Surface Functionalization of Graphene Oxide with Hyperbranched Polyamide-Amine and Microcrystalline Cellulose for Efficient Adsorption of Heavy Metal Ions

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Research Article

Keywords: Adsorption, Graphene oxide, Cellulose, Hyperbranched polymer, Heavy metal ions

Posted Date: September 17th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-860098/v1

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Abstract

Graphene oxide (GO)-based adsorbents have received attention in the removal of heavy metal ions in wastewater due to its large specific surface area and oxygen-containing functional groups, which can enhance the interaction between GO and heavy metal ions. Many researchers are seeking economical and effective strategies to further improve the adsorption capacity of GO. Different from other studies, this study proposed to introduce more active groups with hyperbranched polymer and construct micro/nano 3D bumps with cellulose on the surface of GO to improve the adsorption performance of GO. First, hyperbranched polyamide-amine (HPAMAM) functionalised GO was fabricated by the formation of amide bond between the carboxyl group of GO and the amino group of HPAMAM to endow GO more active groups and increase the affinity of adsorbent with heavy metal ions. Then, dialdehyde cellulose (DAC) obtained through the oxidation of microcrystalline cellulose was grafted onto GO/HPAMAM by forming a Schiff-based structure between the amino group of HPAMAM and aldehyde group of DAC; it is used to fabricate micro/nano 3D bumps on the surface of GO to increase the contact area between the adsorbent and pollutants. The obtained GO/HPAMAM/DAC adsorbent exhibited strong adsorption capacity and good cycle stability for heavy metal ions. The maximum adsorption capacities of Pb(II), Cd(II) and Cu(II) were 680.3, 418.4 and 280.1 mg/g at 298 K, which were better than those of most adsorbents reported. Pseudo-second-order kinetic model and Langmuir isotherm model could describe this adsorption process. The adsorption of Pb(II), Cd(II) and Cu(II) contributed to the chelation or complexation of nitrogen- and oxygen-containing groups on GO/HPAMAM/DAC adsorbent. This study may provide a novel strategy for improving the adsorption performance of GO with hyperbranched polymer and cellulose.

1. Introduction

With the global industrial development, heavy metal ions are used in many fields, such as light industry, batteries and electroplating. Industrial wastewater contains many heavy metal ions (Uoginte et al. 2019). Considering its high toxicity, low degradation and easy bioaccumulation of heavy metal ions (Madadrang et al. 2012), it is important to remove heavy metal ions from wastewater to avoid threats to the ecosystem and human health. Presently, membrane separation, chemical precipitation, photocatalysis, reverse osmosis, adsorption and other technologies have been used to remove heavy metal ions from wastewater (Barakat et al. 2011; Mehdaoui et al. 2018). Among them, adsorption has the advantages of high efficiency, convenience and easy industrial amplification and is widely used in wastewater treatment (Xiang et al. 2017; Duru et al. 2016). Recently, carbon-, polymer- and biomass-based adsorbents have been designed to achieve low-cost and efficient heavy metal-ion adsorption (Zhao et al. 2018).

Graphene has unique electrochemical properties, excellent mechanical and thermal properties and a large specific surface area (Srinivasan et al. 2018). The oxidised graphene contains oxygenous groups, such as hydroxyl and carboxyl groups, which makes graphene hydrophilic and enhances the interaction between graphene and metal ions (Pazat et al. 2017). Therefore, graphene oxide (GO) is an ideal candidate for the adsorbent. The adsorption performance of the adsorbent depends on the contact area
and affinity between the adsorbent and pollutants (Cui et al. 2015). Researchers are committed to modifying GO for more efficient adsorbents. The design of advanced GO-based adsorption materials should follow two principles: Introduce more active groups on the GO surface to enhance its affinity for heavy metal ions and build a micro/nano three-dimensional (3D) structure on the GO surface to increase the contact area with pollutants, which may promote the adsorption process.

Hyperbranched polymers have abundant terminal active groups and many internal cavities formed by branched molecular structures (Manna et al. 2001). Hyperbranched polyamide-amine (HPAMAM) presents a spherical branched molecular structure with developed nano-cavities and many terminal amino groups (Rehim et al. 2011). Adsorbents with nitrogen-chelating ligands, such as amino groups, are more efficient in adsorbing heavy metal ions (Huang et al. 2018). The HPAMAM can be grafted onto GO using an amide bond between the amino group of HPAMAM and the carboxyl group of GO. On this basis, the micro/nano 3D structure needs to be built on GO for a more efficient adsorbent.

Cellulose, containing many hydroxyl groups, can combine with GO dispersed in an aqueous medium through hydrogen bonding (Yakout et al. 2017). The combination of cellulose and graphene is expected to build a micro/nano 3D structure on GO to increase the contact area between GO-based adsorbents and pollutants, creating favourable conditions for an efficient adsorption process. On the other hand, the introduction of cellulose can reduce the cost of GO-based adsorbents. Zhang et al. (2014) reported a porous GO/carboxymethyl cellulose adsorbent prepared using a unidirectional freeze-drying method, which was efficient in the adsorption of Ni$^{2+}$. Zaman et al. (2020) combined microcrystalline cellulose (MCC) obtained from waste jute with GO through a modified Hummers’ method to construct GO/MCC nanocomposite adsorbent.

In this study, HPAMAM and MCC functionalised GO adsorbent for efficient adsorption of heavy metal ions was proposed. First, GO/HPAMAM was prepared through the formation of an amide bond between the carboxyl group of GO and the amino group of HPAMAM to endow GO more active groups and increase the affinity of adsorbent with heavy metal ions. Then, dialdehyde cellulose (DAC) obtained by the oxidation of MCC was grafted onto GO/HPAMAM by forming a Schiff-based structure between the amino group of HPAMAM and the aldehyde group of the DAC; it is used to fabricate a micro/nano 3D bump on the surface of GO to increase the contact area between the adsorbent and pollutants. The characterisation and adsorption performance of GO/HPAMAM/DAC was carried out. The adsorption mechanism of GO/HPAMAM/DAC has also been analyzed. This study may provide an alternative method for enhancing the adsorption performance of GO with hyperbranched polymer and cellulose.

2. Materials And Methods

2.1 Materials

The GO was obtained from Deke Daojin Science and Technology Co., Ltd. (Beijing, China). The HPAMAM was purchased from Hyperbranched Polymers Science & Technology Co., Ltd. (Wuhan, China). The
molecular weight of HPAMAM was about 1900–2200 g/mol and the amino amount was about 12–16 mol/mol. The MCC was provided by Yuanye Biotechnology Co., Ltd. (Shanghai, China). The crystallinity of MCC was 62.9%, and the degree of polymerization was 200–250. The HCl, NaOH, NaIO₄, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), N-hydroxysuccinimide (NHS), Pb(NO₃)₂, Cd(NO₃)₂ and Cu(NO₃)₂ were purchased from Maclin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2 Synthesis of GO/HPAMAM/DAC adsorbent

Typically, 50 mL of deionized water was used to disperse 0.1 g of GO with an ultrasonication. The HPAMAM (1 g) was then added to the GO dispersion and reacted at 70°C for 1 h in the presence of EDC/NHS catalyst to obtain GO/HPAMAM complex. On the other hand, 20 mL of deionized water was used to disperse 1 g MCC. Then, 1 g NaIO₄ was added to MCC dispersion and adjusted the pH to 3.0 with 0.1 mol/L of HCl. After which, the mixture reacted at 30°C for 8 h in the dark to obtain dialdehyde cellulose (DAC). After filtration and washing, DAC was added to the GO/HPAMAM complex and reacted at 70°C for 6 h. Subsequently, the mixture was washed, filtered, and dried to obtain the GO/HPAMAM/DAC adsorbent.

2.3 Characterisation

The FT-IR spectra were detected in a Vertex 80 V spectrophotometer (Bruker, Germany) from 4000 to 500 cm⁻¹ using 4 cm⁻¹-resolution. The XRD patterns were obtained using an Ultima X-ray diffractometer (Rigaku, Japan) with a 5°/min scanning rate. The XPS spectra were conducted in an Axis Ultra DLD X-ray photoelectron spectrometer (Kratos, U.K.) using Mg–Kα (hν = 1253.6 eV) as the radiation source. The SEM pictures were taken using a Supra 55 field-emission scanning electron microscope (Zeiss, Germany). The zeta potentials of GO/HPAMAM/DAC suspension were detected in a Nano-ZS90 Zetasizer (Malvern, U.K.).

2.4 Adsorption experiments

Typically, heavy metal ion solutions (100 mL) of Pb(II), Cd(II) or Cu(II) were mixed with 10 mg GO/HPAMAM/DAC adsorbent and stirred for 24 h at 298 K. After that, GO/HPAMAM/DAC adsorbent was separated from the mixture using a 0.22 µm membrane. The AA-6300C atomic adsorption spectrometer (Shimadzu, Japan) was used to quantitatively detect the content of heavy metal ions in the filtrate. For cyclic adsorption experiments, 0.1 mol/L NaOH and 0.1 mol/L HCl were utilized to desorb Pb(II), Cd(II), and Cu(II) from GO/HPAMAM/DAC.

3. Results And Discussion

3.1 Proposed process concept of GO surface functionalization with HPAMAM and MCC

The GO presents a large specific surface area, hydrophilicity, and good affinity for heavy metal ions due to containing oxygenous groups (such as hydroxyl and carboxyl groups) on its surface, which is deemed
an ideal adsorption material. In order to further improve the adsorption capacity of GO, this study proposed to introduce more active groups and construct a micro/nano 3D structure on the surface of GO to increase the contact area and affinity between the adsorbent and pollutants. The HPAMAM and MCC functionalised GO adsorbent was prepared through the synthesis process shown in Fig. 1. It involves the following steps: (1) chemical grafting of HPAMAM on GO through amide bond in the presence of a catalyst (EDC/NHS), which was expected to increase the active groups on GO, thus increasing the affinity of the adsorbent for the heavy metal ions. (2) The MCC was oxidised, using NaIO₄, to DAC to introduce aldehyde groups on the cellulose molecular chain, thus creating conditions for the grafting of DAC on GO/HPAMAM. (3) The DAC was grafted onto GO/HPAMAM by forming a Schiff-based structure between the amino group of HPAMAM and the aldehyde group of the DAC, which was expected to construct a dense micro/nano 3D bump on the surface of GO to increase the contact area between the adsorbent and pollutants. The use of cellulose to construct micro/nano 3D bump on GO is a highlight different from other studies. The as-prepared GO/HPAMAM/DAC adsorbent had the potential to efficiently adsorb heavy metal ions from wastewater.

### 3.2 Characterisation of GO/HPAMAM/DAC adsorbent

Figure 2a shows the FT-IR spectra of GO, DAC, HPAMAM, and GO/HPAMAM/DAC. For GO, the stretching vibration peak of C = C, C = O and −OH appeared at 1623, 1718 and 3419 cm⁻¹, respectively (Qi et al. 2017). For HPAMAM, the bending vibration peak of −CH₂− appeared at 1417 cm⁻¹. The −NH− flexural vibration peak and −C = O tensile vibration peak of the amide bond appeared at 1500 and 1585 cm⁻¹, respectively. The symmetric and asymmetric tensile vibration peaks of −CH₂− appeared at 2843 and 2936 cm⁻¹. The tensile vibration peak of −NH₂ appeared at 3084 cm⁻¹. The broad peak at 3287 cm⁻¹ was attributed to the superposition of the −NH− stretching vibration peak of the amide bond and the −NH₂ stretching vibration peak. For DAC, the C = O stretching vibration peak of the aldehyde group appeared at 1750 cm⁻¹ (Zhu et al. 2016), confirming the introduction of the aldehyde group on the cellulose molecular chain after oxidation. In contrast, some new peaks appeared in GO/HPAMAM/DAC. The peaks at 1450, 1650 and 3380 cm⁻¹ correspond to the vibrations of −CH₂−, −CONH− and −NH−, respectively (Zeng et al. 2007), confirming the graft of HPAMAM on GO through an amide bond. On the other hand, the C = N vibration peak appeared at 1558 cm⁻¹ and the C = O stretching vibration peak of the aldehyde group at 1750 cm⁻¹ disappeared, indicating that DAC was grafted onto GO/HPAMAM by forming the Schiff-based structure between the amino group of HPAMAM and the aldehyde group of DAC. Thus, each building unit of GO/HPAMAM/DAC adsorbent was connected by a covalent bond to achieve structural stability.

The XRD spectra of GO, GO/HPAMAM and GO/HPAMAM/DAC are shown in Fig. 2b. A strong peak appeared in the XRD spectra of GO, which was caused by the interlayer spacing of GO sheets (Lv et al. 2018). After grafting HPAMAM, the characteristic diffraction peak of GO was reduced, which may be due to the shielding of GO by HPAMAM. In addition, the characteristic diffraction peak of GO was further reduced after grafting DAC, and the characteristic diffraction peak corresponding to the typical crystalline
structure of cellulose appeared at about $2\theta = 23^\circ$. The decrease in the crystallinity of GO may be due to the grafting of cellulose molecular chains, which resulted in the non-uniform content of GO (Liu et al. 2017).

The surface chemical structure of GO/HPAMAM/DAC adsorbent, which affects its absorption performance, was analysed using XPS. As shown in Fig. 2c, a distinct characteristic peak corresponding to N 1s appeared at about 400 eV, which implies the grafting of HPAMAM in the adsorbent. This sharp peak indicates the relatively high nitrogen content in GO/HPAMAM/DAC, which might increase the adsorption capacity. The high-resolution spectrum of N 1s is shown in Fig. 2d. The characteristic peaks corresponding to C–N–C, C–N, N(C)$_3$, C = N and N–C = O appeared at 399.2, 399.8, 400.1, 400.8 and 401.4 eV, respectively (He et al. 2016). The appearance of N–C = O and C = N proves the grafting of HPAMAM and DAC on GO, which is consistent with the results of FT-IR spectra. The primary, secondary and tertiary amines presented in GO/HPAMAM/DAC could promote the adsorption of heavy metal ions.

The SEM images of GO, GO/HPAMAM and GO/HPAMAM/DAC are shown in Fig. 3. The GO (Fig. 3a, b, c) displayed a smooth sheet-layer structure with a certain degree of stacking. After grafting HPAMAM (Fig. 3d, e, f), GO showed a rough surface. This may be due to the branched molecular structure and the nano-cavities of HPAMAM. The abundant active groups in HPAMAM could improve the affinity between adsorbents and heavy metal ions. In addition, the stacking degree of GO was reduced. After the grafting of DAC onto GO/HPAMAM (Fig. 3g, h, i), the surface of GO became rougher and micro/nano 3D bump appeared, which could increase the contact area between the adsorbent and pollutants for an efficient adsorption process. The large number of active groups in HPAMAM and the micro/nano 3D structures fabricated by cellulose would improve the adsorption performance of GO.

### 3.3 Adsorption performance of GO/HPAMAM/DAC adsorbent

As shown in Fig. 4a, the surface charge of GO/HPAMAM/DAC adsorbent in the pH range of 3.0–12.0 was analysed. It was easy to find that the zeta potential of the adsorbent decreased with the increase of pH. When the pH was 8.24, the zeta potential was zero. Therefore, the isoelectric point (pH$_{ip}$) of GO/HPAMAM/DAC adsorbent was 8.24. The surface charge of GO/HPAMAM/DAC adsorbent was positive at pH < 8.24 because the primary and secondary amines in HPAMAM interacted with H$^+$ to form cationic groups (Zhu et al. 2016).

Figure 4b shows the adsorption capacity of the adsorbents for Pb(II), Cd(II) and Cu(II). The unmodified GO had the worst adsorption capacity (42.4, 28.7 and 10.8 mg/g for Pb(II), Cd(II) and Cu(II), respectively). After grafting HPAMAM, the adsorption capacity of GO/HPAMAM was improved (112.8, 58.9 and 24.3 mg/g for Pb(II), Cd(II) and Cu(II), respectively). This was mainly due to the introduction of more active groups on GO, which enhanced the affinity between the adsorbent and heavy metal ions. After grafting DAC, the adsorption capacity of GO/HPAMAM/DAC showed more improvement (401.5, 242.8 and 131.4 mg/g for Pb(II), Cd(II) and Cu(II), respectively). This was mainly because the micro/nano 3D structures
fabricated by cellulose on GO increased the contact area between the adsorbent and the pollutants. Based on the above results, it can be concluded that introducing more active groups using HPAMAM and fabricating the micro/nano 3D structure using cellulose is an effective strategy to improve the adsorption capacity of GO. Subsequently, the adsorption kinetics and adsorption isotherms of Pb(II), Cd(II) and Cu(II) onto GO/HPAMAM/DAC were investigated.

The adsorption kinetics of Pb(II), Cd(II) and Cu(II) onto GO/HPAMAM/DAC adsorbent at 298 K are shown in Fig. 5a. There were two adsorption stages for these three adsorbates. First, the adsorption capacity increased rapidly in the first 150 min. Then, the adsorption process tended to balance, and the adsorption capacity reached a stable level. A large number of active groups and micro/nano 3D bumps in GO/HPAMAM/DAC adsorbent increased its interaction with heavy metal ions. Pseudo-first-order and pseudo-second-order kinetics were fitted to measure the data to investigate the adsorption process.

The pseudo-first-order kinetics is expressed as follows:

\[-\ln (1 - F) = k_1 t + C\]

\[F = \frac{Q_t}{Q_e} = \frac{1}{1 + k_1 t} (1)\]

where \(Q_t\) (mg/g) is the amount of heavy metal ions adsorbed at the contact time \(t\) (min), \(Q_e\) (mg/g) is the amount of heavy metal ions adsorbed at equilibrium, and \(k_1\) (min\(^{-1}\)) is the kinetic rate constant. The curves of \(-\ln(1 - F)\) vs. \(t\) are shown in Fig. 5b, and the \(k_1\) values are displayed in Table 1.

| Adsorbate | Pseudo-first-order | Pseudo-second-order |
|-----------|--------------------|---------------------|
|           | \(Q_e\) (mg/g) | \(k_1\) (1/min) | \(R^2\) | \(k_2\) (g/mg.min) | \(Q_e\) (mg/g) | \(R^2\) |
| Pb(II)    | 148.8              | 0.01522             | 0.9940 | 0.00017              | 169.8          | 0.9977 |
| Cd(II)    | 131.6              | 0.00924             | 0.9857 | 0.00021              | 138.7          | 0.9970 |
| Cu(II)    | 118.2              | 0.01349             | 0.9749 | 0.00016              | 134.2          | 0.9978 |

The pseudo-second-order kinetics is expressed as follows:

\[\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{k_2 Q_e^2}\]

2

where \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the kinetic rate constant. The curves of \(t/Q_t\) vs. \(t\) are shown in Fig. 5c, and the \(k_2\) values are displayed in Table 1.
As shown in Table 1, the $R^2$ of the pseudo-second-order kinetic model for Pb(II), Cd(II) and Cu(II) adsorption were all larger than those of the pseudo-first-order kinetic model. It confirmed that the pseudo-second-order kinetic model can describe the Pb(II), Cd(II) and Cu(II) adsorption onto GO/HPAMAM/DAC adsorbent, and chemical adsorption is the rate-determining step (Xu et al. 2017).

Figure 6a presents the adsorption isotherms of Pb(II), Cd(II) and Cu(II) onto GO/HPAMAM/DAC adsorbent at 298 K. The adsorption capacities of GO/HPAMAM/DAC adsorbent for Pb(II), Cd(II) and Cu(II) increased with the increase of initial concentration of heavy metal ions. The GO/HPAMAM/DAC adsorbent exhibited the strongest adsorption capacity for Pb(II). The Langmuir and Freundlich isotherm models were used to demonstrate the adsorption process of GO/HPAMAM/DAC adsorbent for Pb(II), Cd(II) and Cu(II).

The Langmuir isotherm is expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}$$

where $Q_m$ (mg/g) represents the maximum adsorption capacity of unit weight adsorbent for heavy metal ions, and $b$ (L/mg) is the Langmuir adsorption constant. The curves of $C_e/Q_e$ vs. $1/C_e$ are shown in Fig. 6b, and the $Q_m$ and $b$ values are displayed in Table 2.

![Table 2](image)

| Adsorbate | Langmuir model | Freundlich model |
|-----------|----------------|------------------|
|           | $Q_m$(mg/g)    | $b$(L/mg)       | $R^2$ | $k$(mg/g) | $n$ | $R^2$ |
| Pb(II)    | 680.3          | 0.0284           | 0.9927 | 29.91     | 2.3737 | 0.9123 |
| Cd(II)    | 418.4          | 0.0032           | 0.9909 | 2.74      | 1.5183 | 0.9648 |
| Cu(II)    | 280.1          | 0.0028           | 0.9907 | 19.11     | 4.3397 | 0.8174 |

The Freundlich isotherm is expressed as follows:

$$\ln Q_e = \ln k + \frac{1}{n} \ln C_e$$

where $k$ and $n$ are Freundlich adsorption constants, $k$ (mg/g) is a rough index for the adsorption capacity, $1/n$ represents the empirical parameter of adsorption intensity. The curves of $\ln Q_e$ vs. $\ln C_e$ are shown in Fig. 6c, and the $k$ and $n$ values are displayed in Table 2.
As shown in Table 2, the $R^2$ of the Langmuir isotherm model for Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$) adsorption were larger than those of the Freundlich isotherm model. Therefore, it can be concluded that the Langmuir isotherm model can describe the Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$) adsorption onto GO/HPAMAM/DAC adsorbent. In addition, the $Q_m$ of Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$) were 680.3, 418.4 and 280.1 mg/g at 298 K. Compared to most of the adsorbents listed in Table 3, GO/HPAMAM/DAC adsorbent exhibits a higher $Q_m$ for Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$). All the above results confirmed that GO/HPAMAM/DAC has the potential to adsorb heavy metal ions in wastewater as a promising adsorbent.

### Table 3
The $Q_m$ for GO/HPAMAM/DAC compared with other adsorbents reported.

| Adsorbent                              | $Q_m$ (mg/g) | Temperature | Reference                  |
|----------------------------------------|--------------|-------------|----------------------------|
|                                        | Pb($\text{VI}$) | Cd($\text{II}$) | Cu($\text{II}$) |                     |
| Graphene oxide/cellulose membranes     | 107.9        | 16.7        | 14.3         | 298 K | Sitko et al. (2016) |
| Modified biochar                       | -            | -           | 16.1         | 293 K | Yang et al. (2014)  |
| GO/CMC                                 | 76.7         | 46.1        | 82.9         | 293 K | Zhang et al. (2014) |
| Lignosulfonate-graphene oxide-polyaniline | 216.4      | -           | -            | 303 K | Yang et al. (2014)  |
| Multi-metal binding biosorbent         | 63.4         | 38.3        | 108.1        | 296 K | Abdolali et al. (2017) |
| Cross-linked grapheme oxide sheets via modified extracted cellulose | 186.5 | - | 46.4 | 298 K | Yakout et al. (2017) |
| GO-HBP-NH$_2$-CMC                      | 150.3        | -           | 137.5        | 298 K | Kong et al. (2020)  |
| **GO/HPAMAM/DAC**                      | **680.3**    | **418.4**   | **280.1**    | **298 K** | **This work** |

In addition, cycling stability is an important factor that restricts the practical application of adsorbents. The adsorption capacity of GO/HPAMAM/DAC adsorbent for Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$) in five cycles is shown in Fig. 7. Even after five cycles, more than 90% of Pb($\text{VI}$), Cd($\text{II}$) and Cu($\text{II}$) could be re-adsorbed. The good recycling performance of GO/HPAMAM/DAC adsorbent was attributed to the structural stability contributed by covalent grafting between GO, hyperbranched polymer and cellulose.

### 3.4 Adsorption mechanism of GO/HPAMAM/DAC adsorbent
The GO/HPAMAM/DAC adsorbent with a large number of active groups and micro/nano 3D structure showed strong adsorption capacity for heavy metal ions in wastewater. To study the adsorption mechanism of GO/HPAMAM/DAC adsorbent, FT-IR and XPS were conducted to analyse the adsorption sites of GO/HPAMAM/DAC adsorbent. The FT-IR spectra of GO/HPAMAM/DAC before and after heavy metal-ion adsorption are shown in Fig. 8a. For GO/HPAMAM/DAC, the broad peak at 3000–3500 cm\(^{-1}\) was attributed to the superposition of O–H and N–H vibration, and the peaks at 1650 and 1558 cm\(^{-1}\) were ascribed to O = C−NH and C = N vibration. After the adsorption of Pb(), Cd() and Cu(), the peaks at 3000–3500 cm\(^{-1}\) tended to broaden. This confirms that the hydroxyl and amino groups contributed to the adsorption of heavy metal ions. In addition, the peaks at 1650 and 1558 cm\(^{-1}\) were weakened, suggesting that the nitrogen- and oxygen-containing groups on GO/HAPAMAM/DAC adsorbent could chelate and/or compound heavy metal ions by acting as electron donors.

The XPS spectra of GO/HPAMAM/DAC before and after heavy metal-ion adsorption are shown in Fig. 8b. The Pb, Cd and Cu appeared in XPS spectra after adsorption, confirming the pollutant adsorption on GO/HPAMAM/DAC. Figure 8c, d show the O 1s and N 1s XPS spectra of GO/HPAMAM/DAC before and after Pb(), Cd() and Cu() adsorption. For GO/HPAMAM/DAC, the peaks of O 1s and N 1s appeared at 531.5 and 398.6 eV. After adsorption, these two peaks moved towards high binding energy, indicating the interaction between oxygen-/nitrogen-containing groups and heavy metal ions in the adsorption process. This is consistent with the results of FT-IR.

4. Conclusion

Introducing more active groups with hyperbranched polymer and constructing micro/nano 3D bumps with cellulose on the surface of GO is an effective strategy to improve the adsorption performance of GO. The GO/HPAMAM/DAC adsorbent exhibited strong adsorption capacity and good cycle stability for Pb(), Cd() and Cu(). The adsorption process could be described by the pseudo-second-order kinetic and Langmuir isotherm models. The GO/HPAMAM/DAC adsorbent showed a higher \(Q_m\) for Pb(), Cd() and Cu() than those of most other adsorbents reported. The adsorption of Pb(), Cd() and Cu() was mainly contributed by chelation or complexation of nitrogen- and oxygen-containing groups on GO/HAPAMAM/DAC adsorbent. This study suggests that GO/HAPAMAM/DAC adsorbent may be a promising adsorbent for the efficient removal of heavy metal ions from wastewater.

Declarations

Acknowledgments

This work was financially supported by the Young Elite Scientists Sponsorship Program by CAST (2018QNRC001), the Fundamental Research Funds for the Central Universities (2572019B01), the China Postdoctoral Science Foundation (2019M651241), the Heilongjiang Provincial Postdoctoral Science
Conflicts of interest

The authors confirm that this article content has no conflict of interest.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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Figures
Figure 1

Schematic on the synthesis of GO/HPAMAM/DAC adsorbent.
Figure 2

(a) The FT-IR spectra of GO, DAC, HPAMAM, and GO/HPAMAM/DAC. (b) The XRD patterns of GO, GO/HPAMAM, and GO/HPAMAM/DAC. (c) Full XPS spectrum of GO/HPAMAM/DAC and the high resolution XPS spectrum of (d) N 1s.
Figure 3

The SEM images of (a, b, c) GO, (d, e, f) GO/HPAMAM, and (g, h, i) GO/HPAMAM/DAC.

Figure 4

(a) Zeta potentials of GO/HPAMAM/DAC adsorbent at various pH (3.0-12.0). (b) Adsorption capacity of Pb(II), Cd(II), and Cu(II) on GO, GO/HPAMAM, and GO/HPAMAM/DAC (T = 298 K, t = 24 h, m = 10 mg, V = 100 mL, C0metal = 100 mg/L).
Figure 5

(a) Kinetic adsorption curve of GO/HPAMAM/DAC adsorbent for Pb(II), Cd(II), and Cu(II) (T = 298 K, t = 24 h, m = 10 mg, V = 100 mL, C₀metal = 100 mg/L). (b) Pseudo-first-order kinetic model. (c) Pseudo-second-order kinetic model.

Figure 6

(a) Adsorption isotherms of GO/HPAMAM/DAC adsorbent for Pb(II), Cd(II), and Cu(II) (T = 298 K, t = 24 h, m = 10 mg, V = 100 mL). (b) Langmuir isotherm model. (c) Freundlich isotherm model.
Figure 7

Adsorption capacity of GO/HPAMAM/DAC adsorbent for Pb(II), Cd(II), and Cu(II) in 5 cycles.

(a) The FT-IR spectra of GO/HPAMAM/DAC before and after heavy metal ions adsorption. (b) Full XPS spectra of GO/HPAMAM/DAC before and after heavy metal ions adsorption and the high resolution XPS
spectra of (c) O 1s and (d) N 1s.