Preparation of MnO₂ modified magnetic graphitic carbon nitride composite and its adsorption toward Pb(II) in waste water

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ABSTRACT

Based on graphitic carbon nitride (CN) nanosheets, a novel MnO₂ modified magnetic graphitic carbon nitride composite (MMCN) was prepared via magnetization and in-situ deposition of MnO₂. Then an array of characterizations and experiments were conducted to explore the physical and chemical properties of the synthesized MMCN material. The adsorption behavior and removal mechanism of the MMCN were also discussed intensively. The best pH value of Pb(II) of MMCN was 6. The maximum adsorption capacity of MMCN was as high as 187.6 mg/g, which was much higher than that of MCN and original CN, and removal percentage of Pb(II) was around 99%. The adsorption kinetics and isotherms were accorded with pseudo-second-order model and Langmuir model, respectively. The chemical adsorption of Pb(II) indicated that MMCN was a successful modified sorbent and pretty efficient to remove Pb(II) in aqueous owing to the complexation and ion exchange of ample amino and hydroxyl groups. Moreover, MMCN could be separated easily from aqueous under an external field after reaction with its magnetic performance.

Key words: adsorption, graphitic carbon nitride, magnetic, MnO₂, Pb(II)

HIGHLIGHTS

• A novel MnO₂ modified magnetic graphitic carbon nitride composite (MMCN) was prepared.
• The maximum adsorption capacity of MMCN toward Pb(II) was 187.6 mg/g and removal percentage of Pb(II) was around 99%.
• Characterization and batch experiments were conducted to investigate adsorption mechanism.
• The MMCN was a successful modified adsorbent and efficient to remove Pb(II) in aqueous.

INTRODUCTION

As one of the most critical resources, Water is of enough significance for all creatures. However, much industrial and municipal wastewater contains various metal ions frequently and this seriously exceeds the natural degradation capacity of ecology which have a fatal effect on the whole environment (Xu et al. 2018). Especially, Pb(II), a common heavy metal ion applied widely in the manufacture field can induce the neurophysical disorders of child even with lead content in blood below 10 μg/dL (Uberoi & Shadman 1990; Safruk et al. 2017). The adsorption method which is simple and inexpensive has been considered as a promising approach to address the issue (Bailey et al. 1999; Ngah et al. 2011; Uddin 2017).

Among the alternative materials, graphitized carbon nitride (CN) has been considered as a promising material in research. The basic skeleton of CN is a kind of poly (5-S-triazine) rich in nitri cation defects. The s-triazine ring of CN is a conjugated 2-D polymer structure and easy to form p-conjugated planar layer (Amiri et al. 2016), which offers an excellent chemical and thermal stability. Noticing that the basic functional groups of CN surface are mainly amino-groups, they can bring numerous binding sites and capture Pb(II) quickly and accurately by complexation and ion-exchanged behavior (Zou et al. 2016). However, the original CN can only offer limited reactive sites, and it is difficult to separate from waste water owing to its high dispersion. Researches has shown that the introduction of some compatible materials is an effective method to conquer the conundrum (Guo et al. 2019a).

Herein, Manganese dioxide (MnO₂) modified magnetic graphitic carbon nitride composite (MMCN) was prepared via in-situ deposition and applied in solution for the Pb(II) removal. MnO₂ is chosen as the potential to add into the CN material for the remediation of lead cations. MnO₂ is a transition metal oxide with advantages of low-cost, good stability, and environmental compatibility (Moghaddam & Pakizeh 2015; Xiong et al. 2018).
Especially, MnO₂ possesses a point of zero charge of ca. 2.0 and has a large surface area with ample –OH groups (Murray 1975; Gheju et al. 2016; Zhao et al. 2016), which can provide numerous active sites for Pb(II) in a wide range of pH > 2.0. Moreover, ferroferric oxide (Fe₃O₄) is also chosen as a modifier added to CN material because of its excellent performance separating from solution with an external electric field (Rajput et al. 2016; Zhou et al. 2018; Li et al. 2019).

MATERIALS AND METHODS

Materials

MMCN and MCN was prepared from analytical-reagent grade melamine (C₃N₃(NH₂)₃), manganese sulfate monohydrate (MnSO₄·H₂O), ferric chloride (FeCl₃) and ferrous sulfate heptahydrate (FeSO₄·7H₂O). Lead source was confirmed as nitrate (Pb(NO₃)₂). They were obtained from Tianjin Kemel and Sinopharm. Potassium permanganate (KMnO₄) and the remaining were purchased in Macklin. All water used in the experiment was purified deionized water.

Methods

The obtained adsorbent was characterized by a variety of techniques. Scanning electron microscopy (SEM, VEGA3SBH, CZE) was used to determine the morphology of samples. The surface functional groups of samples were determined by Fourier transform infrared spectrometer (FTIR, Nicolet 6700, USA). Powder X-ray Diffraction (XRD) Specimen samples were characterized by Bruker Advance D8 diffractograph with Cu (Kα) radiation. The surface chemistry of MMCN and the adsorbed MCMN samples were determined using X-ray photoelectron spectroscopy (XPS, Escalab 250, USA). The specific surface area and porosity of samples were analyzed at 77 K by Brunauer-Emmett-Teller (BET, JW-BK132F, China). At room temperature, the potential changes of MMCN samples were detected using the Zeta potential analyzer (DELSA 440SX, USA). Vibration sample magnetometer (VSM, MPMS XL-7, USA) tested the magnetic properties of MMCN samples. And properties of MMCN composite for Pb(II) adsorption was evaluated by the experimental studies. Removal mechanism of the adsorbents were also confirmed to evaluate the application of Pb(II) on MMCN.

Preparation of materials

Preparation of CN, MCN and MMCN

Through the typical pyrolysis method (Guo et al. 2019a), CN was prepared in following steps. 12 g of melamine powder was put in a coppel and roasted at 550 °C for 3 h in atmosphere. After cooling up the faint yellow bulk to room temperature, washed it by water and ethanol for times and dried it at 323 K for 24 h, and grinded bulk into powder for spare finally.

The MCN composite was synthesized through in-situ deposition of Fe₃O₄ particles on the surface of CN. The detailed procedures were described as follows. Under the atmosphere of nitrogen, 1.00 g as-preparation CN, 1.20 g FeSO₄·7H₂O and 2.32 g FeCl₃·6H₂O were mixed in 80 ml deionized water and continued to stir the mixture for 30 min. Then added NH₃·H₂O solution (30%, v/v) in drops until the pH value of aqueous to 10.0. The suspension continued to be stirred for 2 h at 353 K. After filtering, washing and drying the products, collected the black solids by a magnet.

The MMCN composite was prepared by the following steps. 1 g as-prepared MCN and 1.17 g MnSO₄·H₂O were mixed in 80 ml deionized water stirring for 0.5 h at room temperature. Then heating up mixture to 353 K and added 0.5 g KMnO₄ granules into it slowly. The whole reaction system was kept agitating for 5 h to obtain MMCN composite. Finally, washed the black composite with distilled water and ethanol, respectively.

The preparation process of MMCN can be described by the diagram in Figure 1. The synthetic mechanisms of Fe₃O₄ and MnO₂ nanoparticles were expressed as following:

\[
\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 \downarrow + 4\text{H}_2\text{O} \quad (1)
\]

\[
2\text{MnO}_4^- + 3\text{Mn}^{2+} + 4\text{OH}^- \rightarrow 5\text{MnO}_2 \downarrow + 4\text{H}^+ \quad (2)
\]

Adsorption properties

Batch of sorption experiments were displayed to optimize the correlative factor of MMCN material for Pb(II) adsorption. The values of adsorption capacity were calculated by ultraviolet spectrophotometer according to
Therefore, the adsorption quantity of MMCN for Pb(II) was calculated by Equation (3):

$$Q_e = \frac{(C_0 - C_e)}{m} \times V$$

(3)

(1) Different adsorbents and dosage:

CN, MCN and MMCN were conducted here as the adsorbent for Pb(II), 0.02 g adsorbent was added into a conical flask contained 40 mL Pb(II) solution (50 mg/L). To study the effect of dose, MMCN dosages of 0.25–2 g/L were carried out in 40 mL Pb(II) solution at 100 mg/L.

(2) Effect of pH value on adsorption:

The pH of the solution was adjusted by 0.1 mol/L HNO₃ and 0.1 mol/L NaOH solutions to 2, 3, 4, 5, 6, 7, 8, respectively. and 0.02 g MMCN was added into a conical flask with a Pb(II) concentration of 100 mg/L. The pH of the solution was the solution was vibrated for 270 min at 298 K and 170 r/min. The concentration of Pb(II) in the supernatant after adsorption equilibrium was measured and calculated by ultraviolet spectrophotometry. Each sample was repeated at least 3 times.

(3) Adsorption kinetics:

The effect of contact time between 0 and 270 min of Pb(II) on different adsorbents were investigated at 298 K, and the initial concentration of the Pb(II) solution was 30, 100, 250 mg/L and the pH was 6.0. The concentration of Pb(II) in the supernatant was measured and calculated at different contact time.

(4) Adsorption isotherms:

The adsorption isotherm of Pb(II) on MMCN was studied at 298, 308 and 318 K. 0.02 g MMCN were added to 40 mL Pb(II) solution at concentration of 20–180 mg/L for 270 min at 170 r/min, respectively. After Adsorption equilibrium, the concentration of Pb(II) in the supernatant was measured and calculated.

RESULTS AND DISCUSSION

Characterizations of materials

The surface morphology of CN, MCN and MMCN were observed by SEM. As shown in Figure 2, CN had an aggregated, layered and irregular plate-like structure, which was consistent with the reported literature (Guo et al. 2019b). Differently from the smooth surface of CN, the MCN composed of many bulk particles possessed a non-smooth surface morphology. Clearly, there were many nanoparticles were found on the surface of MMCN, which could be due to appearance of MnO₂ on the outer surface of MCN. As for the EDS elemental mapping of MCN and MMCN, the Fe and Mn were uniformly distributed in the synthesized MCN and MMCN material, which proved the mass deposition of Fe₃O₄ on CN, MnO₂ in MMCN and the successful modification of CN.

To further understand the microstructures of CN, MCN and MMCN, the BET characterization of the two materials were studied and shown in Figure 3 and Table 1, which implied an IV type isotherm and a H4 type hysteresis loop according to the classification of IUPAC meaning a mixture of microporous and mesoporous of adsorbent. Obviously, the surface area of MMCN (262.78 m²/g) was much larger than that of MCN (16.45 m²/g) and original CN (5.47 m³/g). MMCN pores were mainly distributed within the mesoporous range with centered pore diameter of 4.89 nm. Generally speaking, higher specific surface area offered more sorption
sites for Pb(II) (Li et al. 2018a). The corresponding pore size distribution plots suggested the MMCN composite had more pores than single CN, which could provide interchange channel for adsorption. The increased surface area and numerous mesopores would be momentous to sorption process.

The FTIR spectra of CN, MCN and MMCN were presented in Figure 4(a) as the importance of functional groups in sorption. The characteristic peak at 806 cm⁻¹ which belonged to the triazine units of CN was observed in the spectra of all adsorbents and several peaks in the range of 1,100 and 1,700 cm⁻¹ meant to the typical stretching vibrations of tri-s-triazine derivatives (Tian et al. 2016), which indicated that MCN and MMCN
retained the structure of tri-s-triazine in CN after modification. The significant band at ca. 588 cm\(^{-1}\) in FTIR spectrum of MCN could be assigned to Fe-O (Shi et al. 2018) signing the formation of Fe\(_3\)O\(_4\) on the CN. For MMCN, a new peak was observed at 516 cm\(^{-1}\), which was due to the stretching of the Mn-O bond (Dubal et al. 2011). Moreover, the broad peak at 3,000–3,500 cm\(^{-1}\) mainly represented the stretching vibration behavior of amino (-NH and –NH\(_2\)) and -OH groups (Tian et al. 2016; Zhang et al. 2019). Noticing the band of 3,000–3,500 cm\(^{-1}\), the central peak of MMCN have a significant shift compared to that of MCN and CN, which suggested enhancement of hydrogen bond interaction owing to appearance of more functional groups (Zhou et al. 2017). The results illustrated that magnetization and modification had been conducted successfully and the process occurred probably through chemical deposition.

The XRD patterns of the CN, MCN, MMCN and MMCN-Pb composite were presented in Figure 4(b). The strong peaks at 13.0° (100) and 27.5° (002) in the XRD spectra of CN indicated an excellent crystallinity. The typical peaks of CN were also observed in other three materials, which illustrated the structural stability of CN. The characteristic peaks of MCN at 2\(\chi\) = 30.5° (220), 35.9° (311), 43.6° (400), 53.5° (422), 57.4° (511), and 63.0° (440) were attributed to the typical crystal faces of Fe\(_3\)O\(_4\) (Chen et al. 2019). As for MMCN, the peaks at 12.3°, 18.6°, 36.9° and 65.7° (PDF 18-0802) belonging to MnO\(_2\) were found in the spectra which could be attributed to the cover of mass MnO\(_2\) on the surface of MCN and the characteristic peaks of Fe\(_3\)O\(_4\) was obscurer than before. The results were fully consistent in that of FTIR. In the XRD pattern of MMCN-Pb composite. Some weak but noteworthy peaks were found at 32°, 36.8°, 52.7°, 62.6° and 65.6° (PDF 03-1156) which suggested the presence of Pb in crystal character and successful adsorption of lead onto MMCN.

Magnetic responsivity was conspicuous characteristic of magnetic materials. The Figure 4(c) showed the magnetic hysteresis loop of MMCN and the saturation magnetization value of 44 emu/g, implying that the MMCN composite
could be isolated from aqueous easily after adsorption by an external ordinary magnet, just like what expressed in inset picture. The loop of MMCN was without any hysteresis and symmetrical about the origin, which meant that the superparamagnetism of MMCN could meet the demand of magnetic separation from aqueous. The MMCN material with excellent separation property provided a sustainable sight for the remediation of heavy metal.

The XPS survey spectra of MMCN and MMCN-Pb composite were shown in Figure 4(d). We could see Pb 4d and Pb 4f peaks in the XPS survey of MMCN-Pb while not appeared in that of MMCN, which indicated the existence of divalent Pb on the surface of MMCN after loading (Xu et al. 2013). The spectrum of Pb 4f in Figure 5(f) exhibited that two characteristic peaks at 143.4 and 138.5 eV were assigned to Pb 4f5/2 and Pb 4f7/2, respectively.

Figure. 5 | XPS high resolution spectra of (a) C 1s, (b) N 1s, (c) O 1s, (d) Mn 2p, (e) Fe 2p, and (f) Pb 4f.
Two peaks at 654.3 and 642.5 eV for Mn 2p$^{1/2}$ and Mn 2p$^{3/2}$ (Figure 5(d)) spin–orbit suggested the chemical state of Mn as Mn (IV) (Li et al. 2018b), while the weak shift of the peak after adsorption was due to the interruption of Mn(IV) (Liang et al. 2017). From the XPS result of Fe 2p in Figure 5(e), the calculated Fe$^{2+}$/Fe$^{3+}$ ratios of the MMCN before and after adsorption were around 0.5, which indicated a fact that the existence of Fe$^{3+}$ in composite (Zhao et al. 2016). As shown in Figure 5(a), three intense peaks were identified at ca. 288.6/288.5 eV, 286.2/286.7 eV and 284.7/284.9 eV, which is corresponding to the sp$^{2}$ C-N bond, C-O bond and the sp$^{2}$ hybrid carbon on the N-containing aromatic ring N=–C=N, respectively (Wu et al. 2019). The XPS spectra of N 1s (Figure 5(b)) could be divided into two peaks at around 399.0 eV and 401.0 eV, the N 1s binding energy of MMCN-Pb showed an obviously higher peak than that of MMCN, which could be attributed to the coordination of N with Pb (Li et al. 2018a). Meanwhile, the O 1s (Figure 5(c)) peaks in MMCN material exhibited a contrary change after load of Pb(II), indicating an interactive effect between MMCN and lead. There was a peak at ca.530 eV in the high resolution of O 1s which could be attributed to Fe-O-Fe and Mn-O-Mn (Zhao et al. 2016). The ratio of the integral area of the surface hydroxyl oxygen (ca. 531 eV) to the total oxygen decreased from 9.64% to 6.92% after Pb(II) adsorption, indicating that the surface hydroxyl was related to the Pb(II) adsorption process (López-Muñoz et al. 2016). In conclusion, the adsorption force of Pb (II) on MMCN is a chemical process and mainly related to ample hydroxyl and amino groups on the exterior of MMCN.

**Effect of adsorbent dosage and pH**

A series of experiments about the effect factors including different adsorbents, adsorbent dosage and initial pH in aqueous on the Pb(II) removal were conducted and the data were exhibited in Figure 6. In Figure 6(a), the capacity of MMCN to Pb(II) was as high as 127.19 mg/g, which was much higher than that of CN and MCN, showing an excellent effect of modification. Distinctly in Figure 6(b), with the increasing dosage of MMCN
from 0.25 to 2.0 g/L, the removal percentage of Pb(II) increased gradually and stabilized at around 99%. Instead, the adsorption capacity negatively correlated with MMCN content. Considering to the experimental loss, so the optimal dosage of MMCN was 1.0 g/L.

pH value is another effective factor of adsorption capacity as shown in Figure 4(d). In the pH range of 2–8, the capacity rose sharply when pH < 4, increased slowly at pH 4–6 and reached a plateau at 6–8 finally. The phenomenon could be explained by the surface charge of MMCN and the species distribution of Pb in aqueous. The pHPZC of the MMCN was confirmed at around 4.63. When pH < 4, lower than pHPZC, the positive charge of MMCN induced by protonation would bring electrostatic repulsion between MMCN and Pb(II) and the ample H⁺ would compete with Pb(II) to unite with negative groups on the surface MMCN. With the pH value increasing, the electrostatic repulsion got weaker and Pb(II) became the dominant species of lead when the pH was lower than 6. As the pH value continued to grow, the lead started to precipitate based on the species distribution of lead obtained from Visual MINTEQ (ver.3.0.). Considering all above results, pH = 6 was chosen as the optimum pH.

Adsorption kinetics study

A bunch of experiments were carried out to study the effect of initial concentration and contact time on MMCN adsorption for Pb(II). From data in Figure 7(a), the adsorption quantity of MMCN rose rapidly in the first 20 min and the rate slowed down 50 min later. Finally, the adsorption equilibrium was approached at around 90 min. The higher rate at start was relevant to higher concentration of Pb(II) and the existence of abundant active sites, which indicated that chemical adsorption occurred primarily in the process. In order to further study the practical application of the sorption, the pseudo-first-order and pseudo-second-order models were chosen to simulate the adsorption kinetic. Both of liner fitting curves and correlative parameters were presented in Figure 7(b), 7(c) and Table 2. As shown, the adsorption capacity worked out by pseudo-second-order model was more relevant to the experimental converts compared with the former, and correlation coefficient closing to 1 suggested that the pseudo-second-order model was more satisfying to approach the actual adsorption kinetics. These results reflected that adsorption was really a chemical process which involved valence forces between adsorbents and metal ions (Liu et al. 2019).

![Figure 7](image-url)

**Figure 7** | (a) Effect of time on the removal process; Fitting curves of (b) pseudo-first-order and (c) pseudo-second-order models.

| Table 2 | Kinetic parameters of MMCN adsorption at different initial Pb(II) concentrations |
|---------|---------------------------------|----------------|----------------|
| C₀ (mg/L) | Qₑ (mg/g) | Qₑ (mg/g) | k₁ (min⁻¹) | R² |
| 30       | 54.17  | 14.42  | 0.016 | 0.92 |
| 100      | 115.82 | 30.11  | 0.020 | 0.69 |
| 250      | 147.81 | 38.32  | 0.017 | 0.72 |
|          |        |        |        |      |
| Qₑ, the adsorption quantity of MMCN from experiment. |
| Qₑ, the adsorption quantity of MMCN from calculation through fitting curve. |
Isotherms and thermodynamic studies of reaction

The thermodynamic and isotherms of MMCN for Pb(II) at 298, 308, and 318 K were exhibited in Figure 8. Obviously, the highest adsorption capacity of Pb(II) onto MMCN occurred at 318 K and \( Q_m \) here was 187.6 mg/g, which showed higher temperature was favorable for the adsorption process. Then these isotherms data were demonstrated by Langmuir and Freundlich models as the following.

**Langmuir model**

\[
\frac{C_e}{Q_e} = \frac{1}{k_L Q_m} + \frac{C_e}{Q_m}
\]

(6)

**Freundlich model**

\[
\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e
\]

(7)

where \( Q_e \) (mg/g) and \( Q_m \) (mg/g) mean equilibrium adsorption capacity and the maximum theoretical monolayer capacity of MMCN, respectively; \( C_e \) (mg/L) is the concentration of Pb(II) at equilibrium; \( k_L \) (L/mg), \( k_f \) (mg/g) and \( n \) represent the Langmuir affinity, Freundlich constant and the intensity of adsorption, respectively.

From Table 3, the correlation coefficient of the Langmuir model was clearly higher than that of the Freundlich, implying the former was more appropriate to describe the Pb(II) removal on MMCN. Therefore, the adsorption behavior seemed to be conducted on homogeneous surface in monolayer according to the fundamental assumptions of Langmuir model. In addition, a dimensionless separation factor (\( R_L \)) was introduced to judge whether the
above characteristics of the Langmuir simulation was credible or not. The $R_L$ was expressed as:

$$R_L = \frac{1}{1 + k_L C_0}$$

(8)

The value of $R_L$ can be used to reveal the feasibility of reaction. There are four situations and one of them is $0 < R_L < 1$ which means favorable; and the bigger $R_L$, the better for the removal. From what shown in Table 3, the obtained $R_L$ values implied the adsorption of Pb(II) on MMCN was favorable.

To evaluate the thermodynamic characteristics of the MMCN composite, the related thermodynamic parameters (i.e., $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$) were studied as the following. The thermodynamic equations can be represented as:

$$\ln (K^0) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(10)

$$\Delta G^0 = -RT \ln K^0$$

(11)

where $K^0$ is equilibrium coefficient of sorption. $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ mean the standard free energy, enthalpy change and entropy change, respectively. They can be calculated by the slope and y-intercept in Van’t Hoff plot (Li et al. 2018a). The calculated negative values of $\Delta G^0$ indicated that the high temperature was conductive to the spontaneous adsorption process of Pb(II) on MMCN. Meanwhile, the positive values of $\Delta H^0$ and $\Delta S^0$ demonstrated a natural endothermic reaction with increasing randomness and it agreed with the above fact that higher adsorption capacity at higher temperature.

Here is a comparison of adsorption conditions and capacity of different adsorbent agents with that in the work. From the data in the Table 4, it is clear to see a better effect of the MMCN than other previous adsorbents in similar studies. So, the MMCN adsorption is an effective and promising method to remove Pb(II) from aqueous.

### Table 3 | Correlative isotherm parameters of MMCN for Pb(II) at different temperatures

| T (K) | Langmuir isotherm | Freundlich isotherm |
|-------|-------------------|---------------------|
|       | $Q_m$ (mg/g)      | $k_L$ (L/mg) | $R^2$ | $R_L$ | $k_f$ (mg/g) | $R^2$ |
| 298   | 150.2             | 0.704             | 0.9992 | 0.006–0.045 | 1.95 | 0.8992 |
| 308   | 165.8             | 0.758             | 0.9986 | 0.005–0.042 | 2.15 | 0.7853 |
| 318   | 187.6             | 0.974             | 0.9995 | 0.004–0.035 | 2.23 | 0.7844 |

### Table 4 | Comparison with recent similar studies

| Adsorbents       | pH     | T(K)  | Adsorption capacity (mg/g) | References             |
|------------------|--------|-------|----------------------------|------------------------|
| FAAS             | 6.0    | /     | 32.48                      | Lu et al. (2016)       |
| SDAC             | 6.5–8.0| 303 ± 2| 46.70                      | Sreejalekshmi et al. (2009) |
| White pottery clay | 5.5  | 293   | 159.24                     | Li et al. (2020)       |
| MWCNTs           | 5.0    | 298   | 91.00                      | Wang et al. (2007)     |
| Pb(II)-IIP       | /      | 298   | 33.15                      | Ao & Guan (2017)       |
| Pb-ICB           | /      | 303   | 177.62                     | Jing et al. (2016)     |
| MMCN             | 6.0    | 318   | 187.6                      | This work              |

### CONCLUSION

A new adsorbent named MMCN for Pb(II) was prepared via magnetization and in-situ deposition of MnO₂. An array of characterizations and experiments were conducted to explore the synthesized MMCN material and removal behavior toward Pb(II). The adsorption kinetics, thermodynamics and removal mechanisms of the
MMCN were also analyzed. The maximum adsorption capacity of MMCN for Pb(II) was as high as 187.6 mg/g, which was much higher than that of original CN, and removal percentage of Pb(II) was around 99%. These results indicated that MMCN was pretty efficient to remove Pb(II) in aqueous by complexation and ion exchange with ample amino and hydroxyl. Moreover, MMCN could be separated easily under an external field after reaction because of its magnetic performance.

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CONFLICT OF INTEREST
The authors declare that they have no conflict of interests.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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