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Magnetic Metal Organic Frameworks (MOFs) Composite for Removal of Lead and Malachite Green in Wastewater

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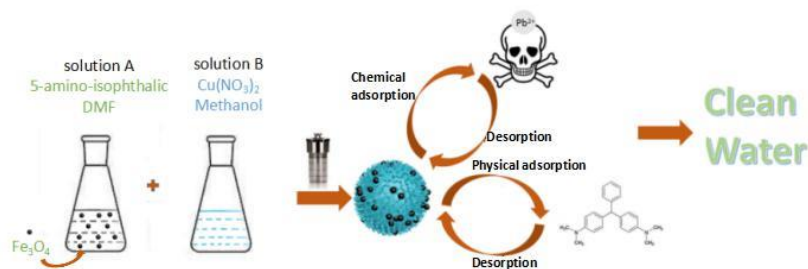
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Graphical abstract



Abstract

We designed and synthesized a magnetic metal organic frameworks (MOFs) composite, Cu-MOFs/Fe₃O₄ as the adsorbent for removal of lead (Pb(II)) and malachite green (MG) in wastewater. This Cu-MOFs/Fe₃O₄ can be easily prepared by in-situ growth of Cu-MOFs with doping Fe₃O₄ nanoparticles. The prepared Cu-MOFs/Fe₃O₄ composite was well characterized by SEM, XRD, and FTIR spectra. The adsorption experiments found that Cu-MOFs/Fe₃O₄ can serve as adsorbent for removal of Pb(II) and MG simultaneously. The adsorption capacities were found to be 113.67mg/g for MG and 219.00 mg/g for Pb²⁺, respectively, which are significantly higher than reported materials. Adsorption isotherm, kinetics and recyclability of Cu-MOFs/Fe₃O₄ for removal of Pb(II) and MG were then studied. Adsorption of Pb(II) and MG exhibited Freundlich adsorption isotherm model, with the adsorption kinetics of available second-order kinetic. Physical adsorption for MG and chemical adsorption for Pb(II) were confirmed by Dubinin-Radushkevich (D-R) isothermal adsorption model. The adsorption of Pb(II) and MG in real water samples were then studied. The Fe₃O₄/Cu-MOFs was found to be recyclable for removal of Pb(II) and MG, can be explored as the potential adsorbent for waste water treatment.

Keywords: Metal organic frameworks;magnetic composite;adsorption; malachite green;Lead;water treatment

1 Introduction

Environmental pollution, in particular water pollution have drawn considerable attention in recently years, because serious problems have been made to humans and other live organisms[1-3]. In addition to the efforts to reduce the discharging of pollutants, developing effective approaches to remove the existing pollutants, such as organic dyes, and heavy metals from contaminated water are essential to ensure the clear water supplying [4, 5]. Both organic dyes and heavy metals are normally existed in waste water, causing several problems for their removal simultaneously [6]. Therefore, it is desirable if the materials used for treatment can remove both dyes and heavy metals from the wastewater before it is discharged into the environment.

Malachite Green (MG) is a basic dye, being widely used in textile and dyestuff industries. Contamination of MG in water causes serious problems for human and animal health due to its poisonous, carcinogenic, mutagenic or respiratory effects being found at high concentration in water [7, 8]. It is well know that lead (Pb(II)) is a hypertoxic, biology accumulative and caustic heavy metal. Especially, this metal shows strong biological toxicities to human and other animals in the end of food chain [9, 10]. This metal is not degradable, can covert to other

chemical forms in live organisms after binding to biomolecules [11-13]. Thus, removal of these organic dyes and heavy metals will directly benefit to both environments and living creatures [14, 15].

Towards this end, a large number of approaches have been applied for removal of dyes from wastewater, such as adsorption, membrane-based separation, electro-coagulation, biochemical degradation and oxidative degradation [16-21]. Among them, adsorption technology has been widely recognized to be one of the most effective methods due to its high efficiency and ease of handling[22]. In particular, the adsorbents and other relevant materials can be recycled, significantly reduced the cost for the wastewater treatment. Traditional adsorbents, such as chitosan/natural zeolites, activated carbon, and silica microspheres, have been generally used in the water treatment by wastewater industries [23]. Those materials are normally applicable for the dyes or heavy metal pollution at low concentrations because their insufficient adsorption capacity.

The use of metal organic frameworks (MOFs) as the absorbent for removal of pollutants has attracted considerable interests in recent years due to its large surface area and adjustable pore size [24, 25]. These materials are also well known as the inorganic polymer that possess unique chemical and physical properties, being widely used in gas separation, photo-electro-catalysis, drug delivery, sensing, adsorption, and gas-storage [26-30]. Cu-MOFs is composed of oxygen, nitrogen, other organic ligands and copper ions from the self-assembly of the coordination polymer. In the preparation of Cu-MOFs, the arrangement of organic ligands and metal ions exhibits obvious direction, and different pore structures can be formed with different adsorption

properties, optical properties, and electromagnetic properties. As a result, Cu-MOFs has shown great potential and attractive prospects in modern material science field [25].

With specific ligands that can coordination with metal ions, MOFs can also be used for removal heavy metals. For example, it is well documented that N atoms from amino group can bind to heavy metal ions, such as Pb(II) through a dative bond [31, 32]. Therefore, amino group terminated Cu-MOFs is expected to be able to adsorption of Pb(II) in waste water in this contribution. In addition, the internal porous structure of amino Cu-MOFs allows adsorption of MG, providing a material for removal both heavy metals and organic dyes simultaneously.

It has been reported that the stability of MOFs can be significantly enhanced in aqueous solution with support by a nano-/micro-composite [33]. In addition to the enhancement of stability, the hybrid composite can also be designed to facilitate the recycling processes for MOFs after adsorption of organic dyes and heavy metals.[34] To this purpose, the magnetic nanoparticle, Fe_3O_4 , could be a good choice as the separation in the water samples can be achieved simply by an external magnetic field [35, 36]. Therefore, preparing magnetic composites combination MOFs with magnetic nanoparticles has significant superiorities in adsorption and separation of pollution.

In this work, a new Cu-MOFs/ Fe_3O_4 composite was designed and synthesized for removal Pb(II) and MG simultaneously (Scheme 1). Integrating of the porous structure of Cu-MOFs with the magnetic Fe_3O_4 particles, Cu-MOFs/ Fe_3O_4 composite was able to be used as an effective adsorbent for MG and Pb(II) removal. Recycling of Cu-MOFs/ Fe_3O_4 composite can also be achieved by an external magnet. The adsorption properties for MG and Pb^{2+} of Cu-

MOFs/Fe₃O₄ composite were discussed, and the kinetics, thermodynamics and adsorption isotherm were further studied. The feasibility of Cu-MOFs/Fe₃O₄ composite as adsorbent for removal of MG and Pb(II) in mixed wastewater samples was finally evaluated.

2 Experimental

2.1 Chemicals and materials

Copper nitrate (Cu(NO₃)₂), N, N-dimethylformamide (DMF), sodium acetate, ethanol (EtOH), ethylene glycol (EG) were obtained from Sinopharm Group Chemical Reagent Company. Malachite Green (92.7 mg L⁻¹), FeCl₃·6H₂O, 5-amino-isophthalic acid, lead nitrate (Pb(NO₃)₂) were purchased from Aladdin Reagent Company (Shanghai). Fresh double distilled water was used throughout the experiment. MG solution with different concentration was prepared by diluting of stock MG solution with water, and stock solution of Pb²⁺ (1000mg L⁻¹) was prepared by dissolving Pb(NO₃)₂ in water.

2.2 Characterization

The chemical composition of Fe₃O₄ and Cu-MOFs/Fe₃O₄ composite were determined by D/max-III C X-ray diffractometer (Shimadzu, Japan). The Fourier transform infrared spectroscopy was measured by a FTIR spectrometer (Perkin Elmer, USA). Scanning electron microscope (SEM) images were obtained using a JSM6510LV scanning electron microscope (JEOL, Japan). N₂ adsorption-desorption analysis was performed on an Accelerated Surface Area and Porosimetry System ASAP2020 (Micromeritics, American). The surface area was estimated using the BET equation, and the pore size distribution was determined by the BJH

model. UV-vis absorption spectra were measured with a Lambda 900 UV/VIS/NIR spectrophotometer (Perkin Elmer, USA). Inductively coupled plasma-mass spectra (ICP-MS, Perkin Elmer, USA) was employed to measure the concentration of Pb(II).

2.3 Synthesis of Cu-MOFs/Fe₃O₄ composite

2.3.1 Synthesis of Fe₃O₄ nanoparticle

The magnetic Fe₃O₄ nanoparticles were synthesized by following reported method [37]. Briefly, 1.73 g FeCl₃·6H₂O and 2.31 g sodium acetate were dissolved in 35 mL ethylene glycol (EG) with stirring for 0.5 h. The mixture was then transferred into a Teflon-lined autoclave, sealed and heated at 200 °C for 8 h. The systems were then allowed to naturally cool to room temperature. The final products collected by centrifugation, washed with ethanol and water for several times to remove any possible remnants, and then dried under vacuum at 60 °C for 8 hours to obtain powder Fe₃O₄ nanoparticles.

2.3.2 Synthesis of Cu-MOFs and Cu-MOFs/Fe₃O₄ composite

For synthesis of Cu-MOFs, 0.4 g 5-amino-isophthalic acid solution in 20 mL DMF was added into a EtOH solution (15 mL) containing 1.2 g Cu(NO₃)₂. The mixture was then transferred into a Teflon-lined autoclave, sealed and heated at 120 °C for 12 h. The formed sediment was collected by filtration, and washed with ethanol and water for three times. For preparation of Cu-MOFs/Fe₃O₄ composite, 0.15 g Fe₃O₄ nanoparticles were added into 20 mL DMF containing 0.4 g 5-amino-isophthalic acid with stirring. After stirring at R. T. for 10 min, 1.2 g Cu(NO₃)₂ in 15 mL EtOH was added. The mixture was then transferred into Teflon-lined

autoclave for heating at 120 °C for 12 h. The products were then collected, and washed with EtOH-H₂O for several times to obtain Cu-MOFs/Fe₃O₄ composite.

2.4 Adsorption experiments

For adsorption of MG, the Cu-MOFs/Fe₃O₄ composite (50.0 mg) was added to 5 mL MG solution at different concentration, and the mixture was shaken for certain time (5-60 min) at 25 °C, 35 °C, 45 °C, separately. The solution was then placed closely to a magnet for 5 min, and then the water solution was removed. The residual MG was then analyzed using UV spectrometer at the wavelength of 620 nm. For investigation the dynamic adsorption, the concentration of MG in water solution was also measured at the different time point.

For adsorption of Pb(II), the Cu-MOFs/Fe₃O₄ composite (50.0 mg) was added into a water solution containing different concentration of Pb²⁺. Shaking at 5 °C, 35 °C, 45 °C, the concentration of Pb²⁺ was measured at each 10 min until the saturated adsorption reached. Then, the concentration of Pb²⁺ in Cu-MOFs/Fe₃O₄ composite was measured by ICP-MS.

2.5 Desorption experiments

For recovery of Cu-MOFs/Fe₃O₄ composite, the used composite was treated with acetone, followed by EDTA. The used Cu-MOFs/Fe₃O₄ composite was mixed with acetone under stirring for 30 min. After repeating for three time, the Cu-MOFs/Fe₃O₄ composite was dried at R. T. for 5 min, and then placed into a solution contains 0.1 M EDTA. Stirring the mixture for 3 h, washing with water for three times before reuse the regenerated Cu-MOFs/Fe₃O₄ composite.

3 Results and discussion

3.1 Characterization of Cu-MOFs/Fe₃O₄ composite

The morphology of the Fe₃O₄ nanoparticles, Cu-MOFs, and Cu-MOFs/Fe₃O₄ composite were characterized by scanning electron microscopy (SEM). As shown in Fig. 1, uniform size and shapes of Fe₃O₄ nanoparticles were obtained with an average diameter of 400 nm. The Cu-MOFs exhibited a spherical flower-like structure before coating of Fe₃O₄ nanoparticles. No significant changes on the shapes of Cu-MOFs/Fe₃O₄ composite was noticed after growth of Fe₃O₄ nanoparticles, but obviously the Fe₃O₄ nanoparticles have been embedded within Cu-MOFs shown in Fig. 1d.

The formation of Cu-MOFs/Fe₃O₄ composite was further confirmed by powder XRD measure of Fe₃O₄ nanoparticles, Cu-MOFs, and Cu-MOFs/Fe₃O₄ composite. As shown in Fig. 2, the diffraction peaks at $2\theta = 18.94^\circ$, 30.16° , 35.54° , 43.07° , 53.6° , 57.1° and 62.70° were obtained, which are in consistent with the diffraction plate PDF#99-0073 at (300), (220), (311), (400), (411), (440). Sharp diffraction of Cu-MOFs was also obtained, suggesting a well crystal structure obtained. The diffraction peaks of Cu-MOFs/Fe₃O₄ composite were well matched with Fe₃O₄ and Cu-MOFs, corroborating the presence of Fe₃O₄ nanoparticles in the composite.

FTIR spectra of the Fe₃O₄, Cu-MOF and Fe₃O₄/Cu-MOFs were presented in Fig. 3. The peak at 3500 cm^{-1} of Cu-MOFs is assigned to amino group termination. The bending vibration of N-H from 5-amino-isophthalic acid can be supported by the peaks observed at $1500\sim 1650\text{ cm}^{-1}$. The peaks at $1230\sim 1030\text{ cm}^{-1}$, can be assigned to the stretching vibration peak of C-N. These

peaks were also clearly observed from Fe₃O₄/Cu-MOFs, suggesting the formation of Cu-MOFs/Fe₃O₄ composite. For the spectra of Fe₃O₄ nanoparticles, the peak at 588 cm⁻¹ can be assigned to Fe-O vibration. The shift of this peak may be caused by the interaction between Fe₃O₄ and Cu-MOFs.

3.2 The adsorption of Cu-MOFs/Fe₃O₄ composite towards MG and Pb(II)

Fig. 4 shows the N₂ adsorption – desorption isotherms and pore size distributions of Cu-MOFs/Fe₃O₄. The Curves show IV type isotherm, which means Cu-MOFs/Fe₃O₄ is with mesoporous structure. Based on the pore size distribution curves, obvious mesoporous distribution can be observed in 3.5 nm, 4 nm and 8.5 nm. The BET surface area and pore volume is 35.4 m² • g⁻¹.

The adsorption properties of Cu-MOFs/Fe₃O₄ composite towards MG and Pb²⁺ were then investigated and the results showed in Fig. 5. Using Cu-MOFs/Fe₃O₄ composite, the removal efficiency for MG was found to be 90 %. The removal efficiency was increased with higher concentration of MG. As shown in Fig. 5b, the removal efficiency for Pb(II) was measured to be 96 % at low concentration at concentration less than 10 mg/L. Upon increasing the concentration of Pb(II), the removal efficiency was gradually decreased. Nevertheless, 80% Pb²⁺ was removed at the concentration of 1000 mg/L, suggesting high efficiency of Cu-MOFs/Fe₃O₄ composite for Pb(II) removal.

The difference of Cu-MOFs/Fe₃O₄ composite for removal of MG and Pb(II) may be attributed to the adsorption processes. In contrast with the physical adsorption for MG, chemical adsorption of Pb(II) is mainly dominated by the coordination of Pb²⁺ with amino from Cu-

MOFs. The removal efficiency could be decreased when the N-Pb bond was saturated.

The maximum adsorption capacities for MG and Pb^{2+} were then calculated. As shown in Table 1, higher adsorption capacity of Cu-MOFs/ Fe_3O_4 composite for MG and Pb(II) removal was obtained in this work.

In order to understand the adsorption ability, traditional adsorbents are compared, and the result is shown in Fig.6.

It is clear that, the removal efficiency of Cu-MOFs/ Fe_3O_4 for MG is a bit better than that of zeolite and activated carbon (Fig. 6 a), the reason may be the physical adsorption for dyes results from the pore size. Even if the surface area of Cu-MOFs/ Fe_3O_4 is not large, but the pore size is with mesoporous structure. The excellent adsorption for MG is due to the appropriate matching of the channel diameter and the dye molecular width[42,43]. Therefore, it can adsorb MG with relative adsorption capacity.

Fig.6 b shows that the removal efficiency for Pb^{2+} is absolutely better than that of zeolite and activated carbon. It can further prove that the adsorption is chemical adsorption which is dominated by the coordination of Pb^{2+} with amino from Cu-MOFs. From the comparison, the Cu-MOFs/ Fe_3O_4 can be proved as an adsorbent for mixed-wastewater treatment.

To examine the superparamagnetic nature of Cu-MOFs/ Fe_3O_4 composite, we placed the Cu-MOFs/ Fe_3O_4 composite close to an external magnet. As shown in Fig. 7, the Cu-MOFs/ Fe_3O_4 composite can be easily separated from the solution within a few seconds. This superparamagnetic nature was not changed after adsorption of MG and Pb(II), indicating the

capability in magnetic recovery of Cu-MOFs/Fe₃O₄ composite after treatment.

3.3 Adsorption isotherms for MG and Pb²⁺

Freundlich model was then selected to study the adsorption isotherm of Cu-MOFs/Fe₃O₄ composite for removal of MG and Pb(II). The Freundlich equation can be described as:

$$Q_e = K_F C_e^{1/n} \quad (1)$$

where K_F and $1/n$ were the Freundlich constant related to adsorption capacity and intensity, respectively. Two linear plots, $\ln Q_e$ against $\ln C_e$ was obtained for adsorption of MG and Pb(II), respectively. It was found that the removal of MG and Pb(II) are following Freundlich adsorption isotherm model.

3.4 Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevich (D-R) isotherm adsorption process was then investigated to understand the principle of adsorption, *i. e.*, chemical adsorption and/or physical adsorption processes [44, 45]. The Dubinin-Radushkevich (D-R) isothermal adsorption model can be described as:

$$\ln Q_e = \ln Q_m - B_d [RT \ln(1 + 1/C_e)]^2 \quad (2)$$

$$E = 1/(2B_d)^{1/2} \quad (3)$$

where Q_e was the equilibrium adsorption capacity of MG and Pb²⁺ on the Fe₃O₄/Cu-MOFs (mol/g), respectively; B_d (mol²/J²) was the activity factor correlated with mean free energy of adsorption, R was the ideal gas constant (8.314 J·mol⁻¹·K⁻¹), T (K) was the Kelvin temperature, and E (kJ/mol) was the average free energy of adsorption. Chemical adsorption

normally showed the energy E at the range of 8-16 KJ/mol, while physical adsorption was happened when E is less than 8.

Linear plots between $\ln Q_e$ and $RT \ln(1+1/C_e)$ at different temperatures were shown in Fig. 9. The D-R constants were estimated using separate intercept and slope of linear plots. For the adsorption process for MG, E was calculated to be 1.81, 5.83 and 9.47 KJ/mol at different temperatures (a, b and c), respectively. This indicated that the adsorption for MG was mainly physical adsorption at low temperature. With the increasing temperature, chemical adsorption was involved besides the physical adsorption. For the adsorption process for Pb^{2+} , E was determined to be 10.64, 12.13 and 13.88 KJ/mol at different temperatures (d, e and f), which are all located in the level of 8-16 KJ/mol, suggesting the removal of Pb^{2+} was mainly dominated by chemical adsorption process.

3.5 Kinetics for the adsorption of MG and Pb^{2+}

To study the kinetics for adsorption of MG and Pb^{2+} , time-dependent adsorptions capacity was then measured at different temperature. The applicability of the pseudo-first-order kinetic model and pseudo-second-order kinetic model were tested by fitting the experimental data. The results showed that the adsorption of MG and Pb^{2+} are following pseudo-second-order kinetic model (Fig. 10). The thermodynamic equilibrium constant (K) and the free energy change (ΔG) were also calculated on basis of the adsorption equilibrium at different temperature, and the results were shown in Table 2. The data of negative free energy (ΔG) and the positive enthalpy change (ΔH) suggested that the adsorption for MG and Pb^{2+} were spontaneous and endothermic processes.

3.6 Recycle of Cu-MOFs/Fe₃O₄ composite

Desorption experiments were then carried out to evaluate the regeneration of Cu-MOFs/Fe₃O₄ composite after MG and Pb²⁺ adsorption. Considering the different adsorption processes, two different eluents, acetone and EDTA were selected to removal of MG and Pb²⁺, separately. As shown in Fig.11. it was found that the MG removal efficiency was 90% after recycling Cu-MOFs/Fe₃O₄ composite for five times. Although the strong chemical adsorption for Pb²⁺, over 85% removal efficiency was obtained after recycling the Cu-MOFs/Fe₃O₄ composite for three time. However, the removal efficiency reduced to 50% if further adsorption performed. These results demonstrated that the Cu-MOFs/Fe₃O₄ composite can be recycled for MG and Pb²⁺ adsorption, which is extremely important for a adsorbent to be potential used in future water treatment industry.

2.6 Removal of MG and Pb²⁺ in real water sample

To evaluate the practical application of Cu-MOFs/Fe₃O₄ composite, adsorption of MG and Pb²⁺ in was then evaluated in a real water sample collected from Yangtze River locally. The water was firstly filtered to remove big solid particles, sand, and live organisms. The water samples were spiked with both MG and Pb²⁺ at certain concentration. Cu-MOFs/Fe₃O₄ composite was then added into the samples with shaking. The Cu-MOFs/Fe₃O₄ composite was further collected by a magnet, and the samples were then analyzed to obtain the removal efficiency.

As shown in Table 3, the removal efficiencies for MG and Pb²⁺ were found to be over 89.92% and 86.75%, respectively. The removal efficiency for both MG and Pb²⁺ are concentration independent. The results demonstrated that Cu-MOFs/Fe₃O₄ composite can be used for

adsorption of MG and Pb^{2+} in real water sample with high removal efficiency.

4 Conclusions

In this work, a recyclable Cu-MOFs/ Fe_3O_4 composite was designed and synthesized for adsorption of organic dyes (MG) and heavy metals (Pb^{2+}). The prepared Cu-MOFs/ Fe_3O_4 composite was well characterized by FTIR, XRD, and SEM. Removal of MG and Pb^{2+} in water sample can be easily achieved by gentle shaking and magnet separation. Removal efficiency was further studied, and the results showed over 90% adsorption efficiency for both MG and Pb^{2+} removal. The maximum adsorption capacity for Pb^{2+} and MG were determined to be 219.00 mg/g and 113.67mg/g, respectively, which is much higher than the reported methods. Studies on adsorption mechanisms demonstrated the removal of MG was mainly dominated by physical adsorption, and removal of Pb^{2+} was based on chemical binding with N of the ligands. Because the physical adsorption for dyes and chemical adsorption for metal ions, the Cu-MOFs/ Fe_3O_4 composite can be potentially applied to real polluted water with the existing pollutants, such as organic dyes, and heavy metals from contaminated water. The Cu-MOFs/ Fe_3O_4 composite was found to be recyclable, can be further used for five times after washing with acetone and EDTA solution. The application of this Cu-MOFs/ Fe_3O_4 composite for removal of MG and Pb^{2+} in practical water samples were then demonstrated. The successful development of this Cu-MOFs/ Fe_3O_4 composite not only provides an effective method for removal of MG and Pb^{2+} in water samples, but also extend the extend the industrial application of inorganic materials.

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ACCEPTED MANUSCRIPT

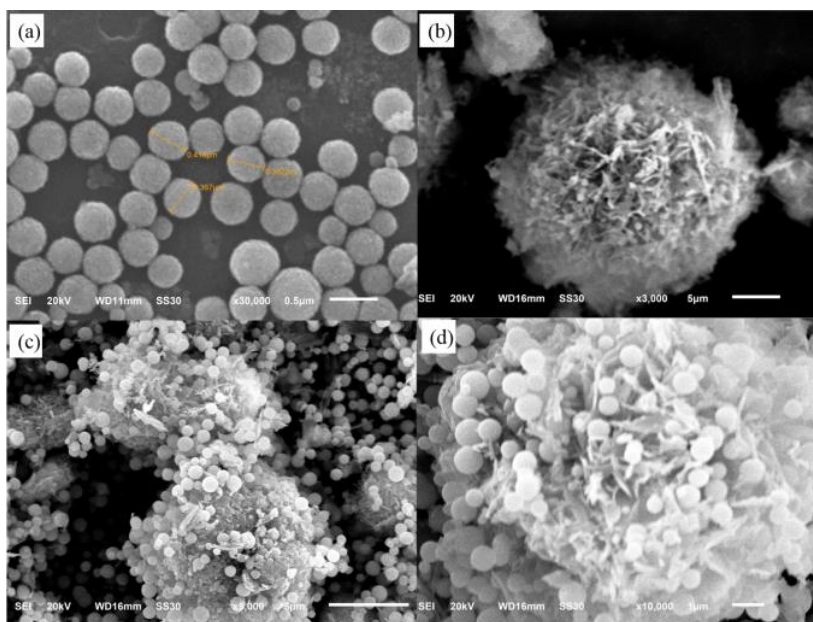


Fig. 1 SEM images of Fe₃O₄ nanoparticles (a), Cu-MOFs (b), and Cu-MOFs/Fe₃O₄ composite (c, d).

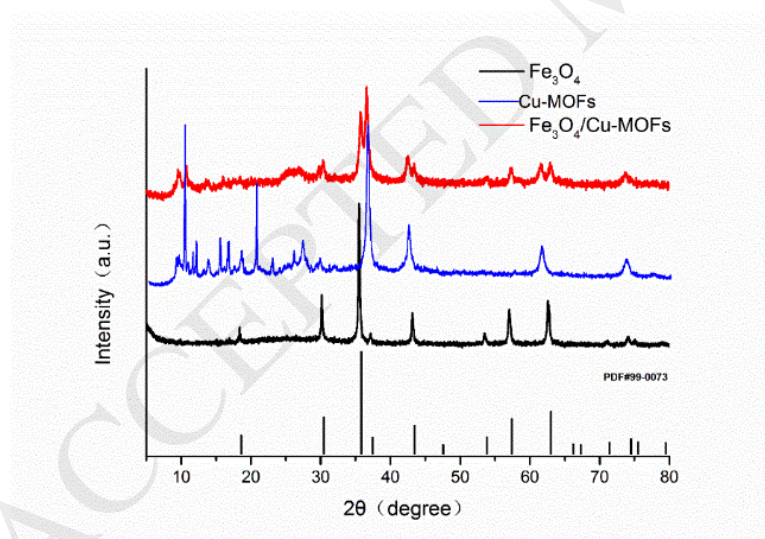


Fig. 2 XRD patterns

Fig. 3 FT-IR spectra of Fe₃O₄ nanoparticles, Cu-MOFs, and Cu-MOFs/Fe₃O₄ composite.

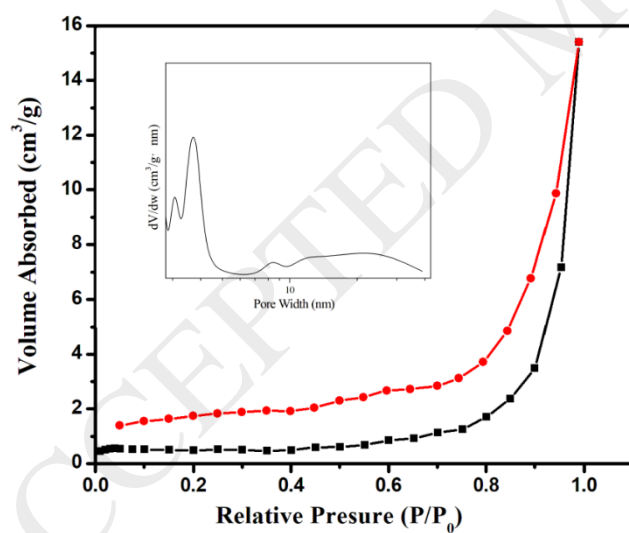
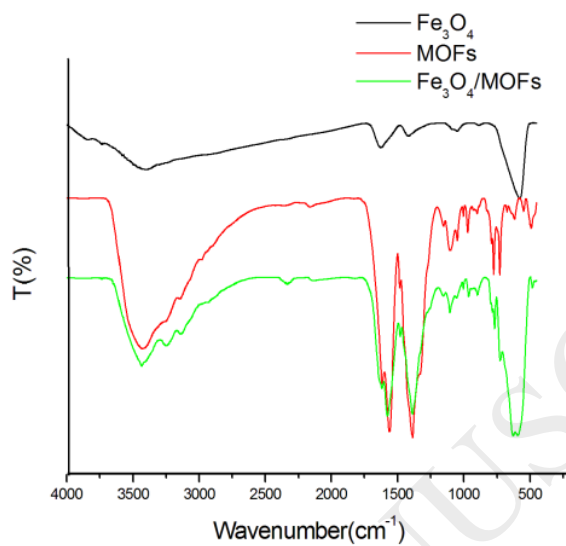


Fig. 4 N₂ adsorption - desorption isotherm and pore diameter distribution profile (insert)

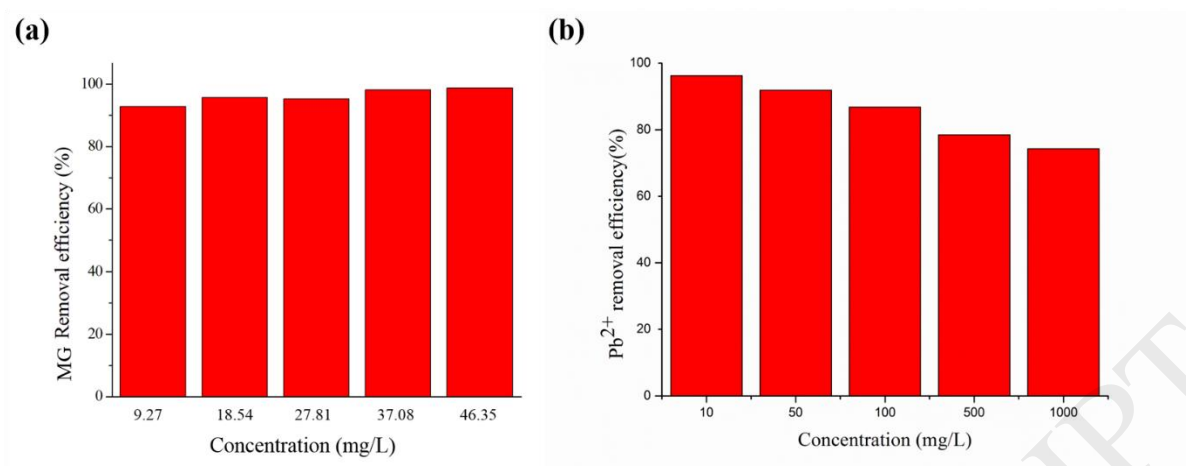


Fig. 5 The adsorption capability of Cu-MOFs/Fe₃O₄ composite towards MG (a) and Pb²⁺ (b) at different concentration.

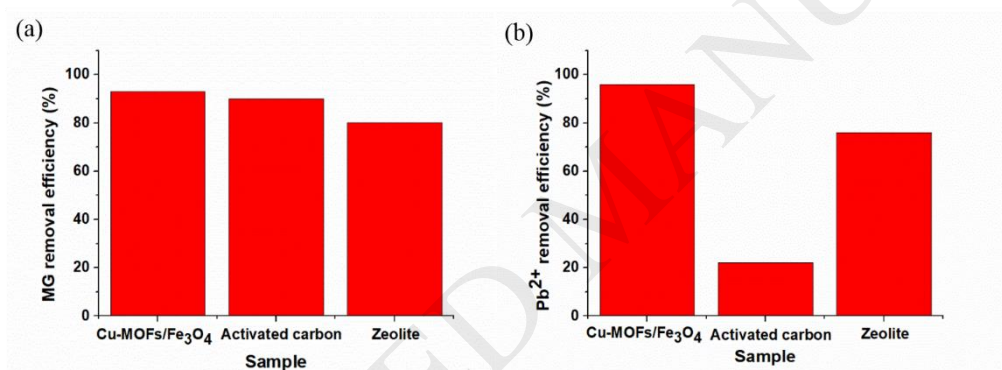


Fig.6 Adsorption for MG (a) and Pb²⁺ on different adsorbents



Fig. 7 Photographs demonstrating the magnetic separation of the Cu-MOFs/Fe₃O₄ composite before (a) and after (b) adsorption of MG and Pb(II).

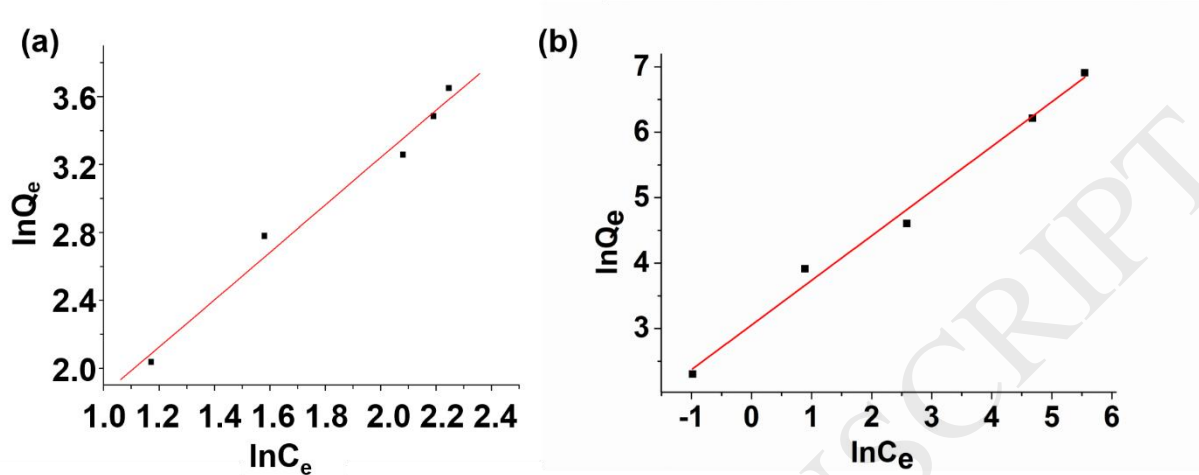


Fig. 8 Freundlich isothermal model of Cu-MOFs/Fe₃O₄ composite for adsorption of MG and Pb²⁺.

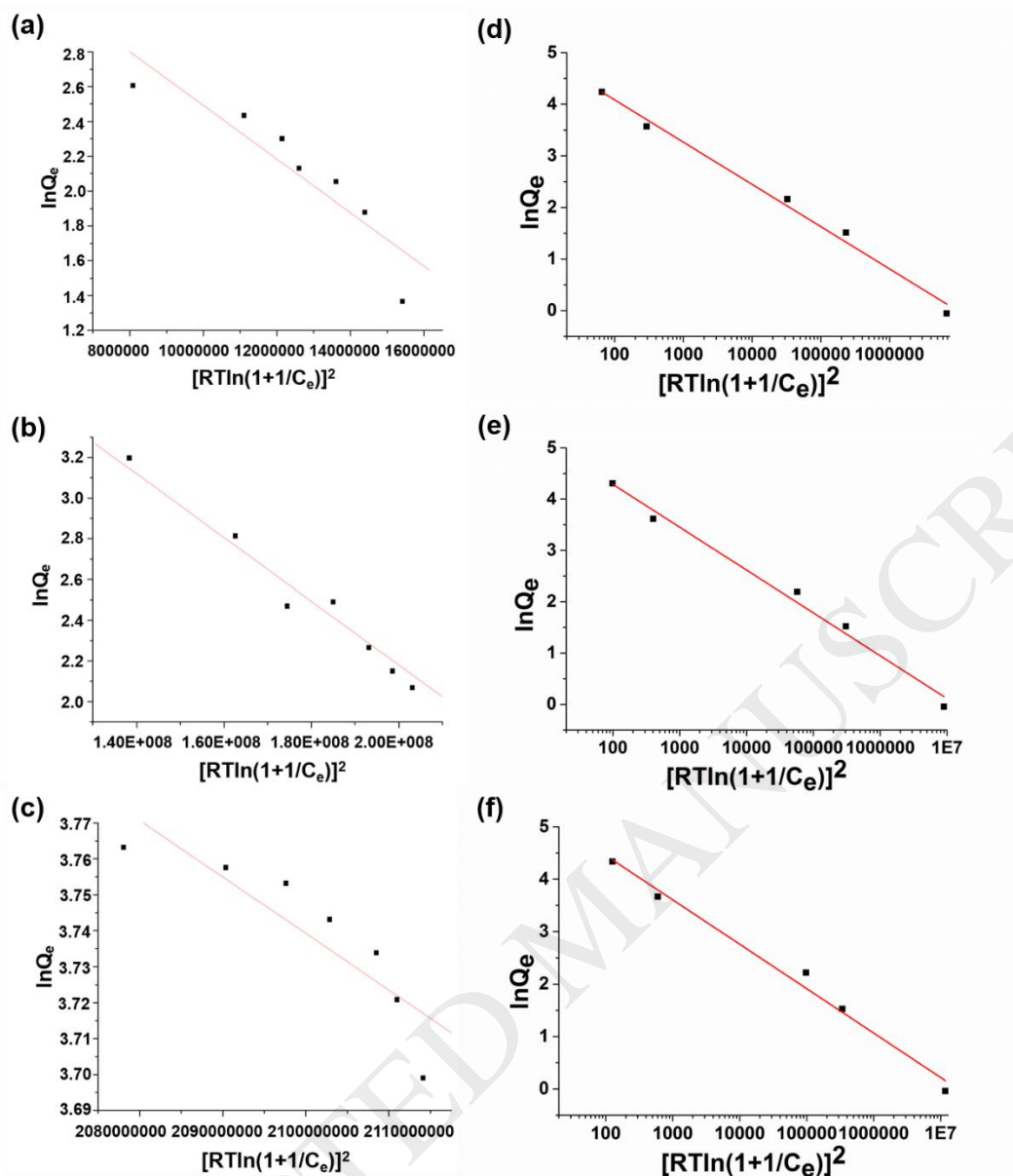


Fig.9 Dubinin-Radushkevich (D-R) isothermal adsorption model of Fe_3O_4/Cu -MOFs for removal of MG at 298 K (a), 308 K (b), and 318 K (c); Pb^{2+} at 298 K (d), 308 K (e), and 318 K (f).

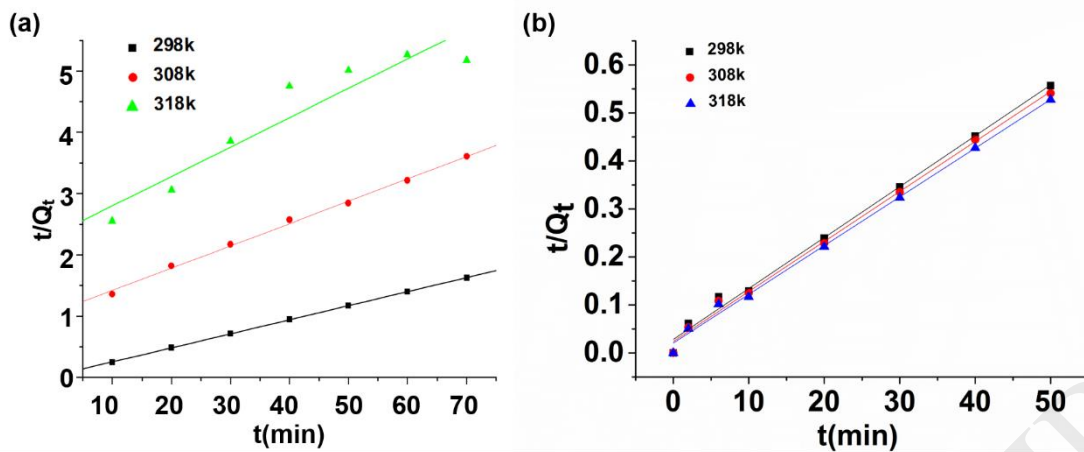


Fig. 10 Plots of pseudo-second-order kinetics for the adsorption of MG(a) and Pb²⁺(b).

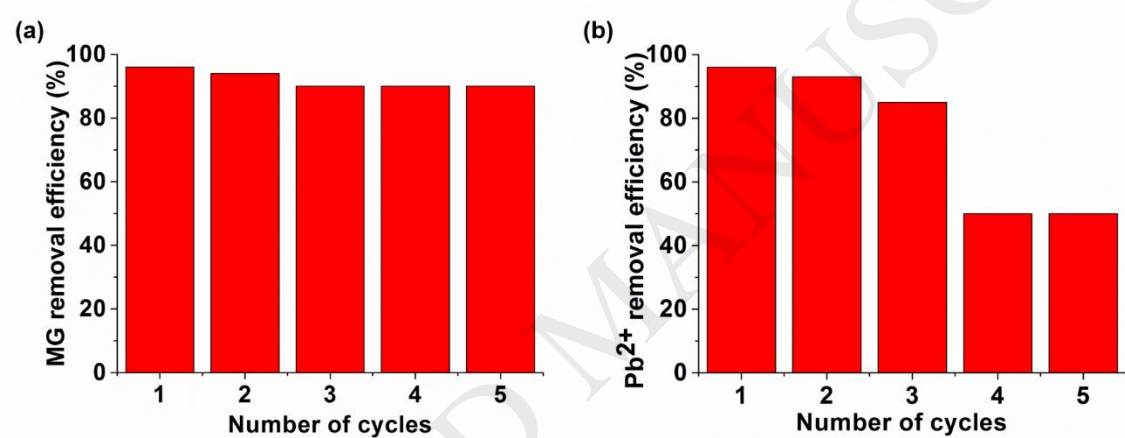
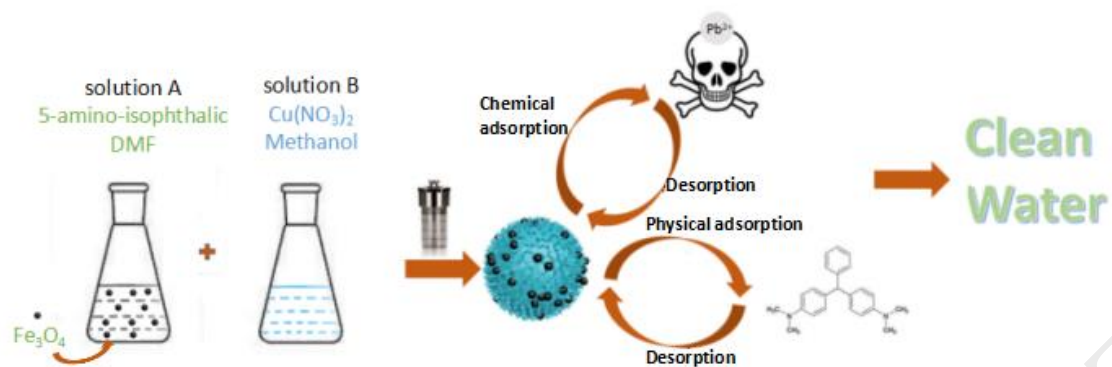


Fig. 11 Recyclability of Cu-MOFs/Fe₃O₄ composite for MG and Pb²⁺ adsorption.



Scheme 1 Schematic illustration the synthesis of Cu-MOFs/Fe₃O₄ composite for removal of MG and Pb(II).

Table 1 Comparison of the Maximum adsorption capacity

| Sample | Adsorbents | Adsorption capacity (mg/g) | References |
|------------------|--|----------------------------|------------|
| Pb ²⁺ | γ -Fe ₂ O ₃ nanoparticles | 48.90 | [38] |
| | Fe ₃ O ₄ @SiO ₂ -EDTA | 114.94 | [39] |
| | Fe ₃ O ₄ /Cu-MOFs | 219.00 | This work |
| MG | Avena sativa (oat) hull | 83.00 | [40] |
| | Diatomite | 23.64 | [41] |
| | Fe ₃ O ₄ /Cu-MOFs | 113.67 | This work |

Table 2 Relative parameters of thermodynamic equilibrium.

| Sample | T(K) | K | $\Delta H(\text{kJ}\cdot\text{mol}^{-1})$ | $\Delta S(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$ | $\Delta G(\text{kJ}\cdot\text{mol}^{-1})$ |
|------------------|------|-------|---|--|---|
| MG | 298 | 3.26 | | | -2.99 |
| | 308 | 6.75 | 49.75 | 176.82 | -4.76 |
| | 318 | 11.49 | | | -6.53 |
| Pb ²⁺ | 298 | 0.88 | | | -1.45 |
| | 308 | 1.19 | 28.76 | 101.39 | -2.47 |
| | 318 | 1.83 | | | -3.48 |

Table 3 Removal efficiency of Cu-MOFs/Fe₃O₄ composite for adsorption MG and Pb²⁺ in real water sample. Final concentration of the solution before (a) and after (b) adsorption by Cu-MOFs/Fe₃O₄ composite.

| Sample | Added | Concentration (mg L ⁻¹) ^a | Found (mg L ⁻¹) ^b | Removal efficiency (%) |
|--------|------------------|--|--|------------------------|
| 1 | Pb ²⁺ | 100.00 | 13.25 | 86.75 |
| | MG | 46.35 | 3.83 | 91.73 |
| 2 | Pb ²⁺ | 10.00 | 0.70 | 93.00 |
| | MG | 46.35 | 3.24 | 93.01 |
| 3 | Pb ²⁺ | 100.00 | 12.46 | 87.54 |
| | MG | 4.64 | 0.47 | 89.92 |
| 4 | Pb ²⁺ | 10.00 | 0.57 | 94.35 |
| | MG | 4.64 | 0.39 | 91.49 |