Synthesis and adsorption properties of $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}/\text{Fe}_3\text{O}_4$ nanocomposites†

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Multifunctional $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}/\text{Fe}_3\text{O}_4$ (HL = pyridine-2-carboxamide) nanocomposites were successfully synthesized by combining $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}$ and $\text{Fe}_3\text{O}_4$ nanoparticles. The characterization was performed by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM), X-ray powder diffraction (XRD) and ultraviolet-visible light absorbance spectrometry (UV-vis). The XRD and TEM analyses reveal that the nanocomposites possess high crystallinity with an average particle size of $\sim 19.43 \text{ nm}$. The VSM and UV-vis demonstrate excellent superparamagnetic behavior and two well-behaved absorption bands of the nanocomposites. The adsorption activity of the nanocomposites was investigated using methylene blue, gentian violet, safranine T, fuchsin basic, methyl orange and Sudan red (III) as probe molecules, and the results reveal that the $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}/\text{Fe}_3\text{O}_4$ nanocomposites have selective adsorption behavior for organic dyes. The recycling performance was observed using basic fuchsin, and the results demonstrate that the nanocomposites exhibit good recyclability and high stability. The $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}/\text{Fe}_3\text{O}_4$ nanocomposites have a promising future for magnetic, optical and biomedical applications.

Polyyoxometalates (POMs) are a well-known class of inorganic clusters consisting of a metal-oxygen framework, which have shown unique physicochemical properties and various applications owing to their highly electronegative and oxo-enriched surfaces, controllable shape and size, tunable acid-base, redox, magnetic, catalytic, and photochemical properties. On the other hand, magnetic $\text{Fe}_3\text{O}_4$ nanoparticles are most widely known for their exceptional physicochemical properties, low cost, non-toxic nature as well as environmentally benign for industrial scale synthesis of fine chemicals. The interdisciplinary integration of POMs and $\text{Fe}_3\text{O}_4$ nanoparticles has accelerated with fundamental curiosity and promising applications. Previously we have prepared $\text{Fe}_3\text{O}_4$ nanoparticles and their hybrids for the promising applications of heterogeneous catalysis, biological medicine, magnetofection, photo-therapy after magnetic separation, simultaneous photo-therapy and hyperthermia. Herein, we report a facile route for the synthesis of $[\text{Cu(L)}_2(\text{H}_2\text{O})]_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})] \cdot 4\text{H}_2\text{O}/\text{Fe}_3\text{O}_4$ nanocomposites using the ultrasonic technique.

Now, a large number of dye-waste water discharged pose a significant threat to the water environment and human health due to their toxicity and even carcinogenicity. It is urgently-needed to find desirable adsorption materials, which not only reduce the pollutant organic dyes with high efficiency and low lost, but also realize selective separation and recovery. The use of nanomaterials as efficient catalysts in aqueous medium has

1 Introduction

In recent years, polyoxometalate/nanoparticle nanocomposites (POMs/NPs) based on polyoxometalates and nanoparticles have attracted considerable interest due to their unique properties resulting from the combination of the polyoxometalates and the nanoparticles. Research has been dedicated to the fabrication of POMs/NPs with a wide variety of POMs and NPs such as $\alpha$-$\text{K}_2\text{P}_2\text{W}_{18}\text{O}_{62}/\text{Pt}$, $\text{Na}_{12}\text{P}_2\text{W}_{15}\text{O}_{56} \cdot 18 \text{H}_2\text{O}/\text{Pt}$, $\text{Na}_3\text{EuW}_{10}\text{O}_{36} \cdot 32 \text{H}_2\text{O}/\text{Pt}$, $[\text{NH}_4]_4\text{Na}_3\text{P}_3\text{W}_{30}\text{O}_{110} \cdot 31 \text{H}_2\text{O}/\text{Fe}_3\text{O}_4$, $\text{H}_2\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$, $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}/\text{TiO}_2$, $[\text{SiW}_7\text{V}_{2}\text{O}_{40}]^{7-}/\text{Bi}_2\text{O}_3$, and $\alpha$-$\text{SiW}_{12}\text{O}_{40}{\text{H}_4}^+/\text{Ag}$ to explore the synergistic properties arising from the nanocomposites. POMs/NPs have successfully been employed for biocatalysis, electrocatalysis, photocatalysis, oxidation of alkenes, bio-sensing, and medicinal chemistry. The assembly of POMs/NPs can provide a path for exhibiting their unique properties in many fields, and the complex structure makes them attractive for future study.

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2 Materials and methods

2.1 Materials

Copper(n) perchlorate hexahydrate (Cu(ClO4)2·6H2O, 98%), pyridine-2-carboxamide (C22H17ClN2, 98%), sodium molybdate dihydrate (Na2MoO4·2H2O, 99%) and phosphoric acid (H3PO4, 85%) were purchased from J&K Scientific Ltd. Iron(n) acetylacetonate (Fe(acac)3, 99.9%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEO–PPO–PEO, Mn = 5800), octyl ether (C8H17OC8H17, 99%), 1,2-hexadecanediol (C14H29CH(OH)CH2(OH), 90%), DMF (HCON(CH3)2, 99.5%), 1,2-ethylene glycol (C2H4(OH)2, 99%), and solvents such as hexane and ethanol were purchased from Aldrich. All materials were used as received without further processing. Distilled water was used throughout.

2.2 Synthesis of Fe3O4 nanoparticles

The Fe3O4 nanoparticles were synthesized according to the reported literature method. A typical experiment was carried out in a 100 mL flask, 0.2541 g of iron(n) acetylacetonate, 0.7859 g of PEO–PPO–PEO as the surfactant, and 0.6468 g of 1,2-hexadecanediol were dissolved in 10 mL octyl ether under vigorous stirring. Subsequently, the reaction mixture was slowly heated to 125 °C within 1 h, homogenized for 1 h at 125 °C, then rapidly heated to 280 °C within 15 min and refluxed at the temperature for 1 h to complete the reaction. After cooling down to room temperature, the black precipitate products was washed with mixed solvents of ethanol/hexane (v/ethanol/hexane = 2:1) several times, and re-dispersed in hexane for further use.

2.3 Synthesis of [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O

The [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O was synthesized using the method similar as the literature method. An aqueous solution containing Cu(ClO4)2·6H2O (0.093 g, 0.25 mmol) and pyridine-2-carboxamide (0.061 g, 0.5 mmol) was stirred at 50 °C for 0.5 h. After cooling to room temperature the solution was added to a 10 mL aqueous solution of Na2MoO4·2H2O (0.242 g, 1.0 mmol), the pH value was maintained at 3 by dropwise adding of concentrated H3PO4 under continuous stirring. Then the mixture was stirred for 0.5 h and then filtered. By filtering the mixture, the powders were stored for the following synthesis. The filtrate was allowed to evaporate at room temperature. After 3 days blue crystals suitable for X-ray studies were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 38.4% based on Mo. Anal calc. for C24H34Cu2Mo5N8O32P2 (1615.30): C, 17.85; H, 2.12; N, 6.94; Cu, 7.87; Mo, 29.70. Found: C, 17.85; H, 2.14; N, 6.92; Cu, 7.88; Mo, 29.66. IR (KBr, cm−1): 3430 (w), 3082 (w), 1716 (m), 1684 (s), 1633 (w), 1565 (m), 1497 (m), 1440 (s), 1307 (w), 1278 (w), 1169 (w), 1133 (m), 1058 (s), 1035 (m), 928 (s), 904 (s), 758 (m), 682 (s), 525 (w).

2.4 Synthesis of [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O/Fe3O4

[Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O/Fe3O4 nanocomposites were prepared by an ultrasonic procedure. A typical synthesis was carried out in a 50 mL beaker, Fe3O4 nanoparticles (5 mg), [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O powders (50 mg) were added in a beaker containing water (10 mL) and ethanol (10 mL) in sequence and obtained an uniform and turbid liquid by ultrasound about 10 h. After the completion of the reaction, the resulting products was collected using a magnet putting on one side of the beaker to separate them from the turbid liquid. The magnetic products were [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O/Fe3O4 nanocomposites, which was washed with water several times.

2.5 Structural characterization and measurements of the nanocomposites

The structures of the synthesized Fe3O4 nanoparticles, [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O and [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O/Fe3O4 nanocomposites were analyzed by X-ray powder diffraction (XRD, X'Pert Pro) and transmission electron microscopy (TEM, JEOL2010F). The UV–vis spectra were measured by an ultraviolet-visible light absorbance spectrometry (UV–vis, HitachiU4100). In the Fourier transform infrared spectroscopy (FTIR) studies, Fe3O4 nanoparticles, [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O and [Cu(L)2(H2O)]H2[Cu(L)2(P2Mo5O23)]·4H2O/Fe3O4 nanocomposites were separately crushed with a pestle in an agate mortar. The individually crushed material was mixed with KBr in about 1 : 100 proportion. The mixture was then compressed into a 2 mm semi-transparent disk by applying a force of 10 T for 2 min. The Fourier transform infrared spectra were recorded in the wavelength range of 500–4000 cm−1 using an Avatar 360 FTIR spectrometer (FTIR, Nicolet Company, USA). The magnetic properties were subsequently investigated by a vibrating sample magnetometry (VSM, Lakeshore 7300).

2.6 Crystallography

Crystallographic data were collected with a Bruker SMART-CCD APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares on F² with
Table 1 Summary of crystal data and refinement results for [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O

| Parameter               | Value                  |
|-------------------------|------------------------|
| Crystal data            | [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O |
| Empirical formula       | C_{24}H_{34}Cu_2Mo_5N_8O_{32}P_2 |
| \( f_{o} \)             | 1615.30                |
| Cryst syst              | Triclinic              |
| Space group             | P1                     |
| \( T \) (K)             | 296(2)                 |
| \( a \) (Å)             | 10.187(3)              |
| \( b \) (Å)             | 10.918(3)              |
| \( c \) (Å)             | 20.739(5)              |
| \( \alpha \) (deg)      | 82.052(4)              |
| \( \beta \) (deg)       | 89.700(5)              |
| \( \gamma \) (deg)      | 88.467(5)              |
| \( V \) (Å^3)           | 2283.6(10)             |
| \( Z \)                 | 2                      |
| \( \Delta l \) (g cm^{-1}) | 2.335             |
| \( \mu \) (mm^{-1})     | 2.423                  |
| Crystal size (mm)       | 0.27 \times 0.18 \times 0.15 |
| \( \theta \) (deg)      | 1.983-25.098           |
| \( \delta \) (mm^{-1})  | 0.0551, 0.1396         |
| hkl range               | -12 \leq h \leq 9,    |
|                         | -12 \leq k \leq 12,   |
|                         | -24 \leq l \leq 24    |
| GOF on \( F^2 \)        | 0.999                  |
| \( R \) (int)           | 0.0433                 |
| No. param               | 671                    |
| Refl. measured/unique   | 8012/5810              |
| \( R_1 \), \( wR_2 \) [I \geq 2\sigma(I)] | 0.0551, 0.1396 |
| \( R_1 \), \( wR_2 \) [all data] | 0.0818, 0.1601 |
| \( \Delta l_{max}, \Delta l_{min} \) (e Å^{-3}) | 1.821, -1.678 |

3 Results and discussion

3.1 Crystal structure description of compound [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O

Selected bond distances and angles for [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O are given in Table 2. The molecular structures along with the atom numbering scheme are depicted in Fig. 1.

2.7 Characterization of adsorption activity

The adsorption activities of the nanocomposites were performed in the dark by measuring the adsorption rate of different dye solutions at room temperature. The dye solutions such as methylene blue, gentian violet, safranine T and fuchsin basic, methyl orange and Sudan red (III) were prepared with a concentration of 15 mg L^{-1} by dissolving the dye powder in distilled water. The reaction was conducted with 50 mg of the adsorbents dispersed in 20 mL of 15 mg L^{-1} fuchsin basic. After each cycle, the adsorbed fuchsin basic were separated from aqueous solution by a piece of magnet and washed with a solvent DMF about 20 mL at room temperature to remove the adsorbed fuchsin basic. Then, the regenerated [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O nanocomposites were added to the initial dye solution of fuchsin basic (20 mL of 15 mg L^{-1}). The concentrations of fuchsin basic solution were determined by measuring the absorbance through a UV-vis spectrophotometer (Beijingpxitongyong TU-1900).

2.8 Characterization of desorption, reusability activities

In order to investigate the regeneration of the adsorbents during the adsorption experiments, a solvent DMF is chosen as the eluents. The stability and reusability of the nanocomposites on removing fuchsin basic were investigated through cycle tests. The fuchsin basic solution was prepared with a concentration of 15 mg L^{-1} by dissolving the dye powder in distilled water. The reaction was conducted with 50 mg of the adsorbents dispersed in 20 mL of 15 mg L^{-1} fuchsin basic. After each cycle, the adsorbed fuchsin basic were separated from aqueous solution by a piece of magnet and washed with a solvent DMF about 20 mL at room temperature to remove the adsorbed fuchsin basic. Then, the regenerated [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O nanocomposites were added to the initial dye solution of fuchsin basic (20 mL of 15 mg L^{-1}). The concentrations of fuchsin basic solution were determined by measuring the absorbance through a UV-vis spectrophotometer (Beijingpxitongyong TU-1900).

![Fig. 1 Structure of [Cu(L)_2(H_2O)]_2[H_2][Cu(L)_2(P_2Mo_5O_23)]·4H_2O with atomic numbering scheme.](image-url)
Single-crystal X-ray structural analysis exhibits that \([\text{[CuL}_2](\text{H}_2\text{O})]_2[\text{H}_2\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) crystallizes in \(P1\) space group. In addition, Fig. 1a shows that compound \([]\text{[CuL}_2](\text{H}_2\text{O})\]_2\text{H}_2\text{[CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) consists of \([\text{[CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})]^{2-}\) polyanion, \([\text{[CuL}_2]^2\] complex fragments and four water molecules in the structural unit of compound \([\text{[CuL}_2](\text{H}_2\text{O})]_2[\text{H}_2\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\). As is well known, the \(\text{P}_2\text{Mo}_5\text{O}_{23}\) cluster can be viewed as two \([\text{PO}_4]\) tetrahedral capping either side of an irregular ring of five distorted \([\text{MoO}_6]\) octahedron linked by one corner-shared and four edge-shared contacts. Each phosphate subunit shares three oxo-groups with the molybdate ring. One of these oxo-groups adopts a \(\mu_2\)-bridging mode, linking one molybdenum atom and a phosphorus atom; while the other two adopt a \(\mu_3\)-bridging mode, linking two molybdenum atoms and a phosphorus atom. Each of two Cu atoms adopts a five-coordinated distorted \([\text{CuN}_2\text{O}_3]\) square-pyramidal geometry surrounded by two pyridine-2-carboxamide ligands and one O atom from \(\text{P}_2\text{Mo}_5\text{O}_{23}\) cluster or one water, respectively. The Cu(1) is coordinated by two N (amide) atoms with Cu–N bond lengths of 1.968(9)–1.970(9) Å, two O (amide) atoms with Cu–O bond lengths of 1.958(7)–1.960(7) Å and one O (qua) atom with Cu–Ow bond lengths of 2.169(7) Å. The Cu(2) atom is coordinated by two N (amide) atoms with Cu–N bond lengths of 1.961 (9)–1.978(9) Å, one O atom of \([\text{MoO}_6]\) octahedron with Cu–O bond lengths of 2.231(7) Å, and two O (amide) atom with Cu–Ow bond lengths of 1.930(7)–1.945(7) Å.

3.2 IR spectroscopy

Fig. 2 compares the FTIR spectra of \(\text{Fe}_3\text{O}_4\) nanoparticles, \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) and \([\text{[CuL}_2](\text{H}_2\text{O})]_2[\text{H}_2\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO nanoparticles. In Fig. 2b, the \(\text{Fe}_3\text{O}_4\) nanoparticles show one strong characteristic band at the position of 600 cm\(^{-1}\) which is associated with the stretching vibration mode of Fe–O.\(^{32-34}\) The IR spectrum of \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) has been depicted in Fig. 2c. It is evident that the characteristic band at 3378 cm\(^{-1}\) is attributed to the O–H stretching vibration of water, while the peaks at 3072 cm\(^{-1}\) are related to the \(\text{N}–\text{H}\) of pyridine-2-carboxamide. A series of strong bands in the range of 1684–1133 cm\(^{-1}\) is also associated with pyridine-2-carboxamide. Bands in the region of 1120–1008 cm\(^{-1}\) are assigned to \(\text{P}–\text{O}\) stretching vibration.\(^{35,36}\) The peaks at 908 cm\(^{-1}\) and 672 cm\(^{-1}\) are attributed to \(\text{N}–\text{O}\) and \(\text{N}–\text{O}–\text{Mo}\), respectively.\(^{36}\) As given in Fig. 2a, these characteristic vibration and bending modes reappear in the FTIR spectrum of the \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO nanoparticles, but instead shifting to the positions of 3389 cm\(^{-1}\) for the O–H stretching vibration and 3174 cm\(^{-1}\) for the \(\text{N}–\text{H}\) of pyridine-2-carboxamide. The result is that \(\text{Fe}_3\text{O}_4\) and \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) are existed in \([\text{[CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})]^{2-}\cdot\text{H}_2\text{O}\) FeO nanoparticles, which demonstrates the synthesis of \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO nanoparticles.

3.3 UV-vis spectroscopy

The optical property of \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO nanoparticles were assessed by UV-visible absorption spectroscopy. Fig. 3a–c shows the UV-vis spectra of \([\text{[CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO nanoparticles, \([\text{CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\), FeO (a), \([\text{CuL}_2](\text{H}_2\text{O})]_2\text{H}_2[\text{CuL}_2](\text{P}_2\text{Mo}_5\text{O}_{23})_4\cdot\text{H}_2\text{O}\) FeO (b) and FeO (c) dispersed in H\(_2\)O.
nanocomposites were recorded by TEM and HRTEM. As given in Fig. 4a, the obtained \([\text{Cu(L)}_2(\text{H}_2\text{O})]\)\(_2\)\([\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\)\(_4\)\(\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites are virtually uniform and nearly spherical in shape with seldom aggregation. The histograms in Fig. 4b shows the size distribution of \([\text{Cu(L)}_2(\text{H}_2\text{O})]\)\(_2\)\([\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\)\(_4\)\(\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites, which are reasonably described by the Gaussian function, showing tight size distribution with average sizes of approximately 19.43 nm in diameter. Fig. 4c represents the HRTEM image of a single \([\text{Cu(L)}_2(\text{H}_2\text{O})]\)\(_2\)\([\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\)\(_4\)\(\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposite. As labeled, the spacing of 2.85 Å corresponds to the (220) reflection of the \(\text{Fe}_3\text{O}_4\) phase. Moreover, with a higher magnification than in Fig. 4a of the same sample, a thin layer with ~1 nm uneven thickness is clearly observed in Fig. 4c. We think that this similarly may be the example of observation of such kind of \([\text{Cu(L)}_2(\text{H}_2\text{O})]\)\(_2\)\([\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\)\(_4\)\(\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) core–shell structure.

3.5 XRD patterns

As shown in Fig. 5, the structure of the \([\text{Cu(L)}_2(\text{H}_2\text{O})]\)\(_2\)\([\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\)\(_4\)\(\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites was recorded by XRD.
and analyzed together with the results of Fe$_3$O$_4$ and [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O. Fig. 5a represents the diffraction pattern obtained from the [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites, in match to the standard diffraction peaks of the corresponding Fe$_3$O$_4$ (JCPDS No.88-0315), the diffraction peaks positioning at 30.2°, 35.6°, 43.2°, 57.3° and 62.7° are indexed to the (220), (311), (400), (511) and (440) planes of the Fe$_3$O$_4$ nanoparticles. Fig. 5b represents the diffraction pattern obtained from the [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O and Fe$_3$O$_4$ are included in [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites.

### 3.6 Magnetic property of [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$

The magnetic property of [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites was studied by VSM. Fig. 6a and b show the hysteresis curves of Fe$_3$O$_4$ nanoparticles and [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites at 300 K, respectively. It is clear that [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites show superparamagnetic behavior with a coercivity tend to ~9.0 Oe and magnetization of ~2.37 emu g$^{-1}$ comparing with a coercivity tend to ~90 Oe and magnetization of ~16.10 emu g$^{-1}$ of Fe$_3$O$_4$ nanoparticles.

### 3.7 Separation and aggregation process of [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$

Fig. 7 visually demonstrates the separation and aggregation process of the [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites in water.

Under the influence of an external magnetic field, [Cu(L)$_2$(H$_2$O)]H$_2$[Cu(L)$_2$(P$_2$Mo$_5$O$_{23}$)]·4H$_2$O/Fe$_3$O$_4$ nanocomposites can be easily collected by a magnet in a water body.
nanocomposites in water change from a purplish grey, homogeneous dispersion (Fig. 7a) to a clear, transparent solution, with the nanocomposites collected by a piece of magnet (Fig. 7b). The collected nanocomposites can be easily and reversibly dispersed by agitation after removal of the magnetic field and the above process can be repeated. The finding that all $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites as prepared could be collected by a magnet, leaving no free $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ visible. In other words, we performed magnetic separation and found that all nanocomposites were collected by the magnet because the $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites are magnetic and there is no more nanoparticles left-over, so nonmagnetic $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O}$ are not present in the samples.

### 3.8 Adsorption properties

Organic dyes such as methylene blue, gentian violet, safranine T and fuchsin basic are important organic dyes which are widely used as a colorant in textiles and food stuffs the dyes are harmful if swallowed by human beings and animals, causing irritation to the skin, eye and respiratory tract. Their breakdown products in the water may be toxic, carcinogenic or mutagenic to life forms, and they have been shown to cause retching, stun, cyanosis, jaundice and tissue necrosis in human. Therefore, an effective and optimal strategy to degrade the dyes rapidly must be developed. In the design of an economical wastewater disposal system, fast adsorption rate is also an important parameter for design and synthesis of the efficient adsorbent.

We investigated the adsorption of $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites using organic dyes such as methylene blue, gentian violet, safranine T, fuchsin basic, methyl orange and Sudan red (III) as probe molecules. Fig. 8 show that $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites were able to adsorb the methylene blue, gentian violet, safranine T and fuchsin basic efficiently in the dark. The intensity of UV-visible absorption peak of each dyes decreases with the increase of time due to the existence of $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites, and the adsorption efficiency of methylene blue, gentian violet, safranine T and fuchsin basic were 79%, 91%, 64% and 83% in 12 min, 45 min, 60 min and 120 min, respectively. In addition, the peak patterns of each dyes are slightly similar and the peak positions are the same except gentian violet which may be due to itself of gentian violet. Fig. 9 show that $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites were not able to adsorb the methyl orange, Sudan red (III) efficiently in the dark. The intensity of UV-visible absorption peak of methyl orange and Sudan red (III) both are almost constant. The reason of the same adsorbent with different effects on removal of dyes is related to the structure of the dye molecules and the structure of the $[\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2\text{[Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{]}\cdot 4\text{H}_2\text{O/Fe}_3\text{O}_4$ nanocomposites.

POMs, as an outstanding family of metal-oxide clusters with controllable shape and size, highly electronegative, and oxo-enriched surfaces, are expected to exhibit good adsorption towards cationic dyes. Firstly, POMs are a kind of hydrophilic metal-oxo cluster compounds. The hydrophilic/hydrophobic property of the framework is modulated by encapsulating the POM molecules, which allows the ingress and egress of the dye molecules. Secondly, POMs with a large number of negative charges encapsulated in the neutral framework may have a stronger force with the positive charges of dyes. The approving...
result is that \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites exhibit rapid adsorption efficiency and high uptake capacity towards methylene blue, gentian violet, safranine T and fuchsin basic than methyl orange, Sudan red (III), which is in accord with literature.\(^{45}\) The magnetic \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites combining \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}和\text{Fe}_3\text{O}_4\) nanoparticles could be collected in adsorption process preferably.

3.9 Stability and reusability behaviours

The stability and reusability of the nanocomposites are another important standard for practical application. It can be seen from the process of magnetic aggregation and dispersion that the \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) are not the mixture of \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O} and \text{Fe}_3\text{O}_4\) nanoparticles but a new nanocomposite, although it is still a challenge to identify the interaction between POM species and magnetic particles. The in-depth study is on the way. As shown in Fig. 10, the IR patterns of the adsorbents regenerated from adsorption and desorption experiments match well with the as-synthesized product, indicating that the structure of the nanocomposites remain intact, which confirms their good stability and recyclability. The properties are significant in improving the use of material without loss of their structure and reducing the adsorption cost. In a word, the nanocomposites are of great significance for the practical use of the absorbents and exhibit good reproducibility.

After adsorption experiments, the adsorbed fuchsin basic can be removed by a solvent DMF. In Fig. 11, it shows that the photographs of three adsorption and desorption cycles. When a solution of DMF was added, digital images show that fuchsin basic molecules in the nanocomposites can be rapidly released. Then, the regenerated \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites were added to the initial fuchsin basic solution (20 mL of 15 mg L\(^{-1}\)), the adsorbents are still capable of removing fuchsin basic up to 91%, 93% and 90% over one cycles, two cycle, three cycle, respectively, as shown in Fig. 12. This means that the dye release is also an ion-exchange process, which also further demonstrate that ionic interaction between dyes and anionic framework is main determinant for selective adsorption and separation of dyes.\(^{46}\)

4 Conclusions

In summary, we have successfully synthesized the nanocomposites of \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) that combining \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O} and \text{Fe}_3\text{O}_4\) nanoparticles. The UV-vis measurement shows the well-defined optical absorption with the nanocomposites dispersed in \(\text{H}_2\text{O}\). The magnetic characterization shows that \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites have superparamagnetic behavior. The dispersion-collection processes in \(\text{H}_2\text{O}\) of the \([\text{Cu(L)}_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu(L)}_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\text{H}_2\text{O}/\text{Fe}_3\text{O}_4\) nanocomposites were...
demonstrated for application readiness. [Cu(L)2(H2O)]H2-
[Cu(L)2(P2MoO7]·4H2O/Fe2O4 nanocomposites have selective adsorption behavior for organic dyes. Meanwhile, the stable and reusable [Cu(L)2(H2O)]H2[Cu(L)2(P2MoO7]·4H2O/Fe2O4 nanocomposites were found to be a good adsorbent and could be employed as an effective adsorbent applicable in adsorption field.

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