Synergistic Photocatalytic-adsorption Removal of Basic Magenta Effect of AgZnO/polyoxometalates Nanocomposite

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Abstract

The bifunctional photocatalytic-adsorbent AgZnO/polyoxometalates (AgZnO/POMs) nanocomposites were synthesized by combining AgZnO hybrid nanoparticles and polyoxometalates $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})]\text{H}_2[\text{Cu}(\text{L})_2(\text{P}_2\text{Mo}_5\text{O}_{23})]\times 4\text{H}_2\text{O}$ ($\text{HL} = \text{C}_6\text{H}_6\text{N}_2\text{O}$) into nanostructures via a sonochemical method. Transmission electron microscopy (TEM) indicated that AgZnO/POMs nanocomposites were uniform with narrow particle size distribution and without agglomeration. X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis confirmed the nanostructure and composition of AgZnO/POMs nanocomposites. The ultraviolet-visible spectra (UV-vis) and photoluminescence spectra (PL) confirmed excellent optical properties of the AgZnO/POMs nanocomposites. 94.0% of basic magenta (BM) in aqueous solution could be removed using the AgZnO/POMs nanocomposites through adsorption and photocatalysis. The kinetic analysis showed that both the adsorption and photocatalysis process conform to pseudo-second-order kinetics. In addition, the removal efficiency of AgZnO/POMs nanocomposites was found to be almost unchanged after 5 cycles of use. The bifunctional photocatalytic-adsorbent AgZnO/POMs nanocomposites with high stability and cycling performance have broad application prospects in the treatment of refractory organic dye wastewater containing triphenylmethane.

1. Introduction

With the development of industry, a large number of toxic and harmful organic wastewater has caused a series of environmental problems, which seriously threaten human health [1–4]. Basic magenta (BM) is a kind of refractory organic pollutant containing triphenylmethane. BM is widely used as a coloring, in industries such as textile and leather, and also as a colorant for the stain of collagen, tuberculosis and muscle [5, 6]. It is urgently needed to be removed from the aqueous solution for the reason of that BM poses a great threat to water resources due to its poor biodegradability, toxicity and carcinogenicity. According to the literature, the removal method of BM in aqueous solution is mainly adsorption [7, 8]. However, the application of BM dye adsorbents subject to the disadvantages of low adsorption capacity, slow kinetic speed and low recovery potential. It is still a challenge to explore a cleaner and more effective method to remove BM from aqueous solution.

Polyoxometalates (POMs), a promising adsorbent, has been applied in environmental protection because of their rich composition and structure, high thermal stability, adjustable acidity and reversible redox properties et al [9–13]. As adsorbent, POMs have been used to synthesize a variety of materials to remove different dyes from aqueous solutions [14–17]. Liu's research group has reported a case of $\text{Fe}_3\text{O}_4/\text{POMs}$ nanomaterial with good adsorption performance for removal of cationic dyes, and a case of $\text{Fe}_3\text{O}_4/\text{Ag}/\text{POMs}$ nanomaterial with rapid removal of methylthionine chloride, indicating that more effective dye removal enhancement performance could be obtained by combining POMs and nanoparticles into a single entity through nanoengineering [18, 19].

AgZnO hybrid nanoparticles have excellent photocatalytic activity and are widely used in the field of photocatalysis. The addition of Ag improves photocatalytic capacity of AgZnO and the charge utilization efficiency and photochemical stability of ZnO [20–24]. Photocatalytic activity of AgZnO nanoparticles has photocatalytic effect on dyes in aqueous solution [25, 26]. In order to explore an effective and environmentally friendly method for removing BM dye in aqueous solution, in this paper, we combined AgZnO hybrid nanoparticles and POMs to obtain bifunctional photocatalytic-adsorbent AgZnO/POMs nanocomposites. The removal experiments of BM demonstrated that photocatalytic-adsorbent AgZnO/POMs nanocomposites possessed both adsorption and photocatalytic effects on BM in aqueous solution with emerging high removal efficiency. The good adsorption, photocatalytic activity and reusability of the nanocomposites indicated that the bifunctional photocatalytic-adsorbent AgZnO/POMs nanocomposites are beneficial to protecting the environment.

2. Experiment Section

2.1. Materials

Silver acetate (Agac, 99%), Zinc(II) acetylacetonate ($\text{Zn}(\text{acac})_2$, 99.9%), PEO-PPO-PEO, n-octyl ether (99%), 1,2-hexadecanediol (90%), Copper perchlorate ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 98%), Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 99%), Pyridinecarboxamide ($\text{C}_6\text{H}_6\text{N}_2\text{O}$, 98%), and NaOH (98%) were purchased from Aladdin company (Shanghai, China). None of the materials were further purified.

2.2. Synthesis of photocatalytic-adsorbent AgZnO/POMs nanocomposites

The AgZnO and polyoxometalates $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]\text{H}_2[\text{Cu}(\text{L})_2\text{P}_2\text{Mo}_5\text{O}_{23}] \cdot 4\text{H}_2\text{O}$ (Cu-POMs) samples were synthesized using the method reported in the literature [21, 19]. Firstly, AgZnO hybrid nanoparticles were synthesized, 10 mL of octyl ether, $\text{Zn}(\text{acac})_2$ (0.0989 g), 1,2-hexadecanediol (0.6468 g), Agac (0.0259 g) and PEO-PPO-PEO (0.7874 g) were added to a three-necked flask stir the mixture. The mixture was heated to 125°C, then quickly raised to 280°C, the experiment was completed. When the temperature is cooled, the AgZnO hybrid nanoparticles were taken out and washed, obtaining pure AgZnO hybrid nanoparticles. Then, Cu-POMs was synthesized, copper perchlorate (0.093 g), 2-pyridinecarboxamide (0.061 g), and 15 mL of deionized water were added to a beaker, and stirred and mixed. When the temperature was cooled to room temperature, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.24 g), and deionized water (10 mL) were added to the solution and mixed well, and keep pH was maintained at 3. The blue precipitate Cu-POMs was obtained by filtration. A mixture of reactants was obtained by adding 50 mg POMs powders and 5 mg AgZnO hybrid nanoparticles into beaker containing 5 mL water and 5 mL ethanol, then ultrasound to obtain a uniform liquid. This process combines the AgZnO hybrid nanoparticles with Cu-POMs to form nanostructures. Finally, the samples were dried to obtain a bifunctional AgZnO/POMs nanocomposite with both photocatalysis and adsorption effects.

2.3. Analysis

The structure and morphology of the photocatalytic adsorbent AgZnO/POMs nanocomposites were analyzed by XRD (X'Pert Pro, Bruker, Germany) and TEM (JEM-2100 JEOL Ltd., Japan) including HRTEM. The optical properties of photocatalytic adsorbent AgZnO/POMs nanocomposites were characterized by UV-vis (Hitachi U4100, Japan) and PL spectroscopy (Hitachi F7000, Japan). The FTIR spectra of nanocomposites were recorded using Avatar 360 FTIR spectrometer (Nicolet Company, USA). The XPS were performed on photoelectron spectrometer (Thermo Fisher Scientific ESCALAB 250XI, United States) Al K α X-ray used as the excitation source.

2.4. Dye removal experiment

The removal activity was researched by analysing the removal efficiency of BM from aqueous solution. In the removal experimental study, a 36 W UV lamp (Philips, Netherlands, emitting mainly 365 nm) and a 500 W Xenon lamp as light source. The dye was dissolved in water to prepare 15mg/L BM aqueous solution (room temperature condition, pH = 6.3). The 5 mg nanocomposites were added into 40 mL (15 mg/L) BM solution for experiments. The solution was magnetically stirred at room temperature. At different time intervals, the about 5 mL solution was removed and centrifuged for 3 min. The absorption peak intensity of BM at the maximum wavelength of 545 nm was analyzed by UV-Vis spectrophotometer.

3. Results And Discussion

3.1. TEM analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

The particle size distribution and morphology of photocatalytic-adsorbent AgZnO/POMs nanocomposites were analyzed by TEM and SEM. In Fig. 1a, the AgZnO/POMs nanocomposites are uniform particles size without agglomeration. By measuring the TEM micrographs of AgZnO/POMs nanocomposites, the histogram of particle size distribution was obtained. The average particle size of AgZnO/POMs nanocomposites was about 19.5 nm, which was consistent with the Gaussian distribution. Figure 1b is the HRTEM image of AgZnO/POMs nanocomposite. Apparently, the nanocomposites are distributed with highly regular lattices, which the spacing of 1.44 Å corresponds to the Ag (220) plane, while the spacing of 2.47 Å is ZnO (101) planes. A spacing of about 1 nm between the blue dotted line and the green dotted line may be distributed with POMs [27]. Element mapping (Fig. 1(c-k)) confirmed the distribution of P, O, Ag, Cu, Mo, N, C and Zn in the AgZnO/POMs nanocomposites, showed that AgZnO and POMs existed simultaneously in AgZnO/POMs nanocomposites. The results confirmed the formation of photocatalytic adsorbent AgZnO/POMs nanocomposites.

3.2. XRD analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

The structure of prepared photocatalytic adsorbent AgZnO/POMs nanocomposites was analyzed by XRD. In Fig. 2c, the diffraction peaks marked by the purple column diagrams of AgZnO hybrid

nanoparticles at 38.2°, 44.4°, 64.6° and 77.4° correspond to the characteristic peaks of Ag (JCPDS No. 04-0783). The peaks marked by the blue column diagrams at 31.7°, 34.5°, 36.5°, 47.6°, 56.7°, 62.8° and 67.7° correspond to ZnO (JCPDS No. 36-1451) characteristic diffraction peak. The peaks at 8.7°-30.7° in Fig. 2b are the diffraction peaks of POMs [19]. In the diffraction pattern of photocatalytic adsorbent AgZnO/POMs nanocomposites (Fig. 2a), the diffraction peaks of POMs (Fig. 2b) and AgZnO hybrid nanoparticles (Fig. 2c) reappear simultaneously. The results confirmed the formation of AgZnO/POMs nanocomposites.

3.3. FTIR analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

The FTIR spectra of AgZnO/POMs nanocomposites, POMs, and AgZnO hybrid nanoparticles had been depicted in Fig. 3 (a-c). As shown in Fig. 3a, the vibration peak at 3370 cm^{-1} is caused by the H₂O hydrogen bond. The vibration peak appearing in the interval of $1680 - 1133\text{ cm}^{-1}$ is attributed to the ligand 2-pyridinecarboxamide. The stretching vibration of the P-O bond appears in the range of $1120 - 1008\text{ cm}^{-1}$ [28, 29]. The vibrational peaks at 905 cm^{-1} and 662 cm^{-1} are attributed to the $\nu(\text{Mo}-\text{O}_{\text{bridging}})$ bond and the $\nu(\text{Mo}-\text{O}_{\text{terminal}})$ bond, respectively [29]. The characteristic absorption peaks in POMs appear in the map of photocatalytic-adsorbent AgZnO/POMs nanocomposites. In Fig. 3c, the strong absorption at 512 cm^{-1} clearly reflects the vibration of the Zn-O bond, and the corresponding peak also appears in Fig. 3b [30]. The above characteristic absorption peaks also exist in the FTIR spectra of photocatalytic adsorbent AgZnO/POMS nanocomposites (Fig. 3b), confirmed that the nanocomposites had been synthesized.

3.4. XPS analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

In Fig. 4, the XPS spectrum was calibrated using C1s (284.8 eV). The peaks of C, O, N, P, Zn, Mo, Cu and Ag can be observed from the full spectrum of XPS (Fig. 4a). In Fig. 4b, the AgZnO/POMs nanocomposites shows two peaks of binding energy at approximately 1022 eV and 1045 eV, corresponding to the main regions of Zn 2p_{3/2} and Zn 2p_{1/2} [31]. The first peak is attributed to the Zn²⁺ ion in the anoxic zinc oxide [32]. The peaks at 367.2 eV and 373.2 eV (Fig. 4c) correspond to Ag 3d_{5/2} and 3d_{3/2} states of metal Ag. Compared with bulk silver (about 368.2 eV and 374.2 eV, respectively), the peaks of the Ag 3d state is significantly transferred to the lower value of AgZnO hybrid nanoparticles, which is attributed to contact between Ag and ZnO [33]. Figure 4d shows peaks at 934.9 eV and 932.4 eV, which are in the energy region of Cu 2p_{3/2} and Cu 2p_{1/2} attributed to Cu²⁺, indicating that Cu is mainly present in the form of Cu²⁺ [34, 35]. Figure 4e shows peaks at 133.2 and 134.1 eV, corresponding to the P-O peaks of P 2p_{3/2} and P 2p_{1/2}, respectively [36]. In Fig. 4f, shows peaks at 235.8 and 232.3 eV, corresponding to the main regions of Mo 3d_{3/2} and Mo 3d_{5/2} respectively, indicating that the valence of Mo is mainly Mo⁶⁺ [37]. The analysis shows that AgZnO/POMs nanocomposites contain AgZnO and POMs.

3.5. UV-vis analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

UV-vis absorption spectrum of photocatalytic-adsorbent AgZnO/POMs nanocomposites in aqueous solution in Fig. 5. The AgZnO/POMs nanocomposites have four absorption bands at 209 nm, 260 nm, 365 nm and 380–420 nm, respectively. The absorption band at 365 nm is the characteristic absorption band of ZnO [21]. The absorption at 380–420 nm reveals the hybridization of ZnO with Ag and the interfacial electron interaction between Ag and ZnO [38]. The absorption bands at 209 nm and 260 nm are attributed to POMs because of electron transfer of $O_{\text{terminal}} \rightarrow \text{Mo}$ and $O_{\text{bridging}} \rightarrow \text{Mo}$ in POMs [19]. The results show that the AgZnO/POMs nanocomposites have excellent optical properties.

3.6. PL analysis of photocatalytic adsorbent AgZnO/POMs nanocomposites

The solid fluorescence emission spectra of photocatalytic-adsorbent AgZnO/POMs nanocomposites were detected under the excitation wavelength of 241 nm (Fig. 6a) and 380 nm (Fig. 6b), respectively. As shown in Fig. 6a, AgZnO/POMs nanocomposites have an emission peak at 393 nm, corresponding to the solid-state fluorescence emission peaks at 393 nm of POMs [39]. Figure 6b AgZnO/POMs nanocomposites shows three emission peaks at 465 nm, 489 nm and 596 nm corresponding to the emission peaks of AgZnO hybrid nanoparticles, respectively. The blue light emission peaks at 465 nm and 489 nm are usually caused by photo-generated holes of ZnO and the oxygen vacancies occupied by the nanocomposites [40]. The emission at about 596 nm is generally thought to be caused by the recombination of electrons and valence band holes in the deep defect layer of ZnO [41]. The results show that the AgZnO/POMs nanocomposites have excellent optical properties.

4. Removal Of Bm

The adsorption and photocatalytic activities of AgZnO/POMs nanocomposites were studied by removing BM from aqueous solution. Figure 7a is the UV-vis absorption spectra of BM solution containing the AgZnO/POMs nanocomposites at different intervals. Figure 7b shows a comparative study for removing BM in the presence of (1) POMs, (2) AgZnO and (3) AgZnO/POMs nanocomposites, in which, the ordinate is C/C_0 , where C is the corresponding concentration of BM at different time intervals, and C_0 is the original concentration of BM. It can be observed in combination with Figure 7(a) and (b), the absorption peak strength of BM gradually decreases in 0-30 min, remaining unchanged in 30-50 min for reaching adsorption equilibrium under stirring in the dark, then after 50 min, decreases with the increase of UV-light irradiation, indicating the adsorption and photocatalysis activities of AgZnO /POMs nanocomposites. In Figure 7b, POMs only showed adsorption, while the adsorption and photocatalysis of AgZnO hybrid nanoparticles were relatively weak, when the two are combined, AgZnO/POMs nanocomposite has enhanced adsorption effect relative to AgZnO hybrid nanoparticles, and shows photocatalytic effect relative to POMs, and finally achieves 94% removal rate of BM in aqueous solution. Figure 7c shows a

comparative histogram of the removal of BM by POMs, AgZnO, and AgZnO/POMs nanocomposites under UV-light and Vis irradiation, respectively. No matter under UV or visible light irradiation, the photocatalytic-adsorbent AgZnO/POMs qualifies higher removal efficiency than the adsorbent POMs and photocatalyst AgZnO. The removal rate of AgZnO/POMs for removing BM is 94%, which is much higher than that of POMs (54%) and AgZnO (73%) under UV-light irradiation.

The N₂ adsorption-desorption isotherms of AgZnO nanoparticles and photocatalytic-adsorbent AgZnO/POMS nanocomposites were determined using the automatic physical/chemical adsorption apparatus. In Figure 8, both samples showed typical type IV isotherms, indicating the presence of mesoporous structures [42]. According to the analysis results of relative position and height of hysteresis loops (Figure 8), the specific surface area (BET) of AgZnO nanoparticles (Figure 8a) is 28.682 m²/g, The BET of AgZnO/POMs nanocomposite (Figure 8b) is 33.535 m²/g. The results indicate that the AgZnO/POMS nanocomposites obtained by the combination of the two have higher specific surface area, which corresponds to the enhanced adsorption performance of the composite under dark conditions.

The pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data of AgZnO/POMs nanocomposites.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \tag{2}$$

In the (1) and (2), *q*₀ is adsorption amount at *t* = 0, *q_e* is equilibrium adsorption amount, *q_t* is adsorption amount at time *t*, *k*₁ and *k*₂ are the pseudo-first-order and pseudo-second-order kinetic rate constants, respectively.

Table 1. Kinetic correlation coefficients (*R*²) fitting parameters.

	Pseudo-first-order	Pseudo-second-order
	<i>R</i> ²	<i>R</i> ²
Dark	0.3471	0.9997
UV light	0.9380	0.9736

The kinetic plots of removing BM by AgZnO/POMs nanocomposites are shown in Figure 9 and the results are shown in Table 1. The *R*² of pseudo-second-order model were 0.9997 and 0.9736 under dark and UV-light respectively which were higher than that of pseudo-first-order model, 0.3471 and 0.9380 under dark and UV-light respectively, indicating that both the adsorption process and the photocatalysis process of removing BM by AgZnO/POMs nanocomposites followed the pseudo-second-order kinetics. The results

demonstrate that the removal rate of AgZnO/POMs nanocomposites is mainly due to the chemical adsorption and electron transfer ability of the composites [27, 43].

When AgZnO/POMs nanocomposites were excited by UV light, the photogenerated e^- and hole (h^+) will be produced by ZnO. Ag acts as an electron acceptor, by which chemisorbed molecular oxygen reacts with photogenerated e^- to form superoxide radicals ($\cdot O_2^-$), facilitating the trapping of photogenerated e^- , and thus the separation efficiency of the photogenerated e^- and h^+ is improved. The h^+ in the valence band of ZnO react with hydroxyl groups to form hydroxyl radicals ($\cdot OH$), the $\cdot OH$ is a strong oxidant for removing the organic chemicals. The h^+ , $\cdot OH$ and $\cdot O_2^-$ produced in the process of photocatalysis are crucial substances for BM removal, in addition to the adsorption between the adsorbent and the dye molecules [19, 27, 44]. As a result, the removal efficiency of AgZnO/POMS nanocomposites was greatly improved by the combination of AgZnO and POMs into a whole through nanoengineering. The photocatalytic-adsorbent AgZnO/POMs nanocomposites are expected to be a new type of dye removers which can remove aromatic organic dyes from water pollution more efficiently, especially for BM, which is difficult to remove.

To investigate the reproducibility of the nanocomposites for removing BM, we collected and washed the AgZnO/POMs nanocomposites. The collected nanocomposites were used to remove BM via five repeated experiments under the same reaction conditions. As shown in Figure 11a, the removal rate of BM in AgZnO/POMs nanocomposites decreased by only 7.0% (from 94.0% to 87.0%) after five cycles, the slight reduction might correspond to the loss of AgZnO/POMs nanocomposites during washing. Figure 11b shows that the FTIR spectrum of the AgZnO/POMs nanocomposites before and after BM removal are similar. It could be proved that the nanocomposites have the well stability and light corrosion of resistance.

5. Conclusions

In conclusion, the photocatalytic-adsorbent AgZnO/POMs nanocomposites were synthesized by combining AgZnO hybrid nanoparticles and POMs. The TEM and HRTEM showed that AgZnO/POMs nanocomposites were uniform with narrow particle size distribution and without agglomeration. The bifunctional photocatalytic-adsorbent AgZnO/POMs nanocomposites could effectively remove refractory BM from aqueous solution with removal efficiency of 94% by adsorption and photocatalysis. The adsorption process and the photo-degradation process of AgZnO/POMs nanocomposites for removing BM followed the pseudo-second-order kinetics. After five cycles, the removal efficiency of nanocomposites for BM remained the same, and the FTIR spectrum of the AgZnO/POMs nanocomposites after the removal of BM were similar to the fresh samples, demonstrating that the nanocomposites have the well stability and light corrosion of resistance. The bifunctional photocatalytic-adsorbent AgZnO/POMs nanocomposites have potential applications in the treatment of refractory organic dye wastewater containing triphenylmethane.

Declarations

Conflicts of Interest

The authors declare no conflict of interest.

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Authors' contributions

Heyun Tian, Jie Luo and Chenguang Ma designed the concept and conducted the experiments. Heyun Tian and Jie Luo, wrote the main manuscript. Heyun Tian, Chenguang Ma, Ke Zhang, Yiyi Qi and Shixia Zhan conducted data processing and analysis. Heyun Tian, Jie Luo, Hongling Liu and Mingxue Li modified the paper.

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Figures

Figure 1

(a) TEM micrographs and illustration shows particle size histogram of AgZnO/POMs nanocomposites, (b) HRTEM of an individual AgZnO/POMs nanocomposite, (c) STEM micrographs and (d-k) corresponding elemental mappings of AgZnO/POMs nanocomposites.

Figure 2

XRD patterns of (a) AgZnO/POMs nanocomposites, (b) POMs, (c) AgZnO hybrid nanoparticles (The purple and blue column charts are the column diagrams of Ag and ZnO labeled cards, respectively).

Figure 3

FTIR spectra of (a) POMs, (b) AgZnO/POMs nanocomposites and (c) AgZnO hybrid nanoparticles.

Figure 4

XPS spectra of AgZnO/POMs nanocomposites (a) full spectrum, (b) Zn 2p map, (c) Ag 3d map, (d) Cu 2p map, (e) P 2p map, (f) Mo 3d map.

Figure 5

UV-vis absorption spectrum of photocatalytic-adsorbent AgZnO/POMs nanocomposites.

Figure 6

(a) Solid PL emission spectra of POMs and AgZnO/POMs with excitation wavelength $\lambda_{ex} = 241$ nm, (b) Solid PL emission spectra of AgZnO and AgZnO/POMs with excitation wavelength $\lambda_{ex} = 380$ nm.

Figure 7

(a) UV-vis absorption spectra of BM solution containing the AgZnO/POMs nanocomposites, (b) Degradation curves of different materials for removing BM, curve: (1) POMs, (2) AgZnO (3) AgZnO/POMs nanocomposites, (c) Histogram of the removal of BM by POM, AgZnO and AgZnO/POMs nanocomposites under UV and Vis irradiation.

Figure 8

(a) N₂ adsorption-desorption isotherm of AgZnO hybrid nanoparticles, (b) N₂ adsorption-desorption isotherm of AgZnO/POMs nanocomposite.

Figure 9

The kinetic plots for removing BM by AgZnO/POMs nanocomposites, (a) and (b) pseudo-first-order kinetics, (c) and (d) pseudo-second-order kinetics.

Figure 10

Schematic illustration of degradation of BM by AgZnO/POMs nanocomposites.

Figure 11

(a) Histogram of recycled removal of BM for five cycles, (b) Comparison of FIRT spectra of AgZnO/POMs nanocomposites before and after five cycles.

Supplementary Files

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