

Construction of 3D BiOBr@hollow carbon sphere hybrids for decontamination of phenol in aqueous solution

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Abstract: In this study, 3D BiOBr@hollow carbon sphere (BiOBr@C) hybrids were synthesized via template-assisted hydrothermal methods. The effect of BiOBr@C on the catalytic decomposition of phenol was investigated. Compared with BiOBr, the BiOBr@C hybrid exhibited a significantly increased specific surface area. Furthermore, the BiOBr@C hybrid also showed improved visible-light absorption capacity because of the synergistic effect between the carbon spheres and BiOBr. Phenol decontamination experiments demonstrated that the BiOBr@C hybrid achieved an optimal catalytic decomposition efficiency of 34% within 24 h, outperforming both pure BiOBr and carbon spheres alone. Kinetic analysis indicated that the phenol decontamination process on BiOBr@C fit the Weber–Morris intraparticle diffusion model, suggesting that the catalytic decomposition mechanism involved multiple processes, including intramolecular diffusion and surface chemical adsorption, rather than simple physical adsorption. This study provides a promising strategy for designing efficient BiOBr-based photocatalysts for phenol decontamination applications.

Key words: BiOBr; hollow carbon spheres; photocatalysis; phenol degradation; adsorption kinetics

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1. Introduction

Phenol, a crucial phenolic compound, has extensive applications in pharmaceutical manufacturing and synthetic material production, with a continuously growing market demand. It is primarily used in the production of preservatives and resins. Statistical data indicate that China's total production capacity reached 6.358 million tons by 2024 [1, 2]. As phenol usage has increased, the incidence of leakage accidents has also increased, drawing increasing attention to the resulting environmental safety concerns across society [3]. Existing phenol decontamination and disposal technologies primarily include electrochemical methods, nano-adsorption techniques, and photocatalytic oxidation [4]. Jiang et al. [5] identified challenges in electrocatalytic applications, such as electrode materials being susceptible to degradation reactions with short lifespans, low mass transfer efficiency in reactors complicating the degradation of low-concentration pollutants, and high energy consumption and electrode material costs, all of which significantly limit their engineering applications. Seham et al. [6] developed Fe₃O₄/SiO₂ core-shell-structured materials enabling rapid adsorbent recovery via external magnetic fields, achieving phenol adsorption capacities of 120 mg/g with excellent regeneration performance. However, some nanomaterials may have unknown ecological impacts and require further

assessment before use. Additionally, researchers have extensively studied the photocatalytic decontamination of phenol using semiconductor materials such as TiO₂ and ZnO. These findings indicate that modified TiO₂ can achieve an 85% phenol degradation rate under UV light, although its response under visible light conditions requires further improvement [7-10].

Photocatalytic technology represents an emerging field that integrates photochemistry, catalysis, and semiconductor physics, where catalysts convert light energy into chemical energy to drive reactions [11, 12]. This technology efficiently decomposes organic pollutants by generating reactive species through light excitation, making it a highly effective deep decontamination technique. In recent years, bismuth-based photocatalytic materials have emerged as a focal point in photocatalyst research because of their outstanding absorption properties in the visible light spectrum, excellent stability, and high degradation efficiency for recalcitrant organic pollutants [13].

Currently, BiOBr materials are widely applied in photocatalysis because of their unique structure and properties [14]. While exhibiting significant absorption in the visible region, their absorption capability sharply decreases beyond this range, directly limiting their quantum yield. Consequently, numerous researchers have employed techniques such as morphology control, elemental doping, and surface modification to increase catalytic efficiency. Liao et al. [15] synthesized BiOBr nanosheets with specific morphologies using ethylene glycol and water as raw materials. The resulting BiOBr nanosheets have a high specific surface area and abundant surface active sites, significantly enhancing photocatalytic reactions. Additionally, carbon materials have garnered significant attention because of their high conductivity, making composites of car-

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bon materials and BiOBr a key research focus [16, 17]. Ma et al. [18] employed a solvothermal method assisted by fullerene (C70) to synthesize a flower-like BiOBr photocatalyst. The involvement of C70 played a crucial role in material structure formation, with the C70 template promoting changes in the specific surface area and inducing the unique flower-like structure of BiOBr. Furthermore, owing to the exceptional electron-accepting capacity of C70, the C70/BiOBr composite achieves high levels of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ generation through its high photoexcited charge separation rate. Under sunlight irradiation, this composite exhibited superior photocatalytic performance for phenol degradation. Liu et al. [19] reported that the hydroxyl, carboxyl, and amino groups present on the BiOBr surface react with the amino groups on the carbon nanotube surface or form hydrogen bonds during the preparation of carbon nanotube/BiOBr composites. This enhances the stability of the composite and facilitates electron transfer. However, these methods suffer from high research costs and technical immaturity [20]. Therefore, the development of novel photocatalysts based on BiOBr materials that feature simple preparation methods, low loading requirements, strong catalytic activity, and high catalytic efficiency is urgently needed in the fields of pollutant degradation and decontamination treatment.

Recent studies have further demonstrated that interfacial engineering is an effective strategy for improving the photocatalytic activity of BiOBr-based composites toward phenolic pollutants. Han et al. reported a C@BiOBr photocatalyst for phenol degradation and reported that carbon modification can enhance pollutant adsorption and charge separation [21]. Chen et al. constructed a PCN/BiOBr hybrid for 2,4-dichlorophenol degradation and confirmed that the improved activity was closely related to enhanced photogenerated carrier separation [22]. More recently, Fe-modified BiOBr was reported to enhance photocatalytic and piezo-photocatalytic phenol degradation, further indicating the importance of defect/metal regula-

tion and ROS generation in BiOBr-based systems [23]. These studies suggest that coupling BiOBr with conductive or functional components is a promising route for improving light utilization, interfacial charge transfer, and phenolic pollutant degradation efficiency. In this study, BiOBr@C hybrid catalytic materials were synthesized via template and hydrothermal methods. The microstructures, crystal structures, and phenol degradation performances of the BiOBr@C hybrid materials were investigated. Kinetic model analysis revealed the photocatalytic mechanism.

2. Experimental Section

2.1. Raw materials

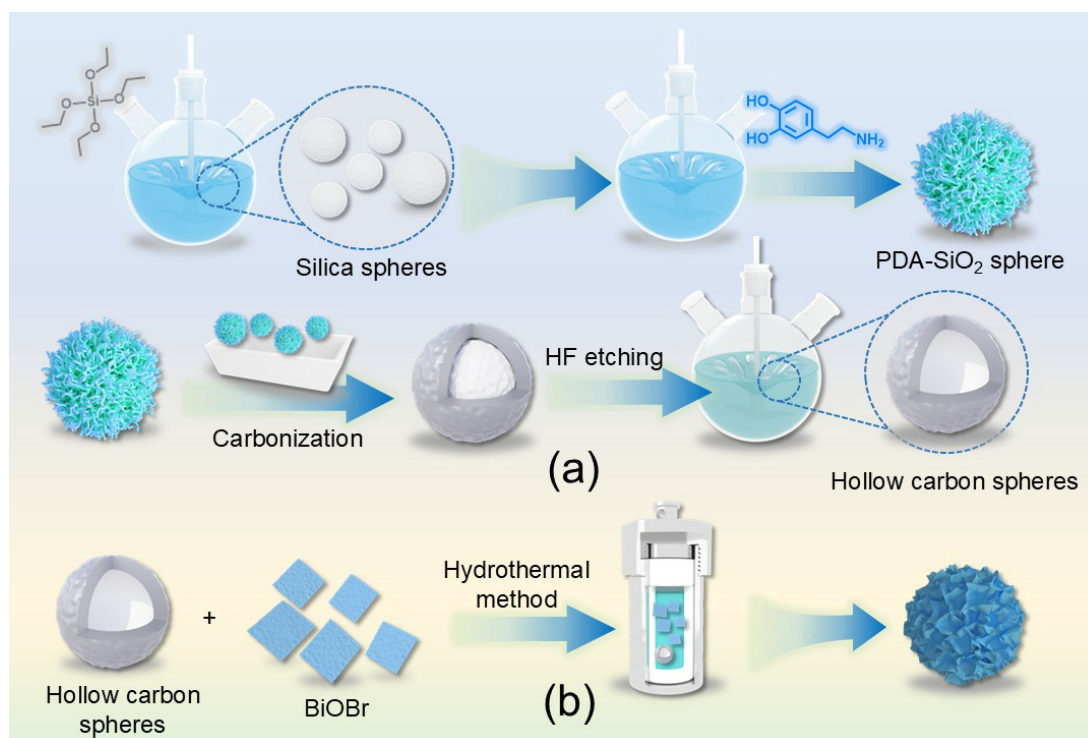
Bismuth nitrate pentahydrate, cetyl trimethyl ammonium bromide (CTAB), hydrogen fluoride, ethylene glycol, anhydrous ethanol, phenol, ethyl orthosilicate (TEOS), and ammonia solution were obtained from Sinopharm Reagent Co., Ltd. Potassium bromide and dopamine hydrochloride were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Preparation of BiOBr@C hybrids

2.2.1. Preparation of hollow carbon spheres

Hollow carbon spheres were prepared via a two-step procedure, as shown in Scheme 1a. First, 1 mL of TEOS and 5 mL of anhydrous ethanol were added to a beaker and stirred for 20 min to obtain the TEOS solution. 5 mL of ammonia solution, 15 mL of deionized water, and 20 mL of anhydrous ethanol were poured into a three-neck flask. The mixture was stirred for 10 min, after which the TEOS solution was added dropwise. The mixture was stirred at room temperature for 12 h, centrifuged at 8000 rpm, and dried, after which SiO_2 was obtained.

Tris-HCl (1.576 g) was added to 100 mL of deionized water. SiO_2 microspheres (0.20 g) were added and subjected to continuous ultrasonic treatment for 6 h. After stirring under



Scheme 1. (a) Preparation of hollow silica spheres and (b) BiOBr@C hybrids

ultrasonication, 2 mL of ammonia solution was added, and 0.2 g of dopamine hydrochloride was dissolved in 100 mL of deionized water. This solution was added dropwise to the previously prepared mixture. The mixture was stirred at room temperature for 24 h, filtered under vacuum, dried, and ground to obtain a gray-black powder. The gray-black SiO_2 powder was placed in a tube furnace. The temperature was increased to 550°C at a rate of 5°C/min and maintained at this temperature for 2 h. A 20% hydrofluoric acid solution was prepared. The calcined powder was added to the solution and stirred slowly for 12 h to dissolve the SiO_2 .

2.2.2. Preparation of BiOBr

Bismuth nitrate pentahydrate was added to ethylene glycol containing CTAB. The mixture was stirred for 30 min and then sonicated for 30 min until a clear solution was obtained. After the addition of KBr, the mixture was stirred for 10 min. The solution was transferred to a 50 mL high-pressure reactor, heated to 160°C, and maintained at this temperature for 6 h. The precipitate was filtered and collected, washed repeatedly with deionized water and ethanol, and then dried at 60°C for 10 h. The product was stored in amber bottles.

2.2.3. Preparation of BiOBr@C hybrids

BiOBr@C hybrids were prepared via a hydrothermal method, as shown in Scheme 1b. Typically, 0.485 g of bismuth nitrate pentahydrate was added to an ethylene glycol solution containing 1.82 g of CTAB. The mixture was stirred for 30 min, after which 0.280 g of carbon spheres was added. The mixture was stirred for 10 min, followed by ultrasonication for 30 min. KBr (0.119 g) was added, and the mixture was stirred for 10 min to ensure complete dispersion of the KBr in the solution. The prepared mixture was transferred into a 100 mL high-pressure reactor. The reactor temperature was raised to 160°C and maintained for 6 h. After the reaction, the mixture was filtered, and the precipitate formed was collected. The samples were washed multiple times with ethanol and purified water and then transferred to an oven for heat treatment at 60°C for 10 h.

2.3. Characterization

The morphological structure of the obtained materials was characterized via a Gemini 500 scanning electron microscope (Germany, Zeiss). The microstructures of the samples were investigated via transmission electron microscopy (TEM) via a JEM-2100 instrument at an operating voltage of 10 kV. The BET specific surface area of the materials was determined via an ASAP 2020 physical analyzer. X-ray diffraction (XRD) was used to characterize the crystalline structure of the materials (Rigaku miniflex600). Optical properties were characterized via

a UV–visible–near-infrared spectrophotometer (UV–vis DRS) manufactured by Shimadzu Corporation, Japan. The surface photovoltaic properties were characterized via a steady-state surface photovoltaic spectrometer (CHF-XM-500 W). The wavelength range was set from 300 nm to 800 nm, with a spectral resolution of 2 nm. EIS measurements were performed via a PAR-STAT MS electrochemical workstation. The experiments employed a standard three-electrode system with the open-circuit voltage amplitude adjusted to 5 mV and the frequency range set between 100 kHz and 10 MHz. The catalytic performance of the corresponding materials was evaluated by analyzing the diameter of the semicircular arc in the AC impedance curve within the Nyquist plot. The prepared materials were characterized by high-performance liquid chromatography-mass spectrometry (HPLC-MS) using an LTQ-Orbitrap XL Fourier transform electrostatic field Orbitrap high-resolution mass spectrometer from Thermo Fisher Scientific (USA). A TOC-L CPH total organic carbon spectrum analyzer (Japan) was used to analyze the carbon composition in the liquid phase before and after catalysis.

3. Results and Discussion

3.1. Morphological characterization

The microstructures of the carbon spheres, BiOBr, and BiOBr@C were characterized by scanning electron microscopy (SEM). As shown in Figure 1a, the synthesized carbon spheres exhibit distinct spherical features with diameters of approximately 200 nm. As depicted in Figure 1b, BiOBr has a typical multilayer lamellar structure with relatively large lamellar widths (exceeding 1 μm). Compared with spherical structures, such structures generally possess more complex internal architectures and larger specific surface areas. Consequently, they generate multilevel light reflection effects, effectively enhancing the light absorption efficiency and demonstrating superior light absorption properties and photocatalytic activity [24]. As shown in Figure 1c, the BiOBr@C hybrid photocatalyst synthesized via high-temperature and high-pressure reactions exhibited a typical composite “sheet-sphere” structure. Hollow carbon spheres are dispersed and attached to both the interior and surface of the BiOBr sheets, confirming the successful synthesis of the BiOBr@C photocatalyst [25].

Furthermore, transmission electron microscopy (TEM) was employed to characterize the microstructures of the carbon spheres, BiOBr, and BiOBr@C composite. The morphology and diameter distribution of the carbon spheres are further illustrated in Figure 2a. In Figure 2b, the TEM image of BiOBr reveals a structure characterized by the coexistence of single-

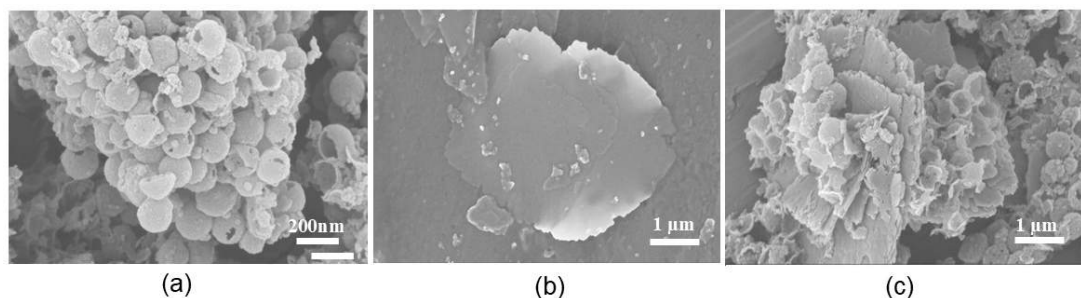


Fig. 1. SEM images of (a) carbon spheres, (b) BiOBr, and (c) BiOBr@C

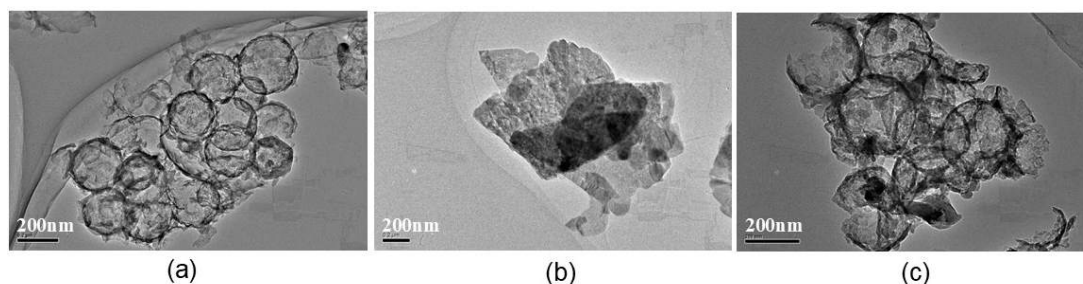


Fig. 2. TEM images of (a) hollow carbon spheres, (b) BiOBr, and (c) BiOBr@C

layer and multi-layer sheets, which corresponds well with the SEM results. Moreover, as shown in Figure 2c, BiOBr@C clearly exhibited a “sheet-sphere” composite structure, further confirming the successful incorporation of hollow carbon spheres onto the BiOBr surface and the successful synthesis of the hybrid material [26].

3.2. BET adsorption–desorption behavior

The N_2 adsorption–desorption isotherms for carbon spheres, BiOBr, and BiOBr@C are shown in Figure 3, and their specific surface areas, pore volumes, and pore size data are summarized in Table 1. All the samples exhibit Type IV isotherms, indicating the presence of mesoporous structures. The carbon spheres have ultrahigh specific surface areas, corresponding to abundant micro/mesoporous structures, providing highly dispersed sites and a conductive network for BiOBr. Pure BiOBr has the smallest specific surface area. BiOBr@C demonstrates a significant increase in isotherm adsorption capacity after carbon sphere incorporation, indicating the formation of multi-level pore channels between the carbon framework and BiOBr, thereby increasing the specific surface area [27].

XRD analysis was employed to characterize the crystalline

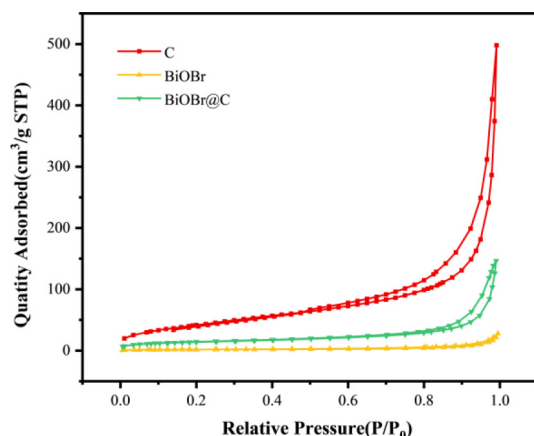


Fig. 3. BET adsorption–desorption isotherms of carbon spheres, BiOBr, and BiOBr@C

Table 1. Specific surface area, pore volume, and pore size data for carbon spheres, BiOBr, and BiOBr@C

Material	Specific Surface Area (m²/g)	Average Pore Size (nm)
Hollow carbon spheres (C)	159.49	19.32
BiOBr	5.88	14.33
BiOBr@C	50.43	10.35

phases of BiOBr, the hollow carbon spheres, and the hybrid catalyst. The XRD patterns of BiOBr, the hollow carbon spheres, and the BiOBr@C photocatalyst are shown in Figure 4. The diffraction peaks of BiOBr appear at 25.1° , 32.2° , 39.3° , 46.2° , 53.4° , and 57.1° , corresponding to the (101), (110), (112), (200), (211), and (212) crystal planes, respectively. These diffraction peak data are similar to the characteristics of BiOBr (JCPDS# 09-0393). Since the XRD pattern of the carbon spheres shows virtually no distinct diffraction peaks, the primary diffraction peaks of BiOBr@C also largely correspond to those of BiOBr [28]. XRD analysis confirmed that, compared with BiOBr, the incorporation of hollow carbon spheres has a negligible effect on the XRD patterns of the BiOBr@C hybrid photocatalyst [29].

UV–Vis diffuse reflectance spectroscopy was employed to characterize the multicomponent nanomaterials and hybrid catalysts. As shown in Figure 5, the carbon spheres exhibit strong

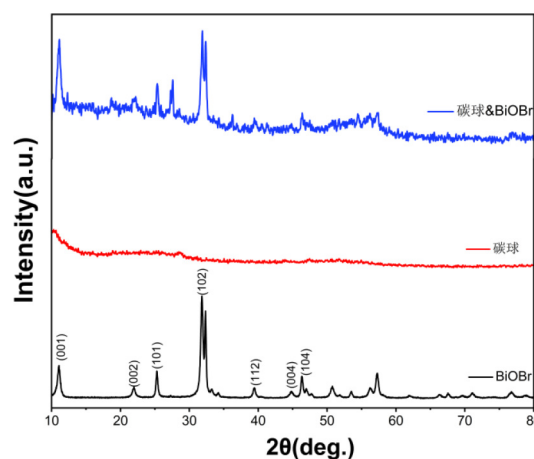


Fig. 4. XRD patterns of BiOBr, carbon spheres, and BiOBr@C

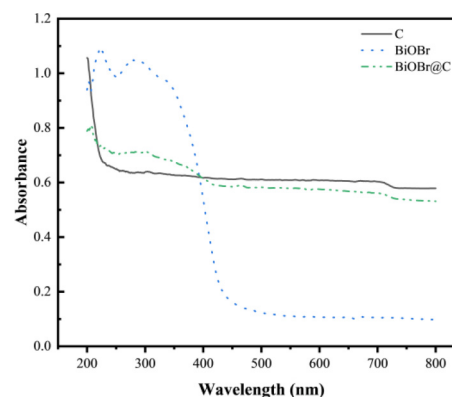


Fig. 5. UV–Vis diffuse reflectance spectra of carbon spheres, BiOBr, and BiOBr@C

light absorption in both the UV and visible regions, with slightly lower absorbance in the visible range. In contrast, BiOBr has high absorption and strong light absorption in the UV region (200–400 nm), but its light absorption capability sharply decreases in the visible region. Therefore, hybridizing BiOBr with carbon spheres enhances the visible-light absorption capacity of the hybrid photocatalyst. On the basis of the above analysis, compared with pure BiOBr, the BiOBr@C photocatalyst demonstrates improved light absorption in the visible region. In nature, sunlight is generally predominant light source in nature, with the visible wavelength range forming its core component. Consequently, enhancing the absorption capacity of photocatalysts in the visible region plays a crucial role in increasing their catalytic efficiency [30, 31].

To evaluate the impact of decontamination type on phenol removal, BiOBr, carbon spheres, and BiOBr@C were tested as decontamination agents under the following conditions: pH = 7, a phenol concentration of 15 mg/L, and catalyst dosage of 50 mg. The effects of BiOBr, C, and BiOBr@C on the phenol concentration in solution under illumination are shown in Figure 6. The BiOBr@C hybrid material exhibited optimal performance in catalyzing phenol degradation, achieving 34% catalytic degradation efficiency within 24 h. BiOBr exhibited lower catalytic efficiency than the BiOBr@C hybrid material during the initial stage, but its degradation rate at 24 h approached that of the hybrid material. The hollow carbon spheres demonstrated the poorest catalytic performance, achieving only a 7% degradation rate after 24 h. On the basis of the previous structural analysis of hollow carbon spheres, it can be inferred that they physically adsorb only on phenol, resulting in the poorest decontamination performance [32, 33]. In the BiOBr@C hybrid material, hollow carbon spheres provide physical adsorption, whereas BiOBr catalyzes phenol degradation in the UV region, demonstrating synergistic catalytic effects [34]. Compared with the hydrothermally prepared BiOBr@C composite, BiOBr&C exhibited a lower phenol removal efficiency, although it contained the same components. These results indicate that simple physical mixing is insufficient to achieve enhanced photocatalytic performance.

Notably, although BiOBr@C exhibited a higher phenol removal efficiency than pure BiOBr at the initial stage, the degradation efficiency of BiOBr gradually approached that of BiOBr@C after 24 h. This phenomenon may be attributed to the different rate-controlling steps during the decontamination process. In the early stage, the hollow carbon spheres in

BiOBr@C provide additional adsorption sites and porous diffusion channels, which facilitate phenol enrichment around BiOBr active sites and accelerate the adsorption-photocatalysis coupling process. In addition, the carbon phase improves interfacial electron transfer, as supported by the reduced EIS arc radius of BiOBr@C. With prolonged irradiation, however, phenol molecules can gradually diffuse to the active sites of pure BiOBr, and the photocatalytic reaction continues to proceed, resulting in a narrowed difference between BiOBr and BiOBr@C at 24 h. Therefore, the role of hollow carbon spheres is reflected mainly in promoting early-stage mass transfer and charge separation.

Catalyst-mediated decontamination of pollutants involves two steps: adsorption and catalytic degradation. The pollutant removal efficiency of a catalyst is closely related to its kinetic characteristics. Solution-phase adsorption processes can be quantitatively described by multiple kinetic models: (1) the quasifirst-order kinetic model, which is based on the Lagergren rate equation and is suitable for describing processes dominated by physical adsorption; (2) the quasissecond-order kinetic model, which involves electronic interactions between the adsorbent and adsorbate and is suitable for chemisorption-controlled processes; and (3) the Weber–Morris internal diffusion model, which is used to analyze the kinetic characteristics of pore diffusion. According to Equation (3.5), if Q_t has a linear relationship with $t_{1/2}$ and passes through the origin, the adsorption process is controlled by a single internal diffusion step. If the line does not pass through the origin, it indicates the presence of multiple control mechanisms in addition to internal diffusion. To evaluate the impact of decontamination type on phenol decontamination performance, BiOBr, carbon spheres, and BiOBr@C were tested as decontaminants [35, 36]. The decontamination conditions were as follows: pH = 7, phenol concentration = 15 mg/L, and catalyst dosage = 35 mg.

TOC analysis was conducted to evaluate the degree of phenol mineralization during photocatalytic degradation over BiOBr@C. As shown in Table 2, the TOC concentration decreased from 30.20 mg/L to 20.52 mg/L after photocatalytic treatment, corresponding to a TOC removal efficiency of 32.1%. These results indicate that phenol was partially mineralized during the BiOBr@C photocatalytic process.

3.3. Kinetic analysis of BiOBr decontamination for phenol

As shown in Figure 7a, the adsorption capacity of BiOBr for phenol tended to increase over time, reaching an equilibrium adsorption amount of 22.1 mg/g after a 24-h adsorption experiment. The adsorption rate decreased with increasing time. The adsorption kinetics of phenol on BiOBr were investigated via three typical adsorption kinetic models: the pseudo-first-order adsorption model, the pseudo-second-order adsorption model, and the intraparticle diffusion model. The results of these adsorption kinetic characteristics are presented in Figures 7b–7d. The fitting parameters for the three kinetic mod-

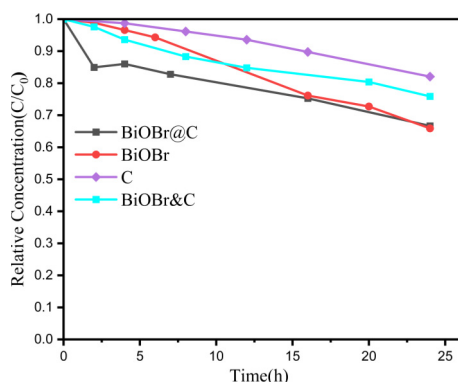


Fig. 6. Phenol removal efficiency over BiOBr, hollow carbon spheres, BiOBr&C and BiOBr@C under illumination.

Table 2. TOC analysis of the phenol solution before and after photocatalytic degradation over BiOBr@C.

Sample	TC (mg/L)	IC (mg/L)	TOC (mg/L)
TOC1	31.47	1.27	30.20
TOC2	20.87	0.32	20.52

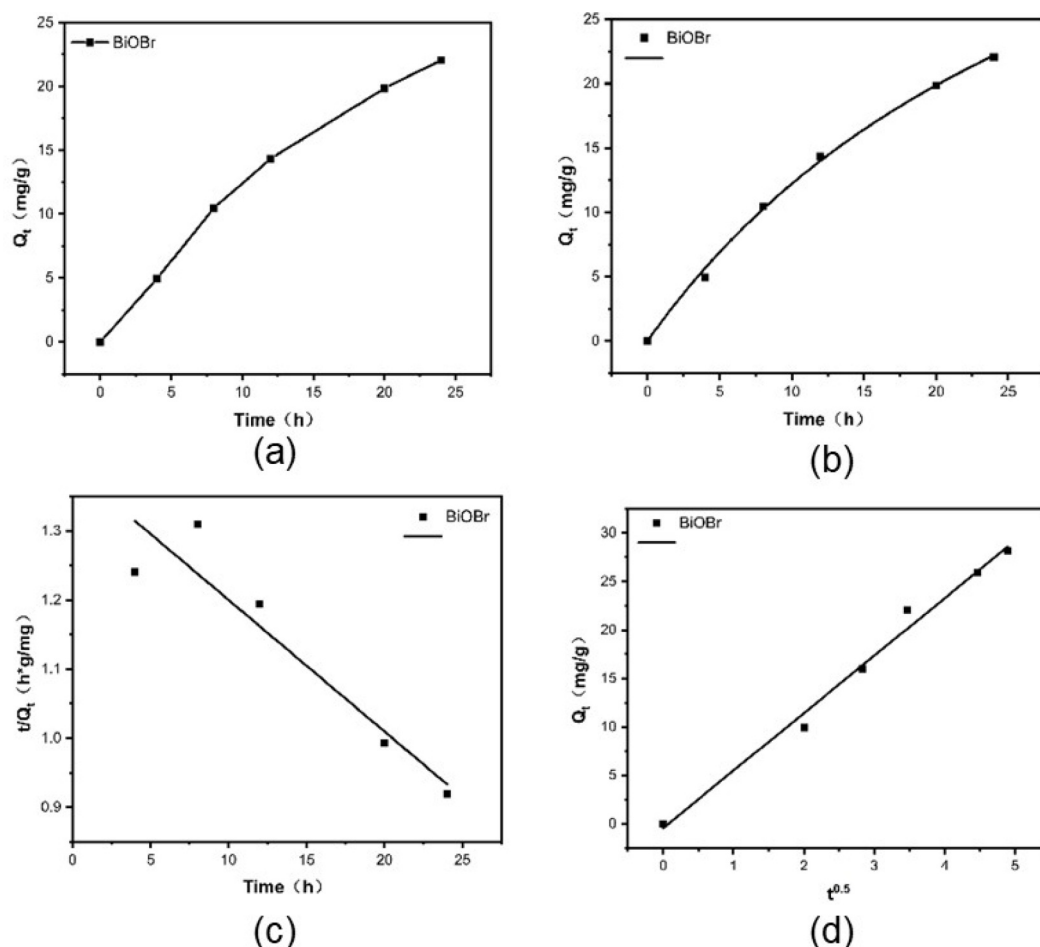


Fig. 7. BiOBr adsorption kinetics curves for phenol: (a) adsorption kinetics curve, (b) Langmuir model, (c) pseudo-first-order model, and (d) intra-particle diffusion model.

els are shown in Table 3. The results of kinetic studies indicate that phenol adsorption on the BiOBr surface conforms well to the pseudo-first-order adsorption model and is also consistent with the intramolecular diffusion kinetic model, with correlation coefficients R^2 of 0.99 and 0.98, respectively. The pseudo-second-order kinetic model exhibited poorer fitting quality ($R^2 = 0.89$) and yielded physically meaningless negative equilibrium adsorption capacities (Q_e). Thus, the adsorption process of phenol on the BiOBr surface does not match the characteristics described by the pseudo-second-order kinetic model. On the basis of the particle–internal diffusion

model fitting results, the intercept value of the linear regression equation significantly deviates from the original value ($C \neq 0$). This finding indicates that, in addition to internal diffusion, other mass transfer mechanisms also participate in controlling the adsorption process. This phenomenon reveals that the adsorption system exhibits multistage controlled kinetic characteristics [37].

3.4. Decontamination kinetic analysis of phenol by hollow carbon spheres

As shown in Figure 8a, the phenol adsorption capacity of the hollow carbon spheres monotonically increased with increasing contact time, reaching a saturated adsorption capacity of 18.2 mg/g at a reaction time of 24 h. The adsorption rate decreased with increasing contact time. In this study, the adsorption kinetics of phenol on hollow carbon spheres via three representative kinetic models: pseudo-first-order adsorption, pseudo-second-order adsorption, and intraparticle diffusion. The detailed results are presented in Figures 8b to 8d. Table 4 details the fitting parameters for the three kinetic models. Adsorption kinetic analysis indicated that phenol adsorption on hollow carbon spheres was poorly consistent with the pseudo-first-order kinetic model ($R^2 = 0.92$) but better consistent with the intraparticle diffusion model ($R^2 = 0.97$). Although the pseudo-second-order model exhibited a high correlation coefficient ($R^2 = 0.99$), it yielded an unreasonable negative equilibrium adsorption capacity (Q_e). Therefore, the adsorp-

Table 3. BiOBr decontamination of phenol: parameters for first-order, second-order, and intraparticle diffusion kinetic fitting

Dynamic Model	Parameters	BiOBr
Pseudo-first-order kinetics	$Q_{e,f}^a$ (mg g ⁻¹)	3.22
	k_1 (h ⁻¹)	0.051
	R^2	0.99
Pseudo-second-order kinetics	$Q_{e,s}^a$ (mg g ⁻¹)	-52.63
	k_2 (g mg ⁻¹ h ⁻¹)	0.00026
	R^2	0.89
Intra-particle diffusion	k_i (mg L ⁻¹ h ^{1/2})	5.93
	C_i	-0.45
	R^2	0.98

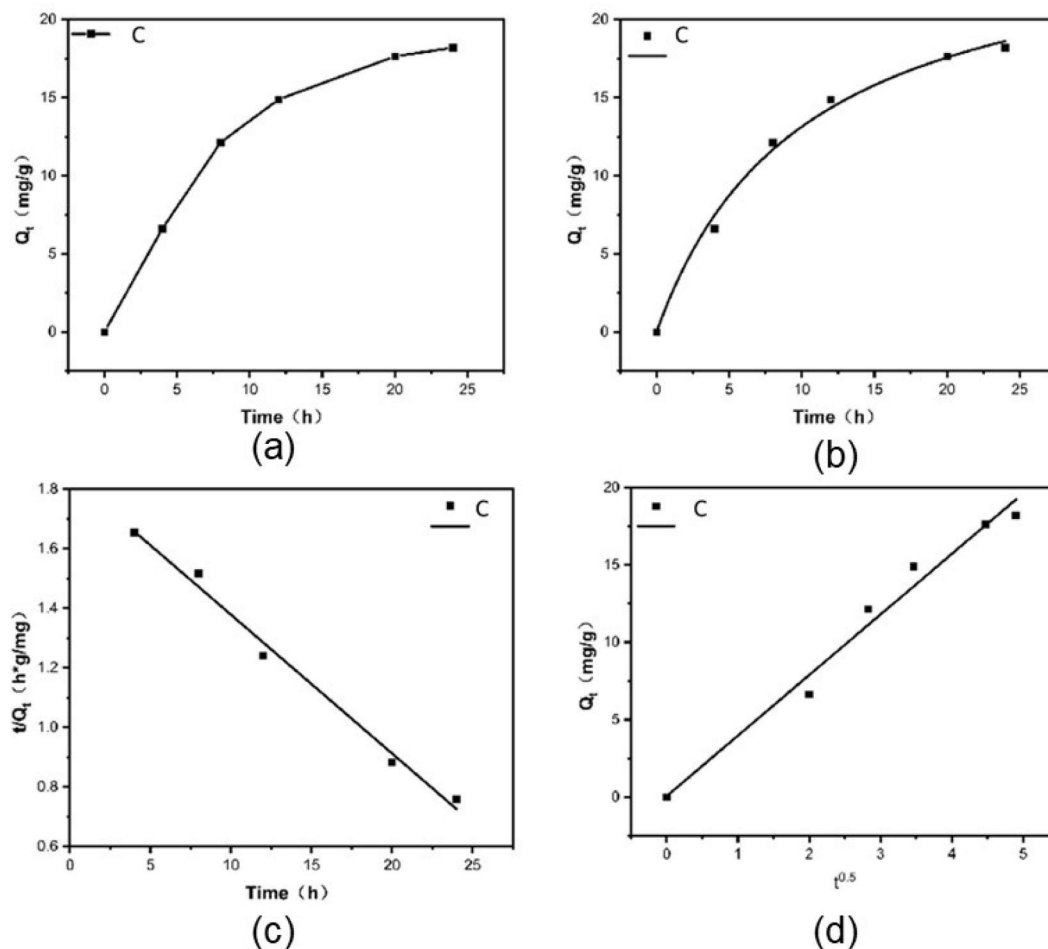


Fig. 8. (a) Adsorption kinetics curve, (b) Langmuir model, (c) pseudo-first-order model, and (d) intraparticle diffusion model for phenol adsorption on carbon spheres.

Table 4. Parameters for the first-order, second-order, and intraparticle diffusion kinetic fits of the carbon spheres for phenol decontamination

Dynamic Model	Parameters	carbon sphere
Pseudo-first-order kinetics	$Q_{e,f}^a$ (mg g ⁻¹)	3.34
	k_1 (h ⁻¹)	0.035
	R^2	0.92
Pseudo-second-order kinetics	$Q_{e,s}^a$ (mg g ⁻¹)	-21.28
	k_2 (g mg ⁻¹ h ⁻¹)	0.0012
	R^2	0.99
Intra-particle diffusion	k_i (mg L ⁻¹ h ^{1/2})	3.92
	C_i	0.054
	R^2	0.97

tion behavior of phenol on carbon spheres does not conform to the pseudo-second-order kinetic model. The phenol adsorption process on hollow carbon spheres involves complex mass transfer mechanisms. Fitting with the intraparticle diffusion model revealed a significant shift in the intercept of the linear equation ($C_i \neq 0$). This phenomenon confirms that, in addition to intraparticle diffusion, other mass transfer steps, such as boundary layer diffusion, also influence the adsorption kinetics. These results indicate that the adsorption system is jointly regulated by multistep mass transfer mechanisms [38, 39].

3.5. Decontamination kinetic analysis of phenol on BiOBr@C

As shown in Figure 9a, the adsorption capacity of phenol on the BiOBr@C hybrid increased with increasing reaction time, reaching an equilibrium adsorption of 28.1 mg/g after 24 h. The adsorption rate gradually decreased over time. In this study, the adsorption kinetics of phenol on BiOBr@C hybrids were investigated via three typical adsorption kinetic models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion. The fitting curves predicted by the three adsorption kinetic models are shown in Figures 9b to 9d, and the specific parameters are listed in Table 5. The adsorption behavior of phenol on the BiOBr@C hybrid fit well with the pseudo-first-order kinetic characteristics, with a correlation coefficient of $R^2 = 0.98$. The adsorption behavior of phenol on the BiOBr@C hybrid also fit well with the pseudo-second-order kinetic model, with a correlation coefficient of $R^2 = 0.97$. However, the Q_e value derived from this model was an implausible negative number, indicating that phenol adsorption on BiOBr did not conform to the pseudo-second-order kinetic model. The phenol adsorption on BiOBr@C closely matched the intramolecular diffusion kinetic model, with a correlation coefficient R^2 of 0.99. These findings indicate that intramolecular diffusion played a dominant role in phenol adsorption on BiOBr@C (Table 6). Furthermore, the fitted line exhibits a non-zero intercept on the vertical axis, suggesting that the adsorption pro-

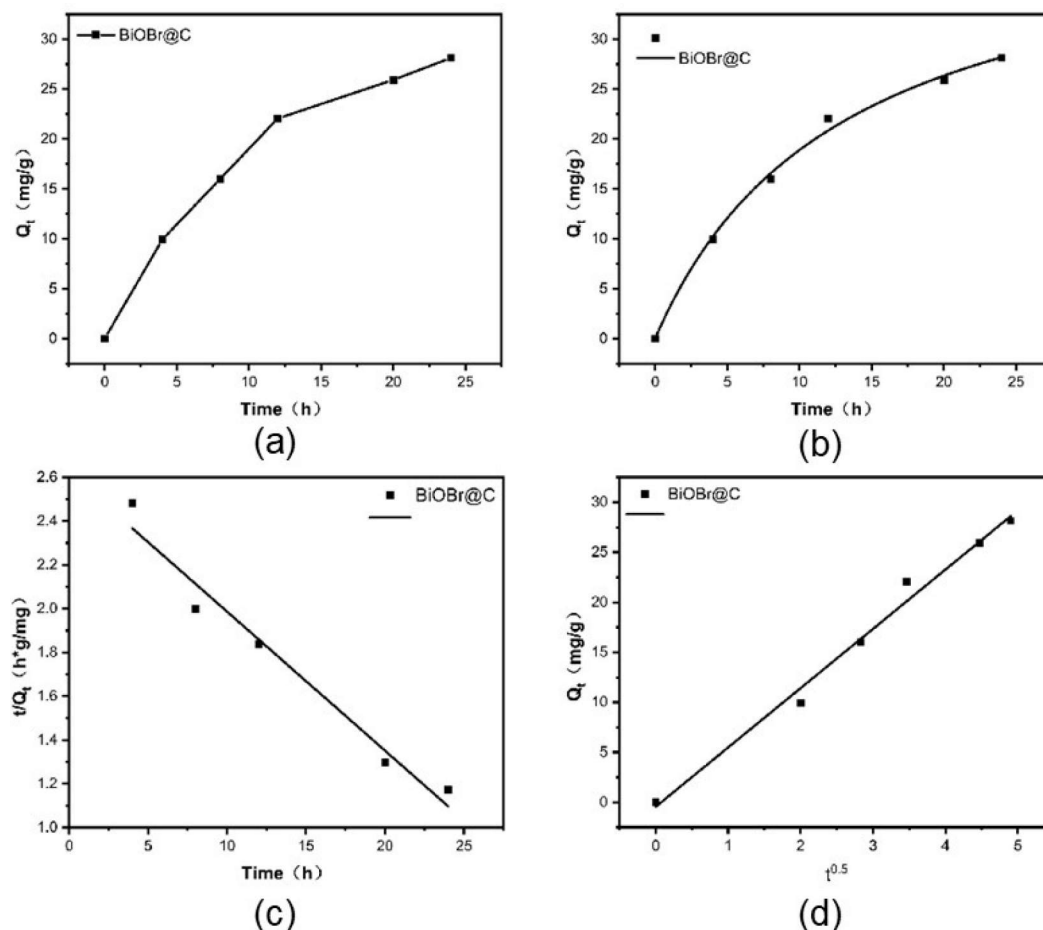


Fig. 9. (a) Adsorption kinetics curve, (b) Langmuir model, (c) pseudo-first-order model, and (d) intraparticle diffusion model for phenol adsorption on BiOBr@C.

Table 5. Fitting parameters for the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetics of BiOBr@C decontamination of phenol

Dynamic Model	Parameters	BiOBr@C
Pseudo-first-order kinetics	$Q_{e,f}^a$ (mg g ⁻¹)	3.23
	k_1 (h ⁻¹)	0.12
	R^2	0.98
Pseudo-second-order kinetics	$Q_{e,s}^a$ (mg g ⁻¹)	-15.63
	k_2 (g mg ⁻¹ h ⁻¹)	0.0016
	R^2	0.97
Intra-particle diffusion	k_i (mg L ⁻¹ h ^{1/2})	5.93
	C_i	-0.45
	R^2	0.99

Table 6. Kinetic models and mechanism analysis for phenol decontamination by BiOBr, carbon spheres, and BiOBr@C

Sample	Kinetic Model	R^2	Mechanism
BiOBr	Pseudo-first-order kinetics	0.99	Physical adsorption
Carbon Sphere	Webber-Morris	0.97	Intramolecular diffusion
BiOBr@C	Webb-Morris	0.99	Intramolecular diffusion

cess is jointly regulated by multiple mass transfer mechanisms rather than being solely controlled by diffusion [40, 41].

3.6. Mechanistic analysis for phenol decontamination

The surface photovoltage spectra of C, BiOBr, and BiOBr@C are shown in Figure 10a. The SPV spectrum of C was extremely weak, nearly zero, whereas that of BiOBr showed two distinct SPV peaks at ~340 nm and ~400 nm. The SPV spectrum of BiOBr@C hybrid was markedly attenuated, with broadened peak shapes and reduced intensity, indicating that BiOBr possessed strong photogenerated charge separation capabilities in the UV-visible region. When carbon spheres were introduced, the SPV signal of the BiOBr@C hybrid significantly decreased, potentially suggesting that the introduction of carbon spheres promoted charge transfer and reduced surface charge accumulation. To further validate the photoelectrochemical properties of the obtained samples, electrochemical impedance spectroscopy (EIS) measurements were performed. The EIS Nyquist plots for C, BiOBr, and BiOBr@C are shown in Figure 10b. A smaller arc radius reflects a lower intrinsic charge transfer resistance. Notably, compared with BiOBr, C has a larger arc radius, whereas BiOBr@C has the smallest arc radius, indicating that the introduction of carbon spheres significantly reduced the charge transfer resistance. Therefore, well-developed interfacial contact between BiOBr and carbon spheres increased the transfer and separation of photogenerated electrons.

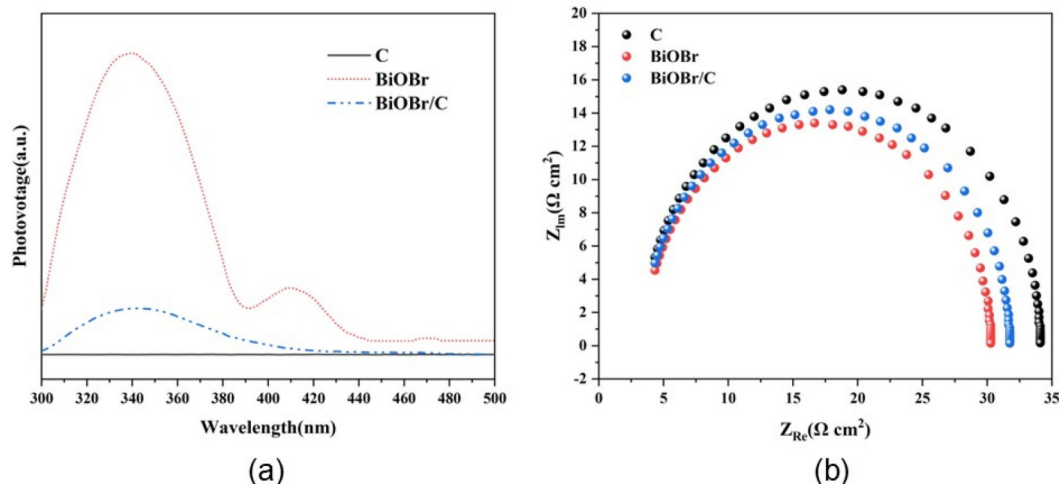


Fig. 10. (a) Surface photoelectric spectra and (b) electrochemical impedance spectra corresponding to the C, BiOBr, and BiOBr@C systems.

ROS trapping experiments were performed to identify the main radicals involved in the catalytic degradation of phenol over BiOBr@C. Isopropanol, KI, and Ar were used as scavengers to quench $\cdot\text{OH}$, h^+ , and $\cdot\text{O}_2^-$, respectively. As shown in Figure 11, all the scavengers inhibited the catalytic degradation of phenol over BiOBr@C, indicating that these scavengers were involved in the photocatalytic process. Among them, isopropanol caused the most significant decrease in degradation efficiency, indicating that $\cdot\text{OH}$ was the dominant radical for the catalytic degradation of phenol over BiOBr@C, while h^+ and $\cdot\text{O}_2^-$ played secondary roles.

To investigate the photocatalytic degradation mechanism of phenol over BiOBr@C, liquid chromatography-mass spectrometry was employed to identify the intermediates involved in the degradation process. As shown in Figure 12, the m/z peaks included 102 (4-hydroxybut-2-eneic acid, M), 109 (hydroquinone or resorcinol, M-1), 151 (para-aldehydebenzoic acid or ortho-aldehydebenzoic acid, M-1), 157 (2-carbonyl-3-enhexanedioic acid, M-1), 171 (2,5-dicarbonyl-3-enhexanedioic acid, M-1), and 203 (2-carbonyl-5-carboxyhexanedioic acid, M-1). On the basis of these predicted chemicals, the photocatalytic degradation pathway is proposed in Figure 13. Phenol first degraded into lower molecular weight intermediates before ultimately decomposing into H_2O and CO_2 .

The potential toxicity of phenol and its degradation intermediates was further evaluated using predicted acute and

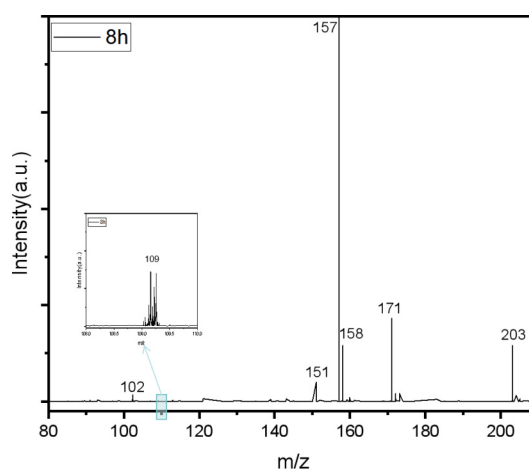


Fig. 12. HPLC test results of catalytic phenol degradation at 8 h

chronic toxicity toward fish, daphnia, and green algae. As shown in Figure 14, phenol and several aromatic intermediates exhibited relatively high toxicity, whereas some ring-opening products showed lower toxicity. These results suggest that although hydroxylation and oxidation may generate toxic aromatic intermediates at the early degradation stage, subsequent ring opening and deep oxidation can reduce ecological risk. Therefore, promoting the complete oxidation of aromatic intermediates is crucial for improving the environmental safety of the photocatalytic degradation process of phenol over BiOBr@C.

3.7. Stability Evaluation of the Catalyst

To evaluate the recycling stability, XRD patterns and SEM-EDS mapping images of BiOBr@C hybrids were obtained. As shown in Figure 15, the XRD pattern of BiOBr@C retained the characteristic diffraction peaks of BiOBr after three photocatalytic degradation cycles, indicating that the crystalline structure of the hybrids was well preserved. SEM-EDS mapping (Figure 16) further revealed the presence and distribution of Bi, Br, and C after three photocatalytic degradation cycles, confirming the structural stability of BiOBr@C during the photocatalytic process.

4. Conclusion

In conclusion, 3D BiOBr@hollow carbon sphere (BiOBr@C)

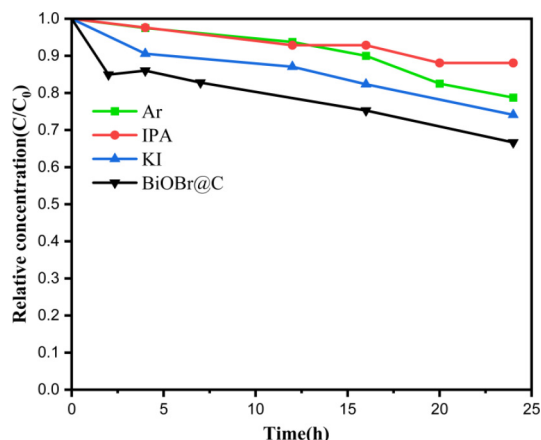


Fig. 11. ROS-trapping catalytic curve

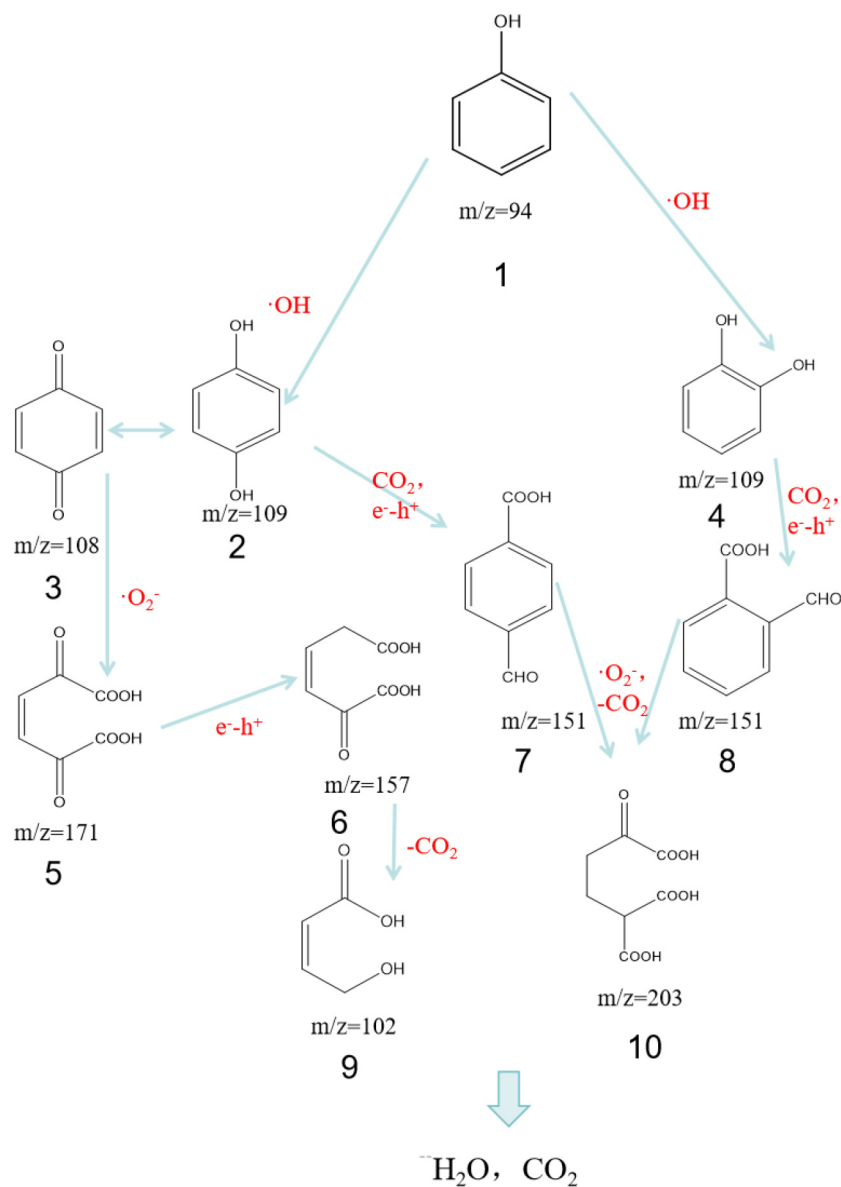


Fig. 13. Proposed degradation pathway of phenol over BiOBr@C.

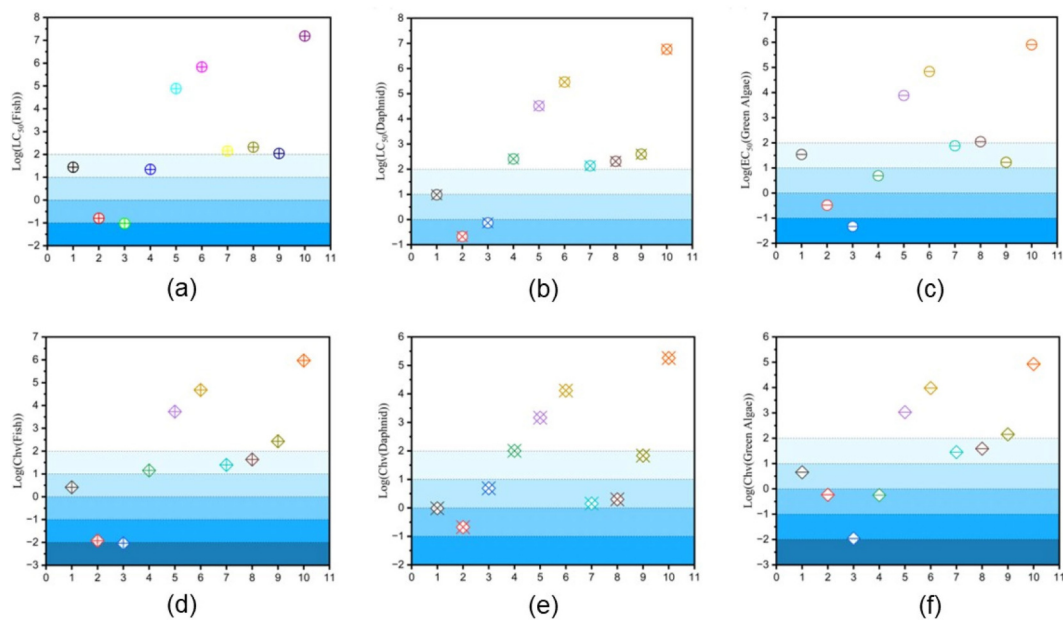


Fig. 14. Predicted toxicity of phenol and its degradation intermediates toward (a, d) fish, (b, e) daphnid and (c, f) green algae.

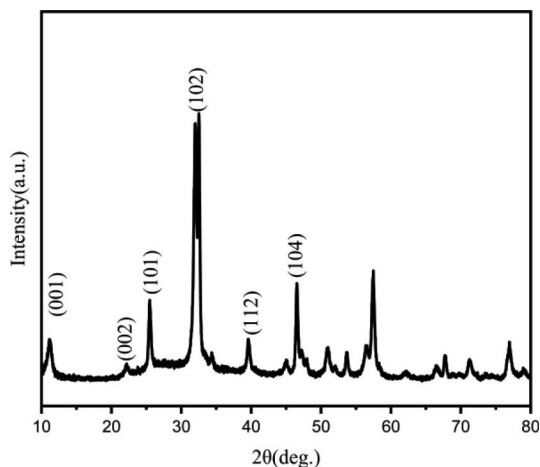


Fig. 15. XRD pattern of BiOBr@C after three photocatalytic degradation cycles.

hybrids were synthesized for the catalytic decomposition of phenol in wastewater. Compared with both pure BiOBr and carbon spheres alone, the BiOBr@C hybrids showed better phenol decontamination efficiency. The adsorption behaviors of phenol decontamination over BiOBr@C fit the Weber–Morris kinetic model well, indicating that the phenol decontamination process was governed by multiple mechanisms, including intramolecular diffusion and surface chemical adsorption. These multiple mechanisms enabled BiOBr@C to exhibit superior phenol decontamination performance compared with BiOBr and carbon spheres. Although BiOBr@C preparation is still somewhat complicated, the hollow carbon spheres provided adsorption sites and diffusion channels, increased light absorption, and improved charge transfer, making this strategy potentially useful for the treatment of phenol-containing wastewater treatment. In future work, the C/BiOBr ratio needs to be adjusted to ensure the scalability of the preparation.

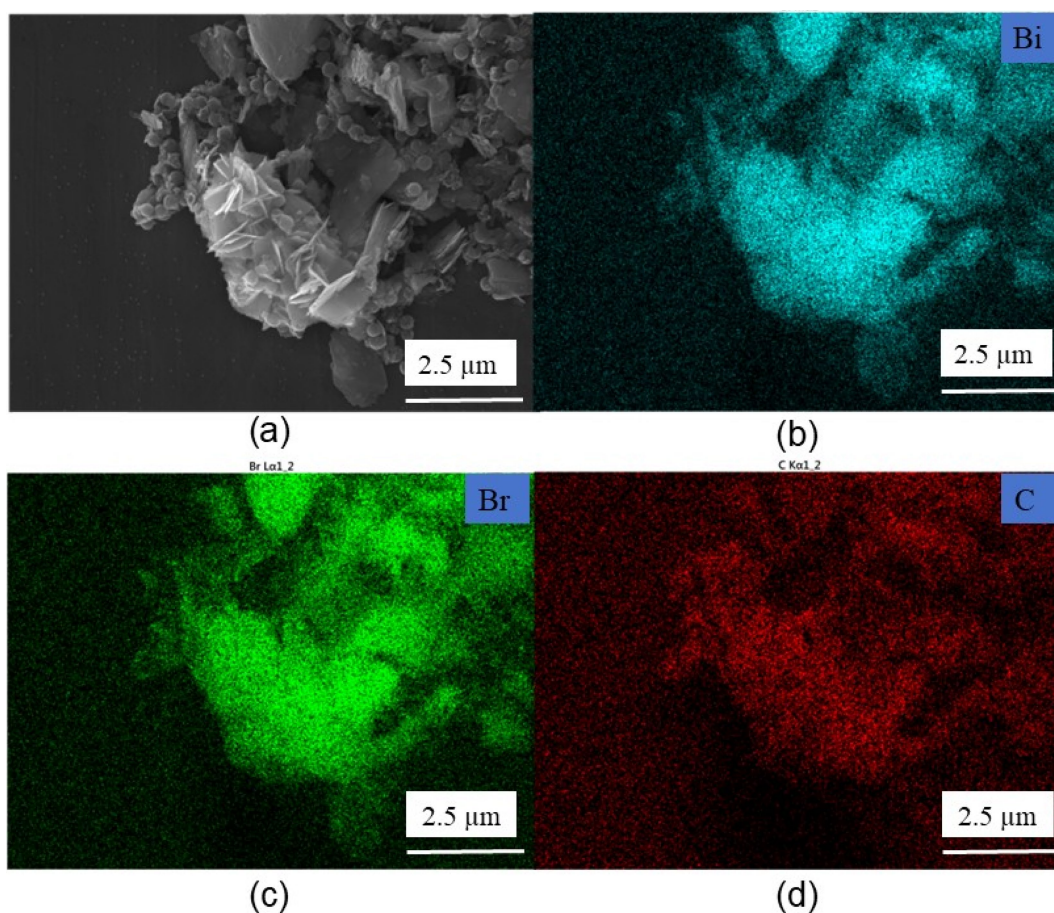


Fig. 16. SEM image and EDS elemental mapping images of BiOBr@C after three photocatalytic degradation cycles.

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Declaration of interests

The authors declare that there are no conflicts of interest in this work.

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