Ternary Photodegradable Nanocomposite (BiOBr/ZnO/WO₃) for the Degradation of Phenol Pollutants: Optimization and Experimental Design

Hager R. Ali† and Eman A. Motawea*

ABSTRACT: The degradation of environmental contaminants with photocatalysts has bright prospects for application in the control of pollution. In this study, BiOBr/ZnO/WO₃ heterojunctions have been documented to be reliable visible-light photocatalysts for phenol deterioration. X-ray diffraction, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, photoluminescence spectral analysis, electrochemical impedance spectroscopy (EIS), EIS Bode plots, linear sweep voltammetry, and UV–visible diffuse reflectance spectroscopy were employed to describe the heterojunction’s structure in addition to its optical features. The results revealed that the BiOBr/ZnO/WO₃ ternary photocatalyst displayed more degradation activity in comparison to single-phase ZnO, WO₃, or BiOBr, which is also higher than that of binary mixture photocatalysts with a phenol degradation efficiency of 90%. The influence of degradation variables, for instance, the potential of hydrogen (pH) and the initial organic contaminant content besides the heterojunction dose, on the deterioration efficiency was optimized using the response surface methodology. The degradation efficiency reached 95% under the optimal conditions of 0.08 g/0.03 L catalyst dose, a pH of 9, and an initial organic contaminant content of 10 mg L⁻¹. However, the optimal phenol degradation efficiency of 39.37 mg g⁻¹ was achieved under the conditions of 0.08 g/0.03 L catalyst dose, pH of 9, and 200 mg L⁻¹ initial phenol concentration.

INTRODUCTION

Treatment of water contaminated with industrial effluents is a persistent global problem today. Several related bodies have raised concerns about the green technology and energy efficiency in wastewater treatment in recent years to reduce the current environmental problems. Phenol is present in the industrial synthesis of adhesive and antiseptic products as an intermediate.¹ An innate deterioration rate of monophenol can happen depending on a condition through various processes. In water bodies, the acceptable limit for phenol is 0.1−1.0 mg L⁻¹. Owing to its toxicity, genotoxicity, and exceptionally high endocrine-disrupting potency, phenol remediation therapies are becoming problems despite the low concentration limit.² One of the best approaches is producing a photocatalyst and its use in process treatment. Some of the rare-earth semiconductors such as BiOBr and ZnO besides WO₃ are used during photocatalytic processes. To start the photocatalytic reaction and ultimately degrade the contaminant, these semiconductors will use sunlight.³ Recently, due to their peculiar properties and possible uses, BiO halogenides (BiOX, where X = Cl, Br, and I) were studied. Bismuth oxybromide is a positive-category semiconductor that has a band gap of 2.80 eV and an enticing photocatalyst for contaminant deterioration under solar light illumination.⁴ Some researchers have reported that photocatalytic activity is strongly dependent on the size, diameter, and structure of catalysts. Nanophotocatalysts’ shape, scale, and structure have therefore been tuned to enhance their activity.⁵ Recently, due to their high crystallinity and ultrathin thickness, the lamellar nanostructures have been gaining greater attention. It is well known that this structure could help in reducing the recombination possibilities of the illumination-created free charge carriers, so that they can easily move toward the surface to degrade the organic molecules.⁶ Fabricating a blend of different p–n types through integrating different transistors with suitable band models is the most efficient way. Besides, an n-type may be generated by hybridizing ZnO with WO₃, which could facilitate the isolation of illumination-produced carriers. Tungsten(VI) oxide (WO₃) nanoparticles (NPs) have
attracted particular interest among researchers in the domain of illumination catalysts owing to their heavy sorption in the presence of solar spectra (almost 500 nm), their sustainable physical and chemical properties, and their resistance toward photocorrosion. Tungstic anhydride (WO$_3$) has exceptional electrical illumination characteristics of a small band gap of $2.40\,\text{eV}$ to $2.80\,\text{eV}$ with a favorable hole dispersion width that may potentially use $\sim 12\%$ solar light. However, because of stagnant kinetics and low charge transfer at the transistor–electrolyte system, WO$_3$ demonstrates a fair photocatalytic activity toward the deterioration of phenolic contaminants. Several techniques have been employed to decorate WO$_3$ to solve these problems, including metal implantation and coupling with other semiconductors. ZnO, additionally defined as the II–IV transistor, contains a broadband energy band gap (3.3 eV), high photosensitivity, and stability. Also, at room temperature, ZnO possessed good heat sustainability and is relatively inexpensive. The variables of a process can be developed, improved, and optimized by the response surface methodology (RSM), which is an assimilation of theoretical and numerical tools used for assessing the significance of differential process factors in the presence of different correlations. RSM is a viable procedure for optimizing responses that are modeled by process parameters. To our knowledge, no previous research has focused on the fabrication of a BiOBr/WO$_3$/ZnO p–n heterojunction and its phenol degradation performance. We present a simple and cost-effective solvothermal synthesis technique for fabricating a unique hybrid BiOBr/WO$_3$/ZnO p–n heterojunction. In the current work, we discuss the effects of p–n heterojunction formation on the visible-light photodegradation properties of phenol and its mechanisms.

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RESULTS AND DISCUSSION

Characterization of NPs. X-ray Diffraction. To characterize the synthesized NPs, various techniques were used. X-ray diffraction (XRD) was used to describe the crystal structure and primary crystal scale. XRD analysis was used to analyze the
BiOBr/WO3/ZnO phase and crystalline composition (Figure 1). XRD detected the pure WO3 as well. The sharp diffraction peaks may be well ascribed to the WO3 phase (JCPDS card no. 024-0747) with 2θ values of 24.35, 26.56, 33.23, 34.15, 35.50, 45.70, and 49.90° and a crystallinity of 79.03%. XRD peaks of the as-prepared ZnO (JCPDS card no. 01-081-8838) were observed at angles of 31.80, 34.46, 36.27, 47.50, 56.60, 62.89, 67.97, 69.11, 72.59, and 76.97° (2θ). The most common diffraction peaks of BiOBr were observed at 2θ angles of 25.16, 31.80, 32.17, 46.16, and 57.17° with a crystallinity of 59.35% and indexed to BiOBr according to JCPDS card no. 52-0084 with a crystallinity of 81.63%. The BiOBr/WO3 XRD pattern (JCPDS file no. 52-0084) and of BiOBr/ZnO (JCPDS file no. 09-0393) corresponded to JCPDS file no. 52-0084; ZnO- and WO3-related peaks were not identified due to the presence of low BiOBr-related ZnO and WO3 amounts. In the BiOBr/WO3/ZnO composites, the XRD pattern corresponded to JCPDS file no. 52-0084. This may be due to the great dispersion of ZnO and WO3 in BiOBr; the position of the peaks showed some changes suggesting the formation of a new compound. Besides, the presence of BiOBr limited the growth of ZnO and WO3 NPs.

Fourier-Transform Infrared Spectroscopy. To evaluate the composition, Fourier-transform infrared (FTIR) spectroscopy was performed. Figure 2 presents the contrast of FTIR spectra for all the prepared photocatalysts; the FTIR spectrum of the synthesized BiOBr/WO3/ZnO composite shows a high peak of absorption at 3508 cm⁻¹ owing to the stretching vibration of nonchemical bond association of OH groups, while a peak at 1637 cm⁻¹ was observed for H–O–H bending vibrations. The peaks are observed due to the existence of CO₂ at 2390 cm⁻¹. For Zn–O, the most characteristic peak at 514 cm⁻¹ is observed, while for the bending vibration of C–H stretching, an absorption peak at about 1392 cm⁻¹ is attributed. The findings mentioned above are in line with the results of XRD. The peak at a lower frequency of 810.84 cm⁻¹ is the product of W–O–W bond stretching vibrations. The presence of W–O–W/O–W (842 and 781 cm⁻¹, respectively) and also a further peak at 507 cm⁻¹ is due to the Bi-O bond that is observed in the FTIR spectra of binary and ternary nanocomposites. These findings further show that the preparation of the ternary nanocomposite BiOBr/WO3/ZnO has been effectively done.

X-ray Photoelectron Spectroscopy. The electronic states and the chemical composition of BiOBr/ZnO/WO3 were examined by X-ray photoelectron spectroscopy (XPS), and the results are given in Figure 3. It can be observed from the survey spectrum in Figure 3a that the characteristic peaks of Zn, Bi, Br, O, and W are present, indicating their coexistence on the surface of the BiOBr/ZnO/WO3 sample. As for the high-resolution Bi 4f spectrum in Figure 3b, two significant peaks are observed at 159 and 164.5 eV, corresponding to Bi 4f⁵/₂ and Bi 4f⁷/₂, respectively, due to the spin–orbital component of Bi³⁺ in BiOBr. Moreover, as shown in Figure 3c, the XPS
spectra of Br 3d consisted of Br 3d 5/2 at 68.2 eV and Br 3d 3/2 at 69.5 eV attributed to Br in the monovalent oxidation state.22 Also, the high-resolution spectrum of W 4f depicted in Figure 3d shows that W 4f 7/2 at 35.4 eV and W 4f 5/2 at 37.5 eV are ascribed to W6+ species.23 From the Zn 2p XPS spectrum in Figure 3e, the fitted peaks at 1045 and 1022 eV can be observed, which were attributed to 2p 1/2 and 2p 3/2 of Zn2+, respectively, in ZnO.24 The O 1s spectrum in Figure 3f could be resolved into four individual peaks, which indicated the presence of four different kinds of O species in the sample. The main peak at 530.4 eV was assigned to O2 ions that are in oxygen-deficient regions. The peak at 533.9 eV was attributed to the crystal lattice O atom in WO3.23 Also, the peak at 531.9 eV was related to the crystal lattice O atom in BiOBr,24 while the peak at 530.6 eV could be attributed to the O atom in

![Figure 3. XPS spectrum of BiOBr/ZnO/WO3: (a) survey spectrum, (b) Bi 4f spectrum, (c) Br 3d spectrum, (d) W 4f spectrum, (e) Zn 2p spectrum, and (f) O 1s spectrum.](image-url)
ZnO. The XPS analysis proves the existence of the BiOBr/ZnO/WO3 composite.

Optical Properties of Photocatalysts. UV–visible diffuse reflection spectroscopy (UV–vis DRS) and photoluminescence (PL) spectroscopy were utilized to identify the optical characteristics of pure ZnO, WO3, BiOBr, and binary and ternary composites (Figure 4). As shown in Figure 4A, the neat BiOBr, ZnO, and WO3 display absorption edges at 425, 420, and 450 nm, respectively, while the binary BiOBr/ZnO and BiOBr/WO3 exhibit absorption edges at 428 and 470 nm, respectively; additionally, BiOBr/ZnO/WO3 shows the highest visible-light absorption edge at 485 nm, confirming the existence of additional energy levels of metal ions in the forbidden gap of BiOBr. The band gap of the prepared photocatalysts was calculated according to the classical equation of Tauc’s plot (Figure 4B,C)

\[
\alpha h\nu = A(h\nu - E_g)^n
\]

(1)

It should be noted that the absorption coefficient per unit length is expressed as \(\alpha\), \(E_g\) represents the band gap energy, \(h\) refers to Planck’s constant, \(\nu\) is the frequency of vibration, \(h\nu\) implies the incident photon energy, \(A\) refers to the proportional constant, and \(n\) is 0.50 for the indirect band-gap semiconductor and 2 for the direct band-gap semiconductor.

ZnO and WO3 have been reported to be attributed, as shown in Figure 4B, to the n-type direct band-gap semiconductor and BiOBr to the p-type indirect band-gap semiconductor (Figure 4C). The band gaps of the synthesized ZnO and WO3 were estimated to be 3.20 and 2.85 eV, respectively, and that of BiOBr was 2.80 eV. By doping BiOBr with ZnO and WO3, the band gap was reduced to approximately 2.75 and 2.70 eV, respectively, while the band gap was reduced to approximately 2.60 eV for the BiOBr/WO3/ZnO composite. This confirms that BiOBr/WO3/ZnO exhibits the narrowest band gap, and this reduction in energy value is due to excessive absorption in the visible region due to the energy level existing in the forbidden gap through the doping of ZnO and WO3.

Furthermore, the conduction band (CB) and valence band (VB) edges of ZnO, BiOBr, and WO3 that are depicted in Table 1 have been studied more as a result of their significant roles in assessing the heterojunction flowchart of photogenerated electrons and holes. WO3 (band gap: 2.85 eV), ZnO (band gap: 3.20 eV), and BiOBr (band gap: 2.80 eV) band-edge positions have been assessed according to the following equations

\[
E_{VB} = X - E_{\text{g}} + 0.5E_g
\]

(2)
Table 1. Values of Calculated $E_{CB}$ and $E_{VB}$ for ZnO, WO$_3$, and BiOBr

| Semiconductor | $X$ (eV) | $E_{CB}$ (eV) | $E_{VB}$ (eV) | $E_g$ (eV) |
|---------------|----------|---------------|---------------|------------|
| ZnO           | 5.790    | $-0.31$       | 2.89          | 3.2        |
| BiOBr         | 6.180    | 0.2           | 3.16          | 2.8        |
| WO$_3$        | 6.49     | 0.615         | 3.36          | 2.85       |

where the VB edge potential is expressed as $E_{VB}$ and $X$ is the semiconductor electronegativity, which is the geometric mean of electronegativity for constituent atoms. The $X$ values are determined as 6.18, 5.79 and 6.49 eV, respectively, for BiOBr, ZnO, and WO$_3$. $E_0$ is the free electron energy of the hydrogen scale (~4.5 eV) and $E_g$ is the semiconductor’s band gap energy. The $E_{VB}$ and $E_{CB}$ values of BiOBr are calculated as 3.16 and 0.20 eV, respectively, while those of WO$_3$ are calculated as 3.365 and 0.615 eV and of ZnO are 2.89 and $-0.31$ eV, respectively.

PL is an efficient tool for investigating the performance of charge carrier transfer, trapping, and separation of photo-generated electrons and holes in heterojunctions. Figure 4D displays the PL spectra of all samples, where the main emission peak is located at 430 nm. The PL spectrum of composite photocatalysts is similar to that of pure BiOBr, while the intensity emission is reduced in the BiOBr/WO$_3$/ZnO photocatalyst. Generally, the intensity of PL emission is derived from free charge carrier recombination, so the lower emission intensity of the BiOBr/WO$_3$/ZnO heterojunction implies a lower electron and hole recombination rate under visible light irradiation. PL results prove that WO$_3$ and ZnO are favorable for charge separation in BiOBr/WO$_3$/ZnO photocatalysts as a result of the lower recombination rate of photogenerated charge carriers.

Photoelectrochemical Measurements. The charge generation, migration, and recombination processes in photocatalysts were investigated by electrochemical impedance spectroscopy (EIS Nyquist spectra); it is evident that the higher the electron and hole separation efficiency, the better the photocatalytic performance. Figure 5a demonstrates that
compared to BiOBr, BiOBr/ZnO/WO₃ has a much lower impedance, as evidenced by the smaller arc radius in the EIS Nyquist plots, implying that BiOBr/ZnO/WO₃ has a lower interfacial layer resistance, beneficial to a faster interfacial
transfer of electron–hole pairs and thus a more effective separation. For better analysis of the EIS data, the corresponding Bode phase plot is presented in Figure 5b; a characteristic of the Bode phase plot is its ability to identify the predominant electrical behavior of the system in a given frequency range. The maximum oscillation frequency \( f_{\text{max}} \) of the impedance semicircle of BiOBr/ZnO/WO\(_3\) is less than that of BiOBr. Thus, the corresponding lifetime of photoelectrons in BiOBr/ZnO/WO\(_3\) increases. This can be ascribed to the efficient separation of light-generated electrons and holes in BiOBr/ZnO/WO\(_3\). In other words, the electrons transferred from the CB of BiOBr to that of ZnO and WO\(_3\), while the holes were transported to the VB of BiOBr. Therefore, the recombination of electron–hole pairs was inhibited, and the lifetime of photoelectrons was prolonged. Figure 5c shows the linear sweep voltammetry (LSV) measurements under visible-light irradiation for the BiOBr and BiOBr/ZnO/WO\(_3\) electrodes. The photocurrent values of both electrodes increased with the upgrade of the applied potential. The photocurrent densities of BiOBr/ZnO/WO\(_3\) were much higher than that of bare BiOBr at the same applied potential, which further indicated that BiOBr/ZnO/WO\(_3\) has higher charge separation and migration.

**Scanning Electron Microscopy, Transmission Electron Microscopy, and Energy-Dispersive X-ray spectroscopy and Electron Microscopy Studies.** The size and morphologies of the prepared BiOBr/ZnO/WO\(_3\) nanocomposite were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For comparison, Figure 6A,E displays the SEM and TEM photos of ZnO NPs; the particles clearly show the spherical structural composition, also nearly spongy-like structural NPs were observed with an average size of 122−193 nm; however, Figure 6B,F shows disc-shaped of agglomerated WO\(_3\) plates and also confirms the orthorhombic shapes of different dimensions with an average size of 71.9−168 nm. Evidently, it is clear that the prepared BiOBr, as shown in Figure 6C,G, contained ultrathin nanocrystals of irregular-shaped nanoplates with an average width of 50−122 nm, whereas ZnO and WO\(_3\) can be observed deposited on the surface of flakes/plates of BiOBr, as shown in Figure 6D,H, and such a structure is expected to provide abundant heterojunction interfaces between BiOBr, ZnO, and WO\(_3\).

Energy-dispersive X-ray spectroscopy (EDX) analysis was utilized to explore the surface chemical composition of ternary BiOBr/ZnO/WO\(_3\). As per Figure 6I, the constituents of Bi, Br,
O, Zn, and W were revealed in the spectrum of BiOBr/ZnO/WO3, implying that the ternary nanocomposite was successfully formed.

Evaluation of Photocatalytic Activity. The efficiency of the prepared photocatalyst toward organic pollutant photocatalytic degradation was investigated by conducting phenol removal. Adsorptive and photocatalytic activities were assessed individually for evaluating and comparing the performance. To screen the best catalyst that can be included in the upcoming experiments and achieve the highest removal of monophenol under visible-light irradiation, the photocatalytic performance of ZnO, WO3, BiOBr, BiOBr/ZnO, BiOBr/WO3, and BiOBr/ZnO/WO3 photocatalysts was evaluated. To attain adsorption-desorption equilibrium, the phenol samples with photocatalysts were shaken in the dark for 1 h. Due to its significant role in the polluted water-treatment process, sorption kinetics was evaluated. At an initial concentration of 50 mg/L, time-dependent phenol adsorption/degradation on the prepared catalysts was evaluated and is presented in Figure 7A as a function of adsorption/degradation capacity and in Figure 7B as a function of adsorption/degradation efficiency. As a result, in the dark, all catalysts reached the adsorption equilibrium after 60 min, while in the presence of visible light, catalysts reached degradation equilibrium after 300 min. From Figure 7A, it can be observed that the maximum phenol degradation capacity reached 27 mg/g with BiOBr/ZnO/WO3 photocatalysts. In the dark, the phenol removal percent was negligible, as depicted in Figure 7B, and decreased in the order of BiOBr/ZnO/WO3 (25%) > BiOBr/WO3 (22%) > BiOBr/ZnO (18%) > BiOBr (17.6%) > ZnO (16%) > WO3 (14%). This may be due to the high surface acidity of ZnO and WO3, which may be attributed to the cationic adsorbents. However, the efficiency of phenol photodegradation under visible light enhanced and is in the order of ZnO (50%) < WO3 (60%) < BiOBr (66.5%) < BiOBr/ZnO (73%) < BiOBr/WO3 (81%) < BiOBr/ZnO/WO3 (90%), which may be attributed to ZnO and WO3 photocatalysts operating as an acceptor of the electron, which is helpful for the efficient isolation of electron-hole pairs generated in the system and prevent their recombination.

The kinetics of the photodegradation of phenol illustrated in Figure 7C implies that the lowest deterioration performance that may be due to the unsuitable band gap under visible-light-induced conditions was shown by pure ZnO and WO3. Under visible-light irradiation, these photocatalysts were hard to be simulated. The deterioration activity of ZnO and WO3 was drastically improved by doping with BiOBr and it reached 90% for BiOBr/ZnO/WO3. We conclude according to the above results that BiOBr/ZnO/WO3 p–n heterojunctions display a high photocatalytic activity rather than the solitary phases of ZnO, WO3, and BiOBr, which is also higher than that of the two component mixture photocatalyst. Compared to an individual or binary components, the improvement of the deterioration activity of the BiOBr/ZnO/WO3 p–n heterojunctions could be related to the creation of heterojunctions through n-type ZnO, WO3, and p-type BiOBr, enabling the interface isolation of electron–hole pairs.

Table 2. Kinetic Parameters and Correlation Coefficients for the Pseudo-First-Order and Pseudo-Second-Order Models

| catalyst              | Pseudo-first-order model | Pseudo-second-order model |
|-----------------------|--------------------------|----------------------------|
|                       | K1 (min⁻¹) | R² | K2 (g mg⁻¹ min⁻¹) | R² |
| dark study            |             |    |                 |    |
| ZnO                   | 0.0019      | 0.998 | 0.00004         | 0.729 |
| WO3                   | 0.0014      | 0.985 | 0.00190         | 0.282 |
| BiOBr                 | 0.0023      | 0.975 | 0.00233         | 0.788 |
| BiOBr/ZnO             | 0.0024      | 0.973 | 0.00350         | 0.882 |
| BiOBr/WO3             | 0.0040      | 0.967 | 0.00791         | 0.946 |
| BiOBr/ZnO/WO3         | 0.0062      | 0.977 | 0.00096         | 0.945 |
| light study           |             |    |                 |    |
| ZnO                   | 0.0025      | 0.970 | 0.00197         | 0.945 |
| WO3                   | 0.0015      | 0.980 | 0.00077         | 0.883 |
| BiOBr                 | 0.0029      | 0.960 | 0.00114         | 0.927 |
| BiOBr/ZnO             | 0.0037      | 0.990 | 0.00101         | 0.976 |
| BiOBr/WO3             | 0.0046      | 0.990 | 0.00095         | 0.939 |
| BiOBr/ZnO/WO3         | 0.0065      | 0.995 | 0.00103         | 0.972 |

Pseudo-first-order and pseudo-second-order models were utilized to evaluate the kinetics of phenol sorption onto photocatalysts, and the values were calculated according to eqs 3 and 4, respectively, whose data are depicted in Table 2. The regression results predicted (R²) demonstrate that, in all cases, the pseudo-first-order model defines phenol sorption rather than the pseudo-second-order model, indicating that phenol degradation depends on the catalyst used. Therefore, the rate of phenol sorption process depending on the pseudo-first-order kinetic model increases in the order of WO3 (0.0014 min⁻¹) < ZnO (0.0019 min⁻¹) < BiOBr (0.0023 min⁻¹) < BiOBr/ZnO (0.0024 min⁻¹) < BiOBr/WO3 (0.0040 min⁻¹) < BiOBr/ZnO/WO3 (0.0062 min⁻¹). BiOBr/ZnO/WO3 was found to be the best catalyst with the best sorption capacity (7.5 mg/g) and a maximum sorption rate (0.0065 min⁻¹) among all catalysts. Experimental data were applied to the pseudo-first-order (eq 3) to obtain more information on the kinetics of phenol deterioration catalyzed by different photocatalysts, where the rate constant K value generally provides an estimate about photocatalyst’s efficiency. The dark and visible-light irradiation catalytic efficiencies of the prepared catalysts are illustrated in Figure 7C. Due to the high band gap of ZnO and WO3 (3.20 and 2.85 eV, respectively), their catalytic efficiencies were significantly limited under visible-light irradiation with nearly 50 and 60 percent, respectively, for monophenol deterioration after 5 h. In the case of BiOBr/ZnO/WO3, the efficiency of removal (K = 0.0065 min⁻¹, and capacity = 27 mg/g) was significantly more than that of ZnO and WO3, indicating that the combination of BiOBr increased the catalytic activity. The p–n heterojunction semiconductor is a convenient system for relatively reliable charge collection and isolation. Typically, the generated electron–hole pairs could be rapidly isolated by the electric field in the charge carriers when the p–n heterojunction was
irradiated by photons. Electrons were diverted to the CB of negative-type semiconductors, driven by an electric field, and holes were diverted to the VB of the positive-type transistors. The Fermi level of positive-type BiOBr moved up when positive-type BiOBr and negative-type ZnO and WO3 were in contact, while that of n-type ZnO and WO3 moved down until the balance state was established. The entire energy band of positive-type BiOBr increased, compatible with the motion of the Fermi level, whereas that of negative-type ZnO and WO3 reduced. Consequently, a charging area was formed in functionalities from negative-type ZnO and WO3 to positive-type BiOBr. Both ZnO and WO3 may simulate to create electron−hole pairs during visible-light irradiation. BiOBr’s photogenerated electrons in the CB would be transported to ZnO and WO3, whereas the holes of ZnO and WO3 in the VB would be transported to BiOBr. The built-in electrical field can endorse such transfers of photogenerated carriers. Therefore, as a consequence of the development of positive−negative heterojunction among positive-type BiOBr and negative-type ZnO and WO3 interfaces, the photogenerated electrons and holes split up successfully. This BiOBr/ZnO/WO3 p−n heterojunction can therefore create VB holes (ZnO and WO3) with a high oxidation activity and CB electrons (BiOBr) with a high reduction activity sequentially and effectively. Photocatalytic reactions may be involved in a greater amount of electrons on the BiOBr surface and holes on the ZnO and WO3 surface, leading to the understanding of the visible-light photocatalytic activity of the BiOBr/ZnO/WO3 p−n heterojunction. From the above results, it can be concluded that BiOBr/ZnO/WO3 is an excellent catalyst for further experimental analysis of degradation.

Optimization Analysis and Design of Experiments. The central composite design, CCD, is a scientific and computational technique that is suitable for modeling tests, multivariate modeling with visual aspect measurements of deferent parameters. Herein, the impact of degradation variables, for instance, the potential of hydrogen (pH), initial monophenol concentration, and BiOBr/ZnO/WO3 dose, on the deterioration efficiency of phenol has been analyzed. The real benefit of CCD is to minimize the number of tests to be held on, also specifying the correlation of operational conditions in addition to maximizing the parameters of degradation.

Combined Influence of Initial Monophenol Concentration and pH on the Deterioration Activity. The initial reactant concentration is recognized as one of the significant parameters of photodegradation of organic compounds. Figure 8A shows how the photodegradation efficiency is affected by the combined effect of initial phenol concentration and solution pH. Evidently, with the increase of the initial phenol

Figure 8. (A) 3D diagram of the combined effect of pH and the initial concentration of phenol for the degradation efficiency of phenol at a BiOBr/ZnO/WO3 dose of 0.08 g/0.03 L, (B) 3D diagram of the combined effect of pH and dose of BiOBr/ZnO/WO3 for the degradation efficiency of phenol at an initial phenol concentration of 10 mg L⁻¹ and a contact time of 300 min, (C) proposed photocatalytic degradation pathway of phenol under visible light irradiation, and (D) total organic carbon (TOC) content in phenol suspension vs visible light irradiation time after degradation with BiOBr/ZnO/WO3 at the initial phenol concentration of 50 mg/L, catalyst dose of 0.08 g/0.03 L, and a pH of 9.
concentration from 10 to 200 mgL\(^{-1}\), the degradation efficiency reduced; the degradation efficiency reached 95 percent at an initial concentration of 10 mg L\(^{-1}\) of phenol and a pH of 9, which is ascribed to the existence of adequate surface area of the catalyst employed, and the reaction of phenol molecules with OH increased. 31 At an initial concentration of 200 mg L\(^{-1}\) and a pH of 9, the degradation efficiency dropped to 52.50 percent. Such related to the possibility of monophenol molecules interacting with OH declines; therefore, excessive oxidant radicals involving OH and O\(_2\) have been needed for improving the oxidation procedure and a lower efficiency of degradation is identified.32

In the photocatalytic process, pH is the core parameter that influences the charging characteristics of the surface of the catalyst, followed by the effects of the sorption activity that influences the photocatalytic degradation.27,36 As seen in Figure 8A, as the pH value increased, there is a clear increase in phenol photodegradation. At a pH of 9 with an initial monophenol concentration of 10 mg L\(^{-1}\), the optimum degradation value (95%) was obtained, although the minimal degradation value (42.80%) was achieved at a pH of 3 with an initial phenol concentration of 200 mg L\(^{-1}\). This is related to the greater H\(^+\) content that in the case of lower pH, it improves the functional protonation of the catalyst surface. In the meantime, a massive amount of H\(^+\) competes for the catalyst binding site with phenol.28 The efficiency of phenol removal steadily increased once the concentration of H\(^+\) in the solution declined. Therefore, the favorite pH for phenol degradation was found to be 9.36

### Combined Effect of BiOBr/ZnO/WO\(_3\) Dose and pH on the Degradation Efficiency.

Photocatalytic studies with various BiOBr/ZnO/WO\(_3\) photocatalyst doses of 0.02, 0.05, and 0.08 g per 0.03 L were carried out. An increase in the photocatalytic dose showed a significant enhancement in the photocatalytic degradation efficiency (Figure 8B), reaching an optimum of 95% degradation at 0.08 g/0.03 L catalyst dose, the pH of 9, and an initial monophenol concentration of 10 mg L\(^{-1}\). The improvement of photocatalytic efficiency with the increase of the BiOBr/ZnO/WO\(_3\) photocatalyst dose may be attributed to the fact that the increase of the photocatalyst’s available surface area and the creation of more OH radicals at the active sites would be sufficient to degrade and mineralize the organic pollutant.31,35,37

The photocatalytic degradation pathway for phenol under visible-light irradiation in the presence of BiOBr/ZnO/WO\(_3\) is depicted in Figure 8C, showing the complete degradation process of phenol. The radical produced on the surface of the BiOBr/ZnO/WO\(_3\) photocatalyst reacts with phenol to produce intermediates, and with continuous photo-oxidation, the benzene ring can open, leading to the formation of an aliphatic compound that mineralized into carbon dioxide and water.

### TOC Content.

The degradation of the organic molecule to CO\(_2\) and H\(_2\)O is the final goal of the photocatalytic process of organic pollutants, where the TOC content at a given irradiation time is reduced. The organic molecule breaks down into intermediate products, which are finally mineralized through the oxidative attack of the hydroxyl radical or by the direct attack of the photogenerated holes. Figure 8D implies that the initial content of TOC (38.2 mg/L) in the phenol suspension decreased gradually with visible light irradiation time. However, the remaining amount in the suspension after...
The photocatalytic treatment of BiOBr/ZnO/WO₃ for 300 min of visible light irradiation decreased to 4.58 mg/L with 88% degradation in the TOC content. These results emphasize the degradation of phenol intermediates to CO₂ and H₂O.

**Analysis of Variance Study.** Analysis of variance (ANOVA) study for the analysis of the quadratic surface and the conditions of the model is presented in Table 3. The ANOVA study covers the degrees of freedom (DF), that is, the amount of freedom to vary values at the end of the computation of the statistics. Fischer’s F-value test is the ratio between the mean square of the model and the residual error where higher F-values with a P-value (probability) are justified as the lowest, as applicable by a highly significant regression model. Also, the probability results greater than 0.05 imply a nonsignificant impact, whereas the results below 0.05 imply a significant impact. The correlation between the practical results and the expected results was quantitatively evaluated with the coefficient of regression R². Adjusted R² is also a monitor of a fit’s perfection, correcting the R² value in the model for the sample by utilizing the DF in its calculations if the adjusted R² is much lower than R²; as a result, the model is not fitted. The R² results implied that the high BiOBr/ZnO/WO₃ phenol degradation coefficient (R² = 0.999) was close to the adjusted R² values (0.998), indicating a significant correlation among the actual and anticipated values and showed that the quadratic modes utilized highly adequate values to achieve the expected results. Model F-values (36.94) also demonstrated that the statistical analysis was appropriate by evaluating probability values (0.0005) lower than 0.05, implying that the model is essential. A nonsignificant number of designs lacking fit (0.200) also demonstrated that the designs created were realistic. The ideal conditions for phenol degradation from the model are the catalyst dose of 0.08 g/0.03 L, pH of 9, and initial phenol concentration of 10 mg L⁻¹ with a predicted 94.40 percent efficiency of phenol degradation. Although the initial efficiency of phenol degradation was 95%, which exemplifies the precision of the models, the optimal phenol degradation capacity of 39.37 mg g⁻¹ was achieved under conditions of 0.08 g/0.03 L catalyst dose, a pH of 9, and 200 mg L⁻¹ initial phenol concentration.

The plots of expected results versus actual BiOBr/ZnO/WO₃ phenol degradation results are shown in Figure 9A; the results were found to be well dispersed near the straight line, expecting an incredible link between the practical and expected output results. The accuracy of the designs was also evaluated and is presented in Figure 9B with the residual plot against the run order; the residuals were non-uniformly dispersed about ±2.50 for the adsorbent. This implied an effective fitting of the model with the practical data. The normal residual probability plot is a graphical description, a diagnostic tool to assess the deviation from the hypothesis whether errors are uniformly distributed or not, where the points will follow a straight line. However, with normal data, some scattering is anticipated. Figure 9C shows the plots of normal residual probability, wherein we can clearly observe that the results were uniformly scattered as the points in the plot form a fairly straight line. For more discussion of the data obtained, Pareto graphical analysis was applied, as depicted in Figure 9D. According to the Pareto diagram, the percentage of efficacy for each phenol degradation variable is in the following order: quadratic effect of initial phenol concentration (23.45 percent) > initial phenol concentration (12.92 percent) > solution pH (12 percent) > catalyst dose used (5.40 percent) > solution pH (12 percent) > catalyst dose used (5.40 percent).

**T-Test.** The T-test has been utilized for investigating the importance of the parameter for the correlation coefficient. A high t-value combined with a small probability value (p < 0.05) of the parameters implies that the corresponding model term is of high significance. In Table 4, the t values, probability values in addition to coefficients are listed, providing all data achieved by Design-Expert software (V.11). The results indicate that the most important parameter is the pH, backed by the monophenol concentration. The coefficient of interaction between the pH and phenol concentration is also significant, followed by the correlation coefficient of the monophenol concentration with the dose of the catalyst.

**Essential and Interaction Influences.** Essential influences reflect the average variation for each variable between the maximum and small degrees. Unless a variable’s influence is positive, the efficiency of degradation increases and the factor shifts from low to high levels. Figure 10A presents the main effects plot, where at a minimum degree of initial monophenol concentration (10 mg L⁻¹), higher degrees of pH of 9, and a catalyst dose of 0.08 g, the maximum design was obtained. The negative value (C = −11.52) of the phenol initial concentration effect indicates that the quantity of deteriorated monophenol decreases in the case of the initial phenol concentration increasing from 10 to 200 mg L⁻¹. The influences of pH and catalyst dose, fortunately, are positive, implying that the response increases with the increase of these two factors. Figure 10B shows an interaction plot; once the variation in the result from a low to a high level for a variable relies on the level of the second variable, the interaction is effective, that is, whenever the layers do not run parallel. The interaction plot exhibits a significant interaction between various factors, where all the lines representing the impacts in the graph quadrants are not parallel. The interaction plot suggests a significant interaction between various factors, where all the lines representing the impacts in the graph quadrants are not parallel.

**Suggested Photocatalytic Mechanism.** For revealing the photodegradation mechanism of phenol by BiOBr/WO₃/ZnO, the formation of oxidative radicals was investigated by adding trapping agents to the phenol solution, such as benzoquinone (BQ) for scavenging the superoxide radical O₂⁻ and isopropanol for scavenging the hydroxyl radical •OH. The results shown in Figure 11A indicate that the addition of the BQ trapping agent significantly suppressed the degradation of phenol to 31.60%, while the addition of the isopropanol trapping agent reduced the degradation of phenol to 44.80%, proving that the superoxide radical "O₂⁻" and the

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**Table 4. Estimated Effects and Coefficients**

| term        | coefficient | T ratio | prob. |
|-------------|-------------|---------|-------|
| constant    | 53.59       | 33.319  | 0.0009|
| A: pH       | 12.00       | 6.7270  | 0.0214|
| B: catalyst dose | 6.764 | 3.7910  | 0.0631|
| C: phenol concentration | −11.525 | −6.6720  | 0.0217|
| AB          | 0.260       | 0.14571 | 0.8975|
| AC          | 4.862       | −2.7250 | 0.0112|
| BC          | 1.687       | −0.94541| 0.4444|
| ABC         | 2.572       | −1.442  | 0.0286|
hydroxyl radical \( \cdot \text{OH} \) play a decisive role in the degradation of phenol by BiOBr/WO\(_3\)/ZnO.

Based on the above findings, the proposed photocatalytic mechanism of phenol degradation using BiOBr/WO\(_3\)/ZnO is illustrated in Figure 11B. ZnO, WO\(_3\), and BiOBr can be activated easily at simulated visible-light illumination which led to the generation of electrons and holes. When the CB electrons of BiOBr were transferred to the CBs of ZnO and WO\(_3\), these excited electrons showed a reduction behavior and react with oxygen \( \text{O}_2 \) to produce the superoxide radical \( \cdot \text{O}_2^- \) and then simultaneously caused the transfer of VB holes of ZnO and WO\(_3\) to the VB of BiOBr. Positive holes can oxidize phenol directly or react with \( \text{H}_2\text{O} \) generating hydroxyl radicals \( \cdot \text{OH} \); generally, the degradation of phenol occurs by oxidation with \( \cdot \text{O}_2^- \) and \( \cdot \text{OH} \) radicals. The \( \cdot \text{OH} \) radical is the most efficient oxidizing species, and it can degrade organic contaminants on the photocatalyst surface. In such a way, it is possible to effectively separate photogenerated electrons and holes and to effectively impede the recombination of electron–hole pairs, which is one of the main elements that can improve the photocatalytic activity. Photocatalytic reactions can result in a greater quantity of electrons on the BiOBr surface and holes on the ZnO and WO\(_3\) surfaces, leading to the superior visible-light photocatalytic activity of the ternary photocatalyst BiOBr/ZnO/WO\(_3\).

**Catalytic Stability Study.** The recyclability and stability of the BiOBr/ZnO/WO\(_3\) photocatalyst toward the degradation of aqueous solutions of phenol were investigated. Figure 11C illustrates the reuse of BiOBr/ZnO/WO\(_3\). For five cycles after desorption with ethanol, the photocatalytic degradation efficiency of phenol after the first cycle was 95\%, which then decreased to 90\% in the fifth cycle. This indicates that the decrease of BiOBr/ZnO/WO\(_3\) photocatalytic activity is negligible and emphasizes the long-term stability of the prepared BiOBr/ZnO/WO\(_3\) photocatalyst.

Based on the degradation efficiency (%) and degradation capacity, a comparative study of the current work and various photocatalysts for the degradation of phenol was done and is discussed in Table 5. The findings listed in the table demonstrate that BiOBr/ZnO/WO\(_3\) is a promising photocatalyst compared to other photocatalysts. Therefore, BiOBr/ZnO/WO\(_3\) is considered a promising catalyst for the simultaneous degradation of phenol in aqueous solutions.

**Investigation of Photocatalytic System Efficiency.** The photocatalytic efficiency of the BiOBr/ZnO/WO\(_3\) ternary nanocomposite was investigated toward the degradation of malachite green in addition to phenol, and the results were compared with the efficiency of commercial TiO\(_2\) P25 nanopowder toward the photodegradation of phenol and malachite green under the same experimental conditions. The results depicted in Figure 11D indicate that the efficiency of BiOBr/
ZnO/WO$_3$ toward the degradation of malachite green (93.6%) is greater than that for the degradation of phenol (90%), while the commercial TiO$_2$ P25 nano-powder has a lower efficiency toward the degradation of both malachite green and phenol that reached 74 and 51.55%, respectively, which emphasize that BiOBr/ZnO/WO$_3$ has a superior photocatalytic activity than the commercial TiO$_2$ P25 nano-powder.

Table 5. Comparative Study of Photocatalytic Degradation Efficiency (%) and Degradation Capacity of Phenol with Various Photocatalysts

| adsorbents           | degradation % | degradation capacity, $q$ (mg/g) | references |
|----------------------|---------------|---------------------------------|------------|
| N-doped meso-titania | 69.2          | 28                              | 2          |
| TiO$_2$/Gr/30PW      | 91.0          | 45.5                            | 35         |
| TiO$_2$/rGO          | 90.0          | 22.7                            | 36         |
| Ag$_3$PO$_4$−Ag$_2$CO$_3$ | 73.9      | 24.6                            | 37         |
| BiOBr/WO$_3$/ZnO     | 95.0          | 39.37                           | current work |

Realistic Application of Refinery Petroleum Wastewater. The efficiency of ternary photodegradable BiOBr/ZnO/WO$_3$ was investigated for the treatment of real refinery wastewater samples. The analytical characterization results of the collected refinery wastewater sample before treatment were as follows: pH, 7.9 ± 0.2; total dissolved solids (TDS), 2.48 ± 0.4 g/L; phenol, 35 ± 0.5 mg/L; chemical oxygen demand (COD), 750 ± 0.8 mg/L; and biological oxygen demand (BOD), 210 ± 0.6 mg/L.

The results depicted in Figure 11E imply that the phenol content of petroleum wastewater decreased drastically with irradiation time rather than the COD and BOD contents, where the removal efficiency of phenol reached 89% after 300 min of irradiation, while that of COD and BOD reached 80.2 and 42.6%, respectively. These results imply the effectiveness of BiOBr/ZnO/WO$_3$ for the treatment of organic pollutants.

Generally, these findings revealed that BiOBr/ZnO/WO$_3$ has the potency to be utilized in the eco-friendly treatment of refinery wastewater with high photocatalytic activity.

Figure 11. (A) Effect of scavengers on the photodegradation efficiency of phenol, (B) suggested photocatalytic degradation mechanism of phenol with BiOBr/WO$_3$/ZnO, (C) photocatalytic stability of BiOBr/WO$_3$/ZnO toward phenol degradation, (D) photocatalytic system efficiency for the degradation of phenol and malachite green at the initial concentration, 50 mg/L; BiOBr/WO$_3$/ZnO and TiO$_2$ P25 dose, 0.05 g/0.03 L; and pH, 6, and (E) realistic application of refinery petroleum wastewater.
Herein, single-nanophase ZnO, WO$_3$, and BiOBr were synthesized, in addition to their binary- and ternary-phase BiOBr/ZnO, BiOBr/WO$_3$, and BiOBr/ZnO/WO$_3$ p–n heterojunctions, by the solvothermal technique. Their catalytic efficiency for phenol degradation was assessed under visible-light irradiation. The results indicate that the ternary BiOBr/ZnO/WO$_3$ p–n heterojunction exhibits the highest photocatalytic activity that reached the degradation equilibrium after 60 min with an efficiency of 90%. RSM was used for optimizing the impact of degradation factors. Under the optimum conditions of 0.08 g/0.03 L catalyst dose, the pH of 9, and an initial monophenol concentration of 10 mg L$^{-1}$, the degradation efficiency reached 95%. Also, the maximum phenol degradation capacity of 39.37 mg g$^{-1}$ was achieved under the conditions of 0.08 g/0.03 L catalyst dose, pH of 9, and 200 mg L$^{-1}$ initial phenol concentration. The radical scavenging test proved that the superoxide radical *O$_2^-$ and the hydroxyl radical *OH play a decisive role in the degradation of phenol by BiOBr/WO$_3$/ZnO.

\section*{EXPERIMENTAL SECTION}

\textbf{Materials and Methods.} All the reagents utilized in this paper were obtained from Shanghai Chemical Company and were of analytical purity, and demineralized water was utilized for all preparations.

\textbf{Synthesis of WO$_3$ NPs.} Sodium tungstate dihydrate powder (Na$_2$WO$_4$·2H$_2$O, 0.003 mol) was first mixed in demineralized water (20 mL).\textsuperscript{40} The final pH of the starting liquid was changed in two phases. First, by magnetic stirring, the pH limit for the liquid was acidified to 1.58 by hydrochloric acid (HCl, 37%) and then a white precipitate was formed. Finally, the liquid was diluted to 40 mL and then the mixture was mixed with oxalic acid (H$_2$C$_2$O$_4$, 0.022 mol) to change the end pH to 2. Sodium chloride (NaCl, 0.068 mol) was added after stirring for 30 min and then heated at 90 $^\circ$C for 3 h. The as-deposited substrate was then rinsed after the reaction was completed; the prepared salt was subsequently washed with demineralized water repeatedly, then calcined at 500 $^\circ$C, and dried in air.

\textbf{Preparation of Nano ZnO.} Nano ZnO was prepared as follows:\textsuperscript{41} 1.48 g of Zn(CH$_3$COO)$_2$·2H$_2$O (Sigma-Aldrich, India) was dissolved in 63 mL of absolute ethanol in a 250 mL Schott bottle and heated with continuous stirring at 60 $^\circ$C. 0.74 g of NaOH was also dissolved separately in 33 mL of absolute ethanol in a 100 mL Schott bottle under the same Zn(CH$_3$COO)$_2$·2H$_2$O condition. After both solutions had been fully dissolved, NaOH was added slowly to Zn(CH$_3$COO)$_2$·2H$_2$O with vigorous stirring at 60 $^\circ$C. The solution mixture was left to stand for 3 h before the reaction was finished. A white precipitate (ZnO) was produced and collected within 10 min by centrifugation at 4000 rpm and washed twice with acetone and once with ultrapure water to eliminate all the impurities. The product obtained was then dried at room temperature and then calcined at 500 $^\circ$C and ground to form a powder.

\textbf{Synthesis of Nano BiOBr and BiOBr/ZnO/WO$_3$ Ternary Photocatalysts.} The hydrolysis solvothermal process method was used for the preparation of BiOBr nanocrystals. Generally, to 0.035 L of 1,2-ethanediol (EG), 2.43 g of bismuth nitrate pentahydrate was added followed by 0.595 g of KBr with vigorous stirring until a transparent solution was obtained. Then, at room temperature, 0.3 L of demineralized water was gradually dropped into a transparent solution, and plenty of precipitate was immediately obtained. The obtained precipitate was purified, rinsed repeatedly with demineralized water, and then allowed to dry at 80 $^\circ$C.\textsuperscript{42} Typically, for BiOBr/ZnO/WO$_3$ synthesis, 2.43 g of bismuth nitrate pentahydrate was added to 0.035 L of 1,2-ethanediol and stirred until the mixture became clear. Then, with vigorous stirring, 0.595 g of KBr was added and continuously stirred until the mixture became transparent. Subsequently, stoichiometric quantities of ZnO and WO$_3$ with proportions of 4BiOBr/1ZnO/1WO$_3$ (0.607 g equal to 25 wt% of bismuth nitrate pentahydrate) were dissolved by ultrasonication in 0.30 L of deionized water and stepwise added to the transparent solution at room temperature. The resultant mixture was collected, rinsed with demineralized water, and dried at 80 $^\circ$C in air.\textsuperscript{43,44}

\textbf{Equipment.} A Shimadzu XRD-600 diffractometer operating at a voltage of 40 kV and a current of 20 mA was utilized to record the patterns of XRD at both low angles (20 range, 0.5–10) and wide angles (20 range, 10–80) with Ni-filtered Cu Kα radiation ($\lambda$ = 1.54 Å). An FTIR spectrophotometer (Perkin-Elmer 720) was used to perform FTIR analysis. The KBr technique was applied nearly in a quantitative manner for all samples under investigation since the sample weight and that of KBr were fixed constant. XPS spectra were collected on K-ALPHA (Thermo Fisher Scientific, USA) with monochromatic X-ray Al Kα radiation of 10–1350 eV and a spot size of 400 μm at a pressure of 10–9 mbar with a full-spectrum pass energy of 200 eV and at a narrow-spectrum of 50 eV. Analysis by SEM coupled with EDS (SEM-EDX) was done using a scanning electron microscope JEOL GSM 6510LV. A transmission electron microscope (JEOL2100, 200 kV) was utilized to observe the particle size and structure morphologies of the synthesized photocatalysts. The photoelectrochemical measurements were conducted with an OrikaFlex-Pack OGF01A/potentiostat–galvanostat (Oriyals, France) system. A UV–vis spectrophotometer (Jasco V-507) coupled with a Shimadzu IRS-2200 was utilized to perform UV–vis DRS and for the detection of malachite green dye concentration at 617 nm. The PL spectral analysis was done using a PL spectrometer (HITACHI F7000). For the quantitative analysis of the reaction intermediates, TOC analysis was employed using a high-sensitivity Shimadzu apparatus (4 μg C L$^{-1}$ to 25,000 mg C L$^{-1}$), model TOC-VCSH.

\textbf{High-Performance Liquid Chromatography Analytical Procedure.} High-performance liquid chromatography (HPLC) was used to analyze the resulting solutions after the reaction time has ended. An Agilent 1200 series (Waldbronn, Germany) HPLC devise model outfitted with an auto-sampler and a photodiode array detector (wavelength set at 190–400 nm in the full UV scan range) was used to analyze the phenol limits. A constant flow level of 1.0 mL/min with a reversed column phase C8 (4.6 × 25 cm, 300 A°, and 5 μm) was used. For elution, the mobile phase consisting of a 40 percent acetonitrile and 60 percent water mixture was utilized. Samples of the solution were taken at different reaction times to evaluate the phenol concentration and then photocatalysts were filtered and collected at 5000 rpm in a centrifuge.

\textbf{Photocatalytic Performance.} The degradation of phenol was utilized to evaluate the photocatalytic efficiency of the synthesized photocatalysts. A batch system was used to perform all experimental runs, where 0.05 g of each prepared...
photicatalyst was put into 30 mL of phenol contaminants (50 mg/l) at ambient temperature (25 ± 2 °C); first, all experimental runs were shaken in the dark for 1 h to reach the adsorption–desorption equilibrium and then visible-light illumination (tungsten lamp 300 W, λ > 400 nm) was switched on for 300 min. Samples were collected at different times, and the residual phenol concentration was assessed using the HPLC instrument. The percentage of phenol removal (R %) and the capacity for adsorption (q, mg g⁻¹) were determined using eqs 4 and 5, respectively.

\[
\text{Adsorption (\%) } = \left( \frac{C_o - C_f}{C_o} \right) \times 100
\]

\[
q_f = \frac{(C_o - C_f)V}{m}
\]

where the sorption capacity of the sorbent at intervals t (mg/g) is represented as \(q_f\) starting phenol concentration as \(C_o\) (mg/L), the remaining phenol concentration at intervals t as \(C_f\) (mg/L), the catalyst mass as \(m\) (g), and the quantity of phenol solution as \(V\) (L).

Relying on the solution concentration, kinetic information was gained by studying the pseudo-first-order kinetic system (eq 6), while depending upon the sorption equilibrium capacity, the pseudo-second-order kinetic model (eq 7) was studied.

\[
\ln \left( \frac{C_o}{C_f} \right) = K't
\]

\[
\frac{t}{q_f} = \left( \frac{1}{K_2q_c^2} \right) + \left( \frac{1}{q_c} \right)t
\]

where the first-order rate constant is given by \(K_1\) (min⁻¹), the second-order rate constant by \(K_2\) (g mg⁻¹ min⁻²), and the quantity of phenol uptake at equilibrium by \(q_c\).

The conversion of phenol intermediates is represented by TOC as the instant TOC and TOC0 as the initial TOC.

**Factorial Design and Optimization.** Depending on the CCD, a simplified RSM has been included to optimize the effect of other variables such as the pH, catalyst dose, and starting phenol concentration on the degradation efficiency. The verity of parameters that indicate the optimum phenol degradation efficiency was analyzed using the CCD model. Each degradation factor has three elevated levels designated as 0, 0, and 0. In the model, the catalyst dose was within 0.02–0.04 g/mg mL, the pH ranged from 3 to 9, and the initial phenol concentration varied from 10 to 200 mg L⁻¹. Design-Expert software (V.11) was used to analyze statistical data. All the optimized tests were shaken in the dark for 1 h until the sorption balance was achieved and then the tests were conducted under visible light for 300 min. The phenol degradation efficiency behavior was described by the following polynomial equation of second order

\[
Y = \beta_0 + \sum_{i=1}^{3} \beta_iX_i + \sum_{i=1}^{3} \beta_{ii}X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij}X_iX_j
\]

where Y is the response variable, \(\beta_0\), \(\beta_i\), \(\beta_{ii}\), and \(\beta_{ij}\) are the regression coefficients for the intercept, linear effect, double interaction, and quadratic effects, respectively, and \(X_i\) and \(X_j\) are the independent variables.

**Realistic Application of Refinery Petroleum Wastewater.** A real wastewater sample was collected from a refinery petroleum company in Egypt. The TDS, pH, and organic constituents of the sample were characterized using standard methods (e.g., American Society for Testing and Materials and American Public Health Association Guidelines, 20th edition) for the examination of water and wastewater. For the degradation treatment, 1 g/L of BiOBr/ZnO/WO3 nanocomposite was dispersed in 100 mL of collected wastewater sample and irradiated for 300 min under visible light. At the end of the degradation time, the treated wastewater samples were separated by filtration, and the treatment efficiency was determined based on the decrease of organic pollutants, including phenol, COD (mg/L), and BOD (mg/L) at different time intervals, where COD and BOD are representatives of organic pollutants in wastewater.

**AUTHOR INFORMATION**

**Author**

Hager R. Ali – Spectroscopic Division, Analysis and Evaluation Department, Egyptian Petroleum Research Institute (EPIR), 11727 Cairo, Egypt; orcid.org/0000-0003-4028-3909; Phone: 002-01227024388; Email: Eman.chemie@gmail.com

**Author Contributions**

1H.R.A. contributed equally.

**Notes**

The authors declare no competing financial interest.

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