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Research Paper

Detoxifying SARS-CoV-2 antiviral drugs from model and real wastewaters by industrial waste-derived multiphase photocatalysts

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HIGHLIGHTS

• Low-cost multiphase photocatalysts are synthesized from industrial waste and WO3.
• Effects of calcination temperature and WO3 concentration are investigated.
• Photocatalysts favor the photocatalytic oxidation of lopinavir and ritonavir.
• Ritonavir is removed with 95% efficiency after visible light irradiation for 15 min.
• No toxicity is detected using Danio rerio for treated ritonavir-containing wastewater.

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ABSTRACT

The use of antiviral drugs has surged as a result of the COVID-19 pandemic, resulting in higher concentrations of these pharmaceuticals in wastewater. The degradation efficiency of antiviral drugs in wastewater treatment plants has been reported to be too low due to their hydrophilic nature, and an additional procedure is usually necessary to degrade them completely. Photocatalysis is regarded as one of the most effective processes to degrade antiviral drugs. The present study aims at synthesizing multiphase photocatalysts by a simple calcination of industrial waste from ammonium molybdate production (WU photocatalysts) and its combination with WO3 (WW photocatalysts). The X-ray diffraction (XRD) results confirm that the presence of multiple crystalline phases in the synthesized photocatalysts. UV-Vis diffuse reflectance spectra reveal that the synthesized multiphase photocatalysts absorb visible light up to 620 nm. Effects of calcination temperature of industrial waste (550–950 °C) and WO3 content (0–100%) on photocatalytic activity of multiphase photocatalysts (WU and WW)

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for efficient removal of SARS-CoV-2 antiviral drugs (lopinavir and ritonavir) in model and real wastewaters are studied. The highest $k_1$ value is observed for the photocatalytic removal of ritonavir from model wastewater using WW4 (35.64 \times 10^{-2} \text{ min}^{-1}). The multiphase photocatalysts exhibit 95% efficiency in the photocatalytic removal of ritonavir within 15 of visible light irradiation. In contrast, 60 min of visible light irradiation is necessary to achieve 95% efficiency in the photocatalytic removal of lopinavir. The ecotoxicity test using zebrafish (Danio rerio) embryos shows no toxicity for photocatalytically treated ritonavir-containing wastewater, and the contrary trend is observed for photocatalytically treated lopinavir-containing wastewater. The synthesized multiphase photocatalysts can be tested and applied for efficient degradation of other SARS-CoV-2 antiviral drugs in wastewater in the future.

1. Introduction

In recent years, epidemic and pandemic viral diseases, such as swine influenza virus (H1N1), Ebola virus disease (EVD), Middle East respiratory syndrome coronavirus (MERS-CoV), severe acute respiratory syndrome coronavirus (SARS-CoV) and others have led to a significant increase in the usage of various antiviral drugs to treat viral infections. Consequently, water pollution with antiviral drugs, as an emerging class of anthropogenic pollutants, has become a global issue that poses a risk to human health and the aquatic environment (Thi et al., 2021) and triggers the development of various antiviral-resistant strains (Jain et al., 2013). An ongoing global pandemic of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) has further increased an unprecedented use of antiviral drugs, accelerating the water pollution with various antiviral drugs (Choudhary et al., 2021). The degradation efficiency of those antiviral drugs in the wastewater treatment plants was reported to be too low due to their hydrophilic nature (Koema et al., 2019), and an additional process is usually required to remove them completely. Therefore, advanced oxidation processes (AOPs) are a favorable alternative for the degradation and mineralization of antiviral drugs with high efficiency.

Heterogeneous photocatalysis is one of the sustainable advanced oxidation processes for efficient removal of various organic, inorganic, and microbial contaminants, where the formed reactive species with oxidation processes for efficient removal of various organic, inorganic, and microbial contaminants, where the formed reactive species with oxidation power (e.g., $\text{OH}, \text{O}_2^•, \text{h}^+, \text{HO}_2^•$, etc.) are actively involved (Ibhadon and Fitzpatrick, 2013). Using commercial TiO$_2$-P25, 1-amantadine, 2-amantadine, and rimantadine were removed with the mineralization efficiencies of 88.7%, 90.8%, and 91.7%, respectively, under UV light irradiation, where the role of $\text{OH}$ species was significantly dominant over the photogenerated holes (An et al., 2015a). Similarly, the contribution of $\text{OH}$ species was substantial compared to the photogenerated holes in the degradation of Tamiflu (oseltamivir phosphate) via forming the typical intermediate species, such as hydration derivatives, hydroxyl substitutes and keto-derivatives (Wang et al., 2015), and in the degradation of acyclovir via hydroxylation, cleavage of isocytosine moieties, and H abstraction (An et al., 2015b) by TiO$_2$-P25. The degradation of zanamivir by TiO$_2$-P25 using a light source with lower irradiance (495 W·m$^{-2}$) was accelerated by a factor of 20, whereas a comparable result was obtained with higher irradiance (2700 W·m$^{-2}$), indicating the limitation by oxygen diffusion (Wocher et al., 2016). Since the UV light makes up a small portion of the solar spectrum and is barely present in indoor premises, it is necessary to involve visible-light-active photocatalysts for the efficient removal of various antiviral drugs. Recently, Z-scheme Bi/BIVO$_4$-CdS heterojunction (Xue et al., 2021) and CdS-decorated BiVO$_4$ (Wu et al., 2020) have exhibited superior performance for the photocatalytic degradation of tetracycline hydrochloride under visible light irradiation, which was also found to have a beneficial effect in preventing the viral infection of SARS-CoV-2 from progressing if it is used in the early stage (Mosquer-à-Sulbaran and Hernández-Ponseca, 2021). Conversely, even though acyclovir was efficiently degraded using the g-C$_3$N$_4$/TiO$_2$ hybrid photocatalyst under visible light irradiation, three persistent intermediates were formed via (i) the mono-hydroxylation of the purine ring and the breakdown of the C–C bond from the side chain of acyclovir (P1), (ii) the breakdown of the purine ring in acyclovir (P2), and (iii) the loss of the side chain from acyclovir (P3), which resisted a complete mineralization, and the aquatic toxicity of the third intermediate (P3) was also two times higher than that of acyclovir (Li et al., 2016). Therefore, it is necessary to conduct ecotoxicity tests for the photocatalytically treated water samples to demonstrate the efficiencies of the photocatalyst and photodegradation process.

Recently, inexpensive, environmentally friendly, and high-value-added materials derived from various wastes have shown efficient photocatalytic and sensing performance (Rodríguez-Padron et al., 2020; Hojamberdiev et al., 2020a). For instance, the ZnS-containing waste from the mining-metallurgy industry was used as a starting material for the synthesis of trigonal ZnIn$_2$S$_4$ layered crystals by a binary-flux method, which exhibited a photocatalytic $\text{H}_2$ evolution rate of 232 mmol·h$^{-1}$ (Hojamberdiev et al., 2018). The ZnS-containing waste was also combined with SnO$_2$ (Hojamberdiev et al., 2020b) and ZnO (Vargas et al., 2022) for the efficient photocatalytic degradation of metoprolol (beta-blocker), carbamazepine (antiepileptic), acetaminophen (nonsteroidal anti-inflammatory drug), and triclosan (antimicrobial) in model wastewater and photoelectrochemical water oxidation, respectively. Also, the antibacterial activity of the ZnS-containing waste was evaluated against four bacterial strains, and the highest antibacterial activity was observed for the inactivation of $E. \text{coli}$ (99%) within 2 h of UV light irradiation (Hojamberdiev et al., 2019).

Tungsten oxide (WO$_3$) is a n-type semiconductor that can absorb visible light up to 480 nm and has good photostability, electron-transport property, and sufficient valence-band potential to drive oxidation reaction (Quan et al., 2020). Previously, we have succeeded in enhancing the photocatalytic activity of the ZnS-containing waste for the degradation of metoprolol, triclosan, and caffeine both in individual and mixed solutions under visible light irradiation by involving hexagonal WO$_3$ and WO$_3$•0.5 $\text{H}_2\text{O}$ (Czech et al., 2020). In this work, we report on the synthesis of inexpensive multiphase photocatalysts by a simple calcination of industrial waste from ammonium molybdate production (WU photocatalysts) and its combination with WO$_3$ (WW photocatalysts). The effects of calcination temperature of industrial waste (550–950 °C) and WO$_3$ content (0–100%) on photocatalytic activity of multiphase photocatalysts (WU and WW) for efficient removal of SARS-CoV-2 antiviral drugs (lopinavir and ritonavir) in model and real wastewaters are studied. The kinetics and mechanisms of the photodegradation of lopinavir and ritonavir by the synthesized multiphase photocatalysts are explored. Further, to analyze the ecotoxicity of the photocatalytically treated water and wastewater samples, the Fish Embryo Acute Toxicity (FET) test is conducted using zebrafish (Danio rerio) embryos according to the OECD Guidelines.

2. Experimental

2.1. Synthesis of multiphase photocatalysts

The WU photocatalysts were prepared by calcination of industrial waste, generated during the production of ammonium molybdate (Almalyk Mining-Metallurgical Complex, Uzbekistan), at temperatures ranging from 550 °C to 950 °C for 2 h. The WU photocatalysts were
denoted as WU1 (as-received), WU2 (550 °C), WU3 (650 °C), WU4 (750 °C), WU5 (850 °C), and WU6 (950 °C) with respect to their calcination temperature. The WW photocatalysts were prepared by mixing the calcined industrial waste at 850 °C for 5 h and WO3 (99.9%, Merck) in different ratios and calcination at 850 °C for 2 h. The WW photocatalysts were labeled as WW1 (10:0), WW2 (8:2), WW3 (6:4), WW4 (4:6), WW5 (2:8), and WW6 (0:10) according to the calcined industrial waste:WO3 ratio.

2.2. Characterization of multiphase photocatalysts

The X-ray diffraction (XRD) patterns were recorded on a MiniflexII (Rigaku) diffractometer to identify the crystalline phases in the synthesized multiphase photocatalysts. The micro- and nanostructures of multiphase photocatalysts were examined by using an S-5200 field-emission-type scanning electron microscope (Hitachi) and an EM-002B high-resolution transmission electron microscope (TOPCON), respectively. The ultraviolet-visible (UV–Vis) diffuse reflectance spectra of multiphase photocatalysts were measured on a UV-3600 UV–Vis–NIR spectrophotometer (Shimadzu). The surface chemical states were analyzed by X-ray photoelectron spectroscopy (JPS-9000SX, JEOL) with non-monochromated Mg-Kα radiation (1253.6 eV). The surface charge density was estimated using the data obtained by potentiometric titration using 0.001 mol·dm−3 NaNO3 as the background electrolyte (Broda et al., 2021).

Metrohm-DropSens (DS110) screen-printed carbon electrodes were used, and all potentials were referenced to the Ag-AgCl reference electrode. The carbon surface of the screen-printed electrodes was modified using only WU6 and WW6 photocatalysts by applying the dip-coating protocol. The suspension was prepared by dispersing 1.0 mg of WU6 or WW6 in 0.5 mL of a mixture solution of ethanol and water (1:1 ratio) under ultrasonication for 10 min, deposited on the electrodes (15 µL suspension), and dried using a heating gun for 10 min. The deposited photocatalyst powders were estimated to be ~0.2 mg·cm−2 for both electrodes. The irradiated geometric area of the photoanodes was 0.13 cm², and the electrolyte volume was 50 µL. The photoelectrochemical measurements were conducted in 0.1 M Na2SO3 (or Na2SO4) N2-saturated solution using a Potentiostat/Galvanostat (DropSens μSTAT200). LED solar light with the irradiance of ~100 mW·cm−2 (Solar Light, G2V) was used. The scan rate for linear sweep voltammetry (LSV) was 2 mV·s−1, and the chronoamperometric (CA) analysis at 0.6 V and 1.2 V vs. Ag-AgCl was performed using a chopped light mode (light-dark cycle: 60–60 s). The stability test was carried out by CA measurement at 1.2 V vs. Ag-AgCl for 60 min under continuous irradiation and in the dark.

The details of photocatalytic tests for the removal of SARS-CoV-2 antiviral drugs (lopinavir and ritonavir) from contaminated model and real wastewaters (A.2.1.) and the Fish Embryo Acute Toxicity (FET) test of photocatalytically treated model and real wastewater samples (A.2.2.) are given in Supplementary Material.

3. Results and discussion

3.1. Characterization of multiphase photocatalysts

The XPS survey spectra of WU6 and WW6 photocatalysts are shown in Fig. A.1a and A.1b, respectively. As shown, the WU6 comprises of iron, molybdenum, magnesium, silicon, aluminum, calcium, oxygen, and adventitious carbon, whereas the WW6 consists of tungsten, oxygen, and adventitious carbon. In Fig. 1, the reflections in the XRD pattern of the as-received industrial waste (WU1) are broad possibly due to overlapping and the presence of amorphous phases. In the WU1, molybdenum exists in the forms of various molybdates, along with calcium, magnesium, iron, etc., with different oxidation states and ordered molybdate intercalates of hydrotalcite-like compounds (3[Mg6Al2(OH)16]2[Mo7O24]48H2O) (Hibino and Tsunashima, 1997). Due to a low concentration of other

Fig. 1. XRD patterns of WU photocatalysts.
elements, iron with a higher concentration is present in the form of Fe$_2$(MoO$_4$)$_3$ (Tian et al., 2011). Thus, the high concentration of iron (FeOOH and Fe$_2$O$_3$) leads to the formation of mixed-valence compounds [Fe$^{III}$MoO$_{4-x}$O$_x$]$^{2+}$ and ammonium molybdoferrate (NH$_4$)$_2$Fe$^{III}$(MoO$_4$)$_3$] and ammonium molybdenum (NH$_4$)Fe$^{III}$(MoO$_4$)$_3$] (Nikolenko et al., 2018). Additionally, the reflections of some natural minerals, including quartz (SiO$_2$), talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$), and hydrotalcite (Mg$_6$Al$_2$(CO$_3$)$_2$(OH)$_{16}$•4H$_2$O), are also observed. After calcination of the as-received industrial waste in the temperature range from 550°C to 750°C (WU2-WU4), Fe$_2$O$_3$, SiO$_2$, Fe$_2$(MoO$_4$)$_3$, MgMoO$_4$, and β-cristobalite become predominant crystalline phases. In this temperature range, the thermal decomposition of hydrotalcites to their corresponding oxides, such as MgO, MoO$_3$, and MgFeAlO$_4$, proceeds along with the simultaneous dehydration and decarbonation of the hydrotalcite structure (Palmer et al., 2009). The high-temperature reaction between MgO and MoO$_3$ results in the formation of MgMoO$_4$ (Yoon et al., 1999).

$$\text{2MgO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{2MgFeAlO}_4$$ (1)

$$\text{MgO} + \text{MoO}_3 \rightarrow \text{MgMoO}_4$$ (2)

A further increase in the calcination temperature of the as-received industrial waste up to 950°C (WU5-WU6) causes a partial decomposition of Fe$_2$(MoO$_4$)$_3$ to Fe$_2$O$_3$ and MoO$_3$ and the formation of FeMoO$_4$.

$$\text{Fe}^{III}_2\text{(MoO}_4\text{)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{MoO}_3$$ (3)

$$\text{Fe}^{III}_2\text{(MoO}_4\text{)}_3 \rightarrow 2\text{Fe}^{IV}\text{MoO}_4 + \text{MoO}_3 + 3\text{O}_2$$ (4)

Also, SiO$_2$ and β-cristobalite were formed at high temperatures (Parise et al., 1994). Due to its low concentration in the as-received industrial waste, the crystalline phases containing calcium are not observed in the XRD patterns of the WU photocatalysts.

In Fig. 2, the industrial waste calcined at 850°C for 5 h (WW1) consists of MgMoO$_4$, FeMoO$_4$, SiO$_2$, cristobalite, MoO$_3$, Fe$_2$O$_3$, and MgFeAlO$_4$. When the industrial waste:WO$_3$ ratio is set to 8:2 (WW2), the reflections assignable to MgWO$_4$ appear as the reaction product of MgO and WO$_3$, whereas the reflections of MgFeAlO$_4$ disappear completely.

$$\text{MgO} + \text{WO}_3 \rightarrow \text{MgWO}_4$$ (5)

When the industrial waste:WO$_3$ ratio is adjusted to 6:4 (WW3), the reflections of MoO$_3$, MgMoO$_4$, and FeMoO$_4$ disappear completely, whereas the reflections of FeWO$_4$ and Fe$_{184}$Mg$_{318}$SiO$_4$ appear. In the industrial waste:WO$_3$ ratios of 4:6 (WW4) and 2:8 (WW5), Fe$_2$O$_3$ and Fe$_{184}$Mg$_{318}$SiO$_4$ disappear, and SiO$_2$ is fully converted to β-cristobalite (Parise et al., 1994), whereas FeWO$_4$ (Sieber et al., 1982) along with MgWO$_4$ and Fe$_2$MoO$_{12}$ become dominant crystalline phases.

$$\text{1/3Fe}_2\text{O}_3 + 1/3\text{Fe} + \text{WO}_3 \rightarrow \text{2FeWO}_4$$ (6)

$$\text{Fe}_2\text{O}_3 + 3\text{MoO}_3 \rightarrow \text{Fe}_2\text{MoO}_3\text{O}_2$$ (7)

As expected, in the industrial waste:WO$_3$ ratio of 0:10, hexagonal WO$_3$ is the only crystalline phase. The XRD results show that Fe$_2$O$_3$ (2% in WU2, 3% in WU3, 9% in WU4, and 3% in WU5), Fe$_2$O$_3$ (26% in WU2, 6% in WU5, and 13% in WU6), MgMoO$_4$ (41% in WU2 and 23% in WU5), FeMoO$_4$ (17% in WU5 and 30% in WU6), and MgFeAlO$_4$ (37% in WU5 and 7% in WU6), crystal phases are dominant in the WU photocatalysts, whereas Fe$_2$O$_3$ (5% in WW2, 6% in WW4, and 14% in WW5), FeWO$_4$ (3% in WW2, 17% in WW3, 26% in WW4, and 30% in WW5), MgWO$_4$ (36% in WW2, 58% in WW3, 50% in WW4, and 47% in WW5), and Fe$_2$MoO$_{12}$ (17% in WW2, 10% in WW3, 8% in WW4, and 11% in WW5) crystal phases are prevalent in the WW photocatalysts. Identifying the crystalline phases present in both WU and WW photocatalysts allows us to understand the photodegradation mechanism of SARS-CoV-2 antiviral drugs (lopinavir and ritonavir) by industrial waste-derived multiphase photocatalysts.

The SEM images of selected WU and WW photocatalysts are shown in Fig. 2.

Fig. 2. XRD patterns of WW photocatalysts.
Fig. 3. The WU1 shows an irregular morphology composed of nanoparticles (Fig. 3a). In contrast, submicron-sized rods are formed on the surface of irregular particles (Fig. 3b) after the calcination of the as-received industrial waste at 950 °C (WU6). These submicron-sized rods possibly belong to one of the crystalline phases formed at 950 °C. Similarly, the WW1 possesses particles of different sizes and morphologies (Fig. 3c). At the industrial waste:WO3 ratio of 4.6 (WW4), the submicron-sized particles belonging to either FeWO4/MgWO4 or Fe2Mo2O8 are formed on the surface (Fig. 3d). The WW6 contains micron-sized cuboids and double-cuboids, formed by the assembly of small and large idiomorphic crystals, along with irregular particles (Fig. 3e). In Fig. A.2a, the TEM image shows that the WW6 has quasi-spherical particles with a size of 200 nm along with rod-like microstructures. The TEM image shown in Fig. A.2b reveals the flake-like morphology consisted of nanoparticles. The HRTEM image and SAED patterns confirm the presence of multiple phases with polycrystalline nature in the WW6 and WW4 photocatalysts. The TEM image in Fig. A.2c shows the WO3 crystals with idiomorphic shape, and the HRTEM image and SAED pattern confirm the high crystallinity and single-crystalline nature of the WO3 crystals, respectively.

The UV-Vis diffuse reflectance spectra of the WU and WW photocatalysts are shown in Fig. 4a and b, respectively. In Fig. 4a, the WU1 shows an absorption edge at about 620 nm, which shifts toward lower wavelengths (600 nm) for the WU2 and WU3 after calcination at 550 °C and 650 °C, respectively. A further increase in the calcination temperature to 750 °C, 850 °C, and 950 °C similarly leads to a slight redshift in the absorption edge (610 nm) for the WU4, WU5, and WU6 photocatalysts, respectively. This suggests that the WU photocatalysts can absorb visible light due to the presence of visible-light-active crystalline phases, such as Fe2O3, Fe3O4, FeMoO4, and MgFeAlO4. The powder color of the WW photocatalysts changes from dark reddish-brown to dark brown with the increase in the calcination temperature up to 950 °C. In the WW photocatalysts (Fig. 4b), the WU1 and WW2 exhibit similar absorption edges at about 610 nm. A further increase in the industrial waste:WO3 ratio leads to a slight bluish shift (about 600 nm) in the absorption edges of the WW3, WW4, and WW5. The WW1-WW5 photocatalysts can absorb more photons from visible light compared with the WW6 because of the existence of visible-light-active crystalline phases, such as Fe2O3, FeMoO4, and Fe2Mo2O8. The WW6, which contains only WO3, shows an absorption edge at 470 nm, which corresponds to the bandgap energy of 2.64 eV. The powder color of the WW1-WW5 photocatalysts changes from reddish-brown to pale brown with the increase in the industrial waste:WO3 ratio, and the WW6 has a light-yellow color.

3.2. Photoelectrochemical characterization

The photoelectrochemical response of the WW6 and WW6, as the representatives of WU and WW photocatalysts, was evaluated using linear scan voltammetry (LSV). Fig. 5a shows the photoelectrochemical response of the WW6 and WW6 photoanodes under continuous light conditions and in the dark. Particularly, the effect of the presence and absence of SO2−4 as a hole scavenger in the aqueous solution was determined. When irradiated, a significant increase in the anodic response as a function of potential was observed, followed by a change in the slope until a pseudo-stationary state in the photocurrent signal was defined at high overpotentials (Bedoya-Lora et al., 2021; Peter, 2018). This is a typical increase caused by the arrival of new minority charge carriers at the semiconductor-electrolyte interface, where holes participate in the chemical reactions with the donor species in the solution (in this case, SO2−4 and H2O) (Ng et al., 2012; Zhang et al., 2014). Very low photocurrent intensities were observed in the absence of SO2−4, which increased at higher potentials, showing kinetic limitations due to the importance of charge carrier recombination processes (Peter, 2018; Zhang et al., 2014). The respective onset potentials (vs. Ag/AgCl) of the WW6 and WU6 photoanodes are 0.41 V and 0.28 V in the presence of SO2−4 and 0.50 V and 0.48 V in the absence of SO2−4, respectively. This is consistent with previous reports on WO3-based electrodes (Ng et al., 2012; Gomis-Berenguer et al., 2018; Patil and Patil, 1996; Costa et al., 2020; Núñez et al., 2019).

Fig. 5b shows the chronoamperometric response at high overpotential (1.2 V vs. Ag-AgCl) for 60 min to confirm the stability of the fabricated WW6 and WW6 electrodes. As shown, a stationary photocurrent density magnitude in a time interval is greater than that of the experimental measurements: 0.17 mA/cm2 for WW6 and 0.12 mA/cm2 for WW6. It is important to compare the photocurrent signals obtained for WW6 and WW6 to understand the effect of different chemical natures of the fabricated photoanodes on their photoelectrochemical response. Fig. 5a shows the photocurrent density vs. potential plot, indicating that the photoanodes differ in the following ways: (i) at high overpotentials, the photocurrent of the WW6 is higher, (ii) the photocurrent signal of the WW6 begins at more negative potentials than that of the WW6, and (iii) at low overpotentials, the WW6 defines higher photocurrent values than the WW6. Changes in material synthesis, chemical composition, crystallinity, particle size, and other factors modified the balance between charge transfer and recombination kinetics differently in the WW6 and WW6 (Patil and Patil, 1996; Hojamberdiev et al., 2021). To elucidate the differences in the photo-redox processes between the WW6 and WW6, it is essential to analyze the photoelectrochemical properties in the presence of SO2−4 in the aqueous solution since a higher photocurrent is guaranteed by its reaction with holes (Zhang et al., 2014). The effect of the photon flux is evident in the modulated illumination condition at different potentials, as shown in the chronoamperometry (CA) results in Fig. 5c and 5d. Because the charge carriers are rapidly deactivated by recombination when the incident photon flux is interrupted, the photocurrent in both electrodes decreases to the values obtained in the dark. The separation of the electron-hole pair occurs quickly as the photonoade surface is re-illuminated, resulting in the concentration of these carriers reaching the level required to maintain the photocurrent observed under continuous illumination (Patil and Patil, 1996; Hojamberdiev et al., 2021).

It should also be highlighted that (i) after the initial seconds of irradiation, an anodic photocurrent peak (overshoot) is detected at low overpotential (0.6 V vs. Ag-AgCl). Undershoots were detected when the light was turned off, as expected for photocatalysts that exhibit surface recombination events. These characteristics are related to the differences in electron and hole relaxation time (Patil and Patil, 1996; Peter et al., 2020). (ii) In both light and dark conditions, stable photocurrents were promptly generated at high overpotential (1.2 V vs. Ag-AgCl), and (iii) the quasi-stationary photocurrent increased with applied potential, indicating the inverse effect between charge transfer and bulk recombination processes (Peter, 2018; Patil and Patil, 1996; Peter et al., 2020). This is consistent with the data reported previously for the WO3/nanoporous carbon composite (Gomis-Berenguer et al., 2018), Fe3O4 (Li et al., 2021), and Fe2O3/WO3 (Müller et al., 2017) photoanodes.

In general, the chemical and structural modifications made by the synthesis method influence the optoelectronic properties, which manifest as a variation in the photoelectrochemical response (Hojamberdiev et al., 2021; Monllor-Satoca et al., 2020). Under light conditions and applied potential, electrons are drawn into the external circuit, but they can also be trapped in new mid-gap states introduced by defects, heterojunctions, and other factors (Monllor-Satoca et al., 2020; Low et al., 2017). The photoelectrochemical response of the WW6 and WW6 photoanodes is then specified by (i) the quasi-stationary potential; (ii) the quasi-stationary photocurrent increased with applied potential, and (iii) the specific property of semiconductors. While the former can be modulated by changing the applied potential, the latter can be evidenced by modifying the photocatalyst structure. When these types of modifications are made, the mid-gap states of the semiconductors and the kinetics of the processes that occur in the spatial charge zone (SCZ) are frequently affected (Monllor-Satoca et al., 2020). The lifetimes of charge carriers in the WO3 photoanode have been found to range from ultra-fast timescales up to the order of seconds, depending on the kinetic
Fig. 3. SEM images WU1 (a), WU6 (b), WW1 (c), WW4 (d), and WW6 (e) photocatalysts.
3.3. Photocatalytic removal of SARS-CoV-2 antiviral drugs

3.3.1. Photocatalytic removal of ritonavir in model wastewater

As shown in Fig. 6a, the photocatalysis of ritonavir (C27H48N6O5S2, 720.94 g mol⁻¹, logKow=6.29) in model wastewater was very fast. After 15 min of visible light irradiation, ritonavir was completely degraded in model wastewater, indicating that ritonavir does not pose a significant risk to the environment. However, lopinavir and ritonavir should be removed with an efficiency of more than 80–90% (92% and 93%, respectively) based on the predicted environmental concentration (PEC) (Kuroda et al., 2021). However, the limited experimental data do not support this. Lopinavir and ritonavir removal rates were significantly lower in African WWTPs (43% to 71% for ritonavir and 192% to 58% for lopinavir), indicating their accumulation in the effluent (Abafe et al., 2018). Because lopinavir and ritonavir are widely used in HIV and COVID-19 treatment (Brown et al., 2021; Kuroda et al., 2021), their predicted environmental concentrations must be higher. Using quantitative structure-activity relationship modeling (considering 100 patients treated out of 100,000 populations a day), studies have predicted that currently used COVID-19 treatment drugs, including lopinavir and ritonavir, can be removed with a low removal efficiency (<20%) during traditional wastewater treatment, and their predicted environmental concentrations in the WWTP effluent can reach 730 ng L⁻¹ each (both unchanged forms and metabolites) (Kuroda et al., 2021). According to another study (Kumari and Kumar, 2021), the PECs of lopinavir and ritonavir in river water or fish might be 186 µg L⁻¹ and 239 µg kg⁻¹ and 128 µg L⁻¹ and 169 µg kg⁻¹, respectively. In African WWTPs, the concentration of lopinavir was up to 25 µg L⁻¹ in influents and 3.8 µg L⁻¹ in effluents, and the concentration of ritonavir was up to 3.2 µg L⁻¹ (Abafe et al., 2018). Interestingly, some enrichment of lopinavir in the treated wastewater (tWW) was observed, highlighting the necessity of properly managing antiviral drug-contaminated wastewater. Due to the direct use of antiviral drug-containing wastewater in agriculture and animals, new strategies for treating antiviral drug-containing wastewater must be developed (Jain et al., 2013; Kuroda et al., 2021; Nannou et al., 2020).

The WW photocatalysts were effective in the photocatalytic treatment of model wastewater containing antiviral drugs. In the dark, the WW6 (100% WO₃) exhibited the highest adsorption, with up to 65% ritonavir adsorbed. In the dark, the WW photocatalysts had a lower adsorption capacity for both antiviral drugs than the WW photocatalyst, with up to 15% ritonavir adsorbed (Fig. 6b). In previous work (Kovalova et al., 2013) on the adsorption of pharmaceuticals onto powdered activated carbon (at 25 mg L⁻¹), more than 70% of ritonavir was adsorbed in less than 24 h. Except for the WWU1 (3[Mg₂Al₂(OH)₁₆]·[MoO₄]·48 H₂O (9%), Fe₆(C₂O₄)₃ (40%), and MgMoO₄ (1%)), all WW photocatalysts showed high photocatalytic activity in the degradation of ritonavir. Surprisingly, the poor removal efficiency (up to 20% after 120 min of irradiation) remained steady, signifying the formation of certain persistent by-products. The chromatograms obtained with the WWU photocatalyst (detection at 254 nm) show only two additional peaks (R₁=1.1 min and R₂=1.9 min), but their relative areas were up to 30% of ritonavir and did not increase appreciably during the photocatalytic reaction (Fig. 6c).

The efficiency of the photocatalytic removal of ritonavir under visible light irradiation for 15 min was compared since the photocatalytic process was quite fast (Fig. 6d). When model wastewater was compared to the WW photocatalysts showed a high efficiency, with the lowest photocatalytic efficiency for the WW2 (3% FeWO₄) and WW5 (30% FeWO₄), despite the presence of FeWO₄. This implies that there are other factors in addition to the crystalline phases affecting the photocatalytic activity. Previously, direct Z-scheme nanocomposite coupling of the visible-light-active FeWO₄ nanoparticles with the C₃N₄ nanosheets exhibited excellent performance for CO production (Bhosale et al., 2019). The O 2p- and Fe 3d-like states hybridize in the valence-band region, whereas the empty Fe 4 s-like states are located at...
the bottom of the conduction band and W 5d-like states are at the higher energy side of the conduction band of FeWO₄ (Rajagopal et al., 2010). In the photocatalytic process, iron, even in the form of FeWO₄, is expected to promote the formation of •OH radicals (Rajagopal et al., 2010; Li et al., 2019).

The WU photocatalysts showed the opposite trend. Despite the fact that direct photolysis of ritonavir was fast within 15 min of visible light irradiation, only photocatalytic treatment with WU3 and WU4 enabled a total removal of ritonavir from model wastewater. In comparison to the photocatalytic removal efficiency of nevirapine (an antiviral drug) over irradiated FL-BP@Nb₂O₅ (68% after 3 h of irradiation, pH = 3, m_cat = 15 mg, C₀ = 5 mg L⁻¹) (Guo et al., 2013), the photocatalytic removal efficiency of ritonavir was substantially greater for the WU3 and WU4 photocatalysts. The presence of Fe₃O₄ (20%), Fe₂(MoO₄)₃ (17%), and MgMoO₄ (35%) phases in the WU3 and WU4 photocatalysts can explain the increased photocatalytic removal efficiency of ritonavir. Co-doping with Fe³⁺Mo was also found to improve the photocatalytic activity of TiO₂ due to retarding the recombination process (Bhembe et al., 2020). The Fe³⁺ ions in the synthesized multiphase photocatalysts can increase absorption of visible light and mediate the charge-transfer process (Liu et al., 2012), whereas the Fe²⁺ ions can assist the heterogeneous photo-Fenton reactions (Kavitha and Palanivelu, 2004; Ruppert et al., 1993). In general, proposing a degradation pathway for lopinavir is challenging because it is thought to be stable under environmental conditions (Seshachalam et al., 2007; Donato et al., 2006).

Despite this, lopinavir is susceptible to •OH attack due to the presence of different ketone, phenyl, and phenoxy groups (Kopinke and Georgi, 2017). The reaction rate constants with •OH radicals (considering molecules with comparable structures or substructures to lopinavir and ritonavir) are estimated to be about 10⁸–10¹⁰ L mol⁻¹ s⁻¹ (Zwiener and Frimmel, 2000). Ritonavir is susceptible to hydrolytic cleavage because of the presence of carbamate and urea moieties (Tiwari and Bonde, 2011; Rao et al., 2010). The formation and decomposition of alkylperoxide radicals leading to the formation of relative alcohols, ketones, and carbon-chain fragmentation, which results in acyclic products, can be considered for the possible degradation pathway of ritonavir (Kopinke and Georgi, 2017).
O$_2^*$ + 2H$_2$O $\rightarrow$ 2 *OH + 2OH$^-$  \hspace{1cm} (12)

OH$^-$ + H$^+$ $\rightarrow$ *OH \hspace{1cm} (13)

O$_2^*$ + Ritonavir/Lopinavir $\rightarrow$ degradation products \hspace{1cm} (14)

*OH + Ritonavir/Lopinavir $\rightarrow$ degradation products \hspace{1cm} (15)

3.3.2. Photocatalytic removal of lopinavir in model wastewater

In the photocatalytic removal of lopinavir (C$_{37}$H$_{48}$N$_4$O$_5$, 628.80 g·mol$^{-1}$, log$K_{ow}$ = 5.94) from model wastewater, all WW photocatalysts were effective (Fig. 8a). After 15 min of irradiation, direct photolysis removed about 80% of lopinavir. However, traces of lopinavir were found in model wastewater after 90 min of irradiation, suggesting that lopinavir is less susceptible to solar-driven degradation. The total decomposition of lopinavir is achieved after the photocatalytic treatment using WW photocatalysts for 15–20 min. In contrast, in the
The photocatalytic removal of lopinavir, the effectiveness of WU photocatalysts was reduced (Fig. 8b). Direct photolysis was outperformed only by the WU1 and WU2. When the photocatalytic removal efficiency of lopinavir from model wastewater is compared after 15 min: $C_{0\text{Lopinavir}} = 10 \text{ mg} \cdot \text{L}^{-1}$, $m_{\text{photocatalyst}} = 0.4 \text{ g} \cdot \text{L}^{-1}$, visible light irradiation, 1–6 refer to the order number of WW and WU photocatalysts. Effects of various parameters on photocatalytic removal efficiency of ritonavir and lopinavir by WU4: (d) pH, (e) DOM, and (f) inorganic ions ($C_0 = 5 \times 10^{-3} \text{ M}$).

### 3.3.3. Effects of various parameters on photocatalytic removal efficiency of ritonavir and lopinavir in model wastewater

The pH-, dissolved organic matter (DOM)-, and competing inorganic ions-dependent experiments were conducted using only WU4 photocatalyst to investigate the factors affecting the photocatalytic removal efficiency of antiviral drugs. As shown in Fig. 8d, an increase in the pH value decreases the photocatalytic removal efficiency of ritonavir while increasing the photocatalytic removal efficiency of lopinavir. At pH below pKa, lopinavir is present in its non-dissociated form as a strong base. Because the surfaces of the synthesized multiphase photocatalysts are acidic (pH$_{ZPC}$ = 9.85 for WW6 and 10.24 for WU6), the obtained results are consistent with the surface charge measurements. This
further hampered the adsorption and photocatalytic degradation of ritonavir and lopinavir. The hydrophobic properties of the tested compounds (logK_{ow} > 4) may imply that they have a higher bioaccumulation potential.

As expected, the photocatalytic removal efficiency of ritonavir and lopinavir was reduced when dissolved organic matter (e.g., tannic acid) was present (Fig. 8e). On the other hand, the impact was slightly linear (R_{ritonavir}^2 = 0.89 and R_{ritonavir}^2 = 0.96). The photocatalytic removal efficiency of lopinavir was dramatically increased from 70% to 90% when a small amount of tannic acid was added to the aqueous solution containing lopinavir (Wang et al., 2014). Possibly, tannic acid may have served as a complexing agent. Tannic acid acted as a superoxide anion or hydrogen peroxide radical scavenger at higher concentrations (Gülcin et al., 2010), lowering the photocatalytic removal efficiency of lopinavir. The introduction of certain inorganic ions altered the photocatalytic removal efficiency of lopinavir, as shown in Fig. 8f. The presence of Cl\(^{-}\), NO\(_3\)\(^{-}\), or SO\(_4\)\(^{2-}\) had no effect on the photocatalytic removal efficiency of lopinavir, and only H\(_2\)PO\(_4\) hampered photocatalytic oxidation. The highest reduction in the photocatalytic removal efficiency of ritonavir was observed when Cl\(^{-}\) was introduced, and both H\(_2\)PO\(_4\) and NO\(_3\)\(^{-}\) similarly reduced the photocatalytic removal efficiency of ritonavir.

The photocatalytic removal of ritonavir and lopinavir was mediated by radicals (Fig. A.3a), and the photocatalytic removal efficiency of both antiviral drugs by WU4 was reduced in the presence of radical scavengers. It can be seen that PBQ as an O\(_2\)• scavenger had the greatest effect on the removal of ritonavir. The most prevalent form of oxygen species was O\(_2\)•\(^{-}\) (k_a of reaction: HO\(_2\) -→ O\(_2\)•\(^{-}\) + H\(^+\) is 4.8 ± 0.1) due to slightly acidic reaction conditions (pH~6.4) (Cavalcante et al., 2016). The effect of holes was noted as the photocatalytic removal efficiency of ritonavir was reduced in the presence of 2Na-EDTA (Gunture et al., 2019). The •OH radicals were also shown by the minor effect. The other pathway for the photocatalytic removal of lopinavir was identified. IPA had the most suppressive impact, followed by PBQ and 2Na-EDTA, showing that O\(_2\)•\(^{-}\) > •OH > h\(^+\) has the greatest effect. IPA is considered as •OH scavenger, with a reaction rate constant of 2 × 10\(^{9}\) M\(^{-1}\) s\(^{-1}\) (Rodríguez et al., 2015). On the other hand, when IPA reacts with h\(^+\), it can behave as an electron donor (Cavalcante et al., 2016). The significantly reduced efficiency in the presence of 2Na-EDTA (a scavenger of h\(^+\)) suggests that both •OH and h\(^+\) were important in the photocatalytic oxidation of lopinavir on the WU1 surface. According to the results of recyclability test conducted using WU6, the effectiveness of the synthesized multiphase photocatalyst showed a slight decrease after the third cycle, indicating their good stability (Fig. A.3b). In the bisphenol AF degradation by FeMoO\(_4\) (Wang et al., 2021), a similar effect of •OH and non-radical singlet oxygen •O\(_2\) was observed. The generation of surface O\(_2\)•\(^{-}\) was favored by the presence of more oxygen vacancies in FeMoO\(_4\) (Zhang et al., 2011). MgWO\(_4\) (Bhyyan et al., 2017), like in the WW photocatalysts, had more active photocatalytic or Lewis acid sites, and the effect of O\(_2\)•\(^{-}\) on the photocatalytic dye removal was noted (Gouveia et al., 2020). Also, •OH was found to be the most reactive species generated when WO\(_3\) was irradiated (Nisar et al., 2020).

3.3.4. Photocatalytic removal of antiviral drugs in real wastewater

The main route for lopinavir and ritonavir to enter the environment is through wastewater. Up to 22% and 37% of unmetabolized lopinavir and ritonavir are excreted with faces, respectively (Kuroda et al., 2021). This may result in the emergence of antiviral drug-resistant virus strains within the bodies of select wild animals (Kuroda et al., 2021). Therefore, the photocatalytic removal of lopinavir and ritonavir in real treated wastewater (tWW) was assessed using the synthesized multiphase photocatalysts. Direct photolysis of ritonavir in model wastewater was fast but slowed in the presence of additional water components, as shown in Fig. A.4a. After 45 min of direct irradiation of tWW with a high dosage of ritonavir, 90% photocatalytic removal efficiency was reached. In the presence of WU4 and WW4 photocatalysts, the photocatalytic removal process was very efficient, and 95% ritonavir was removed after 15 min of irradiation. In both model and real treated wastewaters, lopinavir demonstrated a decreased susceptibility to photocatalytic removal (Fig. A.4b). Also, lopinavir was more efficiently removed using the photocatalytic oxidation of tWW than direct photolysis. Interestingly, when the WW4 was used, the first 45 min of irradiation resulted in a lower susceptibility to irradiation. However, lopinavir was successfully removed after 60 min of irradiation, with a residual concentration of lopinavir of less than 5%. According to Kovalova et al. (2013), the post-treatment of hospital wastewater with powdered activated carbon was effective, removing more than 90% of ritonavir. The presence of tWW components, such as bicarbonates and DOM, is linked to the highest removal rate in tWW. The removal rates for •OH and CO\(_3\)\(^{2-}\) (estimated to be 8.5×10\(^{6}\) L mol\(^{-1}\) s\(^{-1}\)) are significantly higher than the reaction rates of •OH. Particularly, the DOM played two different roles: (i) radical scavenger and (ii) radical chain promoter (Zwiener and Frimmel, 2000).

3.3.5. Kinetics

Three well-known models were used to determine the kinetics of the photocatalytic oxidation of lopinavir and ritonavir by the synthesized multiphase photocatalysts: zero-order, first-order, and second-order (Ahmed and Emam, 2020). Table A.1 shows the rate constant k, half time T\(_{1/2}\), and correlation coefficient R\(^2\). The Chi-squared test (\(\chi^2\)) was used to determine the statistical characteristics of kinetics data (Ahmed et al., 2021). The first-order regime has the highest R\(^2\) and the lowest \(\chi^2\) values, indicating that this kinetics model best fits the experimental data (Zhang et al., 2011; Ahmed et al., 2020). The kinetics of the photocatalytic removal of lopinavir and ritonavir in model and real treated wastewaters by the synthesized multiphase photocatalysts followed a pseudo-first-order regime (Ahmed and Emam, 2019; Zhang et al., 2019).

The k\(_1\) values observed for the photocatalytic removal of ritonavir were higher than that observed for the photocatalytic removal of lopinavir (Table 1). When the WW photocatalysts were used, the difference was one order of magnitude greater. The highest k\(_1\) value was observed during the photocatalytic removal of ritonavir from model wastewater by WW4 (35.64×10\(^{-2}\) min\(^{-1}\)). The obtained values for the photocatalytic removal of lopinavir by WW4 are consistent with the k\(_1\) values obtained by Wang et al. (2015) during the photocatalytic removal of Tamiflu (an antiviral drug) by P2S-TiO\(_2\) under UV-A irradiation (0.040 min\(^{-1}\)). The k\(_1\) values obtained using the WW4 photocatalysts for the photocatalytic removal of ritonavir and the WW photocatalysts for the photocatalytic removal of lopinavir and ritonavir are significantly higher than those obtained using pure anatase photocatalyst (k\(_1\) = (35.64×10\(^{-2}\) min\(^{-1}\)))

| Sample | \(k_1\) (min\(^{-1}\) × 10\(^{-1}\)) lopinavir | \(R^2\) | \(k_1\) (min\(^{-1}\) × 10\(^{-1}\)) ritonavir | \(R^2\) |
|--------|---------------------------------|------|---------------------------------|------|
| WU1    | 4.20                            | 0.8805| 30.49                           | 0.9997|
| WU2    | 4.81                            | 0.7756| 15.46                           | 0.9241|
| WU3    | 0.48                            | 0.5500| 5.84                            | 0.8587|
| WU4    | 1.21                            | 0.5458| 21.22                           | 0.7748|
| WU5    | 0.65                            | 0.4436| 24.57                           | 0.9246|
| WU6    | 1.59                            | 0.439841| 19.78                           | 0.9038|

Table 1 Kinetics of the photocatalytic removal of lopinavir and ritonavir from model and real wastewaters by WU and WW photocatalysts.
According to Kisch and Bahnemann (2015), the reaction rates for the photocatalytic systems based on suspensions of semiconductor powders in dissolved substrates are adequate for comparison. The reaction rates must, however, be measured using the same type of photoreactor under identical irradiation conditions, and the intensity of the incident light must be integrated in the same wavelength range. Finding the most appropriate experimental data that satisfy the above criteria is difficult. Therefore, the photocatalytic performance was compared using the order of magnitude of the pseudo-first-order kinetic constants ($k_1$). Thi et al. (2021) recently compiled the experimental data on the photocatalytic degradation of selected antiviral drugs that had been published so far. It should be mentioned that under UV irradiation at 365 nm and using P25-TiO$_2$ photocatalyst, pseudo-first-order kinetic constants ($k_1$) have been reported (Thi et al., 2021) in magnitudes comparable to those obtained in this study for the photocatalytic removal of lopinavir and ritonavir by the synthesized multiphase photocatalysts (Table 1). Previously, 0.040 min$^{-1}$ at 1.8 mW·cm$^{-2}$ irradiance was reported for the photocatalytic removal of oseltamivir (Wang et al., 2015), and 0.0263 (An et al., 2015b), 0.0542 (An et al., 2011), 0.076 (An et al., 2015a), 0.084 (An et al., 2015a), and 0.102 (An et al., 2015a) min$^{-1}$ were obtained for the photocatalytic removal of acyclovir, lamivudine, 1-aminotadine, 2-aminotadine, and rimantadine, respectively, at 0.36 mW·cm$^{-2}$ irradiance. Therefore, the $k_1$ values obtained for the photocatalytic removal of ritonavir by WU photocatalysts and for the photocatalytic removal of lopinavir and ritonavir by WW photocatalysts are significantly higher than those obtained using pure anatase photocatalyst.

### 3.4. Ecotoxicity

In general, the effect of the photocatalytic treatment is evaluated in terms of the removal efficiency of a target pollutant. However, some toxic by-products or products of the photocatalytic oxidation of the target pollutant can also be generated during photocatalytic treatment, which are potentially harmful to the environment and human beings (Calza et al., 2006). Therefore, a different method must be applied for the assessment of the effectiveness of photocatalytic treatment in detoxifying the water samples containing antiviral drugs, pharmaceuticals, and other emerging pollutants. The bioconcentration factor is used as an indication for predicting bioaccumulation in living organisms. According to the bioconcentration factors (1.32 L·kg$^{-1}$ ritonavir and >1 L·kg$^{-1}$ lopinavir) (Kumari and Kumar, 2021), both antiviral drugs may accumulate in the fish body more than in the surrounding water. There are few studies on the effects of tested compounds on living organisms; however, some modeling studies (Kuroda et al., 2021; Kumari and Kumar, 2021) have predicted that ritonavir and lopinavir may have high chronic toxicity (narcosis) to aquatic organisms due to their high hydrophobicity (PNEC 2.9 ng·L$^{-1}$ for ritonavir and PNEC 4.7 ng·L$^{-1}$ for lopinavir). Furthermore, their metabolites have high toxicity (Kuroda et al., 2021), suggesting that additional wastewater treatment or on-site pretreatment (e.g., ozonation, oxidation, etc.) is required to effectively remove antiviral drugs and pharmaceuticals.

The collected ecotoxicity data show that the variations in Danio rerio can be observed in the 75% diluted tWW solution (Fig. 9a and b). The length of Danio rerio was not altered, but organogenesis was disrupted. The presence of lopinavir in the tWW (Fig. 9c) had an effect on fish embryo mortality; however, no dead fish embryos were found. On the other hand, the length of Danio rerio was reduced up to 40%. Surprisingly, when lopinavir-containing tWW was contacted with fish embryos after photocatalytic treatment using WW4, a 100% mortality rate was noted after exposure to undiluted tWW (100%). The modifications in the fish morphology were observed in the 75% diluted tWW solution (scoliosis). Although no lopinavir was found in the sample, its intermediates or by-products could be harmful to fish. This implies that when advanced oxidation processes are applied to treat real environmental samples, estimating only one parameter - the decreased concentration of the target pollutant – is insufficient, and the final ecotoxicity of photocatalytically treated water samples must be
assessed. Also, Kumari and Kumar (2021) pointed out that priority pollutants in wastewater effluents must be regularly monitored before discharging them into rivers, lakes, and open water reservoirs. As shown in Fig. 9e, the presence of ronitavir in tWW was lethal to Danio rerio. The developed multiphase photocatalysts effectively reduced the toxicity of model and real wastewaters containing ronitavir during photocatalytic treatment (Fig. 9f). According to the number of survived embryos (100%), the application of photocatalytic treatment using the developed multiphase photocatalysts was successful in achieving water with no toxicity, and it is an effective method for removing various toxic chemicals from contaminated water with low ecotoxicity.

4. Conclusions

In summary, multiphase photocatalysts were synthesized by a simple calcination of industrial waste from ammonium molybdate production (WW photocatalysts) and its combination with WO3 (WW photocatalysts). The XRD results showed that Fe3O4, Fe2O3, MgMoO4, FeMoO4, and MgFeMoO12 crystalline phases were dominant in the WW photocatalysts, and Fe3O4, Fe2O3, MgFeMoO12, and FeMoO12 crystalline phases were prevalent in the WW photocatalyst. The WW and WW photocatalysts could absorb visible light up to 620 nm due to the presence of visible-light-active crystalline phases. Effects of calcination temperature of industrial waste (550–950 °C) and WO3 content (0–100%) on photocatalytic activity of multiphase photocatalysts (WW and WW) for efficient removal of SARS-CoV-2 antiviral drugs (lopinavir and ronitavir) in model and real wastewaters were studied. The highest k1 value was observed for the photocatalytic removal of ronitavir from model wastewater using WW4 (35.64 × 10−2 min−1). The synthesized multiphase photocatalysts exhibited 95% efficiency in the photocatalytic removal of ronitavir within 15 min of visible light irradiation. In contrast, 60 min of visible light irradiation was necessary to achieve 95% efficiency in the photocatalytic removal of lopinavir. The ecotoxicity test conducted using zebrafish (Danio rerio) embryos showed no toxicity for photocatalytically treated ronitavir-containing wastewater, and the contrary trend was observed for photocatalytically treated lopinavir-containing wastewater. The synthesized multiphase photocatalysts can also be tested and applied for degradation of other SARS-CoV-2 antiviral drugs in wastewater. The current study demonstrated a simple route for turning the industrial waste from ammonium molybdate production into useful photocatalytic materials for removal of SARS-CoV-2 antiviral drugs.

CRedit authorship contribution statement

Bozena Czech: Investigation, Methodology, Visualization, Writing – original draft, Conceptualization, Validation, Supervision; Anna Wasielwska: Investigation; Anna Boguszewska-Czubara: Investigation, Methodology, Visualization; Kuniyo Yubuta: Investigation, Writing – review & editing; Hajime Wagata: Investigation, Writing – review & editing; Shahlo S. Daminova: Investigation, Writing – review & editing; Zukhra C. Kadirova: Investigation, Writing – review & editing; Ronald Vargas: Investigation, Writing – original draft; Mirabbos Hojamberdiev: Investigation, Methodology, Visualization, Writing – review & editing, Conceptualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.128300.

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