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A review on the potential of photocatalysis in combatting SARS-CoV-2 in wastewater

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ABSTRACT

Photocatalytic technology offers powerful virus disinfection in wastewater via oxidative capability with minimum harmful by-products generation. This review paper aims to provide state-of-the-art photocatalytic technology in battling transmission of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) in wastewater. Prior to that, the advantages and limitations of the existing conventional and advanced oxidation processes for virus disinfection in water systems were thoroughly examined. A wide spectrum of virus degradation by various photocatalysts was then considered to understand the potential mechanism for deactivating this deadly virus. The challenges and future perspectives were comprehensively discussed at the end of this review describing the limitations of current photocatalytic technology and suggesting a realistic outlook on advanced photocatalytic technology as a potential solution in dealing with similar upcoming pandemics. The major finding of this review including discovery of a vision on the possible photocatalytic approaches that have been proven to be outstanding against other viruses and subsequently combatting SARS-CoV-2 in wastewater. This review intends to deliver insightful information and discussion on the potential of photocatalysis in battling COVID-19 transmission through wastewater.

1. Introduction

Novel coronavirus disease 2019 (COVID-19) has been declared a pandemic in most countries since the end of March 2020 and has affected 216 countries causing over 2 billion deaths as of 24 January 2021. This COVID-19 is an illness caused by the new coronavirus emerging in Wuhan, Hubei Province, China, in early December 2019. On 11 March 2020, the World Health Organization declared COVID-19 a pandemic [1]. Since the effects of this novel coronavirus are close to those of extreme acute respiratory syndrome (SARS), it has been named severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) [2]. It is believed that this virus was developed from bats and then moved into other mammalian hosts before jumping to humans. COVID-19 is the third zoonotic epidemic of the twenty-first century, after SARS (2002–2003) and Middle East respiratory syndrome (MERS, 2012) [3]. COVID-19 virus is a positive-stranded ribonucleic acid (RNA) virus with a crown-like appearance under an electron microscope due to the presence of spike glycoproteins on the envelope (Fig. 1) [4]. In addition, the COVID-19 virus is similar to the SARS virus in 2003 but spread faster. Illness caused by COVID-19 is mostly respiratory disease, while symptoms can be cough, fever, nausea, and diarrhoea [5]. The main route of transmission of the COVID-19 virus is inhalation by person-to-person transmission. Based on its symptoms, the transmission can also occur through respiratory droplets and aerosol transmission. For this reason, researchers have focused on various types of transmission, including wastewater, due to the probability that the virus may affect the wastewater from the hospital waste, such as human faecal from infected persons [6].

Many contaminants can be found in wastewater, especially those discharged from the hospital, such as pharmaceutical residues, chemical substances, radioisotopes, and microbial pathogens [7]. Notably, various viruses have been found in the hospital wastewater such as...
adenoviruses, hepatitis A (HAV), and polioviruses. This is according to the media that can be the reason for the viruses to be transmitted, which is water media. Since 2003, drainage plumbing systems have been deemed a possible mechanism for spreading the SARS-CoV-1 coronavirus into the sewage system for coronavirus-infected populations living in apartment buildings [8,9]. The SARS-CoV-2 virus, like SARS-CoV-1, can be transmitted by aerosols or microscopic water droplets [10]. In fact, according to van Rowan et al. (2020) [11], the SARS-CoV-2 and SARS-CoV-1 viruses have comparable stability in aerosols on the surface. Viruses may remain viable and contagious on surfaces (for a few days) and in aerosols depending on the inoculum shed (for hours) [11].

To curb and alleviate infectious drinking water, water purification technologies have advanced significantly in the last century [12–16]. The number of waterborne diseases outbreaks, including cholera and typhoid, has declined because of drinking water disinfection. Water disinfection is the elimination, deactivation, or destruction of pathogenic microorganisms from water. Microorganisms are killed or made inactive, putting an end to their development and reproduction. Sterilisation is a disinfection-related process. During the sterilisation process, all present microorganisms, both dangerous and harmless, are destroyed [17].

Researchers in the Netherlands were the first to detect COVID-19 viruses in the hospital wastewater [18]. Later, Wu et al. [19] also found COVID-19 viruses in the hospital wastewater that is believed transmitted from the human faecal matter of infected person. As in many countries in this world, several studies detected the existence of the COVID-19 virus in the human faecal of COVID-19 patients with or without gastrointestinal symptoms [20]. It should be noted that in some countries, they are not discharged properly. These hazardous contaminants, especially viruses, can represent chemical, biological, and physical risks for public and environmental health.

Conventionally, virus disinfection in water and wastewater divided into two main categories which are physical and chemical methods. Physical disinfection including through heating, adsorption and filtration. Virus will be physically removed from water based on size exclusion. However, due to their small sizes and unique properties of the viruses, they are difficult to remove and deactivate. While, chemical disinfection involved the usage of chemicals to disinfect the virus. Chlorination technique is one the most common technique for virus disinfection that using chlorine gas, chloramines or hypochlorite solution [21–24]. Previous study reported chlorination could remove SARS-CoV-1 efficiently [25]. Unfortunately, chlorination was opposed due to generation of mutagenic and carcinogenic disinfection by-products. Likewise, chlorination also imparts unpleasant tastes and odours to the water. In battling the pandemic, the performance and environmental safety should be taken into serious consideration.

As the current published research of pandemic COVID-19 is focusing on the occurrence, detection, and transmission of viruses in the environment [26–29], this paper aims to provide state-of-the-art technology in battling transmission of SARS-CoV-2 in wastewater via photocatalytic degradation. The concept and limitation of the existing conventional and current advanced oxidation processes for virus disinfection in water systems were reviewed extensively. A broad range of virus degradation by various photocatalysts was also deliberated to understand the possible mechanism to deactivate this deadly virus. At the end of this review, the challenge and future perspectives are included to provide the limitation of current photocatalytic and suggest a reasonable outlook on developing advanced photocatalytic technology as a promising alternative in handling similar forthcoming pandemics. To the best of our knowledge, this is the first systematic review that delivers insightful information and discussion on the potential of photocatalysis in battling COVID-19 transmission through wastewater.

2. Virus disinfection via conventional methods

Physical or chemical disinfectants may be used for disinfection. Chemical pollutants of water, which act as carbohydrates or habitat for microorganisms, are often extracted by the disinfectant. Disinfectants should do more than just destroy bacteria. Disinfectants must also have a residual effect, which ensures that they must stay present in the water after disinfection. After disinfection, a disinfectant can deter pathogenic microorganisms from emerging in the pipes and recontaminating the water. Fig. 2 shows the classification of water disinfection methods [17].

Many wastewater treatment methods aim to inactivate pathogenic microorganisms that are toxic to marine organisms. Recent tests, however, have shown that even after water treatment, a measurable number of pathogens existed in effluents. In hospitals and treatment centres, chlorine is one of the most used disinfectants [30]. In addition to destroying most microbial communities, this detergent has a detrimental influence on the ecosystem and may be hazardous to marine organisms if it reaches waterways [31].

Chlorination can also result in nitrosodimethylamine (NDMA) development, which has been linked to human cancer. The chlorination process will react with organic matter, producing trihalomethanes (THMs), a carcinogenic compound [30]. Conventional filtration methods for wastewater treatment are unsuccessful at eliminating micropollutants like viruses. Furthermore, certain bacteria have been discovered to be immune to such chemical materials [32]. These results are in line with the findings of Al-Gheethi et al., who discovered the existence of viable microbial cells even after the treatment phase [33].

The use of solar-based disinfection (SODIS) technology, especially in water and wastewater disinfection, is a promising approach. This system is ideal because of the abundance of high solar radiation, low capital expense, and long-term feasibility. Meanwhile, nanotechnology’s use in wastewater treatment has also been recorded in the literature. Noman et al., for example, looked at how bimetallic bionanoparticles inactivated antibiotic-resistant E. coli (Gram-negative) and Staphylococcus aureus (Gram-positive) bacteria seeded in greywater [34]. According to the inactivation mechanism, the bacterial cells were inactivated due to disruption to the bacterial cell wall’s carbohydrates and protein structures [35]. The C–C bonds of the functional groups found in the bacterial cell wall were broken. The combination of SODIS and nanotechnology could result in a novel disinfection method for inactivating human viruses. The most popular nanoparticles used for wastewater disinfection are ZnO, which are more efficient when exposed to sunlight, theoretically increasing antiviral activity [36].

As specified by ISO 13408-1, sterility assurance level (SAL) is used to characterise the killing efficiency of a treatment process, with the treatment process being very efficient if the SAL is very poor. Log reduction accepted by the United States Environmental Protection Agency (USEPA) is a term widely used to measure the efficiency of disinfection processes [37]. SAL is generally written as 10^x. Based on the pathogen’s initial concentration, a 10^4 or 10^6 value is most often used.
3. Virus disinfection via an advanced oxidation process

Advanced oxidation processes are a recently discovered technology for the disinfection of viruses in polluted wastewater by generating reactive oxygen species such as hydroxyl radicals as an oxidising agent to treat harmful pathogens. The generation of radicals may be initiated by primary oxidants such as hydrogen peroxide, ozone, sources of energy (UV light, ultrasonic and heat), or catalysts such as titania, iron oxide, or other semiconductors. Hydroxyl radicals are known to rapidly and unselectively bombard organic molecules. The generated radicals degrade the organic molecules found on the virus cell wall and directly deteriorate the virus pathogens. The advanced oxidation processes include ozonation, ultrasound, Fenton process, and photocatalysis, have been effectively and efficiently used in treating virus-contaminated water. The methods offer other diverse approaches to the production of hydroxyl radicals that make it more flexible and therefore provide a better approach to complying with strict guidelines during wastewater treatment.

Ozonation is a common technique in virus disinfection from wastewater that utilises three oxygen atoms (O_3) called ozone into the water. Ozone presents in the form of gas, which is one of the most potent oxidising agents. When ozone is dissolved in water, it produces a broad spectrum of reactive oxygen radicals (ROS) that could oxidise organic materials in virus membranes, which destroys the cell wall leading to cell bursting, causing immediate degradation of the viruses [44]. Previous studies reported that the virus could be removed from wastewater by ozonation [45, 46]. Furthermore, ozone is highly reactive and must be directly used after onsite generation and difficult to store [47]. Ozonation in wastewater could also result in the formation of harmful by-products such as aldehydes, carboxylic acids, and bromate when reacting with dissolved organic matter and bromide [45].

Ultrasound is a longitudinal wave with frequencies in the range of 20–106 kHz [48]. This frequency is above the human hearing range (20 Hz to 20 kHz) but below the mega-sonic range (>600 kHz) [49]. This technique has attracted wide attention in water and sewage system due to simplicity, high decomposition speed, and zero secondary pollution. Ultrasound is evaluated as one of the AOP for the degradation of pollutants in the water system due to the formation of free hydroxyl radicals with oxidising capabilities [50, 51]. Ultrasound technique was reported to disinfect microorganisms and viruses by several mechanisms based on acoustic cavitation [49, 52, 53]. Cavitation is the phenomenon of microbubbles or cavities forming, growing, and collapsing in a liquid in extremely short time intervals (milliseconds) [49]. The mechanism involved are: (1) the viruses could be chemically disinfected by bombarded with hydroxyl radicals generated via ultrasound, (2) the virus could be physically attacked by the high temperature and pressure that results from the momentum of bubble collapse that can kill the viruses, and (3) shear forces that persuaded by microstreaming that could damage the virus. Ultrasound technique can be applied as a stand-alone process or integrated with other disinfection techniques such as chlorination, heating, ozonation, and UV irradiation [53, 54]. However, the utilisation of ultrasound technique in water treatment requires high
### Table 1

**Summary of water disinfection methods.**

| Methods              | Advantages                                                                 | Limitations                                                                                     | References |
|----------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|------------|
| Chlorination         | • Chlorination is a less costly choice than using ultraviolet (UV) or ozone to clean water.  
                         • It is selective against various pathogenic bacteria.  
                         • Dosing rates can be easily managed because they are adjustable.  
                         • Also, after initial treatment, residual chlorine in the wastewater effluent will extend the disinfection phase. It can also be used to measure performance. | • Chlorination may be opposed on an aesthetic basis because it imparts unpleasant tastes and odours to the water. | [21]       |
| Chlorination (sodium hypochlorite solution) | • Both sodium hypochlorite and chlorine gas are effective disinfectants.  
                         • In situ generation, no dangerous chemicals are used. Just softened water and sodium chloride (NaCl) are used.  
                         • Sodium hypochlorite (NaOCl) solutions are less hazardous (1 % concentration) and less concentrated than the normally supplied solution (14 % concentration) when producing onsite demand. | • NaOCl may be purchased commercially or produced onsite, with the latter being the better option for handling. Salt is dissolved in softened water to create a condensed brine solution, diluted, and moved into an electrolytic cell to produce sodium hypochlorite onsite. Because of its explosive nature, hydrogen is therefore produced during electrolysis and must be vented. | [22]       |
| Chlorination (solid calcium hypochlorite) | • Ca(OCl)₂ is safer than chlorine gas and NaOCl since it is in solid form.  
                         • Ca(OCl)₂ can react violently with even very small quantities of water, creating poisonous gases, flame, and spatter.  
                         • Heat will cause Ca (OCl)₂ to decompose easily, resulting in an explosion, a burning fire, and the release of poisonous gases. | • Contamination or inappropriate use of Ca(OCl)₂ will result in explosions, fires, or gas leaks (toxic gases). Every foreign matter should not be allowed to come into contact with calcium hypochlorite (including other water treatment products).  
                         • Ca(OCl)₂ can react violently with even very small quantities of water, creating poisonous gases, flame, and spatter.  
                         • Heat will cause Ca (OCl)₂ to decompose easily, resulting in an explosion, a burning fire, and the release of poisonous gases. | [23]       |

### Table 1 (continued)

| Methods              | Advantages                                                                 | Limitations                                                                                     | References |
|----------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|------------|
| Chloramines          | • Chloramine is a more durable disinfectant than chlorine, but it is not as effective as chlorine in providing long-lasting residual disinfection.  
                         • Chloramination produces no by-products. | • Chloramine concentrations are more difficult to control than chlorine concentrations. | [24]       |
| Ozone                | • Ozone has a high oxidising ability.  
                         • Germs (including viruses) must be destroyed in a matter of seconds, which necessitates a rapid response period.  
                         • Colour and flavour do not change.  
                         • It does not necessitate the use of any chemicals.  
                         • After disinfection, water is given oxygen.  
                         • Algae is destroyed and removed.  
                         • Any organic matter is reacted to and removed. | Since ozone is unstable at ambient pressure, onsite generation is needed.  
                         • Since it is a greenhouse gas, it is poisonous at high concentrations. The ozone 10 photocatalysts - applications and attributes destructor, ozone contact chamber, and generator are the three components of an ozone system. | [41]       |
| Ultraviolet (UV) light | • It reduces the potential for regrowth within the delivery chain, ensuring that the accumulation of biodegradable or assimilable organic carbon (AOC) does not rise.  
                         • By-products such as haemoglobin-associated acetaldehyde (HAA), trihalomethanes (THM), aldehydes, ketoacidosis, and bromate are not produced.  
                         • We can accomplish the same log inactivation of Giardia and Cryptosporidium using UV light, which is less expensive than using chlorine dioxide or ozone.  
                         • There is no development of chlorinated disinfection by-product (DBP) as used in conjunction with chloramines. | There are some limits to UV disinfection in developing countries. The energy demand is the big stumbling block. Electric power supply cannot be assured in certain networks.  
                         • One drawback may be the lack of a single test to check for adequate ray disinfection. Since it leaves no stains, it is only useful as a primary disinfectant. It does not serve as a secondary disinfectant of water, so it does not work against reinfection.  
                         • Chemical structure and the quality of microorganisms found in influent water are also concerns of UV disinfection. To protect bacteria, turbid, cloudy, or water with a significant number of bacteria may be used. Chemical structure is a major issue, as water containing many... | [42]       |

(continued on next page)
operating and maintaining costs due to the high energy consumption and replacement of instruments like the ultrasound probe, which are expensive and may suffer from reliability issues.

Furthermore, due to the instability of the nanosized particle, TiO2 nanoparticles can aggregate, blocking light incidence on the active surface, thereby reducing their photocatalytic activity compared to larger particles. One major practical obstacle for the slurry method is the rapid loss of activity due to the accumulation of ferric sludge that could affect the effectiveness of the treatment. The methods, such as the generation of harmful by-products and utilisation of large volumes of chemicals, have been addressed by the development of second-generation TiO2 catalysts with high separation efficiency and the ability to be recovered and regenerated [63].

4. Virus disinfection via photocatalysis

Photocatalysts are semiconductor oxides that serve as heterogeneous catalysts in the presence of electromagnetic radiation. They act as a disinfection process for water treatment.

Table 1 (continued)

| Methods                        | Advantages                                                                 | Limitations                                                                 | References |
|--------------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------|------------|
| Photocatalytic disinfection    | - Photocatalysis, in contrast to standard treatment techniques, results in the formation of harmless compounds. | - Various toxic chemicals can be found in wastewater. In different drainage sources, the photocatalytic method removes various harmful substances. | [43]       |
|                                | - There are minor reactions. There is less chemical input, and the reaction time is short. | - To some degree, it can be used for hydrogen generation, gaseous phase, and aqueous treatments, as well as solid (soil) phase treatments. |            |

Since then, metal-free photocatalyst like carbon-based photocatalyst and TiO2 catalyst with high separation efficiency and the ability to be recovered and regenerated [63].

*Up to this point, the information presented is consistent with the provided text.*

4.1. Performance evaluation on virus disinfection via photocatalysis

Earlier, TiO2 photocatalyst has shown great potential as a solution for sewage and wastewater treatment because it is non-toxic, cheap, and abundantly available. TiO2 photocatalysts successfully deactivate viruses like phage MS2, bacteriophage Qi8, phage f2, marine norovirus, and human adenovirus [68–72]. Viruses disinfection by photocatalyst could overcome the drawbacks of the conventional disinfection methods, such as the generation of harmful by-products and utilisation of large volumes of chemicals. However, there are main limitations suffered by TiO2 photocatalyst, which are lower bandgap, poor photocatalytic performance and slow photocatalytic degradation rates.

To some degree, it can be used for hydrogen generation, gaseous phase, and aqueous treatments, as well as solid (soil) phase treatments.
capability for carrier charge separation that results in incompetent exploitation of visible light, and low photodegradation performances. Later, coupling TiO$_2$ photocatalyst with other metals such as manganese (Mn) [73], palladium [74], silver oxide (AgO), copper [75,76] and copper oxide [67] to form heterojunction photocatalyst could further enhance the photocatalytic activities on virus degradation through visible light irradiation.

The technology of photocatalysis that employs carbon-based photocatalyst has attracted much attention due to the zero risk of metal leaching into the water system and optimum natural light-harvesting.
The non-metal photocatalysts that have been developed for virus disinfection include carbon-based materials such as fullerene [80,81], carbon nanotube [82], carbon dot [83,84], and graphitic carbon nitride (g-C3N4) [78,85,86].

Fullerene (C60) is a spherical carbon-based molecule made up of carbon atoms kept together by sp2 hybridisation. Fullerenes have a peculiar three-dimensional structure and have high chemical stability. They also have a large specific surface area and strong electrical conductivity. Fullerene offers the generation of ROS under visible light due to its small gap between the highest occupied molecular orbital and lowest occupied molecular orbital, which is approximately 1.6–1.9 eV [87]. A previous study reported that the suspensions of polyhydroxylated fullerene successfully inactivated the non-enveloped viruses like MS2 bacteriophage, enterobacteria phage PRD1, and bacteriophage T7 under UVA irradiation [88]. Hotze et al., determined that the virus inactivation by fullerene material is mainly based on the production of singlet oxygen (1O2), one of the ROS by fullerene aggregates, and resistance of the viruses determined by the structural and composition of non-enveloped virus capsids. However, the potential of fullerene as a photocatalyst in wastewater treatment was limited to the aggregation of the nanoscale particles that reduces the photochemical properties. Therefore, immobilisation of fullerene appeared as the most practical approach to retain the photocatalytic activity in the aqueous system. Moor et al. managed to immobilise fullerene on silica gel and polystyrene resin by the simple nucleophilic addition of a primary amine across a [6,6] fullerene double bond and followed by proton transfer under mild condition as shown in Fig. 4(a) [80]. Based on the SEM images in Fig. 4(b–e), Moor et al., suggested the surface of PS resin and silica gel were covered by monolayer coverage of fullerene and did not exhibit significant aggregation. The immobilisation of fullerene on solid materials also promoted the production of 1O2 in the water under visible light irradiation and deactivated MS2 bacteriophages without exhibiting significant loss of photocatalytic activity after repeated cycles. Besides that C60 fullerene, the immobilised C60 fullerene on MCM-41 also displays antiviral properties towards MS2 in the water system under visible light irradiation [81].

In contrast, g-C3N4 can be synthesised directly from earth-rich, low-cost precursors rich in nitrogen, e.g., heating the melamine [79]. The g-C3N4 consists of organic elements such as carbon, nitrogen, and hydrogen and has the ability to break water and produce hydrogen under visible light irradiation, making it a non-metal catalyst and widely utilised for water treatment [89–91]. To date, g-C3N4 was documented for having antimicrobial and antivirus properties through photocatalytic degradation [92]. The bandgap of g-C3N4 is 2.7 eV that is appropriate for visible-light-driven photocatalyst with a conductive band of 1.1 eV and valence band of +1.6 eV, and normal hydrogen electrode as reference [93].

To evaluate the photocatalytic inefficient of g-C3N4 for virus disinfection under visible light irradiation, Li et al. used bacteriophage MS2 as a model virus [78]. As depicted in Fig. 5(a), bacteriophage MS2 was completely inactivated within 360 min under visible light irradiation. The regrowth test was also conducted in the dark for 72 h. No visible plaques formed, indicating that g-C3N4 had inactivated the virus through the photocatalysis process. As shown in Fig. 5(b), Li et al. also compared the performance of g-C3N4 with other metal-based visible-driven photocatalysts such as nitrogen doped TiO2 (N-TiO2), Bi2WO6
and Ag@AgCl for viral deactivation. They revealed that more than 7-log of MS2 were deactivated by g-CN4, whereas about 1-log and 4-log of MS2 were deactivated by N-TiO2 and Bi3WO6 photocatalyst, respectively. The Ag@AgCl recorded the highest inactivation of MS2, which resulted from the presence of biocidal silver ions and silver nanoparticles that performed as an electron sink to expedite charge separation and enhance the photon harvesting [34]. However, the application of silver-based photocatalyst is costly and may pose health risks in the treated water due to the dissolution of Ag and Ag nanoparticles. As depicted in Fig. 5(c), the degradation mechanism of MS2 by g-CN4 under visible light irradiation mainly involved the oxidation damage on the surface protein of the virus by ROS that resulted in the leakage and destruction of viral materials namely RNA and caused the viral death with no regrowth.

4.2. Mechanism of photocatalysis on virus disinfection

It was first to observe the photocatalysis mechanism by TiO2 to inactivate the virus by destroying the shell and/or capsid of viruses. As a result, genetic materials, minerals, and proteins were released inside the viruses and caused the virus to inactivate. Herein, it should be noted that the photocatalysis mechanism of the virus occurred on the surface of the film and can be explained by photodegradation of the protein capsid of the virus and subsequently efflux of the viral RNA enveloped by the protein layer. When virus reacts with the surface of the catalyst, active radicals such as O2, HO, and HO formed and oxidised the C–H bonds and degraded viruses [95]. It is well known that most photocatalysts are semiconductor materials. The photocatalytic process based on semiconductor materials can be briefly described as shown in Fig. 6. When the semiconductor is irradiated by light, photogenerated electron (e–) and hole (h+) are generated and react with other substances to form ROS, including OH, H2O2, H, and O2, and these ROS participate in the photocatalytic degradation bacteria process. Afterwards, reactive oxygen species attack the cell membrane. The coenzyme A on the cell membrane is damaged, resulting in inhibition of respiration dependent on the intact cell membrane, reduction or loss of cellular respiration activity, and eventually cause cell death.

To view the potential of photocatalysis as an alternative solution for battling COVID-19, understanding the real mechanism of deactivation and destroying the microorganisms, especially coronaviruses, during photocatalytic disinfection is vitally important. It might be helpful to develop a more efficient and powerful photocatalyst by (1) designing the morphology according to virology, (2) hybridising or functionalising with transition metals ions, and (3) fabricating composites or heterogeneous photocatalyst for efficient energy utilisation and recovery.

Typically, microorganisms contain outer membrane, peptidoglycan, and cytoplasmic membranes responsible for structural integrity and retention. The membranes surround an internal liquid-based cytoplasmic matrix that is comprised of genetic material and biochemical systems. Based on the complexity of the microorganisms, the complete mechanism of their degradation by photocatalytic remains partially known. As illustrated in Fig. 7, Regmi et al. reviewed the possible mechanism of photocatalytic degradation by semiconductor and nanoparticles photocatalyst on microbial cells in wastewater environment involving (1) oxidative stress induction; where the excess generation of ROS leads to peroxidation of the lipid membrane and protein attack that depresses the activity of some periplasmic enzyme and directly interact and damage the genetic materials, (2) metal ion release; the metal ions could exempt from semiconductor photocatalyst then passed through the cell membrane and directly reacted with the functional groups of nucleic acid and protein such as −COOH, −NH, and −SH, before finally destroying them, (3) non-oxidative mechanism: reducing the critical cellular metabolism such as amino acid, protein, nucleotide, and carbohydrate metabolism without oxidative stress induction [96].

Nevertheless, only the first mechanism has gained the interest of the researchers, which involved the generation of ROS that plays a major role in virus disinfection. Researchers strongly agreed that the main degradation of microorganism is initiated by the prolonged ROS attack results on the damage of the cell wall, followed by the cytoplasmic membrane and direct attack of intracellular components comprising genetic materials within the microorganism as depicted in Fig. 8 [97].

Viruses and their host bacteria typically co-exist in actual water conditions. Therefore, the efficiency of photocatalytic inactivation in the mixed system of virus/bacteria is of practical importance. For instance, Zheng et al. fabricated Cu-TiO2 nanofibres for the removal of virus bacteriophage f2 and bacteria E. coli 285 [75] (Fig. 9(a)). They compared the inactivation of both virus and bacteria in a single and mixed systems with the presence and absence of source light. Under visible light, both E. coli and bacteriophage f2 were inactivated completely within 240 min, as shown in Fig. 9(b). This indicates bacteriophage f2 is more resistant to photocatalytic oxidation in the virus/bacteria mixed system than E.coli 286. However, in the virus/-bacteria mixed system with the absence of source light, the removal efficiency of bacteriophage f2 decreased significantly compared to that in the single virus system, as depicted in Fig. 9(c). It can be assumed that free ROSs play an important role in phage f2 inactivation and in the bulk.
Virus disinfection in the water system by photocatalysis is also affected by the presence of natural organic molecules. Besides bacteria, the actual water system also contains natural organic matters (NOMs) such as nucleic acids, carbohydrates, and proteins. Their presence could quench the generated ROS and serve as disinfectants [98]. Therefore, the disinfection of viruses must also consider the presence of NOMs. To further explore this situation, Cheng et al. utilised humic acid as NOM representative and Cu–TiO$_2$ nanofibers as a photocatalyst [76]. They found that when the concentration of humic acid was increased from 0 to 15 mg/L, the removal efficiency of bacteriophage f2 declined from 5.00- to 1.89-log. This is due to the presence of humic acid that prevented the viral photocatalytic efficiency of the photocatalyst. It could be inferred that the presence of humic acid also dramatically reduces its stability. Particularly, for the practical application of virus photocatalytic disinfection technology, the existence of NOMs is a non-negligible problem, and more relevant research should be conducted to gain a better understanding of this subject.

5. Challenges and future perspectives

The impressive performance of the virus inactivation through the photocatalysis process in water, as summarised in Table 2, has proven the capability of photocatalysis to disinfect various harmful viruses. However, there are several challenges and barriers in the disinfection of viruses by photocatalysis, especially in battling them in wastewater. First, the difficulty in recovery of the suspended photocatalyst from the solution. Because of the possible toxicity of nanosized photocatalysts and the photocatalysts functionalised with other carcinogen substances, the powdery-shaped and suspended nanosized photocatalysts must be removed before the treated water is reused or released into the environment. The photocatalytic disinfection of the virus could also be more harmful if the released photocatalyst has not gone through a complete reaction, where disinfection has still not occurred, and the photocatalyst is still holding the adsorbed harmful viruses. Second, in real water applications, the nanosized photocatalysts are brittle and prone to aggregation. Aggregation of photocatalyst could hinder the active surface area and reduce the photocatalytic performance. Therefore, those barriers must be overcome if photocatalytic degradation is to be used independently in wastewater treatment.

To address the above challenges, immobilising the photocatalyst into porous or floating substrate could solve the recovery and agglomeration issues of the suspended photocatalysts in the aqueous system [13, 67, 92]. The porous substrate could be an organic or inorganic membrane leading to the development of a bifunctional photocatalytic membrane that acts as a filter and photocatalyst in the same chamber. However,
incorporating the photocatalyst in the substrate might result in the sedimentation of the photocatalyst at the bottom of the substrate. This condition could hinder the maximum light utilisation from activating the photocatalyst. Hence, modification or functionalisation of the photocatalyst and the substrate can be adapted to guarantee the photocatalyst remains at the top surface of the substrate. Other than that, utilisation of translucent or transparent substrate might solve the source light utilisation.

Besides that, the application of electrospun nanofibrous photocatalyst also attracted much attention in virus disinfection in water systems due to their super porosity and high surface area to volume ratio [74, 76, 99]. Nevertheless, electrospun nanofibrous photocatalysts are broadly acknowledged as brittle and fragile, and they can collapse easily due to their large pore size. This condition makes them not suitable to be used in water treatment for long-term application. Post-treatment after fabrication of nanofibrous photocatalytic could enhance the flexibility and mechanical strength of the nanofibrous photocatalyst.

Apart from that, viruses were reported to have stronger resistance towards photocatalytic disinfection than other microbes such as bacteria due to their differences in structural and geometric properties [75]. Unlike bacteria, viruses are the smallest and tiniest germ that can spread easily through the air that can cause various diseases with specifically targeted cells. For example, when a certain virus gets inside a host, it can hijack the specific cellular machinery like blood, respiratory system, liver, or other organs to generate clones of itself, overtaking more cells, and harming the body. In the case of COVID-19, when SARS-CoV-2 gets inside the human body, it specifically attacks the upper and the lower respiratory system like sinuses, nose, throat, windpipe, and lungs before damaging the organs and terminating the whole body. The recent finding through protein simulation revealed that the active SARS-CoV-2 spike protein is more stable than the active SARS-CoV-1 spike protein [106]. In comparison, SARS-CoV-1 moves faster, active, and nonactive, requiring a longer time to attach to human cell because of their instability. Meanwhile, SARS-CoV-2 are more stable and ready to attack which makes the COVID-19 much easily transmitted among human compared to MERS and SARS-CoV-1. The detection of the variant of SARS-CoV-2 through mutation also increases global awareness for improving current wastewater treatment.

Therefore, it is urgently crucial to develop an advanced remedy to deactivate the targeted viruses, especially SARS-CoV-2 in the water system. Development of smart or intelligent photocatalytic membrane could specifically exclude, adsorb, and photocatalytically degrade the virus according to their structural and geometric properties. By integrating stimuli-responsive materials that act as automatic doors by flexible adjustment of pore sizes and surface properties in response to the size or biological properties of the targeted viruses, the intelligent or smart membrane could overcome the bottlenecks of current photocatalytic technology.

6. Conclusion

In conclusion, there has been a significant rise in evidence suggesting the presence of pathogenic novel SARS-CoV-2 in wastewater. Throughout this review, the articles on various viruses disinfection by photocatalyst were evaluated extensively. It is discovered that in the presence of electromagnetic radiation, photocatalysts degrade any microorganism that has spread through surfaces or polluted the air, including the current deadly COVID-19 virus. There are only a few photocatalysts that operate successfully in the presence of UV radiation at the moment. The scientific work on improving the performance of photocatalysts in the presence of visible spectrum radiation, such as solar radiation, is still ongoing. However, the photocatalysts’ stability and protection must be assured before being used in the public domain. If these limitations are overcome, photocatalysis can become a more effective weapon in the fight against the virus’s spread. It is hoped that photocatalysts will be commercialised and adopted on a wide scale in the near future to clean up contamination and kill deadly species like coronavirus.
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optimization, Chemosphere 195 (2018) 551–558, https://doi.org/10.1016/j.chemosphere.2017.12.122.

[87] Y. Pan, X. Liu, W. Zhi, L. Jiang, Z. Liu, G. Zeng, B. Shao, Q. Liang, Q. He, X. Yuan, D. Huang, M. Chen, Advances in photocatalysis based on fullerene C60 and its derivatives: Properties, mechanism, synthesis, and applications, Appl. Catal. B Environ. 265 (2020) 118579, https://doi.org/10.1016/j.apcatb.2019.118579.

[88] E.M. Hotze, A.R. Badreldin, M. Wanner, Enhanced wavelength selectivity of bacteriophage inactivation via singlet oxygen generation in UV illuminated fullerenol suspensions, Environ. Sci. Technol. 43 (2009) 6639–6645, https://doi.org/10.1021/es900111f.

[89] N. Hashimah, J. Jaafar, S. Samitsu, A.F. Ismail, M.H.D. Othman, M.A. Rahman, N. Hidayati, N. Yusof, F. Aziz, T.A.T. Mohd, Efficient removal of partially hydrolysed polycarlyamide in polymer-flooding produced water using photocatalytic graphitic carbon nitride nanofibres, Front. Chem. 11 (2019) 341–4349, https://doi.org/10.3389/fchem.2019.00694.

[90] A. Sudhalk, P. Raizada, P. Shindal, D.Y. Jeong, J.H. Lim, P. Singh, Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous photo dominant pollutants, J. Ind. Eng. Chem. 67 (2018) 28–51, https://doi.org/10.1016/j.jiec.2018.07.007.

[91] V. Hasija, P. Raizada, A. Sudhalk, K. Sharma, A. Kaur, P. Singh, S. Bonnalaagad, V.K. Thakur, Recent advances in noble metal free doped graphitic carbon nitride based nanohybrids for photocatalysis applications in water: a review, Appl. Mater. Today. 15 (2019) 494–524, https://doi.org/10.1016/j.apmt.2019.04.003.

[92] C. Zhang, Y. Li, D. Shuai, W. Zhang, L. Niu, L. Wang, H. Zhang, Visible-light-driven, water-surface-floating antimicrobials developed from graphitic carbon nitride and expanded perlite for water disinfection, Chemosphere 208 (2018) 84–92, https://doi.org/10.1016/j.chemosphere.2018.05.161.

[93] W. Ong, L. Tan, Y.H. Ng, S. Yong, S. Chai, Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation : are we a step closer to achieving sustainability? Chem. Rev. 116 (2016) 7159–7329, https://doi.org/10.1021/acs.chemrev.6b00075.

[94] D. Xia, T. An, G. Li, W. Wang, H. Zhao, P. Keung, Synergistic photocatalytic inactivation capacity of bacteria by graphene sheets and plasmonic Ag eAgX (I / Cl@Br) composite photocatalyst under visible light irradiation, Water Res. 99 (2016) 149–161, https://doi.org/10.1016/j.watres.2016.04.055.

[95] A. Habibi-Yangjeh, S. Asadzadeh-Khaneghah, S. Felizpoor, A. Roushi, Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: Can we win against pathogenic viruses? J. Collid Interface Sci. 580 (2020) 503–514.

[96] C. Regmi, B. Joshi, S.K. Ray, G. Gavvali, Understanding mechanism of photocatalytic microbial decontamination of environmental wastewater, Front. Chem. 6 (2018) 1–6, https://doi.org/10.3389/fchem.2018.00033.

[97] J.A. Byrne, P.S.M. Dunlop, J.W. Hamilton, P. Fernandez-Ibanez, I. Polo-Lopez, F.R. Sharma, A.S.M. Vennard, A review of heterogeneous photocatalysis for water and surface disinfection, Molecules 20 (2015) 5574–5615, https://doi.org/10.3390/molecules2005574.

[98] B. Guo, S.D. Snow, B.J. Starr, I. Xagoraris, V.V. Tarabara, Photocatalytic inactivation of human adenovirus 40: effect of dissolved organic matter and prefiltration, Sep. Purif. Technol. 193 (2018) 193–201, https://doi.org/10.1016/j.seppur.2017.11.012.

[99] A.M. Nasir, N. Awang, J. Jaafar, A.F. Ismail, M.H.D. Othman, M.A. Rahman, F. Saeed, A.M. Mat Yasin, Photocatalytic graphitic carbon nitride nanofibres: Properties, mechanism, synthesis, and applications, Arab. J. Chem. 13 (2020) 965–974, https://doi.org/10.1016/j.arabjc.2019.08.004.

[100] H. Cui, J. Jiang, W. Gu, C. Sun, D. Wu, T. Yang, G. Yang, Photocatalytic inactivation efficiency of anatase TiO2 sol on the H9N2 avian influenza virus, Photocatal. Sci. Technol. 86 (2016) 1313–1319, https://doi.org/10.1016/j.jsc.2017.10.007.63c.

[101] R. Cheng, L. Shen, Q. Wang, S. Xiang, L. Shi, X. Zheng, W. Lv, Photocatalytic membrane reactor (PMR) for virus removal in drinking water: effect of humic acid, Catal. Today 8 (2018), https://doi.org/10.1016/j.cattod.2018.05.163.

[102] R.H. Safey, M.V. Liga, Q. Li, A.R. Barron, Simple route to enhanced photocatalytic activity of P25 titanium dioxide nanoparticles by silica addition, Environ. Sci. Technol. 45 (2011) 1563–1568, https://doi.org/10.1021/es102749c.

[103] M.V. Lija, E.L. Bryant, V.L. Colvin, Q. Li, Virus inactivation by silver doped titanium oxide nanoparticles for drinking water treatment, Water Res. 45 (2011) 535–544, https://doi.org/10.1016/j.watres.2010.12.012.

[104] K. Takehara, K. Yamazaki, M. Miyazaki, Y. Yamada, S. Ruenpeth, A. Jahangir, D. Shoham, M. Okamura, M. Nakamura, Inactivation of avian influenza virus H1N1 by photocatalyst under visible light irradiation, Virus Res. 151 (2010) 102–103, https://doi.org/10.1016/j.virusres.2010.06.011.

[105] Y. Yamaguchi, S. Usuki, Y. Kanai, K. Yamatoya, N. Suzuki, K. Katsumata, H. Saito, H. Tashima, H. Nagai, Silver-decorated TiO2 photocatalyst and visible light, ACS Appl. Mater. Interfaces 9 (2017) 6542–6557, https://doi.org/10.1021/acsami.6b10727.

[106] V.G. Kumar, D.S. Ogden, U.H. Isu, A. Polas, L. Juesepp, L. Moradi, Differential dynamic behavior of prelation spike proteins of SARS coronavirus 1 and 2, Bioinf 2019 (2020) 1–42, https://doi.org/10.1093/bioinformatics/btaa422.