Chemical Engineering Journal 355 (2019) 399–415

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Progress and challenges in photocatalytic disinfection of waterborne Viruses: A review to fill current knowledge gaps

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HIGHLIGHTS

- An overview of antiviral effects of a wide range of photocatalysts is presented.
- Development of photocatalytic reactors for viral inactivation is summarized.
- Key mechanisms of photocatalytic viral disinfection in three views are reviewed.
- Future opportunities & challenges in photocatalytic viral disinfection are included.

ARTICLE INFO

Keywords:
Waterborne viruses
Photocatalysts
Photocatalytic reactors
Inactivation mechanisms

ABSTRACT

Achieving efficient disinfection of waterborne pathogens with minimized harmful disinfection byproducts demands a facile, cost-effective, and environmentally friendly technology. Recently, photocatalytic water disinfection has attracted an ever-growing worldwide attention due to its powerful oxidative capability and promising potential in solar energy utilization. Among waterborne pathogens, viruses, which have been found with very small sizes, high risks of illness, and resistant to environmental inactivation/decomposition, pose a great threat to public health. Over the past a few decades, efforts have been made to employ photocatalysis to achieve effective viral inactivation. Though photocatalysis has been comprehensively reviewed for bacterial disinfection, photocatalytic disinfection of viruses with quite different compositions, structures, and resistance to oxidative stress compared to bacteria was not systematically documented. Here, we present an overview of antiviral effects of a wide range of photocatalysts, including TiO_2-based, metal-containing (other than TiO_2), and metal-free photocatalysts. Moreover, the development of photocatalytic reactors for viral inactivation is summarized to promote practical engineering applications for water disinfection. In addition, key mechanisms that determine the performance of photocatalytic viral disinfection are reviewed. Future perspectives of research opportunities and challenges in photocatalytic viral disinfection are also included. This review will shed light on the development and implementation of sustainable disinfection strategies for controlling waterborne viruses in the future.

1. Introduction

There is a pressing need for providing safe drinking water all around the world. According to a recent report from the World Health Organization (WHO), 844 million people lack access to basic drinking-water services worldwide, including 159 million people mostly in rural areas who use untreated surface water for the drinking purpose [1]. Waterborne pathogenic viruses (such as adenovirus, enterovirus, hepatitis virus, norovirus, and rotavirus, etc.), which are frequently detected in water sources including surface water, groundwater, and even treated drinking water, pose serious health risks to humans [2,3]. For instance, rotavirus and *Escherichia coli* (*E. coli*) in contaminated drinking water are estimated to result in 502,000 deaths per year due to diarrhea [4]. In addition, waterborne viruses can lead to a wide range of diseases and illnesses, including fever, heart diseases, hepatitis, meningitis, paralysis, and respiratory infections [5]. Compared to

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https://doi.org/10.1016/j.cej.2018.08.158
Received 1 July 2018; Received in revised form 20 August 2018; Accepted 23 August 2018
Available online 27 August 2018

bacterial pathogens, viruses have a lower infectious dose of < 10–10^3 particles and a higher illness risk of 10–10,000 times under a similar level of exposure [6], e.g. exposure to one rotavirus particle could have a 31% chance of infection [7]. Therefore, seeking a highly efficient and low-cost inactivation method for waterborne viruses has always been an important topic for the science and engineering community.

A majority of waterborne pathogens can be physically removed by adsorption/filtration or inactivated by chemical disinfectants (such as free chlorine, chlorine dioxide, and ozone) and ultraviolet (UV) light in conventional water treatment processes. Unfortunately, viruses are difficult to be physically removed due to their small sizes and unique surface properties, e.g., granular activated carbon adsorption as a common barrier in water treatment was reported to effectively remove protozoan (oo)cysts and bacteria, but not for viruses [8]. Free chlorine as the most widely used chemical disinfectant exhibits an excellent viral inactivation efficiency, whereas it also increases the likelihood of producing potentially mutagenic and carcinogenic disinfection byproducts (DBPs) [9,10]. Chlorine dioxide and ozone as the strong oxidants are also effective for controlling viruses, but the challenges exist due to complex operations at the same time (e.g., on-site generation) and DBP formation (e.g. chlorite and chlorate from chlorine dioxide and bromate from ozone) [7]. Nowadays, disinfection is moving towards using UV light to control DBP production. Certain viral types such as adenoviruses [11] and rotaviruses [12,13] are susceptible to the inactivation by free chlorine, while they are highly resistant to the inactivation by UV light, resulting in high energy consumption and operational costs [14]. From a green and sustainable perspective, solar water disinfection (SODIS) is promising and advocated by governments [15], especially for developing countries and rural areas. However, indicator viruses (such as bacteriophage MS2) were still detectible after sunlight exposure of a full day, indicating that SODIS may not be effective for viral disinfection and more treatment time is needed for complete inactivation [16]. Encouraged by SODIS, photocatalysis is an alternative disinfection strategy which enhances the performance of viral disinfection, and it overcomes the limitations of conventional disinfection methods. A semiconductor photocatalyst can be excited by light irradiation to activate oxygen in the air or water to generate a series of powerful reactive species (RSs), e.g. h^+, $^{\cdot}O_2^-/HO_2^{\cdot}$, $^{\cdot}OH$, $^1O_2$, and H_2O_2, for waterborne pathogen inactivation under an ambient condition.

In the last decade, the development of photocatalytic water disinfection is ever increasing [17,18]. A number of comprehensive reviews have summarized the advances in photocatalytic disinfection of bacteria [15,18,19], microalgae [20], and parasites [21]. However, the results and conclusions for photocatalytic disinfection of bacteria, microalgae, and parasites cannot be translated to viral disinfection, likely due to unique compositions, structures, and persistence of viruses. With the advance of analytical instruments/methods for viral detection and increasing public health concerns of viruses in safe water supply [22,23], there is an urgent need for understanding photocatalytic viral disinfection as an effective, robust, and sustainable strategy for water purification.

In this review, we aim to provide an overview and summary of current knowledge in photocatalytic disinfection for waterborne viruses based on up-to-date literature. A broad range of photocatalysts for viral disinfection, photocatalytic reactor design for addressing the need in engineering practices, mechanistic understanding of the interplay between viruses and photocatalysts in reaction, and the outlook of future opportunities and challenges are included in this review. To the best of our knowledge, it is the first systematic review to provide insights in photocatalytic viral disinfection for sustainable water purification.

2. Photocatalysts for viral inactivation

As presented in Fig. 1, Sjogren and Sierka [24] were the first pioneers in conducting photocatalytic viral disinfection in 1994, and they explored the inactivation of MS2 by TiO_2 photocatalysis. Since then, most studies focused on the antiviral activity of TiO_2 and TiO_2-based photocatalysts in water. To achieve enhanced virucidal effects, metal-containing photocatalysts other than TiO_2 were also investigated. Specifically, metal-free 'green' photocatalysts prepared from earth-abundant elements/materials arouse our great interest because the photocatalysts support low-cost, sustainable, and safe material fabrication and implementation. Table 1 summarizes these four kinds of photocatalysts reported for viral disinfection in various waters with different matrices, and Fig. S1 presents the various viruses used in photocatalytic viral disinfection.

In general, viral disinfection kinetics are more complex than the first-order profiles usually found for chemical pollutant degradation by photocatalysis, due to the unclear relationship between viral chemical structure after oxidation and viral viability, as well as the complicated and unknown viral repair mechanisms. Therefore, the photocatalytic activity for organic degradation cannot be extrapolated to viral disinfection processes. In addition, different inactivation kinetics of bacteria and viruses were also observed by Cho *et al.* [25]. Virus MS2 was more resistant than the bacterium *E. coli* to the oxidative attack of RS generated from photocatalysts. This can be explained by the difference in the surface structures of bacterial cells and viral particles. *E. coli* is a rod-shaped bacterium with a size of μm and a complex surface structure of lipopolysaccharides, peptidoglycans, and lipid bilayers. Even a slight damage to the bacterial surface can destroy key metabolic systems such as respiration. Nevertheless, MS2 is an icosahedral shaped virus with a size of nm and a simple surface structure of capsid proteins. The viral protein shell is rigid, requiring intensive oxidation to be denatured.

2.1. TiO_2 photocatalysts

Nanostructured TiO_2, one of the most widely studied photocatalysts, was extensively explored for photocatalytic viral disinfection over the past years. Among these studies, Degussa P25 was the most popular photocatalyst due to its high photoactivity, long-term stability, non-toxicity, and low cost [26,27]. A range of disinfection efficiencies for viral inactivation were reported for P25, because of the variation of the photocatalyst dose, viral species and initial concentration, light source and intensity, and water matrix (including solution pH, water temperature, ionic species, etc.) (Table 1). It should be noted that viral inactivation kinetics on P25 cannot be characterized by a single kinetic model, even for the same virus. For example, bacteriophage MS2, some researchers used Chick-Watson model to describe disinfection kinetics [28–30]:

$$\log(C/C_0) = k't$$

where C_0 is the initial titer of viruses, C is the active titer at time t, and k′ is the pseudo-first-order rate constant. However, other researchers observed more complex disinfection kinetics that cannot be simplified with the Chick-Watson model [25]. Consequently, it is impossible to quantitatively compare the photocatalytic viral inactivation efficiency using kinetic rate constants here.

TiO_2 crystalline structures (i.e., anatase or rutile) also impact viral inactivation kinetics (Fig. 2a). Sato and Taya [31] first evaluated the effect of crystalline structures on virucidal activity of TiO_2 particles. The mixture of anatase and rutile TiO_2 particles with an anatase ratio of 70% exhibited the maximal viral inactivation efficiency, which was 2 and 11 times higher compared to TiO_2 with only the anatase and rutile phase, respectively. The enhancement in viral inactivation is attribute to the contact between two types of TiO_2 particles in suspensions, which can promote the quantum yield and thus RS generation during photocatalysis.

The morphology of TiO_2 particles also determines the performance of photocatalytic viral disinfection (Fig. 2b). For example, TiO_2 hollow particles showed improved photocatalytic performance than sphere ones in the degradation of dimethyl sulfoxide due to the multi-scattering of light inside the hollow structure that could increase light