Removing of SARS-CoV-2 from Water and Wastewater with Membrane Technologies-A Brief Review

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Abstract: In the last century, the world has faced many factors that cause pandemics. There have been three major epidemics caused by coronaviruses in the last 17 years. World Health Organization (WHO) announced on March 11 2020 that the most recent outbreak, SARS-CoV-2, turned from epidemic to global pandemic. Although the fact that the major transmission routes of SARS-CoV-2 are inhalation of aerosol/droplet and person-to-person contact, available evidence indicates the viral RNA existence in wastewater. This situation brings out the need for a better understanding of wastewater amongst other human health risks factors. The aim of this article is to review the available knowledge related to SARS-CoV-2 and its presence in wastewater/water, usage of membrane technologies for the removal of SARS-CoV-2 in wastewater/water, and effect of SARS-CoV-2 on public health. Although currently available datas are limited for removal of SARS-CoV-2 with purification techniques, membrane technologies can be a potential candidate for reducing the impact of the ongoing COVID-19 outbreak.

Keywords: SARS-CoV-2, public health, water, wastewater, removal and membrane Technologies.

Membran Teknolojileriyle Su ve Atık Sudan SARS-CoV-22’nin Uzaklaştırılması-Kısa Bir Derleme

Öz: Dünyanın bir asır içinde salgınlar neden olan birçok faktöre karşı karışıma kalkılarak 17 yılda koronavirüslerin neden olduğu üç büyük salgın yaşanmıştır. En son salgın olan SARS-CoV-2 ise Dünya Sağlık Örgütü (DSÖ) 11 Mart 2020’dede salgunandan küresel pandemiye dönüştüğünü duyurdu. SARS-CoV-2’nin ana bulaşma yollarının kişiden kişiye temas ve aerosol / damlaçık inhalasyonu olmasına rağmen, viral RNA’nın atık suda bulunduğunu gösteren mevcut kanıtlar da vardır. Bu durum, insan sağlığı risk faktörleri arasında atık suyun daha iyi anlaşılmasını ihtiyaççısı ortaya çıkmaktadır. Bu makale, SARS-CoV-2 ile ilişkili mevcut bilgileri ve onun atık suculuk varlığı, suculak/ atık suculak SARS-CoV-2’nin giderilmesi için memran teknolojileri ve SARS-CoV-2’nin halk sağlığı üzerindeki etkisi ile ilgili mevcut bilgileri gözden geçirilerek amaçlamaktadır. Hali hazırda mevcut verilerin, sağlaşma teknikleriley SARS-CoV-2 giderimi için sınırlı olduğu için, memran teknolojileri, devam eden COVID 19 salgınının etkisini azaltmada potansiyel bir aday olabilir.

Anahtar kelimeler: SARS-CoV-2, halk sağlığı, su, atıksu, uzaklaştırma ve membran teknolojileri.
INTRODUCTION

The new coronavirus disease, known as Covid-19 (SARS-CoV-2), emerged in Wuhan, China in December 2019. It started to spread rapidly. Public Health Emergency of International Concern announced epidemic on 30 January 2020. World Health Organization (WHO) updated outbreak from epidemic to global pandemic on March11 2020. Globally, 29 November 2020, there have been 61.869.330 confirmed cases of SARS-CoV-2, including 1.448.896 deaths, reported to WHO.

Coronavirus virion is virus that is enveloped, spherical, and about 120 nm in diameter which severe acute respiratory syndrome-related coronavirus in the subgenus sarbecovirus of the family coronaviridae (Kitajima et al., 2020; Rosa et al., 2020). Although it firstly influences the respiratory system of patients, it has a wide series of symptoms, especially the symptoms of the digestive system are common among patients. Also, a significant number of infected people are asymptomatic or have soft evidences, but they can still infect the virus. In the first cases, SARS-CoV-2 transmission was reported to occur from patients with direct contact and sneezing or coughing. However, it has been reported that virus may stay alive on surface and the viability period of the virus may change depending on the surface feature. In addition, SARS-CoV-2 RNA was also identified in human feces in at least 39% of patients tested, thus presenting the possibility of fecal-oral transmission (Lesimple et al., 2020). It is understood that this possibility is a strong assumption considering that the virus enters the cells via angiotensin converting enzyme 2 (ACE 2) receptor. Because ACE 2 receptor has been determined to be highly expressed in epithelial cells of the gastrointestinal tract. That is, SARS-CoV-2 can be actively infected and multiplied in the gastrointestinal tract (Hakim & Sari, 2020).

To date, many studies have been conducted showing that viruses are proliferating in the gastrointestinal tract, and that 2-10% of COVID-19 (SARS-CoV-2) patients have gastrointestinal symptoms, including diarrhea (Chen et al., 2020a, Chen et al., 2020b; Gao et al., 2020; Leung et al., 2003; Wang et al., 2020a, Wang et al., 2020b, Wang et al., 2020c; Zhou et al., 2017). Nowadays, there are many studies demonstrating the presence of viral RNA in feces or anal / rectal swabs (Holshue et al., 2020; Tang et al., 2020; Xu et al., 2020; Young et al., 2020; Zhang et al., 2019).

There has been increasing arguments about gastrointestinal symptoms caused by SARS-CoV-2 infections and the presence of viral RNA, not only in feces of infected individuals but also in wastewater. Wastewater and wastewater treatment is a wide field and complete description of it is not the aim of this review. This work will focus on the literature containing membrane techniques used for virus removal. Usage of model viruses to evaluate the efficiency of wastewater treatment methods and membrane techniques will be introduced. But, current knowledge of the presence of CoVs in wastewater will likely be limited due to the lack of previous environmental research focusing on CoVs. (Hakim & Sari, 2020; Ling et al., 2019; Ong et al., 2020; Yang et al., 2020; Zhang et al., 2019).

This study will provide information that will help us understand the relationship of SARS-CoV-2 in wastewater/water and public health risks.

MATERIAL

The review was prepared based on literature search in the following databases for publications up to 29 November 2020; Pub Med; Web of Science, ScienceDirect, Google scholar and ResearchGate. The keywords utilized for the search were; Coronavirus or Severe Acute Respiratory Syndrome or SARS or SARS-CoV or SARS-CoV-2 or COVID-19 and Wastewater/water or Sewage or Feces or Gastrointestinal infections. All results of the search were scanned manually for related information and their references also searched for additional publications that may be relevant. Articles reporting on SARS-CoV-2 that do not present information on the detection of the virus in feces, wastewater/water, and sewage were only taken into consideration on condition that, they offered information on the structures of these viruses and pandemics.

Survival of SARS-CoV-2 in Water and Wastewater and Its Effect on Public Health: Inactivation of pathogens in water and wastewater is important as it is among the risk factors affecting human health. In many studies, coronavirus has been found to remain in wastewater, chlorine-free tap water, urine and feces for a long time. In the statement made by the world healthy organization; it was stated that there is no evidence that the virus survived in wastewater and drinking water. The statement also claims that it has more sensitivity than most non-enveloped viruses (WHO, 2020d). In this case, existing wastewater treatment plants are sufficient to inactivate SARS-CoV-2. Although limited, some studies have reported that SARS-CoV-2 stays in aquatic environments for a long time and retains its contamination, depending on temperature and physicochemical factors (Pratelli, 2008). When considered from this point of view, identifying and controlling these factors are consequential to state the permanence of SARS-CoV-2 in sewage and environmental waters. The presence of respiratory viruses, including adenoviruses, coxsackieviruses and CoVs in wastewater has been reported in previous studies (Sinclair et al., 2008; Wang et al., 2005a; Wigginton et al., 2015). Although the etiological agent is not often described, there is no uncertainty that swimming in sewage contaminated waters is connected with respiratory disease (Wade et al., 2010).
health effect on garbage collectors and wastewater treatment plant (WWTP) workers (Tschopp et al., 2011). Unlike Tschopp et al., (2011) studies, gastrointestinal effects were seen in three other studies, and two of these three studies attracted attention with effects on respiratory health (Khuder et al., 1998, Lee et al., 2009, Smit et al., 2005). Although there are differences among the studies; wastewater treatment plants pose a risk to both employees and public health. In this case, the first solution that comes to mind is the agents that can be used to remove SARS-CoV-2. Chin et al., (2020) reported that the SARS-CoV-2 was removed with chemicals such as bleach, ethanol, benzylalkonium chloride, povidone iodine and chloroxylenol in the 2020 studies. These studies show that SARS-CoV-2 can be inactivated by temperature and chemicals. It has even been confirmed by the United States Environmental Protection Agency (USEPA) that some disinfectants inactivate SARS-CoV-2 (USEPA, 2020). According to USEPA, suitable disinfectants with proven efficacy against enveloped viruses should be used (eg hypochlorite [bleach], alcohol, hydrogen peroxide, quaternary ammonium compounds and phenolic compounds) (Kitajima et al., 2020). Even if these disinfectants are used, fecal shedding from patients or carriers still pose a risk in common toilets, bathrooms, pools and wastewater. Therefore, in order to remove the virus from these areas, it is first necessary to identify the virus in these areas. It is known that too much research is needed for identification and the difficulty of these researches.

Common areas can be cleaned frequently to avoid possible risks, but this is not the case in wastewater. Casual changes in viral concentrations in wastewater can lead to the asset or nonexistence of a virus, epidemics in the population, and their impact on public health. Therefore, wastewater monitoring can be an important technique to evaluate and deal with viral outbreaks and to protect public health. Considering that SARS-CoV-2 patients with very mild symptoms will not be identified and approximately 80% of the contacts will be missed, monitoring SARS-CoV-2 in wastewater will be important in determining the incidence of the disease. Thus, wastewater-based epidemiology is thought to be an early warning system for public health and future viral disease outbreaks. However, the difficulty of applying this technique is also known. Some of these challenges are the amount and dynamics of viral spills in the feces, viral persistence in the sewer network, change in the wastewater flow from the climate. So, SARS-CoV-2’s surveillance in wastewater is valuable; it is clear that it should be integrated into other public health initiatives. For this, a harmonious approach is required in clinical and wastewater samples (Farkas et al., 2020).

Membrane Technologies in Wastewater Treatment For SARS-CoV-2 Removal: World Health Organization (WHO) emphasized the importance of managing wastewater safely in its temporary guide dated April 23, 2020. This document has been updated on July 29, 2020. In this temporary guide, WHO provides information on virus-related waste management, water, sanitation, hygiene (WASH) and waste management and infection prevention and control (IPC) documentation, including coronaviruses. According to the guideline, providing WASH and waste management practices in communities has a significant role in preventing transmission of pathogens from person to person. In addition, this updated guide includes risks related to feces and untreated sewage, hand hygiene, protection of WASH workers and maintenance and strengthening of WASH services. It is also stated in the guide that water disinfection and wastewater treatment be able to decrease viruses. It is emphasized that by implementing waste management, many other infectious diseases can be prevented and health benefits can be achieved. Although SARS-CoV-2 is possible in untreated drinking water, no infectious virus has been detected in drinking water sources. But, it was shown to state RNA fragments of SARS-CoV-2 in a river in northern Italy. This incident is thought to be influenced by the raw, untreated sewage of the river. Starting in February and March 2020, generally, RNA fragments of SARS-CoV-2 have been found in untreated sewage and sludge in many countries and municipalities (WHO, 2020). These events reveal that wastewater treatment should be well understood and applied. But, the full description of wastewater treatment is not the goal of this review. This work will concentrate on the literature membrane technologies used for virus removal. The effectiveness of membranes in removing virus from wastewater/water will be evaluated. Water filtration membranes are basically divided into four as Reverse Osmosis, Nanofiltration, Ultrafiltration and Microfiltration. Given that the size of the SARS-CoV-2 is 100μm, membranes such as Reverse Osmosis, Nanofiltration and Ultrafiltration should be suitable for its removal (Lesimple et al., 2020). The utmost frequently utilize membrane technologies in wastewater treatment are the microfiltration (0.1–0.2 μm) and ultrafiltration (0.005 ≈ 10 μm). Table 1 is shown details of some studies examining the effectiveness of membranes in removing the virus from water and wastewater.

Ultrafiltration will be a suitable membrane technique for removing coronaviruses with mean viral particle diameter of 120 nm (0.12 μm) and envelope diameter of 80 nm (0.08 μm) (Neuman & Buchmeier, 2016). Their adsorption to solids in wastewater may cause an increase in the removal of coronaviruses. Studies have been carried out in which different viruses and pathogens are removed by the membrane by 50% Chaudhry et al., (2015). Studies involving microfiltration membranes with large pore sizes (0.2–0.4) have also been conducted (Nqombolo et al., 2018). Aani et al., (2020) have examined the bacteria and virus
removal of ultrafiltration in wastewater and reported their use. Gentile et al., (2018) declared that they removed bacteriophage pp7 using a polyethersulfone ultrafiltration membrane with a mean membrane pore size of 67 nm. They also modeled virus and membrane electrostatic interaction forces in their studies. Divalent cations in feed solutions have been concluded to have a negligible influence on viral removal efficacy owing to change of electrostatic interactions. There was no significant change in the size of the bacteriophage with pH or ionic strength in their studies. It has also been stated that at the pH of environmental waters (5 to 8), viruses form minor aggregates and complicate membrane-based disinfection processes. For bacteriophage PP7, changes in pH did not modify modeling estimates for stability and binding. With their results, the authors stressed the significance of electrostatic repulsion in virus removal by membrane filtration. Also, the microfiltration membrane is more suitable for the removal of protozoa and bacteria rather than smaller viruses. This is only separation with sieving mechanisms (Kwarcia-Kozlowska & Wlodarczyk, 2020). Sinclair et al., (2018) varied a microfiltration membranes by utilization a cationic polymer. These membranes were recommended for low pressure water filtration point because of their high water permeability (Lesimple et al., 2020). Among all these pathogens, SARS-CoV-2 is a potentially deadly virus for humans and some measures should be taken to conduct scientific tests. For this, the Center for Disease Control and Prevention (CDC) ensures guidelines for Biosafety and COVID-19 (SARS-CoV-2). In some studies, wastewater testing was performed using murine hepatitis virus (MHV) instead of SARS-CoV-2 against the dangers mentioned in the Guidelines. Murine hepatitis virus (MHV) is a member of the same genus as SARS-CoV-2. MHV was utilized as representative of human CoV in studies. Studies have been conducted examining the efficiency of MHV recovery from wastewater. The efficiency of seven virus concentration methods was evaluated in untreated wastewater samples. They found that ultrafiltration using centrifugal concentration devices may also be appropriate for recovery of MHV. The difference in recovery was due to the difference in surface areas of the devices used, hence, more MHV was lost through adsorption to the membrane via van der Waals interactive forces and / or hydrophobic bonding. The results obtained in this study; Centricon recovered 75% of MS2 coliphage, 61% of Echovirus 1, 95% of Poliovirus 1 and 109% of Coxsackievirus B5; only 33% of 2 of the adenovirus were recovered. The result obtained for MHV is alike to Adenovirus. In this case, it shows that a particular centrifugal concentration device can provide factor recovery for different classes of virus. It was also stated that the recovery performance of diverse representative CoV or SARS-CoV-2 from various volumes of wastewater should be evaluated to better figure out how these variables influence the recovery performance (Ahmed et al., 2020). Reverse osmosis has often been found to be rarely used to remove pathogens from water due to its combination with a pre-treatment system, usually ultrafiltration. However, RO can be utilized with an appropriate pretreatment to remove particulate matter and to complete the removal of residual contaminants after treatment (Tang et al., 2018). In addition, there are studies showing that the membrane bioreactor / reverse osmosis systems have low efficiency in virus removal (Prado et al., 2019). To date, many studies have been carried out with Membrane bioreactor (MBR) treatment for different virus types (Chaudhry et al., 2015; Kuo et al., 2010; Miura et al., 2018; O’Brien & Xagoraraki, 2020; Prado et al., 2019; Purnell et al., 2016; Simmons et al., 2011). Retention or size expention is its main mechanism in removal of viral and other pathogen (Dennis et al., 2020; Lesimple et al., 2020; Ngombolo et al., 2018). Im et al., (2018) applied ceramic membranes after pretreatment to remove virus. They utilized the F-specific bacteriophage MS2 (MS2; NBRC 102619, NITE Biological Research Center, Japan) as a model virus that has a single-stranded RNA encapsulated with a diameter of 24–26 nm. In a pilot plant, they achieved removal of MS2. Membrane fouling, which is a technical challenge that causes a decrease in membrane performance has been reduced with pretreatments. They performed their applications as a pretreatment by combining ozonation, coagulation and ceramic membrane filtration. This work had multiple purposes. Among these objectives was located that to peruse the performance of O₃ + PACl + CMF; to remove virus in O₃ + PACl + CMF; to study the effects of ozonation on virus removal in subsequent coagulation. (coagulation with polyaluminium chloride (PACl)). At the end of the study; they stated that ozonation can considerable abate reversible pollution. However, although ozonation deactivated MS2, it reduced the rate of MS2 removal in after PACl + CMF. This is because ozonation inclined to block MS2 coagulation. The reason for inhibition is the negative charge that increases during ozonation. This makes it difficult for the coagulants to neutralize the surface charge. Coagulation can be said to be a more effective pretreatment for CMF than ozonation in terms of eliminating both viruses (Im et al., 2019). Goswami et al., (2020) discussed the applications of polymeric and ceramic membranes to remove virus from water. The reported removal performances were quite changeable as the reported range was 0.2–7. Present research fields concentrate on ever application of nanotechnology for the solid waste administration, and wastewater treatment due to their diverse antibacterial activity. Chemical activity enhances with their small dimension and large surface areas. For example, noble metal nanoparticles utilize disinfection of E. coli and ensue very well. Nanomaterials also provide a separate, high
efficiency and recyclable water cleaning system that abates water loss and improves quality. It can be applied for bacteria and viruses with a diameter of more than 50-60 nm. Nanomaterials are used to remove and inactivate viruses in wastewater, emerge as a large area. The practice of nanomaterials is deeply connected with their physical properties. For water treatment, nanotechnology has some advantages such as time saving, high efficiency, space saving and simple treatment methods. Fullererens, photocatalysts containing nanomaterials such as CNTs, TiO2 and ZVIs are used in membranes (Indarto et al., 2020; Ojha, 2020; Sahu, et al., 2019). Silver Multiwall nanotubes (Ag-MWCNT), which achieved a 100% removal for several different viruses, were expressed in a study by Kim et al., (2016). They expressed a new MWCNT-silver (Ag) nanofilter, which nanofilter had high permeability. They applied this nanofilter to successfully remove bacterial and viral pathogens from water at low pressure. In former works, a CNT-Ag nanofilter in which Ag nanoparticles were synthesized at the CNT surface was not reported. This filter has been manufactured using key features such as the minor diameter and superior surface area of CNTs, the trends of CNTs to collection and form extremely porous structures, the low melting point of Ag nanoparticles, and the antibacterial activity of Ag nanoparticles. They also stated in this study that viruses can be eliminated by nanotube bundles in the CNT-Ag layer. CNT-Ag nano filter has been specially designed to remove various viruses and bacteria from water in a highly efficient manner. In addition, the lack of supplementary processes to destroy viruses and bacteria makes an important benefit in terms of production costs. Taking all its advantages, it is thought that their CNT-Ag nano filter can provide sufficient solutions for water treatment and other separation processes. Furthermore, researches using CuO / MWCNT filters and a CuO coated MWCNT membrane was carried out to remove MS2 virus from water (Domaga et al., 2020; Nemeth et al., 2019). In a different study, the smectic liquid-crystal ionic membrane removal of three viruses, Q5 bacteriophage, MS2 bacteriophage and Aichi virus were investigated. In all these studies, viruses were reduced (Kuo et al., 2020). They provide upper virus removal for liquid crystal water treatment membranes. Liquid crystal creates 2D layered nano channels that allow excellent virus removal as continuing effective water flow. The removal efficiency is 99.9%.

Table 1. Details of some membranes studies in removing the viruses from water and wastewater.

| Water type          | Methods                                           | Results of Removal for Virus | Reference                      |
|---------------------|---------------------------------------------------|------------------------------|--------------------------------|
| Wastewater          | Membrane Bioreactor (MBR)                         | 50%                          | Chaudhry et al., (2015)        |
| Water               | Polysulfone/ultrafiltration(modelled virus)       | Logarithmic                  | Gentile et al., (2018)        |
| Water               | Microfiltration membrane                          | >5.5 logs                    | Kwarciak-Kozlowska and Wlodarczyk, (2020) |
| Water               | Polyethylene (PEI) coated onto commercially polyether sulfone (PES) | 99.9%                        | Sinclair et al., (2018)       |
| Wastewater          | Electrogalvanic membrane, polyethylene glycol (PEG 8000) precipitation, and ultracentrifugation | from 26.7 to 65.7%          | Ahmed et al., (2020)          |
| Water               | Reverse osmosis                                   | >4 log                       | Tang et al., (2018)           |
| Wastewater          | Membrane Bioreactor / Reverse Osmosis             | 2.3–2.9 log10                | Prado et al., (2019)          |
| Wastewater          | Membrane Bioreactor / Reverse Osmosis and sand-anthracite filters | 0.3 to 0.8 log10          | Prado et al., (2019)          |
| Wastewater          | Membrane Bioreactor (MBR)                         | 2–3 log10                    | Minz et al., (2018)           |
| Wastewater and Potable water | Membrane Bioreactor (MBR) | 2–3 log10                  | Purnell et al., (2016)        |
| Wastewater          | Membrane Bioreactor (MBR)                         | >4 log                       | Chaudhry et al., (2015)        |
| Wastewater          | Membrane Bioreactor (MBR)                         | 1 to 2 log                   | Simmons et al., (2011)        |
| Wastewater          | Ceramic membranes (with model virus)              | >12-log                      | Im et al., (2018)             |
| Wastewater          | Nanomaterials such as CNTs, TiO2 and ZVIs are used in membranes |                        | (Indarto et al., 2020; Ojha, 2020; Sahu, et al., 2019) |
| Water               | Silver Multiwall nanotubes (Ag-MWCNT)             | 100%                         | Kim et al., (2016)            |
| Water               | CuO / MWCNT filters and a CuO coated MWCNT membrane | 99.9%                       | Domaga et al., 2020; Nemeth et al., 2019 |}

**CONCLUSION**

SARS-CoV-2 is a potentially deadly virus for humans, and some precautions must be taken to conduct scientific testing. Therefore, testing was performed using murine hepatitis virus (MHV) instead of SARS-CoV-2 against the dangers mentioned in the guidelines for Biosafety and COVID-19 (SARS-CoV-2) in some studies. When the membranes were examined for virus separation, in most cases, the membranes used for this purpose were micro and ultrafiltration. Here, the relation between the pore size and the virus size is important for a proper separation. Although membranes with larger pore sizes can retain viruses, they cannot be regarded as effective tools for virus separation as they may produce irreversible pore blocking in the membrane. Smaller virus particles may enter the pores of the membrane, which reduces membrane lifetime because of contamination. As a measure to overcome the above mentioned difficulties, some studies put forward an idea of the coating the membrane surface. In the results of these studies, the coating on the membrane surface is not only seen to reduce the pore size, but in some cases the coating interacts with the virus, which increases the efficiency of the removal. Some of these coatings are as follows: CuO / MWCNT filters, a CuO coated MWCNT membrane and silver Multiwall nanotubes (Ag-MWCNT), which achieved a 100% removal for several different viruses. These results
are promising for future studies. The spread of the virus can be greatly reduced by integrating this method into the wastewater management of cities.

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