Photocatalysis of COVID-19 in Wastewater

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The coronavirus (COVID-19) pandemic is currently posing a significant threat to the world's public health and social-economic growth. Despite the rigorous international lockdown and quarantine efforts, the rate of COVID-19 infectious cases remains exceptionally high. Notwithstanding, the end route of COVID-19, together with emerging contaminants' (antibiotics, pharmaceuticals, nanoplastics, pesticide, etc.) occurrence in wastewater treatment plants (WWTPs), poses a great challenge in wastewater settings.

Keywords: Wastewater ; SARS-CoV-2 ; COVID-19 pandemic ; Advanced oxidation process ; membrane bioreactor

1. Introduction

The severe and acute respiratory syndrome, coronavirus-2 (SARS-CoV-2), has been an etiological agent of COVID-19, which, according to the World Health Organization (WHO), is transmitted via respiratory droplets and contact routes [1][2]. According to Hart and Halden [3], SARS-COV-2 belongs to the coronvirinae subfamily made of positive-sense Ribonucleic Acid (RNA) viruses. Additionally, in human cells, this virus uses an angiotensin-converting enzyme (ACE2) as a receptor which is very high in the gastrointestinal system as a courier of ACE2 RNA. SARS-CoV-2 detections in human stools and urine of COVID-19 carriers have been reported to be potent [4]. Successive studies of finding the RNA of this virus in sewage systems raises notable concerns about COVID-19 faucal transmission and its pathogenic effects on sanitation and wastewater systems [3][4].

Municipal wastewater is typically observed as one of the main end routes of different types of emerging contaminants such as pharmaceuticals, endocrine disruptors, antibiotics, microplastics, pesticide and heavy metal residues associated with antimicrobial resistance (AMR) [5]. Sewage streams from the municipal system contain a large number of recalcitrant compounds which are usually excreted by humans and other activities. Notwithstanding, global hotspots for drug-infested countries where drug deals and usages are widespread are usually identified through the sewage systems [6]. Despite this, there are various measures surrounding the movement restriction of about 93% global population to monitor the COVID-19 spread and advisory interventions [3]. As such, extensive testing is required to understand the possible routes of the viral contagion, which is very expensive. Therefore, monitoring the spread of COVID-19 early stages in communities through the wastewater-based epidemiology (WBE) approach is useful [5][6]. Additionally, this could possibly provide rapid results for effective and urgent interventions in the fight against COVID-19.

Conversely, the COVID-19 pandemic has led to a paradigm shift of the world's societal and essential activities with a profound transformation of human life, which poses a global threat to socio-economic growth and development [4][7]. The risk and routine of waste collection and wastewater as an ecological response to address COVID-19 complications in water and wastewater settings has received little attention [8]. In response, this study introduces WBE to monitor the COVID-19 spread and its threats to public health, while analyzing the populated pooled wastewater to mitigate COVID-19 complications. In essence, over the past years, over 1500 pathogens have been discovered, with almost 40 of them emerging from communicable diseases with a major impact on communities [7][9]. These include severe and acute respiratory syndromes (SARS) (2002–2003), H1N1flu/swine flu (2009–2010), Ebola (2014–2016), Zika virus (2015–2016), and COVID-19 (2019–2020) [9]. As it stands, the search of vaccines for recurrence of communicable disease prevention and their treatment, in terms of COVID-19, seems far-reached. This has triggered an international ban at various airports and seaports on travel and social gathering, practicing quarantine protocols, school and church closures, and closures of non-essential industries [10]. According to the WHO report, as of 29 May 2020, over 5 million cases of Covid-19 cases were identified globally with 362,614 deaths and 2,596,004 people recovering [11].

Eventually, SARS-CoV-2 prevention interventions which consist of personal cleanliness, accurate sanitation, hand washing and sanitizing cannot be separated from a safe supply of water. Hence, water and wastewater industries amidst of addressing this global pandemic are going to revel in widespread economic impacts [12]. As a direct consequence of COVID-19 to the global economic system, countries along with South Africa and the United States of America are expected to suffer from huge financial losses of billions of dollars because of revenue discounts of their water utilities [13]. Upon this foundation and many extra anticipated in days to return, studies into figuring out and developing a strong era within the water and wastewater remedy settings to diminish the COVID-19 complications are useful.

2. SARS-COV-2 in Wastewater Possible Treatment Technologies

2.1. SARS-COV-2 Possible Detection Techniques

2.1.1. Magnetic Nanotechnology

Magnetic nanoparticles (Ferromagnetite) have been reported as good substrates for heavy metal adsorption from aqueous solutions [9][14]. The chemistry behind this mechanism could be attributed to the four unpaired electrons in the 3d shell with an iron atom having a strong magnetic moment. Fe^{2+} ions have 4 unpaired electrons in their 3d shell, and Fe^{3+} ions have five unpaired electrons in their 3d shell. Magnetite nanoparticles are susceptible to air oxidation and can be easily aggregated in aqueous systems. The stabilization of the iron oxide nanoparticles by adding surfactants as a type of surface modification is desirable. In this context, ongoing application of magnetic nanoparticles in wastewater settings, which includes the removal of non-magnetic water pollutants like dissolved pollutants, algae, and viruses via magnetic separation has appeared to be very promising techniques [9].

Recently, applications of magnetic separation have been introduced in biotechnology for analytical applications, separation of cells, sewage treatment, protein digestion and purifications [6][9][14][15]. Furthermore, integrating MBs with aptamers opens up additional opportunities in various applications including disease diagnosis using biosensors, cell imaging and labelling and magnetic resonance imaging, disease therapy, water purification, wastewater treatment, sewage treatment, and sample preparation [14][15]. As earlier stipulated, in aptamer-modified MB-based assays, aptamers are utilized as MBs and binding ligands generally utilized for separating the analyte from complex matrices. In aptamer-modified MBs, Surface-Enhanced Raman Scattering (SERS) sensing is employed in the analytical applications of diverse sensor designs (Figure 1).

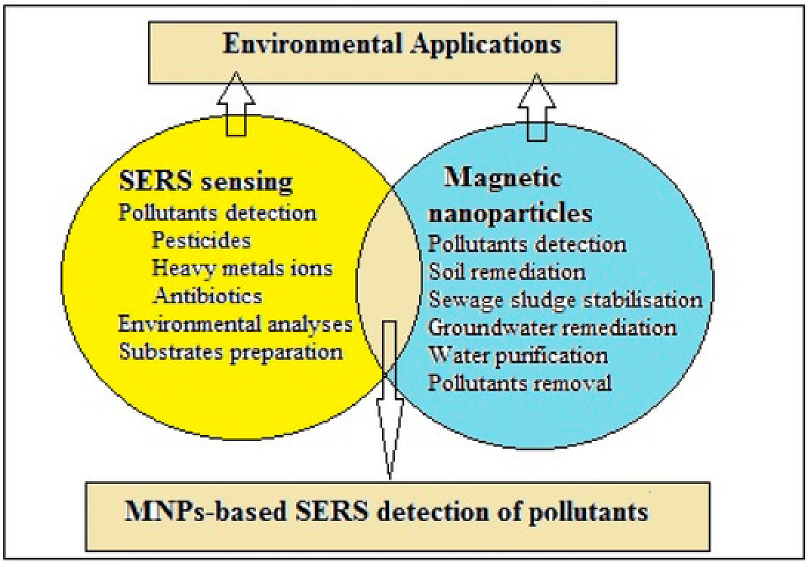

Figure 1. MNP-based SERS detection of pollutants adapted and modified from Pant et al. [15].

2.1.2. Biosensor Technology

Biosensors, as powerful and innovative analytical devices with biological sensing elements, have been employed in many potential fields, which includes drug discovery, diagnosis, biomedicine, food safety, environmental monitoring and security [1][16][17]. For instance, the term “contour” for glucose determination and that of “OneTouch” for glucose and cholesterol determination [17], is a lactose biosensor [16] and a portable system for enzyme immunoassay and polymerase chain reaction analysis [18]. It is reported that the first biosensor was invented by Clark and Lyons [19]. Additionally, the technical revolution in biosensors was found to be the discovery of genetically encoded or synthetic fluorescent biosensors in analyzing molecular mechanisms of biological processes [1][2][18][20]. The development of biosensors is limited by their low stability and the rapid degradation of biological components during storage and use [18]. This makes calibration difficult and reduces reliability. In contrast to biological components, their synthetic equivalents are chemically and thermally stable. Additionally, the utilization of biosensors has acquired paramount significance in the field of drug discovery, food safety standards, biomedicine, defense, security, and environmental monitoring [21]. For decades, it has led to the invention of precise and powerful analytical tools using biological sensing elements such as biosensor [20].

It is found that the topical advances in biological techniques and instrumentation involving fluorescence tagged to nanomaterials have increased the sensitivity limit of biosensors [20][22]. The adoption of aptamers or nucleotides, peptide arrays, antibodies, and molecule imprinted polymers could provide tools to develop innovative biosensors over classical methods [21]. The integrated approaches provide an improved perspective for the development of specific and sensitive biosensors with high regenerative potentials. Several biosensors ranging from nanomaterials, polymers to microbes could provide broader potential applications. The integrated strategies also involve multiple technologies ranging from electrochemical, electromechanical, and fluorescence with optical-based biosensors and genetically engineered microbes [18][20][21]. The majority of these biosensors have tremendous applications with prospects in disease diagnosis and medicine. The mandate and necessity for the use of biosensors for rapid analysis with cost-effectiveness require bio-fabrication that will pave the way to identify cellular to whole organism activity with a detection limit of high accuracy for single molecules [21]. Previous studies have reported that the rapid diagnosis of infectious diseases and apt initiation of appropriate treatment are typically assigned as determinants for the promotion of optimal clinical outcomes and that of the health of the public [7][23][24]. Other studies have reported that the conventional in vitro diagnostics for infectious diseases are time-consuming, requiring centralized laboratories, experienced personnel, and bulky equipment [25].

Recent advances in biosensor technologies have the potential to deliver point-of-care diagnostics that match or exceed conventional standards with regards to time, accuracy, and cost [7][18][20]. Despite the clinical need, the translation of biosensors from research laboratories to clinical applications remains limited to a few notable examples, such as the glucose sensor [20]. Some of the reported clinical challenges that are overcome by biosensors include sample preparation, matrix effects and system integration [26][18]. The vast range of sewage microbial diseases have been found to cause remarkable morbidity and mortality everywhere throughout the world. Sewage gives a perfect developing condition to various sorts of micro-organisms, including yeasts, fungi, algae, protozoa, viruses, and bacteria [6]. According to Mishra et al. [22], the level of heterotrophic, autotrophic, saprophytic, non-pathogenic, and pathogenic forms varies with their sources. Tobore [27] predicted that the concentration of some pathogenic viruses and parasites like Giardia and Cryptosporidium in wastewater is directly connected with the disease rate in the populace. This could narrow the general medical issues, other non-pathogenic faucal bacterial like RNA bacteriophages, total coliforms and E. coli mostly found in wastewater with a negligible effect on the lives of people [28][29]. Therefore, monitoring SARS-CoV-2 in sewage treatment facilities with biosensors in the sewage is useful. Leustean et al. [30] also added that the identification of waterborne infections is crucial to kill and control their harmful impact as pathogens. In essence, the recent invention of biosensors can be applied with magnetic nanomaterials to improve the precision and effectiveness of detecting several pollutants, including viruses in the sewage systems.

2.2. SARS-COV-2 Possible Wastewater Treatment Technologies

2.2.1. Membrane Bioreactor

Membrane technology has emerged as a preferred choice for reclaiming water from different wastewater streams for reuse. With a significant reduction in the size of equipment, energy requirement and low capital cost, membrane technology offers many prospects in wastewater treatment [31]. According to Obotey Ezugbe and Rathilal [32], membrane technology has the potential of bridging the economic and sustainability gap, amid possibilities of low or no chemical usage, environmental friendliness, and easy accessibility to many. Thus, membrane technology has proven to be a more favorable option in wastewater treatment processes in recent times. Figure 2 shows the schematic representation of the different paths of the membrane process.

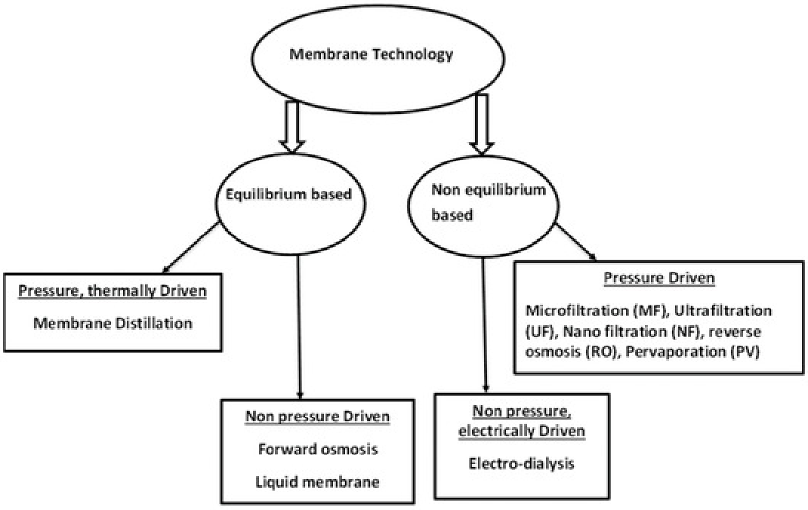

Figure 2. Schematic representation of the membrane processes adapted and modified from Obotey Ezugbe and Rathilal [32].

Over the past decades, membrane bioreactors (MBRs) have reached a significant market share in water and wastewater settings, which is expected to grow at a compound annual growth rate (CAGR) of 13.2% [13][32]. This seems to be higher than that of other advanced technologies, thereby increasing its market value from USD 337 million in 2010 to USD 627 million in 2015 [13]. The main limitation for their widespread application is their high energy demand between 0.45 and 0.65 $kWh.m^{-3}$ for the highest optimum operation from a demonstration plant, according to recent studies [20][33]. Past research articles had reported that, although MBR technology did not come into play when it was earlier introduced by Smith and his co-workers in the late 1960s, it has been playing an important role in wastewater treatment for reuse since the mid-1990s [20]. Rigorous regulations on effluent discharge and the reduction of membrane capital cost could be regarded as the principal drivers for the present widespread use of this technology worldwide [33]. The present emergence in the wastewater treatment market of the membrane bioreactors gives a clue of the degree of maturity reached by this technology. The most cited market analysis report indicates an annual growth rate of 9.0% and predicts a global market value of USD 3.7 billion by 2023 [2]. Predominantly outstanding in this case are China and some European countries with an implementation rate of over 50% and 20%, respectively. The technological advancement in the urban wastewater market is also reflected under two major categories: the diversity of technology suppliers and the upward trend in plant size. It has been found that since 1990, the number of MBRs have grown exponentially with an estimate of over 50 different providers by the end of 2009 [31]. MBR processes make use of their microbiological and metabolic potential for treating wastewater. In relation to that, MBR processes are analogous to conventional activated sludge (CAS) processes [34][31]. These are designed and operated with much longer solids retention times (SRT) than that of CAS processes. Longer SRT operations result in different treatment performances and other associated situations [31].

2.2.2. Advanced Oxidation Process

Current emerging micropollutants contaminants (RNA of COVID-19, pesticides, antibiotics, endocrine disrupting compounds) in WWTPs discharges impacts on the likelihood to reuse these waters after treatment [35][36]. When aquatic animals inject the micropollutants contaminants, they alter their endocrine system due to the endocrine-disrupting compounds [37][38]. A possible prospect for removing micropollutants from tertiary WWTP is hydrogen peroxide (H2O2)/ultraviolet (UV) as an advanced oxidation process (es) (AOPs) [39]. Recently, the Gold Bar Wastewater Treatment Plant applied this method in Edmonton, Canada, to treat secondary sewage [40]. Since then, the process has received much attention because it uses hydroxyl radical (•OH), which is highly reactive to destruct intractable chemicals found in wastewater [41]. Hydroxyl radicals are known to bombard organic molecules nonselective and rapidly. Additionally, the process offers other diverse approaches of producing hydroxyl radicals making it more versatile and consequently gives a better approach to adhering to strict guidelines during wastewater treatment. AOPs which include Photocatalysis, ultrasonic process, Fenton and photo-Fenton processes ($Fe_2^+/UV/H_2O_2$ and Fe_2^+/H_2O_2), H_2O_2/UV, ozone combined with catalysts (O_3/catalysts), UV irradiation (O_3/UV) and ozone combined with hydrogen peroxide (O_3/H_2O_2) or both ($UV/H_2O_2/O_3$) have been effectively utilized in treating wastewater [35][36][41][42]. A remarkable feature realized during the process was the eco-friendliness of the end-product, giving it a more efficient outlook to mineralize a broad spectrum of organic pollutants, including COVID-19. The process is eco-friendly, which can rely on solar energy instead of artificial light sources which is hazardous and costly [36][42]. Furthermore, due to the highly reactive nature of •OH, it can attack almost any organic materials without any discernment. The advantages and disadvantages of AOPs in WWTPs are tabulated in Table 1.

Table 1. Advantages and Disadvantages of AOPs in WWTPs.

Advantages	Disadvantages
Converts organic materials into stable inorganic compounds	**Residual peroxide removal may need to be considered**
Treat nearly all organic compounds and remove some heavy metals	**Complex chemistry tailored to specific contaminants**
Do not introduce new harmful substances theoretically into the water	**Relatively high capital and maintenance**
No sludge production as with biological or chemical processes	**Energy intensive**
Does not concentrate waste for further treatment	
Disinfection of pathogens especially using UV	
Rapid and robust technology	

3. Conclusions and Recommendations

In the midst of COVID-19 wastewater remediation, magnetic nanomaterials were found to be promising (biomagnetic separation, immunoassays, and medical imaging techniques) to provide opportunities to effectively target emerging contaminants that the conventional systems fail to remove. Thus, contaminant-loaded magnetic particles could be easily separated from the solution via an external magnetic field. Thereby, employing them in the wastewater treatment settings can enhance the stability of the viral RNA and other pathogens for the biosensor detections. Comprehensive studies on the toxicity of magnetic nanoparticles have proven to have little or no negative environmental impacts. Hence, integrating magnetized nanomaterials into the wastewater treatment settings, due to their super-magnetic properties, could facilitate the treatment and separations, while the rest of the composite is meant to provide a high surface area for the adsorption of the virus RNA for detection and quantification. Therefore, integrating magnetic biosensor diagnostics into wastewater treatment systems, via wastewater-based epidemiology (WBE) could be a possible way to investigate the spread of COVID-19 in communities around the globe for health policy development and to minimize the diagnostic cost of testing.

Other recommendations and future works include:

- In the application of WBE, which requires routine sampling for diagnostic testing, all safe work protocols and effective personal protective equipment are encouraged to be used to protect personnel from SARS-CoV-2 exposure.
- To avoid discrepancy of results, future work of developing optimized and standardized protocols for detection and quantification of SARS-CoV-2 in wastewater is crucial. This assay needs to be compared and connected with centralized hospital laboratories to help generate effective regional reports.
- To improve the assay of biosensors with the aforementioned capabilities to mitigate and safeguard COVID-19's spread, its sensitivity and detection with magnetic nano-based materials are recommended. Future work can focus on integrating biosensors with biosecurity coupled with smart-phone apps connected to a centralized hospital database to help track carrier status.
- The prospects of photocatalysis to inactivate SARS-CoV-2 in wastewater settings is very high, owing to its appreciable used for sterilization of clinical devices, degradation of protein and virus RNA. Therefore, future research should focus on its safe nanotechnology and bioengineering line to combat the COVID-19 pandemic.

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