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REVIEW

Biosensing capabilities of bioelectrochemical systems towards sustainable water streams: Technological implications and future prospects

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Bioelectrochemical systems (BESs) have been intensively investigated over the last decade owing to its wide-scale environmentally friendly applications, among which wastewater treatment, power generation and environmental monitoring for pollutants are prominent. Different variants of BES such as microbial fuel cell, microbial electrolysis cell, microbial desalination cell, enzymatic fuel cell, microbial solar cell, have been studied. These microbial bio-electrocatalytic systems have clear advantages over the existing analytical techniques for sustainable on-site application in wide environmental conditions with minimum human intervention, making the technology irrevocable and economically feasible. The key challenges to establish this technology are to achieve stable and efficient interaction between the electrode surface and microorganisms, reduction of time for start-up and toxic-shock recovery, sensitivity improvement in real-time conditions, device miniaturization and its long-term economically feasible commercial application. This review article summarizes the recent technical progress regarding bio-electrocatalytic processes and the implementation of BESs as a biosensor for determining various compositional characteristics of water and wastewater.

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[**Key words:** Environmental monitoring; Bioelectrochemical systems; Biosensor; Chemical oxygen demand; Toxicity; Self-powered]

Bioelectrochemical systems (BESs) emerge as a new mode of gaining energy while treating wastewater. In the past decade, remarkable progress has been made in the field of bio-electrochemical processes for bioelectricity generation, salinity removal and chemical production with concomitant wastewater treatment using different variants of BESs [microbial fuel cell (MFC), microbial electrolysis cell (MEC), microbial desalination cell, enzymatic fuel cell, microbial solar cell] (1–4). In the two-electrode assembly of MFC, the anode electrode serves as the electron donor, while in its counterpart, strong oxidizing agents act as the terminal electron acceptors at the cathode electrode. A cation exchange membrane, mainly a proton exchange membrane separates the two chambers (anode and cathode)and both electrodes are connected through an external resistance. In the continuous mode operation, MFC harvests continuous power by degrading the organic content present in the anodic chamber by microbial metabolism and the produced power either can be stored in an external capacitor or used on-site to power sensors and telemetric devices (3). The generated power can be utilized for online monitoring and determination of the concentration of various constituents present in water and wastewater samples. The conventional offline analysis for micro-pollutants deals with extended processing time and a lack of information on biological responses. Hence, the microorganisms-based analytical systems can be used for bio-sensing and bioassay applications in diversified ways. Biological oxygen demand (BOD), the milligrams of oxygen consumed per liter of the sample during 5 days of incubation at 20 °C is one of the most widely used parameters for wastewater characterization as an indicator of organic pollution of water. However, the existing dilution method demands 5 days to complete the analysis. Other limitations of the test method involve inaccuracy and irreproducibility of the analysis. Hence, the conventional BOD_5 test is not feasible for real-time monitoring of wastewater samples. The removal of chemical oxygen demand (COD) during wastewater treatment is another essential factor, which is based on the initial COD concentration and the acquired treatment process. This method is a preferable method for water quality analysis as compared to BOD because it indicates the amount of oxidizable organic matter remaining in the water that is inversely proportional to the dissolved oxygen (DO) levels. Higher COD, which corresponded to lower DO levels, can result in the creation of anaerobic conditions, which is detrimental to the survival of higher aquatic life forms. If the techniques of in-line monitoring of COD and BOD concentration can be tailored to collect real-time data, it would indeed bring advantage to the wastewater treatment

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facilities. Application of BES-based biosensors can be a useful alternative for such measurements (5,6).

Anaerobic digestion (AD) technology is one of the most well established wastewater treatment processes for biological degradation of pollutants due to its comparatively inexpensive and more competent way of operation for the production of methane as biogas. It has been shown in the past that the activity and viability of the activated sludge process, AD and other biological wastewater treatment techniques are profoundly affected when a sudden increase in toxic compounds is detected in the influent stream (7). A monitoring system for the detection of toxic compounds is a prerequisite to control the deleterious effects of toxic compounds on microbial growth and to tune the AD parameters for effective wastewater treatment (7). On-line monitoring is the key to achieve a more efficient AD process, establishing a stable and overall efficient treatment. Therefore, the application of cost-effective and reliable BES-based biosensor for AD processes has been proven more suitable in various research studies (8). To date, the BES has been successfully utilized in lab-scale studies to monitor volatile fatty acids (VFA) (9), BOD (10) and substrate quality analysis, but not commercialized yet for real-time application. For example, fast, cost-effective and sensitive detection of fumarate (food spoilage indicator) is required, and it can be used to determine the food spoilage as well as a cancer diagnosis (2,10). In general, high-performance liquid chromatography and ion chromatography techniques are used for quantification of fumarate in different animal and fruit juice samples (12). These available physicochemical methods require sample pre-treatment and expensive types of equipment for detection, making this detection process economically unviable. Hence, there is a need to develop a new cost-effective biosensor device for fumarate measurement. Use of untreated groundwater as drinking water is prevalent in many countries. There are reasonable chances of groundwater contamination with heavy metals, such as iron, manganese, and arsenic. Long-term consumption of such contaminated water may cause severe physiological malfunctions in the human nervous system (13). Micro-biosensors can potentially apply for rapid monitoring of such heavy metals present in groundwater during field-scale monitoring with less installation cost (14). Yi et al. (15) demonstrated that the optimum values of external resistance in an MFC changed as pollutant changed. The obtained result shows that optimal values for detecting heavy metals, tetracyclines and avermectins were 680 Ω, 330 Ω and 100 Ω, respectively (15). All MFC-based biosensors should optimize for external resistance for increased sensitivity towards the sensing pollutant. Buk et al. (16) fabricated and characterized the feasibility of carbon quantum dot and gold nanoparticle-based electrodes for BES-based biosensing of glucose. Zhao et al. (17) developed a sequential flow membraneless MFC biosensor using both biocathode and bioanode for toxicity monitoring. The presence of toxicants depends on the type of wastewater. As they affect the pH of the wastewater stream, the microorganisms useful for the biological treatment are inhibited (18). Hence, MFC-based biosensors can serve as robust systems for a variety of applications including early detection of toxic compounds in the different wastewater streams (19).

BIOELECTROCHEMICAL SYSTEM AS A BIOSENSOR: PRINCIPLE AND WORKING MECHANISM

BES can directly convert the biochemical energy available in organic matter (wastewater) to bioelectricity (for MFC) or biohydrogen (for MEC). MFC comprises anodic and cathodic chambers separated by proton exchange membrane. In the anodic chamber, electro-active bacteria form a biofilm over the electrode surface. In the absence of oxygen or any other oxidizing compounds like sulfates and nitrates, extracellular electron transfer takes place via direct or mediated pathways to the anode. The current produced by electroactive bacteria in an MFC is directly related to the metabolic activity of the developed biofilm. Therefore, when the process parameters such as pH, temperature, and conductivity of feed are constant, any disturbance in metabolic activity can be observed as a sudden change in the current generation in MFC. The electroactive biofilm on the anode surface can work as the recognition component. The rate of electron flow to the anode (transducer) is affected by the specific disturbance to the electroactive biofilm, and transduced into a measurable change in current production. Lorenzo et al. (20) defined the sensitivity for BES as the electrical signal per unit change of medium concentration in the anodic chamber, which is affected by the electrode surface area (Eq. 1).

$$\text{Sensitivity} = \frac{\Delta I}{\Delta c} \cdot \frac{1}{A} \tag{1}$$

where Δc (mM) is the unit change in the anolyte concentration, A is the electrode surface area, and ΔI (mA) represents the unit change in the current output. The sensitivity equation shows that the shift in current generation plays a vital role in the determination of toxic compounds and other parameters of wastewater, such as a change in BOD and COD concentration. Stein et al. (21) demonstrated the importance of over potentials in MFC-biosensor and their study suggested that the anode potential between −400 mV and −350 mV vs. Ag/AgCl derives the most stable operating voltage for attaining a constant current density. The electro-active microbial biofilm at the anode's electrode surface can work as a low-cost quantitative sensor as compared to other biosensors. The BES-based biosensor can be used as an *in-situ* environmental or bioprocess-monitoring device for real-time applications. The bases include indirect electron transfer by small redox mediators, primary metabolites and their intermediates and direct electron transfer through electron shuttling by bacterial outer-membrane c-type cytochromes and conductive pilli (nanowires) (22,23).

BIOELECTROCHEMICAL SYSTEM AS BIOSENSOR FOR POLLUTANT DETECTION IN WASTEWATERS

Detection of acetate Acetate is a primary organic compound present in wastewater. Jiang et al. (24) investigated the MFC-based detection of acetate using four anodic chambers with one common cathodic chamber. The response time was reduced, while the sensor ability was increased due to the application of novel cathode sharing MFC. Reducing the anodic volume reduces the detection time for acetate measurement. Sun et al. (25) developed a new, more sensitive MFC-based biosensor for detection of acetate of an AD reactor. This biosensor showed a linear relationship between the acetate concentration (0.5–20 mM) and current density at different time range (1–5 h) with varied temperatures (37 °C-55 °C). The measured acetate concentration in AD was comparable with concentrations measured through gas chromatography (25). Cheng et al. (26) developed a marine MFC-biosensor for detecting the acetate concentration (up to 10 μM), which can also be used for real-time measurement of an even low level of acetate present in seawater. The reliability of sensor signals was confirmed by obtaining a linear relationship of the obtained peak currents with the increasing acetate concentrations. The detection limit for acetate in this study was found to be as low as 5 μM.

Detection of assimilable organic carbon Detection of assimilable organic carbon (AOC) is generally used to measure the growth potential of microbes in water. Measuring these compounds

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can help to find out the microorganisms that may be the cause of biofouling to the membrane used for the desalination of seawater in the reverse osmosis process. Therefore, the knowledge of AOC can help to develop anti-biofouling strategies, where the AOC level should be determined online, in-situ, in real-time, accurately and automatically. Cheng et al. (26) developed a marine MFC type biosensor for the detection of AOC regarding acetate measurement. The MFC-biosensor operated in a fed-batch mode with 0.5 g/L of marine broth mixed with 5 mM of sodium acetate in real seawater as anodic substrate. The cathodic chamber was filled with 100 mM potassium hexacyanoferrate (HCF(III)). The developed biosensor could sustain under the oxygenated environment of the anodic chamber. The presence of HCF(III) enabled the development of an adapted biofilm that transferred electrons to HCF(III) rather than oxygen. The HCF(III) in medium works as an electron accepter and after receiving electron, it reduced to HCF(II). Therefore, the reduced HCF(II) could easily transfer an electron to the anode electrode while being reoxidized to HCF(III). For the anode, +200 mV cell potential was used to overcome the effect of dissolved oxygen. According to this study, the aerobic bacteria preferred HCF(III) as a better electron acceptor than oxygen, when both were present (26). Yoshida et al. (27) investigated that a high concentration of HCF(III) can function as an electron mediator between the electrode and aerobic microorganisms such as *Pseudomonas*. The HCF(III) concentration of 0.2 mM was added to the anodic chamber of marine MFC, to overcome the adverse effect of DO in the media. As a result, within 1 h, MFC-biosensor started to produce precise and reproducible signals (27). The obtained results confirmed that the low level of AOC in oxygen-saturated seawater could also be recorded without any additional process for oxygen removal. The coulometric signals were linearly proportional to the acetate concentration; however, the coulombic efficiency strongly depended on the added HCF(III) concentration and presence of DO in the anodic chamber of MFC. Moreover, the peak current is dependent on the rate of microbial oxidation of AOC (28). Cheng et al. (26) also demonstrated that the anodic biofilm with a low concentration of HCF enables the development of marine MFC-biosensor to detect a trace level of AOC in the non-deoxygenated seawater (26). Quek et al. (29) developed a marine MFC for detecting AOC in water samples. A linear relationship (R^2 = 0.98) was observed with produced electrical signals in response to AOC concentration in the range of 0–3600 μM in the marine biosensor. The marine MFC-biosensor took 36 days for the development of biofilm on the anode surface. When the current production was stable, the biosensor was ready to determine AOC. At high AOC concentrations (3600–10,800 μg/L), the electric signal did not show the linear relationship. At a lower level, marine MFC-biosensor was tested successfully for 80 days (29). This MFC-biosensor was used as an indicator of biofouling potential in the seawater reverse osmosis system, but the DO present in the environment suppressed the output signals remarkably. To overcome the presence of oxygen, Quek et al. (30) developed an electrochemical cell for DO removal combined with an MFC-biosensor for AOC measurement in seawater. In this study, a linear relationship (R^2 = 0.991) was observed with the current generation and AOC concentration. The combined system could monitor the AOC concentration in anoxic seawater as well as the aerobic seawater. The combined approach can be used for in-line monitoring of AOC in the seawater desalination reverse osmosis plants (30).

Detection of BOD_5 As earlier mentioned, the conventional method of BOD_5 determination takes 5 days, and it is unsuitable for real-time monitoring and process control. Hence, a new suitable method for BOD determination is a pre-requisite. Lorenzo et al. (31) tested an air cathode single-chamber MFC (SCMFC) as a biosensor for BOD determination (Fig. 1A). With the use of artificial wastewater as feed, biosensor showed a linear relationship with BOD concentration (up to 350 mg BOD/cm^3). The results showed high reproducibility and stability for 7 months of the process. The response time was reduced by reducing the total volume of the anodic effluent from 50 cm^3 to 12.6 cm^3 in SCMFC. The similar results were also obtained with real wastewater in the operating temperature ranging from 20 °C to 30 °C (30). Kim et al. (32) applied air cathode and membrane

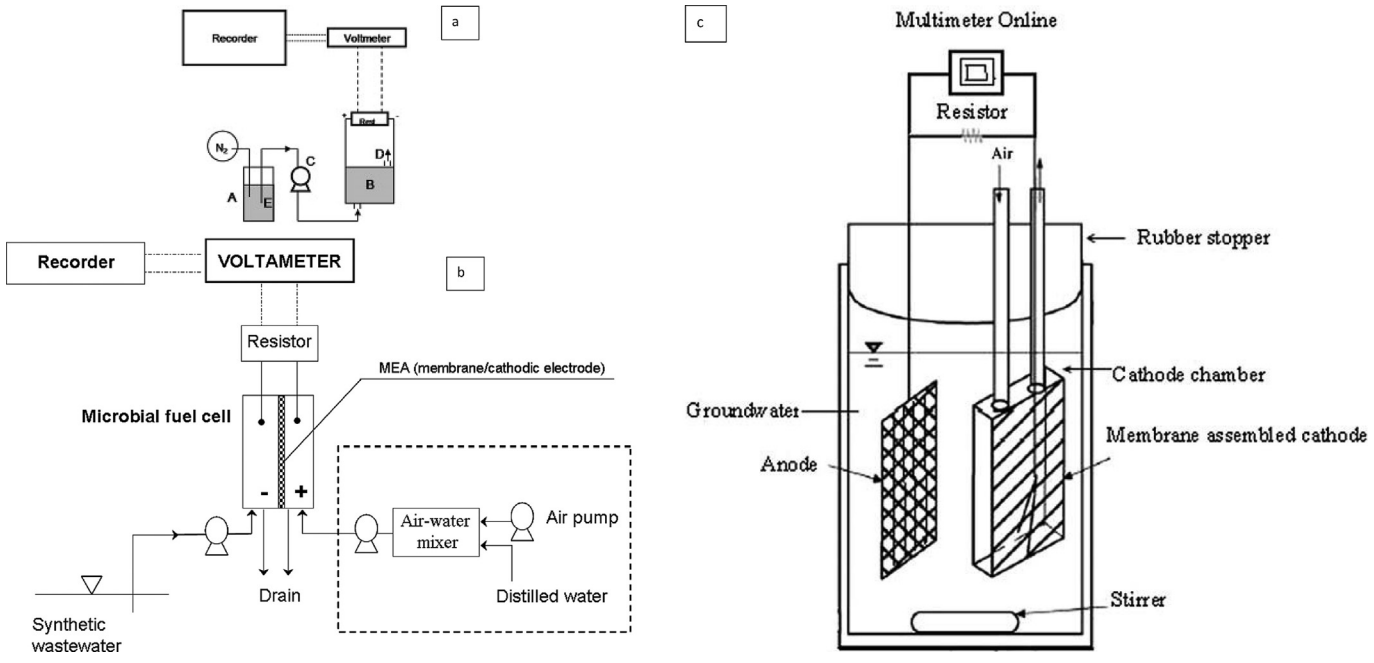

FIG. 1. Different Layouts of BES for Monitoring BOD: (A) System layout of SCMFC. In this A, feed tank; B, MFC; C, peristaltic pump; D, tube outlet; E, tube inlet (30). (B) Schematic figure of the MFC system installed with MEA (31). (C) Schematic figure of the SUMFC sensor (33).

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electrode assembly (MEA) to an MFC type biosensor for acquiring higher performance (Fig. 1B).

The MEA was fabricated with an optimal hot pressing of 120 °C and 150 kg/cm pressure for 30 s. Use of MEA and air cathode for construction of the BOD sensor enhanced the generated total coulombs to 4.56C from initial 0.52C, while the power density was increased to 60.08 W/m^3 from 0.880 W/m^3. Due to the increase in power generation, the sensitivity of the biosensor was enhanced from 1.2 x 10^{-3} to 1.8 x 10^{-2} C per mg/L of BOD (32). Zhang and Angelidaki (33) developed a biosensor based on a submersible MFC (SUMFC) for *in-situ* monitoring of BOD and microbial activity in groundwater. In this study, the biofilm-colonized anode was used to determine the BOD while new electrodes were utilized to determine the microbial activity. Fig. 1C shows the schematic diagram of the SUMFC sensor used in this study. The obtained current density shows a linear relationship with BOD content (up to 250 mg/L) with a response time of 40 min. The SUMFC equipped with a new anode electrode showed a linear relationship with an active microbe's concentration from 0–6.52 nmol-ATP/L. The primary factors affecting the sensor activity were pH, temperature, conductivity and inorganic solid content. The sensing time of SUMFC-based biosensor was enhanced from 40 min to 180 min while used in groundwater. The SUMFC presents a new way for in-situ quantitative measurements for BOD and microbial activity in bioremediation of groundwater. Likewise, Yang et al. (34) developed a low-cost SCMFC for the determination of BOD with use of carbon felt and activated sludge. In this study, the effect of different parameters including temperature, pH, organic matter concentration and response time was optimized for the better performance of the BOD sensor. The response time was 132 min for BOD determination in synthetic wastewater (BOD concentration 200 mg/L). The response signal (voltage) increased with an increase in BOD of synthetic wastewater. This developed biosensor performed equally well with the use of real wastewater; the obtained results have a standard deviation from 2.08 to 8 % compared to the standard BOD_5 method. The negative effect of oxygen diffusion from cathodic to the anodic chamber in SCMFC was overcome by using sulfonated polyether ether ketone membrane, in a study where BOD was being measured in artificial wastewater (35), showing a linear relationship with BOD (up to 650 mg/L). The usage of the sulfonated polyether ether ketone membrane facilitates the enhancement of 62.5% sensing ability compared to the traditional MFC-biosensor. Hsieh and Chung (36) developed a mediator-less MFC-biosensor with mixed microbial culture as an inoculum for the determination of BOD in wastewater. A linear relationship between BOD and obtained cell voltage was observed with long-term stability and higher reproducibility for the biosensor. The optimum conditions for external resistance, temperature and measurement time were 5 KΩ, 35 °C, and 12 h, respectively. The MFC-biosensor successfully measured the BOD concentration below 240 mg/L in real wastewater.

Commault et al. (37) demonstrated a new type of BOD sensor using a *Geobacter* enriched biofilm with ethanol as the only carbon source in the anodic chamber. The high diversity in the biofilm allow microorganisms to adapt to different carbon sources rapidly. In this study, BOD shows a linear relationship (R^2= 0.96) with a total reaction time of 17.5 h. The measured BOD range was 174 mg/L to 1200 mg/L. This biosensor was also tested for cow's milk with reproducibility of 94 %, with an error of 7.4 % compared with the conventional BOD_5 test. Similarly, Logrono et al. (38) also developed a new type of SMFC-biosensor for BOD determination of synthetic rice washed wastewater and this sensor measured the BOD level up to 200 mg/L.

Detection of COD Organic content in wastewater play a crucial role as the treatment process of wastewater strongly depends on the COD and other pollutants present in it. Online monitoring of COD efficiently generates information about its reduction efficiency. The effect of the anode electrode surface area in SCMFC-biosensor for determining the COD of wastewater was studied (30). In this study, two different graphite granules (thickness of 0.3 cm and 1 cm) were used as an anode electrode. Due to the increase in granule surface area to 1 cm, the response time was reduced by 65%, showing the importance of the surface area of the electrode in COD monitoring of wastewater. AD is used extensively for wastewater treatment due to its low operational cost and bioenergy production. Liu et al. (39) developed a new MFC-biosensor that is portable, robust and cost-effective for online monitoring of the AD process. The MFC-biosensor was installed in the recirculation loop of an up-flow anaerobic fixed bed reactor for real-time tracking of COD (Fig. 2).

The obtained MFC-biosensor signals showed a good correlation with pH, gas flow rate and COD for over 6 months duration with receiving enhanced MFC signals at a flow rate of 7.74 mL/min (39). The linear relationship was monitored between MFC-biosensor and organic content (up to 200 mg COD/L). The MFC-biosensor signals showed the Monod-type kinetics with substrate concentration; the highest power was produced with the external resistance of 200 Ω (39). Feng and Herper (40) investigated an MFC based biosensor integrated with an artificial neural network model in field and laboratory analysis of wastewater samples. The developed MFC-biosensor showed a regular peak in the laboratory with a known substrate, while in the real-field study, the peaks acquired irregular shapes and smaller magnitude due to variation in pollutant level in the wastewater. The MFC-biosensor showed a linear relationship (R^2= 0.99) with organic matter present in wastewater. The anode respiring bacteria activity was faster in 20 mL anodic chamber volume compared to 40 mL anodic volume (40). A new biocathode-MFC-tubular membrane bioreactor was constructed to be used as a biosensor for continuous COD monitoring (41). The COD concentration was slowly increased to 1000 mg/L from 100 mg/L, resulting in the increased current generation with quick response time to observe the change in COD concentration. The biosensor showed a linear relationship (R^2 = 0.97) with COD up to 1000 mg/L. The generated bioelectricity in biocathode MFC was evaluated based on the COD reduction patterns, mixed liquor suspended solids concentration, transmembrane pressure, and presence of extracellular polymeric substances. This biocathode MFC-biosensor showed an *in-situ* measurement of COD with a faster and reliable response as compared to the chemical-based COD analysis (41). Jia et al. (8)

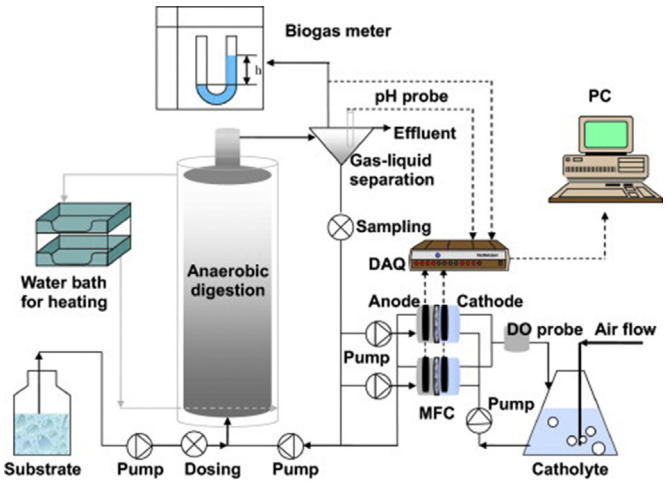

FIG. 2. Integration of anaerobic biodegradation system with MFC-based sensor for online monitoring of COD (39). DAQ, data acquisition systems.

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studied a hybrid integrating MFC sensor with an up-flow anaerobic sludge blanket (UASB) reactor for online monitoring of operating parameters. The MFC consumed only 0.94 % of influent COD for biosensing and the integrated system showed potential for real-time monitoring. With different COD loads, the generated voltage showed a linear relationship and highly reproducible results.

Detection of DO The DO is a very important parameter concerning water quality and wastewater treatment process; it also plays a very vital process in biochemical reaction in the aerobic digestion process. Presently used methods for measuring DO concentration are highly reliable on electrochemical sensors and expensive instrumental that requires expensive electrode material. The present common used method for DO determination are time-consuming. At present DO use, methods also need an external power supply source; these are not suitable for remote sensing DO measurements (42). The application of BES for measuring DO did not require any external power source, so it can be used to determine of DO in the remote areas. As per the DO measurement in the MFC, the number of electrons generated during oxidation in the anodic chamber is donated to the anode electrode and these further transferred to the cathode electrode while using the external circuit. The protons generated during oxidation in the anodic chamber are transferred in the cathodic chamber via using the ion-exchange membrane. At the cathode electrode, the electrons and protons react through a redox reaction with the presence of an oxidant. O_2 work as terminal electron acceptor in the cathodic chamber. Due to the reaction of the anodic and cathodic chamber of BES, the generated bioelectricity could be correlated with DO concentration in water and wastewater streams (42).

A SUMFC biosensor has been developed for *in-situ* and real-time monitoring of DO in tap water (42). The current density (5.6–462 mA/m^2) and DO show a linear correlation (R^2= 0.991) up to the DO level of 8.8 mg/L, with a maximum response time of 4 min. Varying the external resistance, the value of current density was changed, showing a linear relationship with DO. The MFC was later tested with different COD concentrations (100, 300, 500 and 1000 mg/L) to power the device while treating domestic wastewater. The organic matter present in domestic water was sufficient to power the MFC while simultaneously determining the DO concentration (42). Various environmental parameters such as temperature, pH, conductivity and various electron acceptors can influence the oxygen reduction potential at the cathode electrode (43,44). The influence of different pH (5.5–9.0) on sensor performance was also investigated. With all pH, a linear relationship was achieved between current density and DO level; however, the regression coefficient was different in all conditions. At lower pH, higher current density was produced due to improved oxygen reduction efficiency at the cathode electrode. Similar trend was also observed with varying temperatures. Different conductivity levels were tested up to a range of 200 μS/cm, and no effect of conductivity was found on current production. The presence of nitrate (2.5, 5 and 10 mg-N/L) was also investigated. When the DO level was higher than 2.03, the effect of nitrate on current production was minimal; however, at lower DO concentration, nitrate can work as a prevalent electron acceptor affecting the level of the current output. The developed SUMFC-biosensor was also used for DO measurement in seawater, lake, bioreactor sample, and tap water, depicting the wide range of applications of such biosensor for online monitoring of water samples (42).

Detection of volatile fatty acids Monitoring the volatile fatty acids (VFAs) concentration is vital in the AD and MFC process. Acetate, butyrate, and propionate are the intermediate compounds produced in the metabolic pathways of fermentation, methanogenesis and bio-electrogenesis process. In general, VFA is measured in offline mode by using GC (45) or high-performance liquid chromatography (46). VFA concentration plays a significant role in AD, causing microbial stress in the presence of high concentration; hence, the online monitoring of VFAs is necessary. MFCs can be considered for the on-line monitoring of VFAs. Kaur et al. (47) investigated the correlation between VFAs concentration and voltage/current response in MFC-biosensor. In this study, two methods were employed to monitor the VFAs, namely coulombic efficiency and cyclic voltammetry. The oxidation peaks were measured using cyclic voltammetry at a constant scan rate, and these showed a linear relationship with VFA concentration in a rapid response time of 1–2 min. However, the coulombic efficiency method required more than 20 h duration at the VFA concentration of 20 mg/L. For attaining a broader range of stable VFA measurements, anode electrode was modified for improving the overall performance of the MFC-biosensor (48). For a quick response, microorganisms were immobilized on the anode electrode by using natural polymers and polypyrrole. As a natural binder, three different polymers were used, namely (i) agarose and neutral red mediator, (ii) polyacrylamide and *N,N,N,N*-tetramethylenediamine mediator and (iii) polyvinyl alcohol + calcium alginate + carbon powder. The modified anode electrode improved the voltage output, start-up time, current generation, stability, and recovery rate of the MFC-biosensor's response substantially. The positive functional group of pyrrole alkyl ammonium (Ppy^+) enhanced the voltage signals while the modified electrode of (Ppy^+)-based MFC-biosensor measured the VFA concentration up-to 60 mg/L (48). MEC was used as a biosensor for online measurement of VFA in the AD process (49). Initially, synthetic wastewater was used in the AD and obtained linear correlation (R^2 = 0.99) between VFA concentration (5–100 mM) and current densities (0.03 to 2.43 A/m^2).The adopted MEC biosensor performs well under varied MEC operating parameters (external voltage, media ionic strength, VFA ratio) with a linear correlation results between the current density and VFA concentration. In the MEC cathodic chamber, H_2 is also produced, so this is a self-sustainable system and cost-effective method for VFA monitoring in the AD and other anaerobic processes. Schievano et al. (50) demonstrated an air cathode membrane-less MFC for VFA monitoring in the AD process. This system worked as a shock warning in the AD system when the VFA concentration increased more than 4000 mg/L. The MFC-based biosensor potentials were negatively correlated with all four substrates used in the AD system, namely as cheese whey, kitchen waste, citrus pulp and fishery waste. So single-chamber MFC can be used for early warning for the AD process, thus preventing VFA's inhibitory effect overall microbial communities (50). The sensing abilities of BES-based biosensors for the detection of essential elements/components of wastewater treatment are summarized in Table 1 (24,26,30,31,33,35,40,51–57).

BIOELECTROCHEMICAL SYSTEM AS BIOSENSOR FOR METAL ION DECTECTION

Hexavalent chromium sensor A dual-chamber submerged MFC was tested for hexavalent chromium detection in water (58). Chromium Cr (VI) reduction at the cathode and microbial acetate oxidation at the anodic chamber have taken place, resulting in the generation of voltage as an indicator of available Cr (VI) concentration. The MFC-biosensor successfully measured the Cr (VI) concentration from 10 mM to 300 mM in the acidic environment of a cathodic chamber (pH 1.0 or 2.0).

Iron and magnesium sensor In a study with lithotrophic iron-oxidizing MFC (LIO-MFC) system as a biosensor, Tran et al. (59)

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TABLE 1. BES-based biosensors for sensing acetate, BOD, COD and VFAs.

Sensing element/compound	Configuration (inoculant)	Detection limits (μM/mg/L)	Reference
Acetate	Dual chamber MFC (MFC effluent)	250–750[a]	24
Acetate	Dual chamber MFC (marine sediment)	5–80[a]	26
COD	Double- chamber MFC (marine sediment)	6.4–64[b]	30
COD	Membrane electrode assembly (anaerobic sludge)	100–500[b]	31
BOD	Submersible MFC (primary clarifier)	10–250[b]	33
BOD	Membrane electrode assembly (anaerobic sludge)	65–100[b]	35
COD	Membrane electrode assembly (activated sludge)	5–200[b]	40
Acetate	Dual chamber MFC (marine sediment)	10–170[a]	51
Acetate	Single -chamber MFC (*Geobactersulfurreducens*)	79–1600[a]	52
BOD	Dual-chamber MFC (activated sludge)	20–100[b]	53
BOD	Dual chamber MFC (MFC effluent)	5–235[b]	54
BOD	Single-chamber MFC (mixture sludge)	32–1280[b]	55
VFAs	Double-chamber MFC (primary clarifier)	5000–100000[a]	56
VFAs	Single-chamber MFC (secondary biofilms)	50–2000[a]	57

[a] μM.
[b] mg/L.

demonstrated a mechanism to detect manganese and iron in water samples. The neutrophilic iron-oxidizing bacterial consortia were enriched and used in LIO-MFC. The graphite granules and graphite rod were used as the electrodes; the anodic chamber was feed with M9 medium (0.0146 g/L $CaCl_2$, 0.20 g/L $MgSO_4 \cdot 7H_2O$, 0.5 g/L NaCl, 0.34 g/L K_2HPO_4, 0.44 g/L KH_2PO_4 and pH 7.0) and the cathodic chamber was filled with buffer solution (0.44 g/L KH_2PO_4, 0.34 g/L K_2HPO_4 and 0.50 g/L NaCl). When the LIO-MFC system produces stable current, different concentration of Fe^{2+} was added in the anolyte. The produced current and the concentration of Fe^{2+} ions shows a linear relationship ($R^2 = 0.98$) for the Fe^{2+} concentration range 3–20 mM. The different operational parameters such as pH, temperature and external resistance were also investigated to see the effect on the current generation (59). The MFC performed well between the temperature of 30 °C to 40 °C and up to 50 Ω, external resistance was used for higher current generation. The endurance of the LIO-MFC's towards starvation (fed/renewed without the anolyte, Fe^{2+}) reported to be up to 14 days. The detection of manganese was also tested in LIO-MFC where the different concentration of Mn^{2+} (as sole e^- donor) was added in the anolyte and relationship between the current generation and Mn^{2+} concentration was compared. It was found that beyond 3 mM concentration of Mn^{2+} ions, the current generation starts decreasing (59). Table 2 summarizes other studies demonstrating the detecting capabilities of BESs biosensor for metal ions and heavy metals (1,11,14,19,21,59–64).

DETECTION OF TOXIC COMPOUNDS BY USING BIOELECTROCHEMICAL SYSTEM AS BIOSENSOR

Depending on the sources, municipal or industrial wastewater may contain various potential toxicants. Microbial activity is largely inhibited if the toxic compounds are in higher concentration. MFC can be used as an early detection device for the measurement of toxic compounds in wastewater, where the decrease in power generation can be an indicator of the system failure due to the presence of such compounds in higher concentration. At present, the toxic ion detection is carried out by analytical methods such as high-performance liquid chromatography–MS and GC–MS (65). These tests are complicated and time-consuming; therefore, a need to develop a biosensor that can run the online measurement was realized. The change in the current generation in the presence of toxic compounds in wastewater is the key to its quantitative determination. The presence of toxic compounds in the anodic chamber of MFC resulted in a decreased power production, even after supplying fixed current (65). Shen et al. (66) developed a real-time monitoring MFC based toxicity biosensor for active monitoring of acid toxicity in wastewater. When the sudden change occurred in the anodic medium, there was a sudden decrease in voltage production. However, the system recovered fast after toxicity exposure. The sensitivity of the MFC-biosensor was increased with a decreased HRT of 3.5 min from 22 min, which facilitated an enhanced mass transport rate. The optimized external resistance was reported as 5 Ω with the maximum power generation of 0.23 mW while treating domestic wastewater. In another study, an MFC-based biosensor was developed to measure the wastewater toxicity and to monitor the level of substrate concentration. The Butler–Volmer–Monod model was used in this study to describe the generation of current in the steady-state conditions (61). Shen et al. (60) investigated the effect of shear rate on the response of the MFC toxicity sensor to Cu(II). In this study, the impact of shear force caused by N_2 sparging on the anodic film was investigated. When Cu(II) was added in 5 or 7 ppm to wastewater, an immediate decrease in voltage was observed. The inhibition ratio at 7 ppm of Cu(II) for a flow rate of 12 and 24 mL/min was 50%

TABLE 2. BES-based biosensors for detection of metal ions/heavy metals.

Sensing element/compound	Configuration (inoculant)	Detection limit (mg/L)	Reference
Cu(II)	Single-chamber MFC (primary wastewater, biofilm)	>6	1
Cr(VI)	Single-chamber MFC (domestic wastewater)	1	11
As(III)	Single-chamber MFC (mutant *Shewanella oneidenesis*)	3	14
Cd(II)	Membrane electrode assembly (MFC effluent/activated sludge)	0.001 to 0.1	19
Cu(II)	Double-chamber (MFC effluent)	85	21
Fe(II)	Double-chamber MFC (natural mud)	167.5	59
Cu(II)	Membrane electrode assembly (domestic wastewater)	5	60
Ni(I)	Dual-chamber MFC (MFC effluent)	10	61
Hg(II)	Double-chamber MFC (activated sludge)	1	62
Pb(II)	Double-chamber MFC (activated sludge)	1	62
As(III)	Double-chamber MFC (*Enterobacter cloacae*)	0.33	63
As(V)	Double-chamber MFC (*Enterobacter cloacae*)	3.45	63
Fe(III)	Single-chamber MFC (*Geobacter sulferreducens*)	2.8	64

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and 60%, respectively, which was much higher than the study with 5 ppm Cu(II) at the same flow rates. The inhibition ratio is inversely proportional to the shear rate. When the flow rate was increased to 24 mL/min from 1.3 mL/min, the thickness of the biofilm was changed to 100 μm from 300 μm. The high flow rate facilitates an enhanced biofilm density up to 380 g VSS/L. In the thicker biofilm (300 μm), the Cu(II) was penetrated up-to 150 μm of the biofilm. Therefore, denser biofilm with lower thickness was preferable to establish the MFC-biosensor as a toxicity bio-monitoring system (60).

Jiang et al. (67) investigated the sensitivity of MFC-based Cu(II) toxicity sensor by applying flow through the electrode and controlled anode potential. The electrical signals generated by soil microorganisms were useful in enhancing the sensitivity by 15–41 times, for the flow-through anode compared to the flow-by anode. Furthermore, the MFC-biosensor worked well at a constant cell potential of −410 mV–100 mV rather than utilizing a fixed external resistance. Anode potential of −150 mV was found to be the most suitable for detecting Cu(II) with the highest sensitivity. Jiang et al. (24) developed a novel MFC-biosensor with a biocathode sensing element. The biocathode-based MFC sensor showed high sensing abilities (7.4 ± 2.0 to 67.5 ± 4.0 $mA\%^{-1}\ cm^{-2}$) compared to the anode-based MFC sensor (3.4 ± 1.5 to 5.5 ± 0.7 $mA\%^{-1}cm^{-2}$). An enhanced sensitivity was observed with the biocathode-based MFC sensor with the increased DOC's and catholyte conductivities. The biocathode MFC sensor can measure the lower concentration of formaldehyde (0.0005 %), while the bioanode MFC-biosensor can be used for the same chemical in higher concentration (above 0.0025%). Another research group developed a dual-chamber self-powered MFC-biosensor for detecting toxicity in water, containing heavy metals (68). Concentration of 2 ppm in solution of 6 different heavy metal ions (Cd^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}, $Zn^{2+}$and Cr^{3+}) were tested and the inhibition ratio of exo-electrogenic bacteria were obtained as 9.29 %, 5.59 %, 12.56 %, 13.99 %, 8.81 %, and 1.95 %, respectively, showing sensitivity of such bacteria in the presence of heavy metals.

The *p*-nitrophenol (*p*-NP) is a chemical industry contaminant that causes environmental and health damage due to its toxicity (69). The presently adopted technique involves complex and time-consuming pre-treatment processes, which is unsuitable for the *in-situ* determination of *p*-NP (70). Chen et al. (71) developed a dual-chamber MFC-biosensor for *in-situ* real-time monitoring of *p*-NP. In this biosensor, the anodic chamber was aerobic with *Pseudomonas monteilii* LZU-3; this microbe can make biofilm on the anode electrode in the presence of *p*-NP as a sole substrate. The MFC-biosensor performed well at 30 °C with a 7.8 pH and external resistance of 1000 Ω. The generated current and concentration of *p*-NP showed the linear relationships when *p*-NP concentration was ranging between 10 and 48.50 mg/L. The noteworthy findings of BES biosensors towards the detection of toxic compounds are summarized in Table 3 (1,11,24,62,64,71–79).

DETECTION OF HAZARDOUS CHEMICALS BY USING BIOELECTROCHEMICAL SYSTEM AS BIOSENSOR

Acetaldehyde sensor Low-cost detection of acetaldehyde is necessary because of its nature of being an organic environment pollutant. Zhang et al. (43) developed a novel self-powered MFC-biosensor for acetaldehyde detection. The biosensor was first run without any acetaldehyde dose, where it produced the maximum open-circuit voltage of 640 mV and maximum power density of 28.5 $\mu W/cm^2$ at 340 mV voltage output by using ethanol as a substrate in the anodic chamber. When the first dose of 10 μM acetaldehyde was added, the open circuit cell potential and power density were reduced to 630 mV and 25.6 $\mu W/cm^2$, respectively. The addition of acetaldehyde enhanced the reversible enzymatic reactions and reduced feedback inhibition. Thus, the power production was decreased in the MFC-biosensor. The increasing concentration of acetaldehyde (10–610 μM) showed a linear relationship of a gradual reduction of power density with an R^2 value of 0.998.Acetaldehyde shows excellent selectivity in a range of 5–200 μM with a low detection limit of 1 μM (43).

Fumarate sensor Fumarate is used as food spoilage indicator in beverages, baking powders, candy and other food industries. It is also used as a potential biomarker for early diagnosis of fumarate hydratase associated cancer disease (80). Si et al. (2) developed an electrochemical whole-cell biosensor system for fumarate detection. The model microorganism *Shewanella oneidensis* MR-1 was selected because of its ability to transfer an electron from the solid electrode surface. The periplasmic fumarate reductase of *S. oneidensis* MR-1 is actively associated with the electron transfer pathway linked with the cell membrane (81). Hence, the developed biosensor produced current peaks immediately upon fumarate addition in the system. The determination limit of fumarate was 2 μM–10 mM (2). The applied external potential of −600 mV was used for fumarate reduction and a negative current was produced due to inward electron transfer, which was increased immediately on fumarate addition. The obtained result demonstrated that increased current is

TABLE 3. BES-based biosensors for detection of toxicants.

Sensing element/compound	Configuration (inoculant)	Detection limit (mg/L/mM/%)	References
Chloramine	Single/double chamber MFC (primary wastewater, biofilm/planktonic)	0.16[a]	1
Nitrate	Single-chamber MFC (domestic wastewater)	>48[a]	11
Formaldehyde	Double- chamber MFC (MFC effluent)	0.0005[c]	24
Polychlorinated biphenyl's	Double-chamber MFC (activated sludge)	1[a]	62
Formaldehyde	Double-chamber MFC (*Geobacter sulferreducens*)	0.01–0.1[c]	64
p-Nitrophenol	Double-chamber MFC (*Pseudomonas monteilii* LZU-3)	9[a]	71
Levofloxacin	Single-chamber MFC (NA)	100[a]	72
Tobramycin	Single-chamber MFC (MFC effluent)	100[a]	73
Diazinon	Double-chamber MFC (activated sludge)	1[a]	74
Ticarcillin	Double-chamber MFC (*Escherichia coli*/*Staphylococcus aureus*)	75[a]	74
Imidazole	Single-chamber MFC (primary wastewater)	0.02[b]	75
Azide	Single-chamber MFC (primary wastewater)	0.02[b]	75
Cyanide	Single-chamber MFC (primary wastewater)	10.40[a]	75
Toulene	Single-chamber MFC (*Escherichiacoli*)	50[a]	76
Sodium dodecyl sulfate	Double-chamber MFC (MFC effluent)	10–50[a]	77,78
Bentazon	Double-chamber MFC (MFC effluent)	1[a]	78
Glyphosate	Double-chamber MFC (cyanobacteria CAWBG64)	0.169–0.507[a]	79

[a] mM.
[b] mg/L.
[c] %.

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linked to fumarate reduction in *S. oneidensis* and this phenomenon can be taken into account for fumarate quantification. In the whole-cell biosensor, the current peak is used as the bio-sensing output. The enzyme (fumarate reductase) showed a good correlation with the cell growth phase, while in the stationary phase (16 h), the enzyme obtained its maximum activity. With the addition of fumarate, distinct current peaks were generated at varying concentrations. Therefore, these results can be used for accurate online monitoring. The current peaks and fumarate concentration (2–10 mM) shows a linear relationship ($R^2 = 0.997$). When different molecules like succinate, citrate, malate, and glucose was added, fumarate was determined accurately demonstrating the specificity of the biosensor, despite the presence of other biochemicals (2).

DETERMINATION OF WATER QUALITY USING BIOELECTROCHEMICAL SYSTEM AS BIOSENSOR

The purity of drinking water is essential to ensure public health. If any type of chemical toxin is present in the drinking water, it should be removed, and the intake of contaminated water should be stopped (82). Therefore, rapid and online detection methods are needed to detect the occurrence of chemical toxins in drinking water systems. Stein et al. (61) developed an MFC-biosensor for the detection of nickel in drinking water. The MFC-biosensor showed a good response time with a sensitivity of 0.0027 A/m^2/mg Ni/L at an anode potential of −400 mV. The produced current showed a reverse correlation with an increase in nickel concentration, due to flux of nickel towards the proton exchange membrane and catholyte. Stein et al. (77) studied the effect of the magnitude of external resistance on sensitivity and recovery time in an MFC-biosensor. At the lower resistance, higher current generation occurred due to a substantial change in signal. The sensor is more accurate at higher external resistance, reflecting shorter recovery time. The massive shift in signal occurred at high current (≥0.5 mA) or higher anode potential (≥−0.4 V). In both the conditions, external resistance played a crucial role and it facilitated the biofilm present inside the biosensor, to be accustomed and adjusted under both varied cell voltages and anode potentials.

In another study, Lorenzo et al. (20) tested an SCMFC for continuous quality monitoring of drinking water. The SCMFC-biosensor can detect the Cd^{2+} in drinking water. Inside this biosensor, acetate was used as a feed, and a linear relationship was observed between the acetate concentrations (3–164 ppm) and the sensitivity (0.5 μA$mM^{-1}cm^{-2}$), concerning the total surface area of the anode electrode. The cadmium in water was detected with higher sensitivity (0.2 μg L^{-1} cm^{-2}) with a lower limitation limit of 1 μg/L The SCMFC-biosensor can detect cadmium in the range of 1–25 μg/L. Yang et al. (83) developed a micro-liter sized MFC for monitoring the toxic compounds, such as formaldehyde, in water. A reference electrode Ag/AgCl was introduced into the micro-sized MFC to ensure the accurate monitoring of toxic compounds. Formaldehyde showed a fast inhibition rate of bacterial metabolic activity. A rapid change in current profile was observed during the increase of formaldehyde concentration, at the rate of 10 μl/min, to 0.1 % from 0.001 % and under poised anode cell potential of 200 mV (vs. Ag/AgCl). The bacterial activity at the anodic chamber was recoverable by the addition of fresh growth medium, ensuring the reusability of this biosensor.

PROSPECTIVE AND FUTURE TRENDS OF THE BIOELECTROCHEMICAL SYSTEMS AS BIOSENSORS

BES provides a suitable solution for online monitoring of various pollution parameters, such as DO, COD, BOD and other toxic contaminants of drinking water and wastewater, in a comparatively cheaper, faster and accurate manner. Lab-scale operation of MFC-biosensors has been successful; however, the real-time applications are yet to be established. The techniques of using the bio-anode- and biocathode-based MFC-biosensors have promising potential for direct and rapid monitoring of pollutants and biological respiration activity in groundwater and wastewater. The MFC-biosensor shows excellent performance, high linearity, long-term stability, and good reproducibility, having vast potential for routine commercial use. However, the length of response time and sensitivity has to be further improved before considering these technologies for industrial applications. MFC-biosensor provides a new approach to reflect the real-time microbial activity in the AD process while detecting the organic content in the wastewater.

The on-line monitoring of water toxicity through BES-based biosensors will be a breakthrough in wastewater treatment facilities with healthier drinking water supply chains. The biocathodes MFC-biosensor can directly be applied for clean water monitoring (drinking water, reclaimed water). It also has fewer chances of experiencing the combined shock of organic matter load and toxicity. A deeper understanding of the mass-transfer phenomenon, which alter post biofilm formation, is required; as active electroactive biofilm on anode electrode may potentially plays, a key role in designing of BES-based biosensor with enhanced sensitivity for a wide range of compounds and better detection limits. In addition to this, the interferences in output signals during simultaneous detection of BOD and toxic elements are still prevalent, which needs to be addressed in the future by utilizing the sensing abilities of biocathode with different redox potential, rather than using bioanode system. The integration of microfluidic technology in BES based biosensors facilitate high fabrication throughput and ease of scaling-up by configuring miniature, portable and low-cost systems (84). The practicality of the application of BES-based biosensors can be enhanced further to fit for real-time applications by accurately modifying the selectivity and amalgamating the specific receptor proteins of toxins and the extracellular electron mediators like flavins (85). However, more effort is needed to enhance the early warning process of BES-based biosensors by replacing the existing signal-to-noise detection systems with updated data-driven estimation models (artificial neural network and fuzzy) and relevant detection algorithms (86). Tackling the discussed challenges and technological issues in BES-based biosensing technology paves the systems to touch the industrial markets in the nearby future only for real-time monitoring/detection of pollutants and toxic compounds of wastewater streams.

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