

Chemical And Biosensor Technologies For Wastewater Quality Management

Nor Arymaswati Abdullah, Saliza Ramli, Nor Hana Mamat, Samia Khan, Chandima Gomes

Department of Electrical Engineering, Faculty of Engineering,
Universiti Putra Malaysia, Serdang, 43400, Selangor, Malaysia

Department of Computer and Communications Engineering,
Universiti Putra Malaysia, Serdang, 43400, Selangor, Malaysia
chandima@upm.edu.my

Abstract: Chemical-sensor and bio-sensor technologies commonly used for quality management of wastewater have been critically reviewed. The applications of electrochemical, opto-chemical, piezoelectric, acoustic wave, Biochemical Oxygen Demand (BOD), amperometric BOD, bio-enzymatic, bio-acetylcholinesterase and bio-optical algal sensors are detailed. The effectiveness of sensor measurement in terms of accuracy, selectivity, overall cost, and practicality are the main attributes for appropriate selection of sensor technologies in wastewater quality management. This study provides up-to-date information for researchers who look forward to developing better improved and improvised sensors for the future.

Keywords: Wastewater, quality management, chemical sensor, biosensor, electrochemical, opto-chemical

1. Introduction

Wastewater reuse especially from municipal wastewater has become a viable alternative to solving the lack of fresh water sources for various applications. The reclamation and reuse of wastewater are now recognized as an integrated part of the conservation of water resources, especially, in water-scarce countries as reclaimed water can substitute the valuable natural water resources [1],[2]. The use of wastewater after proper treatment process gives rise to the need for adequate monitoring of the water quality. Before the reclaimed water can be used for various applications, its quality should satisfy the standard regulations, where the removal of hazardous pollutants is an essential and critical requirement. The need for continuous wastewater quality management has encouraged the development of various monitoring techniques to measure the level of contamination before, during and after the appropriate treatment the public sewage processes. As reported by Azman et al [3], the public sewage contributes the highest percentage of total sewage in Malaysia as it is shown in Fig. 1. Besides public sewage, other major contributions to sewage are the individual septic tanks, pour flush and regional plants which collectively contribute to 56.4% of the total discharge. The contaminants in wastewater from sewage are removed by many methods including physical, chemical and biological process. Typically, the chemicals and contaminants in wastewater come from industrial processes, for instance, pharmaceutical, textile, fuel, pesticide, plastic, and agrochemical which may harmful to the environment due to the presence of poisonous chemical components in these discharges. Such detrimental constituents in the effluents are heavy metals, radionuclides, petroleum by-products and chemical compounds etc. [4]. Not only environment, even living beings are exposed to the toxic intake. Therefore, the development of sensors for the detection of wastewater constituents has attracted many scientists in the last decade. Chemical sensors play a major role among such sensor technologies.

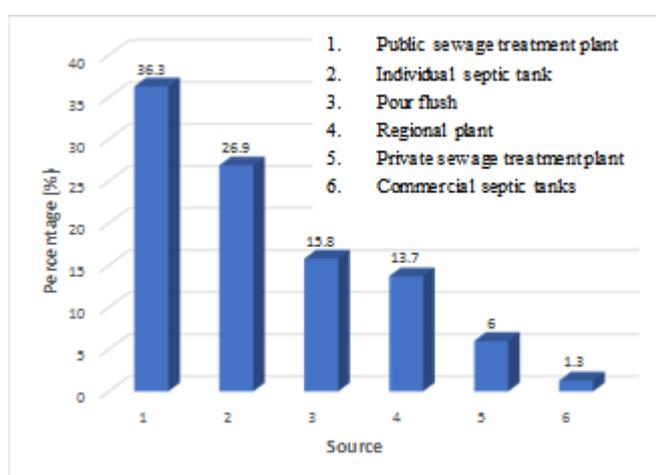


Figure 1: Percentage of sewage sources in Malaysia
(Statistics extracted from [5])

The challenges are not only in detecting and determining the contaminants but also in easy fabrication, user-friendliness, low cost and most importantly the sensing effectiveness of the sensor. Thus, numerous researchers have investigated chemical sensors; optical chemical sensors [6]–[8], electrochemical sensor [4], [9]–[11], online measurement sensor [12], acoustic sensor [13] and many other types. Biosensors are also important for successful wastewater quality management, especially in biological wastewater treatment processes, where the influent quality is vulnerable to the toxicants that present. This is due to the fact that this treatment process relies on biological entities for degradation of organic materials and nutrient removals [14]. Influent toxicity can adversely affect the biological treatment plant; thus, an appropriate and effective bio-sensing method is needed. This is also crucial to prevent harmful effects to the environment and human health due to a biological organism. During the last few years, a number of technologies have been developed in chemical and biosensor fields of which many could be applicable in wastewater quality management. However due to the rapid development of the field created a sizable vacuum of critical review on the pros

and cons of the techniques. Although there are few reviews that address some specific cases of chemical processes on wastewater treatment [15]–[17], critical information focused on sensor technologies is scarce. Such information is vital in further improving and improvising better techniques. This paper fills this existing void in the knowledge gap.

1. Chemical Sensors

A chemical sensor is an essential element of an analyzer-device that converts chemical reaction into the analytically viable signal. The device that transforms analytical variation into the signal is called a transducer. The transducer is a critical part of an automated system, working by sampling, sample transportation, signal processing and data processing [18]. As an example, the steam boiler or bioreactor transform chemical energy of the fuel (such as gas, oil or coal) or organic matters into the mechanical energy. This energy performs the movement of the turbine to generate electrical energy [19]–[21]. The chemical sensor may be divided into different categories based on the principle of the transducer. They are described below.

1.1 Electrochemical sensors

Electrochemical devices convert the effect of the electrochemical interaction at analyte-electrode into an electrical signal. Among all sensors the Clark type sensor is widely used since it was introduced by Clark, 1959 and Kanwisher, 1959 in order to determine COD. The electrochemical sensors using various types of electrodes evolved in order to meet the optimum performance, in the recent years. Electrode-surface grinding, which was investigated in several studies, shows that the system measurement is rapid and practical to detect COD in water quality management but the clogging flow limits the sensor detection efficiency [22]. However, similar detection objectives in nanocomposite-derived sensors, based on different inorganic electrocatalysts, only CuO/ AgO based agents show good correlation with sensor responses [23]. In contradiction to COD, wastewater also comprises toxic gases like sulphide gas, methane gas, carbon dioxide and in-sewer gases that may lead to pollution of the environment, high maintenance cost and safety issue. Both methane gas and carbon dioxide may lead to climate change and sulphide gas may give rise to a corrosive and poisonous atmosphere. In recent years, gases such as nitrous oxide and hydrogen sulphide have been investigated through Clark type nitrous oxide microelectrodes and RAE 032- 0102-000 sensor elements [24],[25]. Besides lower gas flows, the microelectrodes could be able to determine nitrous oxide in low-range from the gas stream. It does not be influenced by humidity and pressure. Electrochemical methods have successfully been applied in detecting heavy elements such as lead and cadmium ions, cyanide ions and chlorophenols. Investigations have been carried out with the type of electrodes including bulk modified electrode with graphitic carbon particles, carbon electrode with immobilized silver hexacyanoferrate nanoparticles and nanocomposite of CTAB and ZnSe QD [26]–[28]. The implication of these studies demonstrates a wide range of impacts including clean and green, toxic free, easy to prepare (even in big amounts), stable, with lower detection boundary, highly sensitive method compared to other modified carbon nano-electrode sensors and conventional sensors. In the recent years, nickel-based materials have been studied in the emergence of

electrochemical sensors in wastewater treatment analysis. However, many of these p-type semiconductor electrochemical sensors show results with low accuracy in electro-catalytic performance because of the low electric conductivity of Ni (OH)₂ [29].

1.2 Optical chemical sensors

Optodes and optical sensors are the same devices in chemical sensor range where chemical reactions and spectroscopic measurements are incorporated. This sensor has small selectivity in sensing and identifying the analytes, which is done via emission or absorbance of different wavelengths in the visible spectrum. Normally, in order to increase the selectivity of sensing, a chemical selective film/membrane is inserted [30],[31]. Numerous studies have attempted to adopt optical sensors in monitoring wastewater treatment which covers the use of membrane-based 4-hydroxy salophen on tri-acetyl cellulose membrane to identify the Cd (II) [32]. This technique produces yellow colour from colourless membrane but the sensitivity is lower even though the response time is shorter compared with that of previous optical sensors. Cr(VI) is determined by conjoining with Aliquot 336 and ortho- nitrophenyl octyl ether as a plasticizer. This simple preparation needs an additional cost [30]. The same sensor is also used for the determination of Cu(II) in wastewater where fibre optics together with planar glass chip of top plate PDMS in micro flow system is employed in the process [33]. Besides above techniques, optical-chemical sensors have been developed by means of optical fluoresce. Such sensors are considered to have simplicity in fabrication and signal processing. Most importantly they are highly cost effective. Several experimental investigations have been conducted to explore Fe (III), Hg (II) and zinc ions in wastewater treatment using optical fluorescent sensors [34–36]. In past two years, the emergence of the optical sensor in wastewater quality management has been improved and improvised in many ways; increased selectivity with fewer interferences, workability at room temperature and broader linear span with high precision. This optical sensor, which is based on a tri-acetyl cellulose membrane using immobilization of 6-Bromo-3-(2-methyl-2,3-dihydrobenzo[d]thiazol-2-yl)-2H-chromen-2, one can identify the amount of copper (II) under the range of 7×10^{-7} M to 1.0×10^{-4} M [6]. Besides that, copper could also be detected via PCTS optical sensor in DMSO solution [7]. To measure pH in wastewater, the immobilization of Giemsa could be employed, which indicates good dynamic pH range detection and is stable up to six months of storage in water [8]. In a recent investigation, the optode has been fabricated into indication solution by coating tri-acetyl cellulose membrane deeply to detect the amounts of Praseodymium ions [37].

1.3 Other chemical sensors

Another type of chemical sensor utilized in wastewater treatment is the mass sensitive device which uses piezoelectric and acoustic wave techniques. The ability of the device to generate ultrasound infiltration makes piezoelectric membrane to reduce the fouling rate via the rising flux. The past studies show that the PDVF membrane is polled while filtration process is done by fluctuating the voltage. However, a recent study shows that by acting as water filtration membrane, a piezoelectric ceramic disk is capable to lessen the fouling [38]. Moreover, piezoelectric

could degrade acid orange 7 dye in wastewater when it acts as mechano-catalyzer when it is synthesized hydrothermally [39]. Methylene blue in wastewater is reduced while coupling effect of FeS/ZnO with piezo-phototronic/photocatalytic is taking place. Integrated with solar energy, this method produces a high efficiency of photocatalytic and small recombination ratio [40]. As mention above, an acoustic device is also utilized in wastewater treatment such as ADCP by wave profiling and dilution estimation from temperature as well as salinity. The technique detects pattern characteristics of wastewater plume dispersion. Current studies show a complicated pattern of plume dilution [41] which needs further improvement for increasing the detection accuracy. Studies are also underway to use monochromatic ultrasonic waves to have better sensor qualities. Such ultrasonic waves could be used for remote measurements where the reflection of the wave provides information on the water quality [42]. It has also been reported that different component of eosin Y (EY), methylene blue (MB) and phenol red (PR) may give different selectivity degree by applying ultrasonic in the methodology for dyes removal in wastewater [43]. The unique magnetic and mechanical properties of magnetic composite materials make such materials a reliable sensor in many applications including wastewater treatment. The research on these materials attracted many researchers and last two years. The available research outputs show that the materials possess good strain sensitivity. These materials could be augmented with reinforced polyester polymer and magnetite Fe₃O₄ micro- and nanoparticles. The improved device could evaluate the effect of Fe₃O₄ particles using glass transition temperature as shown in DMTA [44]. The improvement of the structural characteristics of the materials has been shown through the composition of MAG nanoparticle, carbon nanotubes and graphene oxide which produce new hybrid properties [45]. As discussed above, in the past decade there are many chemical sensors that have been investigated and applied in wastewater treatment. The studies have shown the emergence of these sensors and transforming into better quality in order to make sure that wastewater dispersion from various industries makes no harm to the environment. The types of chemical sensor technologies in wastewater quality management are summarized in Table 1-3.

2. Biological Sensors (Biosensors)

Over the past decades, biosensors have been established as the standard technique over the conventional analytical methods for quality-detection in wastewater management, especially for measuring the Biochemical Oxygen Demand (BOD). Biosensors work as a sensor that concedes the measurement and interpretation of the biological response and reforms it to an electrical signal.

Table 1: Types of electrochemical sensors used in wastewater quality management

Types of sensor material	Parameters	Additional information	Ref
Electrode-surface grinding	COD	Clogging flow	[46]
Nanocomposite-derived	COD	Not all inorganic give good response	[23]
Clark type nitrous oxide microelectrodes	Nitrous oxide	Lower gas flows, low-range N ₂ O	[24]
RAE 032- 0102-000 electrochemical sensor element	Hydrogen sulfide		[25]
Bulk modified electrode with graphitic carbon particles	Lead and cadmium ions	Toxic-free	[26]
Carbon electrode with immobilized silver hexacyanoferrate nanoparticles	Cyanide ions	Lower detection limit	[27]
Nanocomposite of CTAB and ZnSe QD	Chlorophenols	Sensitive reading	[28]
Nickel-based materials	Phosphate	Poor electric conductivity	[29]

Table 2: Types of optical sensors used in wastewater quality management

Types of sensor material	Parameters	Additional information	Ref
Containing Aliquat 336	Cr(VI)	Low cost and easy technique	[30]
4-hydroxy salophen cellulose membrane	Cd(II) Ions	Lower time response but not sensitivity (less than 5µg/L)	[32]
PDMS with fibre optic	Cu(II)	Minimum sample and reagent utilization	[33]
Optical fluorescent	Hg(II), Fe (III), zinc ion	Simplicity and low-cost techniques	[26][35][36]
Triacetylcellulose membrane	Cu(II)	Range of [7e-7,1e-4]M and long lifetime	[6]
Phthalocyaninetetrasulfonic	Cu(II)	In DMSO solution	[7]
Triacetylcellulose membrane	pH	Range of [3.0,12.0] and stable up to 6 months	[8]
Triacetylcellulose membrane	Praseodymium ions	Mesoporous SBA-15paste	[37]

Table 3: Types of others chemical sensors used in wastewater quality management

Types of sensor	Parameters	Additional information	Ref
Piezoelectrc ceramic	Flux	de-fouling functionality	[38]
Piezoelectric fiber	Acid orange 7 dye	Piezoelectric Pb(Zr0.52Ti0.48)O3 fibers	[39]
Piezo-phototronic	Methylene blue	coupling effect FeS/ZnO, use solar energy alternatively	[40]
Ultrasonics	Methylene blue, phenol red, eosin y, dyes	Components selectivity are different toward one dye	[43]
Monochromatic ultrasonic	Water surface position	Remote measurement	[42]
ADCP	Temperature and salinity	Limited response due complicated patterns	[41]
Magnetite Fe3O4	Temperature transition	Compose with Polyester polymer	[44]
Magnetic nanocarbon hybrids	Temperature decay	Compose with graphene oxide	[45]

Biosensors have many advantages over the conventional method such as it could be turned into a portable sensor, on-site operability and ability to be miniaturized [47]. Additionally, for direct monitoring and management of environmental pollutants, biosensors have clear and incisive advantages in comparison with the standard analytical methods since the system is uncomplicated, fast and scrupulous. It is characterised with low maintenance, and rapid monitoring of water treatment [48]. A summary of the biosensors is given in Table 4.

Table 4: Summary of biosensors

Type of Biosensor	Parameter Detection	Applications
BOD ₅	BOD	Sewage disposal
Microbial BOD	BOD	Fermentation industry
Microbial using Bacillus licheniformis BOD	BOD	Saline water, Seawater, Starch wastewater
Microbial using Geobacter -dominated biofilm BOD	BOD	Dairy effluent, Beverage industry effluent
Microbial Fuel Cell	BOD, COD, pH, output load, temperature, Organic concentration	Rubber latex industry, food processing wastewater, corn stove, swine wastewater and sanitary waste
Amperometric	BOD	Wastewater treatment plants
Urease	Chromium Ion	Industry effluent, heavy metal detection
Tyrosinase	Phenolic content, COD	Olive oil wastewater
Cynadiedihydratases	Cyanide Ion, BOD	coal gasification, metal plating, gold and silver leaching, coal coking, synthetic fibres, pharmaceuticals, agrochemicals, plastic
Acetylcholinesterase	Concentration of Paraxon, organophosphate pesticides	pharmaceutical, bioanalytical, food processing industry and environmental control
Alkaline Phosphatase	Concentration of toxic chemical,	Heavy metal detection

Anaerobic Granule	pH, temperature Concentration of Copper Ion and phenol content	Activated sludge
-------------------	---	------------------

2.1 BOD Sensors

BOD is a typical parameter that has been measured in monitoring wastewater systems. It can be characterized as the quantity of dissolved oxygen in milligrams per litre, needed by the microorganism to break down the degradable organic carbonaceous that exist in the water through their bioprocess or biochemical under the reaction situation [49].

2.1.1 BOD₅ Sensors

BOD₅ test also called as the traditional 5-day test is a method to observe the anaerobic process for high BOD levels. This method was first proposed by Royal Commission on Sewage Disposal. BOD will be determined by using the manometric method by measuring the oxygen consumption due only to carbonaceous oxidation [14],[50]. However, researchers have consistently shown that there are few disadvantages of BOD₅ with respect to the time consumption that makes it unsuitable for real-time monitoring and process control. Apart from the requirement of 5-day incubation, to get reproducible results, the technique demands an operator with good experience and technical skills [47],[50]-[52].

2.1.2 Microbial BOD Sensors

Several studies have reported that online BOD can be determined using microbial sensors by immobilizing the microbial-based on respirographic methods. These methods are widely used for pollutant monitoring of nitrifying populations [53],[54]. The established biosensor was invented by incapacitating the microbial consortium on cellulose acetate (CA) membrane closeness to an electrode probe. Various cell biomass concentrations could be used by immobilizing it in order to obtain the optimum response time [14],[51]. A pilot study using Microbial BOD has investigated the potential of Trichosporoncutaneum on the oxygen electrode which paves the way to the development of the first biosensor [55]. Many other studies have investigated the potential of immobilized Pseudomonas putida bacterium membrane to observe the fluorescence signal [14][50]. Microbial BOD Sensors have been used widely in the fermentation industry effluent to harvest the microbial consortium. Besides that, it can be applied in real-time operations and reliable controls in an activated sludge treatment plant. This biosensor offers a better performance in determining the BOD value than the conventional method and BOD₅ method. [56],[57].

2.1.3 Microbial using Bacillus licheniformis BOD Sensors

The microbial BOD biosensor has been fabricated using the Bacillus licheniformis that was immobilized based on the Clark oxygen electrode confined from starch, wastewater, and mild saline water. Researchers have found that it can be utilized for observing the low concentration BOD in seawater [51]. This sensor provides a reliable, perfectly linear, fast and sustainable response. It may work in high saline environments and an efficient method for observing the seawater BOD [50],[51].

2.1.4 Microbial using Geobacter-dominated biofilm BOD sensor

Several studies have given rise to the development of microbial BOD biosensor using Geobacter-dominated biofilm that considers ethanol for biofilms that would be useful in monitoring the quality of dairy effluents and beverage industry effluents [58]. The high organic content of processed milk produces about 0.2 -10 litres of effluent per litre of product. Blooms of toxin-producing microbes have been caused by microbial growth stimulation in the dairy effluents due to the excessive organic content [58]. An ethanol-selected exo-electrogenic biofilm will be allowed when the biosensor operates with an external voltage. The current will be generated without limit by reduced oxygen that reacts at the cathode or the system internal resistance. The biosensor will have wide substrate utilization due to the existence of Geobacter and capable to maintain complex medium and fast response. However, some improvements need to be done to increase the sensitivity of the response.

2.1.5 Microbial Fuel Cell Biosensor

Although the BOD₅ method has been commonly used in the field, there is an increasing concern that some of the BOD₅ are being disadvantageous due to their inability to use in process control and online monitoring [53]. Thus, an anaerobic process treatment for high BOD levels in wastewaters, such as that from factory and rubber latex industry, has been developed by a cell-based biosensor which utilizes immobilized mixed culture of microorganisms and converts it into a transducer using an oxygen electrode and sensing element. This biosensor offers a requisite treatment in avoiding the discharge of deleterious wastes by rubber latex industry that produces a large amount of wastewater, consisting suspended solids and high absorption of organic matter [50],[53]. This biosensor that is also called a microbial fuel cell (MFC) has extensively been studied as another BOD detection method for the process control. It has been considered as a biosensor since it offers benefits like wide measurement range, very fast response, high sustainability, and productivity. This sensor is a bioreactor that transforms chemical energy through a chemical process of microorganisms in organic composition to electrical energy. The main advantages of this sensor are its capability of giving results and conclusions relatively fast, broad linear limit, reusability and sustainability [47],[59]. A BOD sensor on activated sludge has been identified as a good solution for wastewater monitoring, in several studies, due to the simplicity of oxygen electrode and low-cost. Several recent developments in wastewater management sector have checked the possibilities to utilize this BOD sensor in combination with an oxygen electrode, to monitor mixed culture in factory treatment ponds, especially the wastewater from concentrated latex process and an anaerobic treatment process. Apart from BOD measurement, the sensor could also determine Chemical Oxygen Demand (COD), total dissolved solids, pH, organic concentration, output load and temperature [20]. Despite the availability of SCMFC and 2CMFC, the air-cathode MFC offers significant advantages over the two-chamber systems since it has a compact biosensor and a low-cost of operation. It also offers added advantages as there is no aeration, recycling, and nonchemical regeneration of catalytic needed. It also provides good oxygen supply to the cathode as the limit of BOD concentrations can be extended [20]. Several other

researchers have also identified the benefits of MFC biosensor which it can help in breaking down the organic matter in wastewater treatment facilities since major solutions are presented to offer another mode of electricity production. MFC offers an alternative potential for in situ process monitoring and control, and it can be used as a sensor for pollutant analysis other than aforementioned applications. Since it contains microbes that are capable of removing the sulphides and have great operational stability, it is able to biodegrade a variety of organics and can be applied in many biomass sources such as food processing wastewater, corn stover, swine wastewater and sanitary wastes [20]. By using a suitable energy harvesting technique, MFC could generate the required voltage to provide a wireless sensor network that can observe parameters such as pH value in monitoring the environment without the having any impact of the observation process on the subject (environment in this case). The activity of micro-organism in the community of microbial and the conductivity of the substrate would be changed by the temperature variation, thus, the temperature sensor detects the flow of bacteria and nutrients in the wastewater. [20].

2.2 Amperometric BOD sensor

Although BOD sensors such as BOD₅ have the time-consuming issue in monitoring wastewater quality, it would still be applicable in regular monitoring processes. An amperometric biosensor has been introduced to reduce the time factor where its response time could be around 90 minutes. It has been widely used many publicly owned wastewater treatment plants, due to its low cost, good reproducibility, and repeatability [60]. The response time of the sensors has further been optimized in the recent years by incorporating it with a computer-aided processing system. Popularly used in beverage industry wastewater management these days, the BOD sensor will measure the BOD load using steady state method where it could facilitate instant monitoring [61].

2.3 Enzymatic Biosensor

2.3.1 Urease Based Biosensor

Several studies show that observation of chromium ions in heavy metals that are discharged by industrial effluents is tedious, due to considerable time consumption and high cost. It has been found that soil contamination caused by heavy metals could be determined by a new type biosensor, which uses altered sol-gel immobilization method. In this method, a non-woven cellulose swab was immobilized to form *Dolichosuniflorus* and Crude urease. These were in turn utilized for the analysis of water pollutant since it is less selective [62]. The biosensor works based on the activity level of urease and concentration of urea using a spectrophotometric method which can present good reproducibility and storage sustainability, small size, high sensitive and low power consumption. However, since it used interdigitated gold electrode, the cost of this sensor is relatively high [48],[62].

2.3.2 Tyrosinase enzyme Biosensor

For the last decade, several researchers have been focusing on abatement of olive oil wastewater pollutants due to the oil industry as the environmental laws in Europe become tighter. Tyrosinase enzyme Biosensor has been developed in olive

mill wastewater to evaluate the utilization of hydrogen peroxide as well as titanium dioxide in observing the photocatalytic treatment. The biosensor consists of various kinds of heterogeneous membranes that are attached with catalyst and it can determine the total phenolic content. The advantages of the biosensor are high sustainability, high detection performance, low cost and fast COD determination [63].

2.3.3 Cynadiedihydratases (CynD) enzyme Biosensor

Various industrial activities such as coal gasification, metal plating, gold and silver leaching, coal coking can release cyanide compounds into the wastes which can cause serious health hazard in human beings and degradation in ecosystems. Additionally, the production of synthetic fibres, pharmaceuticals, agrochemicals, and plastic also can cause damage to the ecosystems. Some research has been conducted on the utilization of enzymes to reduce the environmental pollution caused by cyanide compounds by breaking down the cyanide microbial. Many biosensors offer low toxicity since their specific activities do not need any cofactors, however, these methods may require regular replacement of enzyme [64].

2.4 Acetylcholinesterase (AChE) biosensor

Solvent tolerance of enzymes is crucial for maintaining their functional operability in various applications such as pharmaceutical and bioanalytical industry, food processing industry and environmental control. However, inactivation of the enzymes could be caused by organic solvents with high concentrations, particularly water miscible. Even stable enzymes depend on the hydrophilicity of the solvent. There are several organic phase enzyme electrode (OPPE) biosensors that have been developing in the recent years, which are less sensitive and stable in non-aqueous media. Hydrogels and organogels are used in the OPPE to protect the enzyme from the organic solvent. Consequently, immobilized AChE biosensor has been developed to detect the effect of hydrophilic biocompatible polymer and chitosan as it shows significantly low solvent tolerance [65,66]. The main advantage of AChE Biosensors is the enzyme stability which can be further improved to protect it from the damaging effects of solvents since it can retain water essential layer. This method could detect the paraoxon in the nM concentration and other organophosphate pesticides.

2.5 Optical Algal Biosensor using Alkaline Phosphatase Enzyme

Some heavy metal detection methods based on existing sophisticated techniques such as ionic chromatography, mass spectrometry, and polarography are unsuitable for continuous observation. Therefore, enzyme sensors have been focused in order to provide easy and low-cost biosensor-technology for controlling the environment. Alkaline phosphatase has been tried to detect heavy metals as it is attached to the cell membrane exterior and is easily accessible to pollutants [67]. With that, the consequence of long-term activity loss can be reduced and it offers a reliable and fast response time. However, the inhibitor detection limit need to be improved as an optimal enzyme concentration is required in the biosensor. An algal biosensor optical fibre also has been proposed to determine the herbicides and quantify the toxic chemical concentration based on chlorophyll-a fluorescence kinetic measurements in

immobilized *Chlorella Vulgaris* cell. The temperature and pH also can be measured by the biosensor and it is very practical for the toxic substance recognition such as alachlor and glyphosate which affects the photosynthesis. These biosensors are easy to handle, low-cost, maintenance-free and highly stable [67],[68].

2.6 Anaerobic Granule (AGB) Biosensor

There is a new biosensor which has been developed based on anaerobic granules for quick online detection device to limit the toxic to the biological process in activated sludge by measuring the concentration of Copper Ion and phenol content. The AGB biosensor would be another way to overcome the drawbacks of current biosensors, by offering simple construction, high sensitivity, stability, easy replication, rapid response and low cost. This new biosensor also can be applied in actual working conditions and a broad range of environmental stresses [69].

3. Needs for the future

One of the foremost challenges of wastewater management is the diverse nature of contaminants of wastewater based on the origin and collection/flowing atmosphere. Different industries contribute different constituents to the wastewater. A general guide to the substances that could be found in various industry-related wastewater is tabulated in Table-5. Note that apart from the industries and domestic sources, it is gravely envisaged that agro-fields contribute many toxic compounds into both groundwater and wastewater, due to the heavy usage of insecticides, pesticides, herbicides and chemical fertilizers [70],[71]. Such toxicities may be added into the wastewater during its storage and flowing process, via running rainwater [72]. The quality control also depends on the mode of final discharge or usage. If the wastewater is purified for reusing purposes much stricter monitoring techniques should be applied than that in the case of wastewater being discharged to large freshwater masses or sea. The highest attention is required when the recycled water is used for potable purposes. The above complexity of wastewater quality management demands multi-constituent detectable sensors for the future. At present, a large number of chemical and biosensors are needed to cover the wide spectrum of wastewater environments. Thus, the future developments may focus on integrated compact sensors that can detect, analyze and monitor any given wastewater system. Improvements are also required with respect to the response and decision-making time intervals. Especially in the case of wastewater management for re-cycling, immediate actions may be taken for emergency cases such as drastic increment in toxic contamination (such as cyanide concentration). Such cases demand high accuracy and highly sensitive sensor/signal transmission system that can send warning information within a reasonable time frame. Thus, the current sensor technology may be integrated with artificial intelligence to upgrade the total system to a robotic structure.

Table-5 Sources of wastewater contaminants

Wastewater constituent	Pollutant sources
Metals (chromium, nickel, zinc, cadmium, iron and titanium compounds)	Iron and steel, other metal industries, electroplating, vehicle repair, textile and leather, petrochemical, mining, ore-processing, coal power, building material,
Metals (lead and mercury)	Iron and steel, pulp and paper, Organic chemicals, agro-supplements, Aircraft plating and finishing, Petrochemical refining, microelectronic
Metals (Silver)	Silver ore processing, photo processing, silver-compound manufacturing plants, jewellery manufacturing, microelectronic and printed circuit board
Biodegradable organic materials	Iron and steel, textile and leather, pulp and paper, petrochemical, agro-supplements and agro-products, prawn farms, dairies, breweries, sweet industry
Odour emitters (Acrolein, amines, mercaptans, dibutyl sulphide, H ₂ S, SO ₂)	Cement factories, lime kilns, pulp and paper, pharmaceutical industries, food processing, fisheries, rubber, textile and leather, paper and pulp, fertilizer, livestock
Non-metallic solids	Textile and leather, paper and pulp, agro-supplements, building material, food processing, domestic and municipal wastes, hotel industry, dairies, breweries, sweet industry
Cyanide	Iron and steel, other metal industries, food processing, agro-supplements, chemical
Phenols, sulphates, Chlorinated organic compounds and acids	Iron and steel, petrochemical, textile and leather, microelectronics, mining, coal power, water purification, prawn farms, soap and detergent manufacturing, laundries
Inks and dyes	Textile and leather, ceramic, vehicle repairing, paint, food processing, printing, soap and detergent manufacturing
Mineral oils	Petrochemical, iron and steel, other metal processing industries, power system component manufacturing
Bio-oils	Domestic, food processing, oil industry, hotel industry, soap and detergent manufacturing
Infectious microbial	Food processing and meat industry, healthcare waste disposal, hotel industry, domestic and municipal wastes, animal husbandry and livestock

4. Conclusion

Development of sensor technologies for use in the management of wastewater quality has been motivated by the challenges to obtaining fast and accurate detection of contaminants that are practical to be applied in wastewater treatment ponds. At the same time, they should be economically viable for installation in significantly large numbers and maintain in the long run. For chemical sensors, the technologies used vary based on the type of ions to be detected and the selectivity and sensitivity. In the biological treatment of wastewater, the process can be adversely affected by influent toxicity itself. An efficient method using an improvised biosensor for wastewater treatment can eliminate this problem and optimize the plant operation.

Acknowledgement:

The Authors would like to thank the Faculty of Engineering, Universiti Putra Malaysia for inter-departmental facilities provided to make this project a success.

REFERENCES

- [1]. Peters, E.J., 2015. Wastewater reuse in the Eastern Caribbean: a case study. Proceedings of the Institution of Civil Engineers-Water Management, 168(5), pp.232–242
- [2]. Pang, Y.-C. et al., 2015. Prevalence of antibiotic-resistant bacteria in a lake for the storage of reclaimed water before and after usage as cooling water. Environ. Sci.: Processes Impacts, 17(6), pp.1182–1189.
- [3]. Mat, E.A.T., Shaari, J., and How, V.K., 2011. Wastewater Production, Treatment, and Use in Malaysia, Sarawak Sewerage Services Department's Inventory of Wastewater Treatment Facility
- [4]. Xiao, Z., Qin, W. and Shi, L., 2016. A electrochemical sensor based on poly (sulfosalicylic acid) film modified electrode and application to phenol detection in oilfield wastewater. International Journal of Smart Home, 10(6), pp.299–308.
- [5]. Mat, E. A. T., Shaari, J. and How, V.K., 2011. Wastewater production, treatment and use in Malaysia. Water Supply and Environmental Sanitation Program Annual Report-2011, Sarawak Sewerage Services Department- Inventory of Wastewater Treatment Facility pp.1–13.
- [6]. Pourbasheer, E. et al., 2015. Design of a novel optical sensor for determination of trace amounts of copper by UV/vis spectrophotometry in the real samples. Journal of Industrial and Engineering Chemistry, 26, pp.370–374.
- [7]. Kumawat, L.K. et al., 2015. A novel optical sensor for copper ions based on phthalocyanine tetrasulfonic acid. Sensors and Actuators, B: Chemical, 212, pp.389–394
- [8]. Khodadoust, S. et al., 2015. Design of an optically stable pH sensor based on immobilization of Giemsa on triacetylcellulose membrane. Materials Science and Engineering C, 57, pp.304–308.
- [9]. Zhou, H. feng et al., 2016. Nitrogen-doped carbon spheres surface modified with in situ synthesized Au nanoparticles as electrochemical selective sensor for simultaneous detection of trace nitrophenol and dihydroxybenzene isomers. Sensors and Actuators, B: Chemical, 237, pp.487–494.
- [10]. Hudari, F.F. et al., 2016. Multi-responses methodology applied in the electroanalytical determination of hair dye by using printed carbon electrode modified with graphene. 28(5), pp.1085–

1092.

- [11]. Bashami, R.M. et al., 2015. The suitability of ZnO film-coated glassy carbon electrode for the sensitive detection of 4-nitrophenol in aqueous medium. *Analytical Methods*, 7(5), pp.1794–1801.
- [12]. Yu, H. et al., 2015. On-line sensor monitoring for chemical contaminant attenuation during UV / H₂ O₂ advanced oxidation process. *Water Research*, 81, pp.250–260.
- [13]. Lee, H.H. et al., 2015. An ultrasonic multi-beam concentration meter with a Neuro-Fuzzy algorithm for water treatment plants. *Sensors (Switzerland)*, 15(10), pp.26961–26977.
- [14]. Xiao, Y. et al., 2015. Toxicity measurement in biological wastewater treatment processes: A review. *Journal of Hazardous Materials*, 286, pp.15–29.
- [15]. Dahiru A. R., Nordin, N. B., Ishak, M. N., Mislan M. S. B., and Gomes, C., 2017. Chemical method for wastewater management: Developments of Fenton process. *International Journal of Advanced Research and Publications*, 1 (3), pp. 33-42.
- [16]. Petrie, B., Barden, R., and Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. *Water Research*, 72(1), pp. 3-27.
- [17]. Sandra, A., Jamil, N.A.M., Jabbar, S., Sakyat, S. and Gomes, C., 2017. Aerobic and Anaerobic Sewage Biodegradable Processes: The Gap Analysis, *International Journal of Research in Environmental Science*, 3 (3), pp. 9-19
- [18]. Hulanicki, A., Glab, S. and Ingman, F., 1991. Chemical sensors: Definitions and classification. *Pure and Applied Chemistry*, 63(9), pp.1247–1250.
- [19]. Chen, P. and Shamma, J.S., 2004. Gain-scheduled 1-optimal control for boiler-turbine dynamics with actuator saturation. 14, pp.263–277.
- [20]. Pietrelli, A. et al., 2016. Electrical characterization of MFC for low power Applications. , 8(1), pp.8–12.
- [21]. Martínez-Huitle, C.A. and Ferro, S., 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chemical Society Reviews*, 35(12), pp.1324–40.
- [22]. Jeong, H., Kim, H., and Jang, T., 2016. Irrigation Water Quality Standards for Indirect Wastewater Reuse in Agriculture: A Contribution toward Sustainable Wastewater Reuse in South Korea, *Water*, 8(4), pp.169-175.
- [23]. Gutiérrez-Capitán, M. et al., 2015. Electrochemical nanocomposite-derived sensor for the analysis of chemical oxygen demand in urban wastewaters. *Analytical Chemistry*, 87(4), pp.2152–2160.
- [24]. Marques, R., Oehmen, A. and Pijuan, M., 2014. Novel microelectrode-based online system for monitoring N₂O gas emissions during wastewater treatment. *Environmental science and technology*, 48(21), pp.12816–12823.
- [25]. Lim, J.S. et al., 2013. SewerSnort: A drifting sensor for in situ Wastewater Collection System gas monitoring. *Ad Hoc Networks*, 11(4), pp.1456–1471
- [26]. Kempegowda, R.G., and Malingappa P., 2012. A binderless, covalently bulk modified electrochemical sensor: application to simultaneous determination of lead and cadmium at trace level, *Anal Chim Acta*, 30,728, pp.9-17.
- [27]. Noroozifar, M., Khorasani-Motlagh, M. and Taheri, A., 2011. Determination of cyanide in wastewaters using modified glassy carbon electrode with immobilized silver hexacyanoferrate nanoparticles on multiwall carbon nanotube. *Journal of Hazardous Materials*, 185(1), pp.255–261.
- [28]. Li, J. et al., 2013. A sensitive electrochemical chlorophenols sensor based on nanocomposite of ZnSe quantum dots and cetyltrimethylammonium bromide. *Analytica Chimica Acta*, 804, pp.76–83.
- [29]. Miao, Y. et al., 2014. Biosensors and bioelectronics electrocatalysis and electroanalysis of nickel , its oxides , hydroxides and oxyhydroxides toward small molecules. *Biosensors and Bioelectronic*, 53, pp.428–439. Miyako, E. et al., 2016. Design, synthesis, characterization and properties of magnetic nanoparticle-nanocarbon hybrids. *Carbon*, 96, pp.49–56.
- [30]. Güell, R. et al., 2007. Development of a selective optical sensor for Cr(VI) monitoring in polluted waters. *Analytica Chimica Acta*, 594(2), pp.162–168.
- [31]. Heineman, W.R. et al., 2012. Spectroelectrochemistry as a strategy for improving selectivity of sensors for security and defense applications. , 8545, p.854509
- [32]. Ensafi, A.A., Meghdadi, S. and Fooladgar, E., 2008. Development of a new selective optical sensor for Cd(II) ions based on 4-hydroxy salophen. *IEEE Sensors Journal*, 8(11), pp.1794–1800.
- [33]. Leelasattarakul, T. et al., 2007. Greener analytical method for the determination of copper(II) in wastewater by micro flow system with optical sensor. *Talanta*, 72(1), pp.126–131.

- [34]. Gunigollahalli K. R. and Malingappa, P., 2012. A binderless, covalently bulk modified electrochemical sensor: Application to simultaneous determination of lead and cadmium at trace level. *Analytica Chimica Acta*, 728, pp.9–17.
- [35]. Zhang, G. et al., 2012. Facile fabrication of a cost-effective, water-soluble, and electrosynthesized poly(9-aminofluorene) fluorescent sensor for the selective and sensitive detection of Fe(III) and inorganic phosphates. *Sensors and Actuators, B: Chemical*, 171–172, pp.786–794.
- [36]. Hosseini, M. et al., 2010. Fluorescence “turn-on” chemosensor for the selective detection of zinc ion based on Schiff-base derivative. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 75(3), pp.978–982.
- [37]. Dashtian, K. and Zare-Dorabei, R., 2017. Preparation and characterization of a novel optical chemical sensor for determination of trace amounts of Praseodymium ion by UV/Vis spectrophotometry. *Sensors and Actuators B: Chemical*, 242, pp.586–594
- [38]. Krinks, J.K. et al., 2015. Piezoceramic membrane with built-in ultrasonic defouling. *Journal of Membrane Science*, 494, pp.130–135.
- [39]. Lin, H. et al., 2014. Piezoelectrically induced mechano-catalytic effect for degradation of dye wastewater through vibrating Pb(Zr_{0.52}Ti_{0.48})O₃ fibers. *Applied Physics Letters*, 104(16), pp.1–5.
- [40]. Guo, X. et al., 2016. High-efficiency sono-solar-induced degradation of organic dye by the piezophototronic/photocatalytic coupling effect of FeS/ZnO nanoarrays. *Nanotechnology*, 27(37), pp.375704–375714.
- [41]. Lucas, A.J. and Kudela, R.M., 2015. The fine-scale vertical variability of a wastewater plume in shallow, stratified coastal waters. *Estuarine, Coastal and Shelf Science*, pp.1–15
- [42]. Nichols, A. et al., 2013. A non-invasive airborne wave monitor. *Flow Measurement and Instrumentation*, 34, pp.118–126.
- [43]. Dashamiri, S. et al., 2017. Multi-response optimization of ultrasound assisted competitive adsorption of dyes onto Cu (OH)₂-nanoparticle loaded activated carbon: Central composite design. *Ultrasonics Sonochemistry*, 34, pp.343–353.
- [44]. Dragatogiannis, D.A. et al., 2016. Effect of magnetite particle loading on mechanical and strain sensing properties of polyester composites. *Meccanica*, 51(3), pp.693–705.
- [45]. Miyako, E., Pichon, B. P., Ménard-Moyon, C., Vacchi, I. A., Lefèvre, C., Bégin-Colin, S., and Bianco A., 2016. Design, synthesis, characterization and properties of magnetic nanoparticle–nanocarbon hybrids, *Carbon*, 96, pp.49-56.
- [46]. Geun Jeong, B. et al., 2007. Performance of an electrochemical COD (chemical oxygen demand) sensor with an electrode-surface grinding unit. *Journal of environmental monitoring: JEM*, 9(12), pp.1352–1357.
- [47]. Di, M. et al., 2009. A single-chamber microbial fuel cell as a biosensor for wastewaters. *Water Research*, 43(13), pp.3145–3154.
- [48]. Nepomuscene, N.J., Daniel, D. and Krastanov, A., 2007. Biosensor to detect chromium in wastewater. *Biotechnology and Biotechnological Equipment*, 21(3), pp.377–381.
- [49]. Al-Dasoqi, N. et al., 2011. Use of Sensors in Wastewater Quality Monitoring—A Review of Available Technologies. *World Environmental and Water Resources Congress 2011*, pp.3379–3388.
- [50]. Velling, S. and Tenno, T., 2009. Chemical different calibration methods of a microbial BOD sensor for analysis of municipal wastewaters. *Sensors and Actuators: B. Chemical*, 141(1), pp.233–238.
- [51]. Jiansheng, C., Xiaohui, W. and Gaizhen, W., 2009. A BOD biosensor using salt-tolerant bacillus licheniformis for sea water. , pp.1–4.
- [52]. Lei, H. and Yi, L., 2009. A novel BOD sensor immobilized active sludge bacteria for rapid determination of biochemical oxygen demand in industrial wastewater. 2009 International Conference on Energy and Environment Technology, pp.382–384
- [53]. Kumlanghan, A. et al., 2008. Microbial BOD sensor for monitoring treatment of wastewater from a rubber latex industry. *Enzyme and Microbial Technology*, 42(6), pp.483–491.
- [54]. Melidis, P., Vaiopoulou, E. and Aivasidis, A., 2008. Development and implementation of microbial sensors for efficient process control in wastewater treatment plants. *Bioprocess and Biosystems Engineering*, 31(3), pp.277–282
- [55]. Hsieh, M.C., and Chung YC., 2014. Measurement of biochemical oxygen demand from different wastewater samples using a mediator-less microbial fuel cell biosensor, *Environ Technol.* 35(17-20), pp.2204-2211.
- [56]. Verma, N. and Singh, A.K., 2013. Development of biological oxygen demand biosensor for monitoring the fermentation industry effluent. *ISRN Biotechnology*, 2013(November 2012), pp.1–6.
- [57]. Woo, M. et al., 2008. Real-time remote monitoring of small-scaled biological wastewater treatment plants by a multivariate statistical process control

and neural network-based software sensors. 43, pp.1107–1113.

- [58]. Commault, A.S. et al., 2016. Geobacter -dominated biofilms used as amperometric BOD sensors. *Biochemical Engineering Journal*, 109, pp.88–95.
- [59]. Du, Z., Li, H. and Gu, T., 2007. A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy. , 25, pp.464–482.
- [60]. Czolkos, I. et al., 2016. Prediction of wastewater quality using amperometric bioelectronic tongues. *Biosensors and Bioelectronic*, 75, pp.375–382.
- [61]. Liu, Y., Song, Q. and Wang, L., 2009. Development and characterization of an amperometric sensor for triclosan detection based on electropolymerized molecularly imprinted polymer. *Microchemical Journal*, 91(2), pp.222–226.
- [62]. Ntihuga, J.N., 2006. Biosensor to detect heavy metals in waste water, Woodhead Publishing Limited.
- [63]. Martini, E., Tomassetti, M. and Campanella, L., 2014. Monitoring photocatalytic treatment of Olive Mill Wastewater (OMW) in batch photoreactor using a tyrosinase biosensor and COD test. , (February 2013), pp.5–7.
- [64]. Martínková, L. et al., 2015. Cyanide hydratases and cyanide dihydratases: emerging tools in the biodegradation and biodetection of cyanide. pp.8875–8882.
- [65]. Warner, J. and Andreescu, S., 2016. An acetylcholinesterase (AChE) biosensor with enhanced solvent resistance based on chitosan for the detection of pesticides. *Talanta*, 146, pp.279–284.
- [66]. Andres, R.T. and Narayanaswamy, R., 1997. Fibre-optic pesticide biosensor based on covalently immobilized acetylcholinesterase and thymol blue. *Talanta*, 44(8), pp.1335–1352.
- [67]. Durrieu, C. and Tran-Minh, C., 2002. Optical algal biosensor using alkaline Phosphatase for determination of heavy metals. *Ecotoxicology and Environmental Safety*, 51(3), pp.206–209.
- [68]. Naessens, M., Leclerc, J.C. and Tran-Minh, C., 2000. Fiber optic biosensor using *Chlorella vulgaris* for determination of toxic compounds. *Ecotoxicology and environmental safety*, 46(2), pp.181–5.
- [69]. Jiang, X., Park, J. and Ellis, T.G., 2014. Use of an Anaerobic Granule Biosensor (AGB) as Upset Early Warning Detection (UEWD) Devices.
- [70]. Mark Steil, 2017. Iowa farmers won water pollution court fight; water still polluted. MPR News.
- [71]. B, P.-F. et al., 2017. Thioarsenate toxicity and tolerance in the model system *arabidopsis thaliana*. *Environmental Science and Technology*, 51(12), pp.7187–7196.
- [72]. Carvalho, F.P., 2017. Pesticides, environment, and food safety. *Food and Energy Security*, 6(2), pp.48–60.