Review

Microfluidics and materials for smart water monitoring: A review

Janire Saez [a, b, **], Raquel Catalan-Carrio [a, c], Róisín M. Owens [b],
Lourdes Basabe-Desmonts [c, d, e, f], Fernando Benito-Lopez [a, e, f, *]

[a] Microfluidics Cluster UPV/EHU, Analytical Microsystems & Materials for Lab-on-a-Chip (AMMa-LOAC), Group, Analytical Chemistry, University of the Basque Country UPV/EHU, Spain
[b] Bioelectronic Systems Technology Group, Department of Chemical Engineering and Biotechnology, Philippa Fawcett Drive, Cambridge, CB3 0AS, UK
[c] Microfluidics Cluster UPV/EHU, BIOMICs Microfluidics Group, Lascaray Research Center, University of the Basque Country UPV/EHU, Vitoria-Gasteiz, Spain
[d] Basque Foundation for Science, IKERBASQUE, Spain
[e] Bioaraba Health Research Institute, Microfluidics Cluster UPV/EHU, Vitoria-Gasteiz, Spain
[f] BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain

HIGHLIGHTS

- Microfluidic devices are reviewed for drinking, sewage, continental and seawater.
- Functional materials became alternatives to conventional valves & sensors in microfluidics.
- Microfluidic systems for water monitoring are reaching commercialization.
- Functional materials and microfluidics improve deployable water systems.

GRAPHICAL ABSTRACT
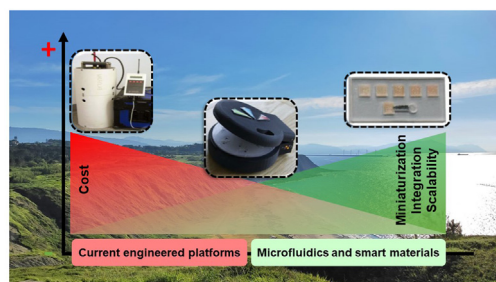
ABSTRACT

Water quality monitoring of drinking, waste, fresh and seawaters is of great importance to ensure safety and wellbeing for humans, fauna and flora. Researchers are developing robust water monitoring microfluidic devices but, the delivery of a cost-effective, commercially available platform has not yet been achieved. Conventional water monitoring is mainly based on laboratory instruments or sophisticated and expensive handheld probes for on-site analysis, both requiring trained personnel and being time-consuming. As an alternative, microfluidics has emerged as a powerful tool with the capacity to replace conventional analytical systems. Nevertheless, microfluidic devices largely use conventional pumps and valves for operation and electronics for sensing, that increment the dimensions and cost of the final platforms, reducing their commercialization perspectives. In this review, we critically analyze the characteristics of conventional microfluidic devices for water monitoring, focusing on different water sources (drinking, waste, fresh and seawaters), and their application in commercial products. Moreover, we introduce the revolutionary concept of using functional materials such as hydrogels, poly(ionic liquid)

---

*Corresponding author. Microfluidics Cluster UPV/EHU, Analytical Microsystems & Materials for Lab-on-a-Chip (AMMa-LOAC), Group, Analytical Chemistry, University of the Basque Country UPV/EHU, Spain.

**Corresponding author. Microfluidics Cluster UPV/EHU, Analytical Microsystems & Materials for Lab-on-a-Chip (AMMa-LOAC), Group, Analytical Chemistry, University of the Basque Country UPV/EHU, Spain.

E-mail addresses: js2409@cam.ac.uk (J. Saez), lourdes.basabe@ehu.eus (L. Basabe-Desmonts), fernando.benito@ehu.eus (F. Benito-Lopez).

hydrogels and ionogels as alternatives to conventional fluidic handling and sensing tools, for water monitoring in microfluidic devices.

Contents

1. Introduction

Water security is recognized as one of the great challenges of the 21st century by many international organizations. For instance, the World's Health Organization (WHO) sets water quality assessment as a top global priority, including safe water supplies for drinking and recreation, hygienic sanitation and good water management for human health [1]. Unfortunately, water pollution and water-related diseases have negative consequences on the body [2] such as diarrhea, which kills around 900,000 people every year in developing countries [1,3,4]. Moreover, environmentally speaking, alterations in the nutrients and oxygen balance can result in eutrophication; the uncontrolled growth of plants or algae in water bodies [5].

Therefore, continuous monitoring of water resources such as fresh water, seawater, and, in particular, wastewater and drinking water, for human and animal consumption, is essential [6]. To do that, physicochemical parameters such as temperature, pH, salinity, oxygen balance, acid neutralizing capacity and nutrient concentrations (nitrates and nitrites, phosphates, ammonium, silicates, sulfates, etc.) need to be monitored and controlled, to guarantee optimal water quality [7]. Traditionally, water samples are collected at the point-of-need, by trained personnel, and transported to specialized analytical laboratories for quality control [8−14]. Advantages of laboratory-based methods include the possibility of analyzing many samples with high accuracy and precision, obtaining low limits of detection (LOD) and quantification (LOQ), with automated equipment. Their main disadvantage is that this equipment is not generally portable, therefore neglecting *in situ* analysis and potentially compromising the stability of samples. Economically speaking, this equipment is expensive and requires trained personnel to prepare and handle the samples. However, this type of technology is evolving continuously, generating more compact, easy to use and cheap equipment which can be operated at conventional laboratory facilities. This is the case of portable kits that allow on-site testing and have become very useful when resources are limited since they are fast, simple and inexpensive. The downside of portable devices is that they require trained personnel during use and do not offer accurate results. They often only provide estimations of the composition of water and as such, do not

fully meet user needs [15]. As an alternative to portable kits, water quality analysis probes have been developed and commercialized. The main advantage of these devices, together with their portability, is their high accuracy. The most advanced versions integrate wireless sensor networks, where data can be collected and delivered through the internet [16]. However, they are not always affordable due to their elevated costs and the need for manual labor during data collection.

The natural evolution of this technology presents a future where humanity will make use of effective, deployable and autonomous sensors in lakes and rivers, water supply systems and even connected to municipal and industrial wastewater treatment plants, for accurate and precise water monitoring at the point-of-need. Furthermore, the information will be made available to citizens through the Internet. In the future, these sensors may also become wearable, and the user able to monitor his/her surrounding water environment.

Despite the huge efforts to develop innovative sensors [17], the current state-of-the-art for autonomous environmental devices to monitor the chemical and biological status of our water resources is based on autonomous flow systems [18] that employ conventional pumps, valves and fluid handling components, and because of this, these systems are usually expensive (often > €20K per unit). Therefore, the goal is to generate autonomous devices that integrate all necessary steps for defined (bio)-chemical analysis such as sampling, sample transport, filtration, dilution, chemical reaction, separation and detection without the need for conventional components. This concept is called micro Total Analysis System (μTAS) [19]. Indeed, a μTAS or a lab-on-a-chip (LOC) has the potential to shrink the technology of an entire laboratory to a chip format. Reviewers stated that LOC and electrochemical sensing-based portable monitoring systems are good alternatives to conventional methods [6] and present the advances of different methodologies within microfluidic-based sensors for water quality monitoring [2]. In particular, two main aspects are rapidly developing and adapting to the new needs of water monitoring:

(1) the engineering of the equipment used for analysis both in lab and in field, that has evolved towards the miniaturization of the device and to the incorporation of more precise

detection technologies for the creation of integrated systems. These systems have experienced the evolution from simple sampling and handling to more complex automated sampling units that allow higher control and a larger number of samples to be analyzed [20]. A major benefactor to this evolution has been microfluidic technology, which permits fast and cheap analysis of samples on-site and with low reagent consumption [21]. This novel formatting saves protocol-time, reduces the risk of sample loss or contamination and reduces costs, by avoiding the use of bulky expensive laboratory instrumentation. Furthermore, microfluidics allows easy operation, full automation, increase throughput and improve repeatability by reducing human errors.

(2) the use of novel functional materials for sensing [22−24], under controlled laboratory conditions, exhibits improved performance compared to conventional sensors. Therefore, these new types of sensors have the potential to upgrade environmental analysis systems.

Despite these exciting developments, there are hardly any examples of these types of systems in real deployment sites. Perhaps, the key to change the current model is to drive down the cost per unit, making autonomous environmental devices available for €500 or even €20. It is essential to be able to develop integrable microfluidic sensors and actuators, fabricated through innovative breakthroughs emerging from fundamental materials science research. They should be fabricated at a reasonable price by using scalable fabrication techniques, compatible with mass production and commercialization, reducing device dimensions without losing any of the advantages of existing technology (Fig. 1) [25].

This review summarises the current state-of-the-art in autonomous microfluidic devices and systems for environmental water monitoring, focusing on different water sources such as drinking water, wastewater, fresh waters (rivers, lakes …) and seawater. Moreover, the review will give a material science perspective, where the integration of functional materials, as an alternative to conventional fluidic handling and sensing features, is fundamental in ensuring device commercialization at an affordable cost.

2. Microfluidic devices for water monitoring

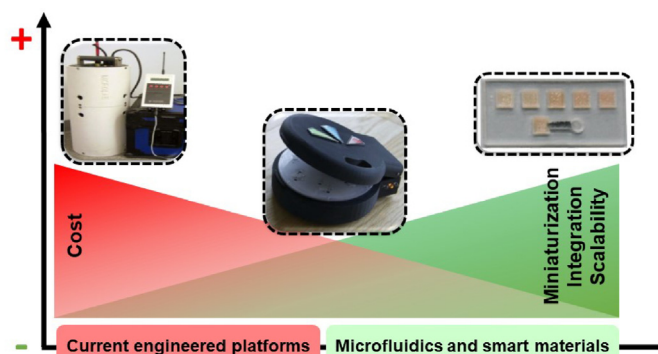Microfluidic devices provide a way to perform analysis in

Fig. 1. Schematic of the strategy used in this review. Pictures in bubbles are developed platforms for water monitoring (left: multianalysis commercial probe; center: a handheld system based on a centrifugal microfluidic device [26]; right: point-of-need microfluidic device [27]. (1) Current platforms are expensive, bulky and difficult to miniaturize and integrate to meet scalability. (2) Truly scalable device development comes through the integration of innovative breakthroughs in materials research and microfluidics.

remote locations, enabling *in situ* analysis at the point-of-need [28]. Reduced measurement times, improvements in sensitivity, enhancement of selectivity and high repeatability are advantages of microfluidic devices when integrated into μTAS [29]. Despite the huge efforts of researchers in providing fully integrated, portable and feasible platforms for environmental sensing, μTAS are hardly used in commercial products. Several examples have reached the market, such as the 2100 Bioanalyzer of Agilent Technologies, micromixers and microreactors from Micronit, and multiflux by Dolomite, but are mainly focused on point-of-care diagnostics [30]. Moreover, to the best of our knowledge, they are not commercial examples of this type of technology used as integrated or standardized analytical processes for water monitoring.

In 2010, Royce W. Murray highlighted that the analytical chemistry community is facing the challenge of developing environmental platforms for water monitoring [31]. Nowadays, these platforms are becoming available through microfluidics but are still struggling with reliability. George Whitesides referred to this issue in 2014 stating that "LOC technology is now shifting from fundamental areas to serious explorations of uses and to demonstrations and applications with real potential to provide the incentive for further and more extensive industrial engineering development, and ultimately to incorporate into products" [32]. Today, this is a reality, as it is now possible to produce microfluidic technology on a large scale. The next step is to merge the knowledge coming from research with the needs of industry, to translate this technology into commercial success [33].

Over the last few years, microfluidic devices and platforms have been delivered for the monitoring of pollutants in a variety of water sources: drinking water, waste and sewage waters, fresh water (rivers, lakes, …), and seawater. Drinking water devices are normally fabricated to detect pathogens and bacteria. In contrast, waste and sewage, fresh water and seawater devices need to be deployable for long periods, under harsh environmental conditions. There are many reviews available that give a wider perspective of microfluidic technology for environmental monitoring [2,18] but none of them summarized the existing technology for different water sources.

In the following sections, the state-of-the-art of deployable microfluidic devices and field-deployable microfluidic systems for *in situ* biological and chemical analysis in different water sources will be reviewed in Table 1. Besides, the general operation; the type of data obtained; the designing factors that determine the effectiveness and the challenges facing their commercialization will be described.

2.1. Drinking water

One of the biggest concerns, which justifies the need of monitoring water quality, is the possible presence of bacteria [36,37], parasites [73,74], or other pollutants [37,38,75−84] that could be harmful to humans, through the consumption of water. Since bacteria, parasites and pathogens are presented in very low numbers in potable water, large volumes of water need to be condensed and to reach the threshold of detection for current detection methods. This is a limitation of the existing technology, therefore multiple methods, including force spectroscopy [85], cytometry [86], laser scattering [73], electrochemical [87] and electrophoresis [17] were adopted by microfluidic technology to overcome the extremely low number of bacteria or pollutants to be analyzed in the sample. Another approach to improve detection is to exploit the intrinsic electrical properties of bacteria by the combination of two electrical techniques such as dielectrophoresis (DEP) and impedance measurements [88]. Their combination with microfluidic devices has the potential of developing accurate, cost-

Table 1
Application of microfluidics for the detection of organisms/pollutants in drinking water, wastewater, fresh water and seawater.

Real sample/matrix	Organism/target pollutant	Microfluidic device/detection technique	Ref
Drinking water/ potable	E. Coli	Poly(methyl) siloxane (PDMS) device. Loop-mediated isothermal amplification (LAMP) detection.	[34]
	Bacteria (E. coli, Salmonella, and Pseudomonas) and viruses (MS-2 and Echovirus)	Gold-deposited glass slide. Electrophoretic transport and electrostatic trapping.	[35]
	E. Coli	PDMS chip. Dielectrophoretic focusing and impedance.	[36]
	Lindane	Polycarbonate (PC). Electric Cell-substrate Impedance sensing	[37]
	Copper (Cu^{2+}), zinc (Zn^{2+}), potassium dichromate and 3,5-dichlorophenol	Glass/silicon wafers. Bioluminescent-cell-based sensor.	[38]
Wastewater	Copper (Cu^{2+})	Glass/PDMS microfluidic device. Fiber optic sensor.	[39]
	Nitrite	Glass/silicon. Colorimetric.	[40]
	Aromatic amines	Cyclic olefin copolymer. Electrophoresis and fluorescence detector.	[41]
	Potassium and nitrate	Not described. Low temperature co-fired ceramic-based potentiometry/ion selective electrodes.	[42]
	Sulfide	Polylactic acid. Sulfide-based electrode/potentiometry.	[43]
	Ammonium	PDMS. Ammonium-selective electrodes/potentiometry.	[44]
Fresh water	Phosphorous	Silicon. Yellow vanadomolybdo-phosphoric acid method/absorbance.	[45 −47]
	pH	Poly(methylmethacrylate) (PMMA). Photodiode/absorbance.	[48]
	Sulfite and nitrite	PDMS. Fluorescence.	[49]
	Ammonium	PDMS/glass. Fluorescence.	[50]
	Nitrite and nitrate	Urethane acrylate and pre-polymerized UA photoresist. Absorbance.	[51]
	Nitrite and nitrate	Not described. Absorbance.	[52]
	Organophosphate	Glass/PMMA holder. Potentiometry.	[53]
	Hydrogen peroxide	Glass. Chemiluminescence.	[54]
	Mercury (II)	PDMS/PMMA. Chromoionphore film/absorbance.	[55]
	Mercury (II)	PDMS/PMMA. Fluorescence.	[56]
	Lead (II)	Cyclo olefin copolymer (COC). Voltammetry.	[57]
	Ethinylestradiol	PMMA. Amperometric.	[58]
	Atrazine	Silicon. Chemiluminiscence.	[59]
	Bacteria	PDMS/glass. Fluorescence.	[60]
	Phosphate	PMMA. Absorbance.	[61]
	Phosphate	Paper. Absorbance.	[62]
Seawater	Salinity	PDMS/Glass. Conductivity/voltage.	[63]
	Cadmium	COC. Electrochemical.	[64]
	Nitrite	PMMA. Absorbance.	[65,66]
	Mercury (II)	Glass/PMMA. Fluorescence.	[67,68]
	Nutrients	Polycarbonate. Absorbance.	[69]
	Silicate	PMMA. Absorbance.	[70]
	Phosphate	PMMA Absorbance.	[22,71]
	pH	PMMA. Absorbance.	[23]
	pH	PDMS. Absorbance.	[72]

effective and simple-to-use portable platforms. Regarding pre-concentration of large volumes of sample, the use of integrated commercial membranes within PDMS-based devices have demonstrated to capture ~10^{-1} μm-scale particles with high efficiency, due to the complementary advantages offered by microfluidics [34]. It is particularly challenging to accurately quantify microorganisms when present in water at low numbers (<100 CFU mL^{-1}). In order to decrease the LOD and achieve high-throughput analysis, a device able to increase bacteria concentrations by positive dielectrophoretic impedance *E. coli* focusing was proposed, achieving a LOD of 300 CFU mL^{-1} with a sensitivity of 100 CFU mL^{-1} [36], Fig. 2A. As an alternative to the use of commercial membranes, electrical forces can be used to pre-concentrate samples, by exploiting the negative surface charges of bacteria and viruses [35].

Interestingly, mammalian cells have been used as sensors for toxicity measurements of toxicants like lindane [37]. It is known that a major limitation of using a mammalian cell-based biosensor for field-testing is the difficulty of maintaining cell viability and sterility outside of a cell culture facility. Therefore, devices reliant on cells will be not practical to scale for commercialization. By adding a self-contained disposable media delivery system to the sensor, cells are kept alive, but still, the model does not meet market requirements as bulky fluidic handling is necessary.

Other analytes of interest in drinking water that have been investigated in microfluidic devices are metals, such as copper [38,75,80,84], lead [76], semimetals like arsenic [81], water safety indicators such as nitrite and nitrate [77,82], the total concentration of calcium and magnesium [78], chlorine [79] and iodine [83]. For instance, the presence of copper in drinking water usually does not exceed more than few milligrams per liter, although higher

concentrations could be detected in waters coming from newly installed copper pipes. For this reason, it is of great importance to be able to effectively monitor copper in pipes. Bioluminescent analyzers that use living organisms as sensors, integrated within microfluidic systems, allow the monitoring of heavy metal ions such as copper and zinc. As an example, these devices were used for the analysis of water samples taken from Tønsberg's pipes in Norway. However, the sensitivity of the system is fairly low and can only sense acute toxicity and more appropriate as a warning device, rather than an actual quantifier of toxicants [38]. Higher sensitivity would be necessary to be able to commercialize these types of drinking water household systems.

Numerous microfluidic-based developments have been made to improve safety in drinking water. As mentioned above, most of the reviewed articles, which use microfluidics, focused on bacteria detection, finding little literature about metals. These systems often employ conventional fluidic handling devices thus, it is hard to find examples implemented in real-life scenarios or reaching competitive markets. Therefore, accurate, portable microfluidic systems to monitor safety in potable water have not been delivered to society yet, despite their continuous evolution.

2.2. Wastewater

Waste and sewage waters are generated by a variety of sources, where the concentration and type of contaminants found in the present high variability. Therefore, the detection methods employed for analysis should be adaptable and comply with regulations and quality standards. Water quality can be affected by several factors including the presence of chemical pollutants and pathogens, which harm human and ecosystem health. As an
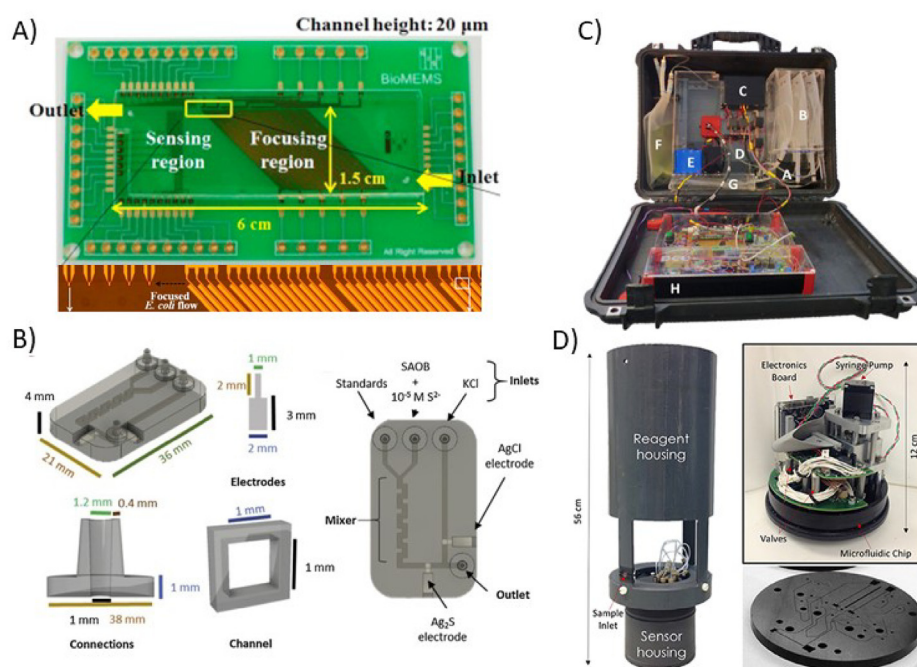

Fig. 2. LOC systems developed for different water matrixes. A) Bacteria sensor consisting of a region that utilizes positive dielectrophoresis for *Escherichia coli*-focusing, and an *E. coli*-sensing region that employs dielectrophoretic impedance measurements in drinking water samples, modified from Ref. [36]. B) Scheme of the fabrication and functioning of a 3D microfluidic device showing locations of the electrodes and dimensions used for the detection of sulfur in wastewaters, modified from Ref. [43]. C) Picture of an autonomous sensing platform for phosphate analysis in fresh waters. Inside picture: (A) inlet system, (B) bags holding the sample, high calibration standard, and low calibration standard, (C) detection chamber housing the microfluidic chip, LED (375 nm), and photodiode, (D) poly(methyl methacrylate) (PMMA) fluidic board, (E) battery, (F) reagent bag, (G) waste bag and (H) electronics, modified from Ref. [61]. D) Pictures of a LOC phosphate sensor deployed in seawater. (Left) A fully assembled sensor with reagent housing. (Top-right) LOC sensor before placement in the watertight sensor housing. (Bottom) One of the PMMA layers of a phosphate LOC (Sensor 1) showing the micromilled microfluidic channels prior device sealing, modified from Ref. [71].

example, wastewater systems are currently being monitored to determine the levels of the SARS-COV-2 virus [89,90], to identify and monitor the incidence of the virus in a community. For this reason, the routine monitoring of pollutants in wastewater systems, involving simple and inexpensive technologies, is a priority in society. In this sense, microfluidics has demonstrated simultaneous quantification and monitoring of the presence of a wide range of pollutants in wastewaters [91].

For instance, copper is a recurrent metal to be determined in water. In this regard, a hybrid glass/PDMS microfluidic device coupled to an optical sensor was developed for the determination of Cu (II) in industrial wastewater [39]. This technology seems very promising for commercialization and possible implementation in industrial wastewater systems and could set the basis for the development of an automatic system for direct monitoring of Cu (II) in municipal treatment plants.

As a step forward to get deployable devices, micro-flow-injection analysis (μFIA) coupled to microfluidics was used for nitrite determination using the Griess-Ilosvay reaction. It is remarkable to mention that the system was placed on-line in a wastewater treatment plant. The optical measurements were performed using a light-emitting diode (LED) as an emitter and a photodiode as a detector. This system proved to be accurate in two concentration ranges (0–50 and 0–250 mg L^{-1}) with features comparable to those provided by conventional methods [40].

Aromatic amines, which have been demonstrated to be carcinogenic and mutagenic, even at very low concentrations, can be released into the environment from the industry. In response, a simple, sensitive and rapid method which combines electrophoresis within microfluidics was developed. It presents a remarkably low LOD (nm L^{-1} range), good repeatability and recovery rates (85–110%). Moreover, if a pre-concentration technique is applied to this method, concentrations in the range of pmol L^{-1} could be determined [41].

Microfluidic technology has not only been applied to land-based samples. This technology has also been used in space engineering [42]. For example, a low temperature co-fired ceramics, with a continuous flow potentiometric microanalyzer, was developed to simultaneously monitor the presence of potassium and nitrate in samples from the water recycling process in space missions. The system integrated a microfluidic device and two ion-selective electrodes, built with nitrate and potassium polymeric membranes and a screen-printed Ag/AgCl reference electrode. Through the development of this system, integrated and compacted devices for the simultaneous determination of multiple analytes on-field was demonstrated.

Integration and portability are key factors in obtaining devices that could be implemented on-field and thus, commercialized. For instance, a sulfide-selective potentiometric sensor integrated into a 3D microfluidic system was tested in wastewater samples, Fig. 2B. The device was validated with real samples, showing no significant differences when compared to conventional methods [43]. The same year, a transducer coupled to a microfluidic device for ammonium-selective sensing in the sewers of the Berlin network was published, with a LOD of 4.10^{-5} M and a response time between 10 and 12 s. The key feature of this device was its ability to perform electrochemical measurements combined with passive microfluidics in real-time [44]. The use of passive flow for sampling eliminated the need for external pumps and valves and thus, reduced power consumption, while incremented portability and integration. As demonstrated in this section, there is a growing interest in the development of integrated microfluidic devices for the analysis and monitoring of wastewater at the point-of-need. A commonality between these systems is their accuracy, low reagent consumption and negligible waste generation; three important

aspects to deliver robust deployable systems. However, at this moment, they still lack commercial application as they depend on conventional fluidic equipment.

2.3. Fresh water

Fresh water bodies are defined as flowing waters, lakes, reservoirs and groundwater. For example, when rain falls to the ground, water keeps moving along the land surfaces to form streams or lakes. It evaporates into the atmosphere and soaks into aquifers from which the public drinking water is obtained. Unfortunately, the groundwater can be contaminated by chemicals or pollutants and thus, the sources of public water [92]. Therefore, the continuous monitoring of these waters is of great importance to manage and protect water ecosystems. In this context, microfluidic based devices and sensors are capable of monitoring water quality and so, identifying pollutants in fresh waters.

Many developments have been published for the monitoring of nutrients within fresh waters. In the following section, we will briefly introduce some of the most inspiring examples. Diamond's group was a pioneer, by publishing a microfluidic device sensor for long-term phosphate monitoring, which incorporates fluid sampling, reagent storage, detection and wireless communication into a portable platform. The device was improved over the years in terms of fluidic handling, to reduce dimensions and the final cost of production [45–47]. Later on, the same group presented a portable and fully autonomous sensor platform for *in situ* pH measurement of water samples. This sensor has the advantage of having integrated reagents storage, which is stable for up to 8 months with proved reproducibility and good repeatability. This research group has made remarkable progress over the years in the field of portable and autonomous water sensors, devices and systems [61,93], Fig. 2C. At the same time, examples of simultaneous determination of sulfite/nitrite in pond and river waters [49], ammonium in rain a river waters [50], nitrite/nitrate in lake [51] and river [52] have appeared. Overall, these sensors comprise valves, pumps, fluidics and reagents handling. Some of them are deployed for over three weeks, measuring more than 160,000 samples. In this case, despite the high measurement frequency, the fluid consumption of the sensor was remarkably lower than those in previously reported systems [52]. Low fluid consumption is important as this, along with power considerations which determines the length and/or measurement frequency of sensor deployment.

Regarding the analysis of pollutants, organophosphate nerve agents such as paraoxon and methyl parathion were detected in river water samples. The integrated system offered rapid and simultaneous measurement at micromolar levels of both poisons [53]. Hydrogen peroxide, when present in rainwater, is an efficient oxidizer of sulfur dioxide to produce sulfuric acid, an important compound in acid rain formation. Hydrogen peroxide was collected from rainwater and snow and analyzed by chemiluminescence [54]. In addition, metals present in fresh waters can seriously affect marine fauna and flora therefore, Hg (II) [55,56] and Pb (II) [57] were analyzed in river water samples using microfluidic technology.

As for potable and drinking water, the control of bacteria and pathogens growths in fresh waters is of great importance to avoid intoxications and ensure humans safety in recreational waters. In this regard, immunosensors have been selected as the gold standard for rapid quantification of acethinylestradiol [58] and antrazine [59] in river water samples. These devices showed high versatility and suitability for point-of-care analysis, with the possibility of building up array systems. Recently, bacteria have been detected by counting active bacteria stained with fluorescence

dyes, 6CFDA- and SYBR Green II-staining. The number of bacteria analyzed with the portable microfluidic system was compared to the conventional fluorescence microscopy method, showing no significant differences. However, smaller cells such as esterase-active cells were not accurately determined [60].

Czugala et al. [94] described a wireless paired emitter detector diode device as an optical sensor for water quality monitoring in a lab-on-a-disc device. This technology allows the analysis of a high amount of water samples at the point-of-need without the need for any external energy input. The microfluidic platform was applied for quantitative pH and qualitative turbidity monitoring of water samples. Fresh river water samples were analyzed, obtaining a very good correlation with standard bench-top systems.

It is important to mention that paper microfluidics have emerged as a cheap alternative to polymer-based microfluidics. They also offer less reagent consumption and easier on site measurement. Jayawardane et al. [62] evaluated a paper-based device for the determination of reactive phosphate in natural and soil waters based on the formation of phosphomolybdenum blue. The described device had low cost, fast and portable features and the device used less reagent than conventional laboratory devices. A general drawback found in microfluidic paper-based devices is their lack of robustness when long-term deployment is needed. It is a new technology in continuous development, which will bring smart solutions to deployable water monitoring devices.

Nevertheless, microfluidic sensors for fresh water monitoring, are still using slow sensors with complex architectures, requiring microfabricated manifolds, multiple valves and pumps.

2.4. Seawater

The quality of seawater depends, to a great extent, on the equilibrium in the concentration of compounds like nitrite, nitrate, ammonium and phosphate, which are denominated as nutrients, and salinity. An excess in the concentration of nutrients could lead to a detrimental state for the marine fauna and flora. In addition, physicochemical parameters such as pH, temperature, and conductivity among others are of importance to monitor water quality and to prevent deterioration, which may be lethal for marine ecosystems. Microfluidic devices may be integrated with industrial processes such as desalination plants. In this regard, integrated microfluidic sensors that measure temperature, conductivity, and salinity from harvested water from a pilot-scale desalination plant over a short period have been developed [63]. pH has been measured in a LOC by colorimetric assays coupled to a robust optical set-up and short-term deployed in European waters with high accuracy (0.001 pH, n = 20) and precision (0.004 pH) [23]. Others, worked on pH colorimetric assays based on meta-cresol purple as indicator dye, featuring high resolution (0.002 pH units for the 7.500−8.200 range), and linearity (R^2 of 0.9994) but lacking fully autonomous performance [72]. The work presented by Yûcel et al. [95] evidenced a clear example of an integrated deployable microfluidic device submerged in the deep ocean and set in seafloors for two days.

During the development of LOC devices, fluid flow analysis, highly integrated systems with fast analysis capabilities became a trend. It is difficult to find examples of integrated sensors that can continuously monitor, for long periods, with high accuracy, low consumption and strong anti-interference ability seawater sources [70]. Therefore, microfluidics capable of performing long-term autonomous sampling for seawater environmental monitoring have not been widely reported yet. Nevertheless, several examples of on-site water analyzers for cadmium [64], nitrite [65,66], phosphorous [22,71] and mercury [67,68] determination were published.

Autonomous systems for the determination of phosphorous in seawater, based on the valadomolybdate method, were published [22,71]. We would like to highlight the work done by Gran et al. where not only the long-term deployment of a phosphate LOC analyzer was demonstrated, but also the proximity in terms of accuracy and precision to reference standard methodologies [71], Fig. 2D.

Despite the huge efforts made in the development of autonomous microfluidic devices for seawater applications, no examples of real implementations have reached the market yet. Deployable devices should appear in the coming years to reduce the gap between laboratory experimentation and product commercialization, through device validation in real scenarios.

In particular, is interesting to mention the use of centrifugal microfluidics for seawater analysis. The simultaneous determination of nitrate, nitrite, ammonium, orthophosphate, and silicate in coastal seawater samples, collected from Chunsu Bay, South Korea, was presented [69]. The device integrated all processes (sample filtering, metering, mixing, reaction, colorimetric detection) and liquid flow was controlled by laser irradiation on ferrowax-based microvalves. This device could be potentially used on site if an autonomous CCD platform similar to Ref. [24] would be adapted. Despite centrifugal microfluidics gaining attention in biomedical applications, companies fail to commercialize these products in the environmental sector due to the elevated cost of both, the disposable device and the platform.

As explained in section 2, microfluidic systems for water monitoring still lack realistic commercial applications due to the many challenges observed in each water matrix. As a common drawback, the low integrability and portability of these devices are mainly due to the use of conventional fluidic machinery. This makes current microfluidic systems very difficult to deploy in aqueous locations. We believe that the integration of novel miniaturized sensors, valves and pumps inside microfluidic devices could overcome this limitation.

3. Functional materials integrated into microfluidic devices

Even though microtechnology allows for the fabrication of small devices, the components needed for fluidic control (pumps, valves, mixing units) and detection are usually bigger than the device itself, reducing their applicability in real scenarios and limiting their commercial value [96]. Here is where functional materials, commonly named as smart materials, arise as suitable alternatives to conventional components for microfluidics, mainly as sensors and actuators.

Functional materials are stimuli-responsive materials, with an autonomous behavior in response to changes in their local environment. These behaviors are dictated by the functional groups present within their polymer chains. These materials can change some of their mechanical properties, such as shape or position, in response to a chemical change [97], magnetic field [98], electricity [99], pressure [100], or light [101] induction and variations in temperature [102], or humidity [103] being able to perform functions, by those external stimuli, without human manipulation, as actuators and fluid controllers. Moreover, if sensing functionalities are incorporated within these materials, they can be used as sensors [104], Table 2. Several groups are working on the integration of functional materials into microfluidic devices for water monitoring [105]. The uses of functional materials under controlled laboratory conditions, exhibit integrability, and low-cost options compared to conventional materials. Some of these materials include the use of carbon nanotubes for the generation of actuators and for dielectric elastomers to create flexible electrodes [106]. Therefore, these new types of actuators, fluid controllers and sensors, with integrated

Table 2

Functional materials used as actuators, fluid controllers and sensors in microfluidic devices for water analysis.

Material	Actuator/Fluid driver	Sensor
Poly(*N*-isopropylacrylamide) (pNIPAAm) hydrogel	Light [94]	–
	Temperature [148]	
pNIPAAm ionogel	Temperature [144–147,152,154]	Colorimetry: Nitrates [27,173], pH [24]
Poly-ionic liquid tributylhexylphosphonium sulfopropylacrylate (PSPA)	Temperature [137]	–
Spiropyran hydrogel	Light [127]	–
Spiropyran ionogel	Light [161,162]	–
Graphene modified pNIPAAM	–	Electrochemical: pH [142]
Alginate hydrogel	pH [157,158]	–
Agarose hydrogel	–	Fluorescence: Nitrite [169]

functional materials, have the potential to improve environmental analysis systems.

Stimuli-responsive materials present switchable chemical properties, mechanical strength, tuneable permeability and mouldable surface characteristics, making them very suitable alternatives to conventional fluidic equipment [107]. The functional materials employed in microfluidics can be encompassed in metallic composites [108], hybrid materials [109], magnetic material [110], and polymeric materials [111]. These materials have the ability to change their shape, stiffness, position, natural frequency, damping, and/or other mechanical characteristics in response to a chemical, temperature variation, electric field, and/or magnetic field [112]. Hydrogels, being one of the first functional materials integrated into microfluidics, are three-dimensional structures of hydrophilic polymeric chains cross-linked into an insoluble, but also form highly hydrophilic swollen structures in water [96]. The nature of the monomers of the structure the functional groups and the crosslinker's present, define the properties exhibited by the material. For example, shape-changing behavior may be due to volume expansion (and contraction) when a specific stimulus is applied. Hydrogel materials are evolving by changing the solvent used during synthesis from water to ionic liquids (ILs) in order to enhance their mechanical and hygroscopic properties. Ionic liquids are solvents more thermally and electrochemically stable than water, composed by cations (*e.g.* ammonium, phosphonium, imidazolium, or pyridinium) and anions (*e.g.* dicyanamide, chloride, or acetate), with a melting point below 100 °C and high flexibility [113]. By choosing the appropriate ion pair, the physicochemical properties of the IL such as viscosity, density, melting point and conductivity can be tuned to suit a particular need. The combination of an IL and a hydrogel component, such as organic [114], inorganic [115], or hybrid organic-inorganic [116] are called ionogels. For instance, when comparing the swelling behavior and the stability of hydrogels and ionogels, an enhancement of the properties of the material is found as a consequence of the incorporation of the IL in the structure of the gel [117–121]. Moreover, due to their low vapor pressure and their ability to plasticize the gel network, ionogels exhibit high resistance to cracking and drying, which renders them as attractive materials in soft actuators for microfluidic applications. Several applications have been already presented in the literature regarding ionogels in microfluidics, some of them out of the scope of this review [122,123]. Temperature-responsive materials have been the most widely studied for the creation of *in situ* devices, nevertheless, the need for heaters to induce actuation is an enormous drawback. Therefore, light irradiation, which allows for non-contact operation and possible independent and remote manipulation of multiple fluids, is becoming an alternative to generate actuators in microfluidic devices. To this end, many research groups have studied photo-responsive polymeric materials, mainly functionalized with azobenzene, leukochromophore and spirobenzopyran [124–127].

The natural evolution of functional materials has led to the recent incorporation of poly(ionic liquid) (PILs) hydrogels that are polyelectrolytes that feature a combination of IL monomers, connected through a polymeric backbone to form a polymeric architecture [113]. Although most research is focused on linear PILs, several reports are dealing with crosslinked PIL networks [128–133] used as membranes [134], electrolytes [135], sensors [136], and actuators [137–139] in microfluidic devices.

In the next section, the different functional materials will be introduced and linked to their type of actuation/sensing capabilities. In general, we will try to evidence that, by incorporating different stimuli-responsive materials, as actuators or sensors in microfluidic devices, the complexity of the device can be reduced when used for environmental applications, increasing their potential marketability. We will critically review the integration of functional materials into microfluidic devices, as actuators or fluid controllers and sensors, to eliminate external pumps and valves or to improve sensing capabilities. These materials will be cataloged by emphasizing their advantages when incorporated in water monitoring systems, which could lead to marketable devices. Moreover, it is worth mentioning that there is a wide range of functional materials to be investigated and exploited for the development of water monitoring systems. Here, we will present some of them, when integrated into microfluidic devices.

3.1. Actuators and fluid controllers in microfluidics

Traditionally, fluidic control in microfluidics uses pneumatic and hydraulic valves and pumps that require additional external equipment, reducing the portability and increasing the price of the final device. Nonetheless, by introducing functional materials as an alternative to conventional fluidic handling equipment, both portability and price reduction are accomplished, favoring commercialization. This section intends to review the different materials used as actuators and fluid controllers but not the actuator mechanism, which has been reviewed elsewhere [106,140].

As mentioned before, the temperature is widely used to generate actuators in microfluidic devices [141–143]. pNIPAAm is one of the most popular temperature-sensitive multifunctional hydrogels used in microfluidics [144–147]; however, none of these works reveals their applicability for environmental monitoring. pNIPAAm hydrogels, being a dynamic polymer, are controlled by electronic heating elements [148,149], magnetic fields [150,151], or light [152–154], introducing the necessity of external controllers that are not wanted in portable devices. Nevertheless, a drastic change in the volume of a material can be triggered by other stimuli, such as pH. Some authors have developed actuators that respond to changes in pH in a physiological range [155], or even actuators with combined responses [156]. Moreover, pH-sensitive hydrogels can also be used for other purposes, for instance, to control the bidirectional transport of reagents in microfluidic
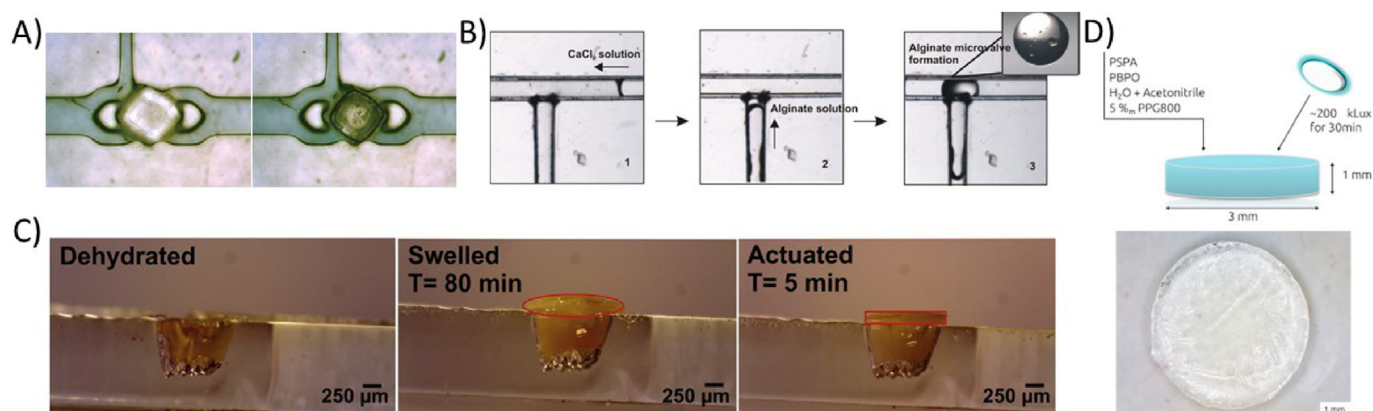
Fig. 3. (A) Photograph of the bidirectional valve right actuated by changes in the pH due to the introduction of ethanol, modified from Ref. [157], B) Photographs showing the generation of an alginate microvalve formation, modified from Ref. [158], (C) Photograph showing the swelling of a photoswitchable spirobenzopyran valve, modified from Ref. [162], (D) Photograph showing the structure of a poly-ionic liquid, modified from Ref. [137].

devices, Fig. 3A [157]. In particular, alginate hydrogels, which are networks of sodium alginate chains typically polymerized with Ca (II) ions, are biocompatible alternatives to be used as thermos-actuators in microfluidic devices for environmental monitoring [158], Fig. 3B. Likewise, most of the ionogels used in microfluidic devices are based on the polymerization of pNIPAAm, using a variety of ILs [159]. These ionogels have been integrated into lab-on-a-disc as temperature responsive actuators [148,149]. Additionally, the swelling properties of ionogels can be employed for liquid flow control in paper devices when the ionogel is used as a passive pump [160].

Another strategy to solve the need for external pumping or mixing [125,126] is the introduction of spiropyran in the pNIPAAM hydrogel [161]. Spiropyran is a photochromic organic compound whose structural change is induced by light and pH. The swelling/shrinking mechanism is reversible and tunable, allowing the control of the flow and mixing in microfluidics, Fig. 3C [162]. Additionally, the mechanism can be auto-induced by the copolymerization of spiropyrans hydrogels with acrylic acid that introduces the necessary flow of protons needed for the reversion of the structure. Is remarkable to find out that, these types of materials were actuated for up to two months in a continuous mode without losing their properties [127]. Spiropyran-based hydrogels have been also implemented in centrifugal microfluidics for controlling fluid motion without the need for external equipment. A white light LED actuated the ionogel valve, making the valve shrink and allowing the fluid to flow while applying centrifugal forces [162]. In this regard, material robustness and actuation speed of the materials, used as actuators, is of high importance for the development of microfluidic analyzers for long-term deployment, Fig. 3D. Moreover, the reversibility of the swelling, the ability to absorb water [137] and the possibility of controlling flows, make these materials very interesting for the generation of valves and pumps in microfluidic devices for water control.

Therefore, considering the type of materials and publications on this matter, pNIPAAm is an exceptional material easily integrable into water analysis systems to improve valving capabilities and thus, reduce system dimensions and price. Additionally, the chemical tunability of the properties of this material might provide water analysis systems with the possibility of multiple actuation processes to control water samples and liquid reagents storage in the same device. Conversely, reversibility is still a challenge for polymeric pumps and valves being, at this point, less reproducible than external mechanical components. Nevertheless, these materials will be accepted as microfluidic components in commercial

microfluidic devices, as long as their price and environmental impact becomes low enough to make the component or the full device disposable.

3.2. Sensors

The IUPAC defines a sensor as a device able to detect physical or chemical information and transforms it into an analytically useful signal. For that, three basic parts are required: an actuator that controls flows when a sensor is working, the sensor itself, that responds to the change in the environment and the transductor that recognizes this change and transforms it into an electric signal. Traditionally, electrodes, electric systems, or lasers have been used as transductors [163], increasing the size and final price of the sensors. The emergence of functional materials was a great advance for miniaturization and for lowering the costs of a sensor since they can act as both actuators and optical or electrochemical sensors themselves [164].

The ability of hydrogels to change shape by responding to an external stimulus such as pH or temperature is widely exploited for the fabrication of chemical [165] and optical [166] sensors. Hydrogel sensors consist of two main parts: a hydrogel element and a transducer in charge of converting the swelling signal of the hydrogel into an electrical (change in conductivity or current) or optical (change of fluorescence intensity, diffraction, or refractometry) domain [167]; this transducer can be incorporated into the hydrogel in the form of particles. For instance, conductive particles and materials such as graphene can be immobilized in hydrogels to be used as transducers, allowing the use of electrochemical methods [142,168]. In general, these types of microfluidic devices have been developed in the field of biomedicine and biotechnology [140]. Besides their responsive behavior, hydrogels are usually transparent, which is a useful feature for sensing colorimetric or fluorometric reactions. For example, hydrogels of agarose derivatives were used for the fluorescence detection of nitrate in different matrixes, including water, see Fig. 4A [169], obtaining LODs in the order of μM. Although traditional methods can detect nM concentrations, this is a good example of a sensor that could be integrated into a microfluidic device for water analysis.

The flexibility of ionogels allows their integration into wearable devices [170]. Despite the historical toxicity of some ionic liquids in water [171], the overwhelming majority of ionogel sensors have been developed for biomedical and biotechnological applications due to their biocompatibility, flexibility, and similar properties to
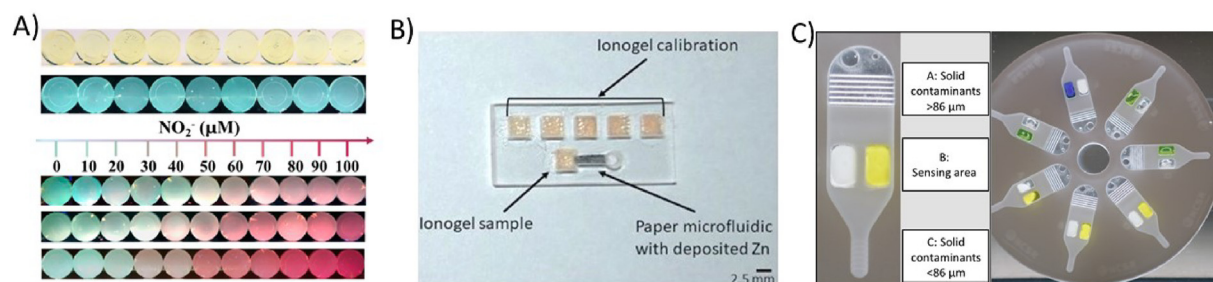
Fig. 4. A) Fluorescence detection of nitrate using an agarose based hydrogel, modified from Ref. [169], B) Photograph of an ionogel-based microfluidic device for the simultaneous detection of nitrate and nitrite, modified from Ref. [27], C) Photograph of a lab-on-a-disc ionogel-based microfluidic device for the simultaneous detection of pH and the turbidity of water samples at point-of-need, modified from Ref. [24].

biological tissues [172]. In environmental monitoring applications, an ionogel was used by us for the detection of nitrite in water as a proof of concept, Fig. 4B [27,173]. The detection of nitrite was carried out using the Griess reaction. The system demonstrated the use of a portable microfluidic device with an ionogel matrix, for water monitoring. Another example of the use of ionogels for the monitoring of water was demonstrated in a lab-on-a-disc format for the simultaneous colorimetric study of the pH and turbidity of water, Fig. 4C [24]. On the other hand, PILs, although have not been fully implemented as sensors yet, have been broadly developed as redox modulated supercapacitors and for energy applications [136,138], thus their ionic structure makes them suitable as electrochemical sensors [139].

Although sensors based on functional materials have been already used for biomedical applications [174], they have not often been applied to environmental analysis, despite their great potential. This could have several explanations, on the one hand, the economic interest in environmental monitoring is lower than healthcare systems. On the other hand, traditional water analysis methods are part of the scientific community for so long, that the acceptance of these novel methods, based on microfluidics, will be difficult. Therefore, environmental agencies should validate and implement these devices before reaching the market. Strong collaborations between different disciplines in the LOC field, such as engineering, material science, biology and environmental chemistry are essential to take this technology from the laboratory to the market.

4. Conclusions

The increasing number of publications every year and their high quality demonstrate the great importance that microfluidic devices are acquiring in water monitoring.

Water is principally analyzed by traditional methods such as liquid chromatography and mass spectroscopy despite the huge efforts adopted to incorporate microfluidics in environmental monitoring. Features like miniaturization of the analytical device, *in situ* analysis at the point-of-need, multiplexing, ease of manipulation and control of the device, and low-cost during device fabrication will soon bring microfluidics to the forefront of water monitoring research.

On the other hand, the use of microfluidic devices requires an in-depth study of functional materials and device implementation, to eliminate miniaturization engineering problems such as with valves, sensors, improving LODs and the possibility of multiple analyte detection. The incorporation of functional materials in microfluidic devices improves automation with novel actuators and sensors, minimizing the need for external bulky components. This will lead to the online, continuous, fast and inexpensive control and

monitoring of water sources. Moreover, it will enable a faster and more adequate response to water contamination, even at the point-of-need.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] https://www.who.int/news-room/fact-sheets/detail/drinking-water.
[2] S.A. Jaywant, K.M. Arif, A comprehensive review of microfluidic water quality monitoring sensors, Sensors 19 (2019) 1–37.
[3] B. Benelam, L. Wyness, Hydration and health: a review, Nutr. Bull. 35 (2010) 3–25.
[4] B.M. Popkin, E.K. D'Anci, I.H. Rosenberg, Water, hydration, and health, Nutr. Rev. 68 (2010) 439–458.
[5] S.R. Carpenter, Eutrophication of aquatic ecosystems: bistability and soil phosphorus, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 10002.
[6] A. Jang, Z. Zou, K.K. Lee, C.H. Ahn, P.L. Bishop, State-of-the-art lab chip sensors for environmental water monitoring, Meas. Sci.Tech. 22 (2011), 032001.
[7] L. Kortazar, J. Sáez, J. Agirre, J.K. Izaguirre, L.A. Fernández, Application of multivariate analysis to the turbidimetric determination of sulphate in seawater, Anal. Meth. 6 (2014) 3510–3514.
[8] A. Lewenstam, M. Maj-Zurawska, A. Hulanicki, Application of ion-selective electrodes in clinical analysis, Electroanalysis 3 (1991) 727–734.
[9] S.G. Silva, J.A. Nóbrega, B.T. Jones, G.L. Donati, Evaluation of Mg and Mn determination in water and plants using continuum source tungsten coil atomic fluorescence spectrometry, Microchem. J. 117 (2014) 250–254.
[10] D. Kusic, B. Kampe, P. Rosch, J. Popp, Identification of water pathogens by Raman microspectroscopy, Water Res. 48 (2014) 179–189.
[11] C. Erger, T.C. Schmidt, Disk-based solid-phase extraction analysis of organic substances in water, TrAC Trends Anal. Chem. (Reference Ed.) 61 (2014) 74–82.
[12] B.S. Gentle, P.S. Ellis, M.R. Grace, I.D. McKelvie, Flow analysis methods for the direct ultra-violet spectrophotometric measurement of nitrate and total nitrogen in freshwaters, Anal. Chim. Acta 704 (2011) 116–122.
[13] M.J. Duane, S. Facchetti, On-site environmental water analyses by ICP-MS, Sci. Total Environ. 172 (1995) 133–144.
[14] D.V. Biller, K.W. Bruland, Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS), Mar. Chem. 130 (2012) 12–20.
[15] N.T.J. Ong, S.K. Yee, Review on water quality monitoring technologies,

[16] A.T. Demetillo, M.V. Japitana, E.B. Taboada, A system for monitoring water quality in a large aquatic area using wireless sensor network technology, Sustain. Environ. Res. 29 (2019) 12.

[17] V.A. VanderNoot, R.F. Renzi, B.P. Mosier, J.L. Van de Vreugde, I. Shokair, B.L. Haroldsen, Development of an integrated microfluidic instrument for unattended water-monitoring applications, Electrophoresis 31 (2010) 2632–2640.

[18] M. Yew, Y. Ren, K.S. Koh, C. Sun, C. Snape, A review of state-of-the-art microfluidic technologies for environmental applications: detection and remediation, Glob. Challeng. 3 (2019), 1800060.

[19] D.R. Reyes, D. Iossifidis, P. Auroux, A. Manz, Micro total analysis systems. 1. Introduction, theory, and technology, Anal. Chem. 74 (2002) 2623–2636.

[20] D. Mark, S. Haeberle, G. Roth, F. von Stetten, R. Zengerle, Microfluidic lab-on-a-chip platforms: requirements, characteristics and applications, Chem. Soc. Rev. 39 (2010) 1153–1182.

[21] N. Convery, N. Gadegaard, 30 years of microfluidics, Micro, Nano. Eng. 2 (2019) 76–91.

[22] F.E. Legiret, V.J. Sieben, E.M. Woodward, S.K. Abi Kaed Bey, M.C. Mowlem, D.P. Connelly, E.P. Achterberg, A high performance microfluidic analyser for phosphate measurements in marine waters using the vanadomolybdate method, Talanta 116 (2013) 382–387.

[23] V.M. Rerolle, C.F. Floquet, A.J. Harris, M.C. Mowlem, R.R. Bellerby, E.P. Achterberg, Development of a colorimetric microfluidic pH sensor for autonomous seawater measurements, Anal. Chim. Acta 786 (2013) 124–131.

[24] M. Czugala, R. Gorkin 3rd, T. Phelan, J. Gaughran, V.F. Curto, J. Ducree, D. Diamond, F. Benito-Lopez, Optical sensing system based on wireless paired emitter detector diode device and ionogels for lab-on-a-disc water quality analysis, Lab Chip 12 (2012) 5069–5078.

[25] T. Thorsen, S.J. Maerkl, S.R. Quake, Microfluidic large-scale integration, Science 298 (2002) 580–584.

[26] M. Czugala, D. Maher, F. Collins, R. Burger, F. Hopfgartner, Y. Yang, J. Zhou, J. Ducrée, A. Smeaton, K.J. Fraser, F. Benito-Lopez, D. Diamond, CMAS: fully integrated portable centrifugal microfluidic analysis system for on-site colorimetric analysis, RSC Adv. 3 (2013) 15928–15938.

[27] J. Saez, G. Arana, L.A. Fernandez-Cuadrado, F. Benito-Lopez, Ionogel-based nitrite and nitrate sensor for water control at the point-of-need, Process Eng. 168 (2016) 518–521.

[28] A.M. Nightingale, A.D. Beaton, M.C. Mowlem, Trends in microfluidic systems for in situ chemical analysis of natural waters, Sensor. Actuator. B Chem. 221 (2015) 1398–1405.

[29] R. Pol, F. Céspedes, D. Gabriel, M. Baeza, Microfluidic lab-on-a-chip platforms for environmental monitoring, TrAC Trends Anal. Chem. (Reference Ed.) 95 (2017) 62–68.

[30] L.R. Volpatti, A.K. Yetisen, Commercialization of microfluidic devices, Trends Biotechnol. 32 (2014) 347–350.

[31] R. Murray, Challenges in environmental analytical chemistry, Anal. Chem. 82 (2010) 1569.

[32] G. Whitesides, The lab finally comes to the chip!, Lab Chip Miniaturisation Chem.Biol. 14 (2014) 3125–3126.

[33] M.I. Mohammed, S. Haswell, I. Gibson, Lab-on-a-chip or Chip-in-a-lab: challenges of commercialization lost in translation, Proc. Tech. 20 (2015) 54–59.

[34] Q. Liu, X. Zhang, Y. Yao, W. Jing, S. Liu, G. Sui, A novel microfluidic module for rapid detection of airborne and waterborne pathogens, Sensor. Actuator. B Chem. 258 (2018) 1138–1145.

[35] A.K. Balasubramanian, K.A. Soni, A. Beskok, S.D. Pillai, A microfluidic device for continuous capture and concentration of microorganisms from potable water, Lab Chip 7 (2007) 1315–1321.

[36] M. Kim, T. Jung, Y. Kim, C. Lee, K. Woo, J.H. Seol, S. Yang, A microfluidic device for label-free detection of Escherichia coli in drinking water using positive dielectrophoretic focusing, capturing, and impedance measurement, Biosens. Bioelectron. 74 (2015) 1011–1015.

[37] T.M. Curtis, M.W. Widder, L.M. Brennan, S.J. Schwager, W.H. Van Der Schalie, J. Fey, N. Salazar, A portable cell-based impedance sensor for toxicity testing of drinking water, Lab Chip 9 (2009) 2176–2183.

[38] X. Zhao, T. Dong, A microfluidic device for continuous sensing of systemic acute toxicants in drinking water, Int. J. Environ. Res. Publ. Health 10 (2013) 6748–6763.

[39] T. Leelasattarathkul, S. Liawruangrath, M. Rayanakorn, B. Liawruangrath, W. Oungpipat, N. Youngvises, Greener analytical method for the determination of copper(II) in wastewater by micro flow system with optical sensor, Talanta 72 (2007) 126–131.

[40] M. del Mar Baeza, N. Ibanez-Garcia, J. Baucells, J. Bartroli, J. Alonso, Microflow injection system based on a multicommutation technique for nitrite determination in wastewaters, Analyst 131 (2006) 1109–1115.

[41] R. Li, L. Wang, X. Gao, G. Du, H. Zhai, X. Wang, G. Guo, Q. Pu, Rapid separation and sensitive determination of banned aromatic amines with plastic microchip electrophoresis, J. Hazard Mater. 248 (2013) 268–275.

[42] A. Calvo-Lopez, E. Arasa-Puig, M. Puyol, J.M. Casalta, J. Alonso-Chamarro, Biparametric potentiometric analytical microsystem for nitrate and potassium monitoring in water recycling processes for manned space missions, Anal. Chim. Acta 804 (2013) 190–196.

[43] R. Pol, F. Céspedes, D. Gabriel, M. Baeza, Fully integrated screen-printed sulfide-selective sensor on a 3D-printed potentiometric microfluidic

[44] J. Gallardo-Gonzalez, A. Baraket, S. Boudjaoui, T. Metzner, F. Hauser, T. Röbler, S. Krause, N. Zine, A. Streklas, A. Alcácer, J. Bausells, A. Errachid, A fully integrated passive microfluidic Lab-on-a-Chip for real-time electrochemical detection of ammonium: sewage applications, Sci. Total Environ. 653 (2019) 1223–1230.

[45] M. Bowden, M. Sequiera, J.P. Krog, P. Gravesen, D. Diamond, Analysis of river water samples utilising a prototype industrial sensing system for phosphorus based on micro-system technology, J. Environ. Monit. 4 (2002) 767–771.

[46] C. Slater, J. Cleary, K.T. Lau, D. Snakenborg, B. Corcoran, J.P. Kutter, D. Diamond, Validation of a fully autonomous phosphate analyser based on a microfluidic lab-on-a-chip, Water Sci. Technol. 61 (2010) 1811–1818.

[47] M. Bowden, D. Diamond, The determination of phosphorus in a microfluidic manifold demonstrating long-term reagent lifetime and chemical stability utilising a colorimetric method, Sensor. Actuator. B Chem. 90 (2003) 170–174.

[48] PerezdeVargasSansalvador, IsabelM, C.D. Fay, J. Cleary, A.M. Nightingale, M.C. Mowlem, D. Diamond, Autonomous reagent-based microfluidic pH sensor platform, Sensor. Actuator. B Chem. 225 (2016) 369–376.

[49] S. Fujii, T. Tokuyama, M. Abo, A. Okubo, Fluorometric determination of sulfite and nitrite in aqueous samples using a novel detection unit of a microfluidic device, Anal. Sci. 20 (2004) 209–212.

[50] S. Xue, K. Uchiyama, H.F. Li, Determination of ammonium on an integrated microchip with LED-induced fluorescence detection, J. Environ. Sci. 24 (2012) 564–570.

[51] L.N.N. Nóbrega, L.d.O. Magalhães, A. Fonseca, A urethane-acrylate microflowanalyzer with an integrated cadmium column, Microchem. J. 110 (2013) 553–557.

[52] A.M. Nightingale, S. Hassan, B.M. Warren, K. Makris, G.W.H. Evans, E. Papadopoulou, S. Coleman, X. Niu, A droplet microfluidic-based sensor for simultaneous in situ monitoring of nitrate and nitrite in natural waters, Environ. Sci. Technol. 53 (2019) 9677–9685.

[53] J. Wang, M.P. Chatrathi, A. Mulchandani, W. Chen, Capillary electrophoresis microchips for separation and detection of organophosphate nerve agents, Anal. Chem. 73 (2001) 1804–1808.

[54] L. Marle, G.M. Greenway, Determination of hydrogen peroxide in rainwater in a miniaturised analytical system, Anal. Chim. Acta 548 (2005) 20–25.

[55] B.Kuswandi Nuriman, W. Verboom, Optical fiber chemical sensing of Hg(II) ions in aqueous samples using a microfluidic device containing a selective tripodal chromoionophore-PVC film, Sensor. Actuator. B Chem. 157 (2011) 438–443.

[56] J. Wang, H. Chen, P. Zhang, Z. Zhang, S. Zhang, J. Kong, Probing trace Hg2+ in a microfluidic chip coupled with in situ near-infrared fluorescence detection, Talanta 114 (2013) 204–210.

[57] W. Jung, A. Jang, P.L. Bishop, C.H. Ahn, A polymer lab chip sensor with microfabricated planar silver electrode for continuous and on-site heavy metal measurement, Sensor. Actuator. B Chem. 155 (2011) 145–153.

[58] N.A. Martinez, R.J. Schneider, G.A. Messina, J. Raba, Modified paramagnetic beads in a microfluidic system for the determination of ethinylestradiol (EE2) in river water samples, Biosens. Bioelectron. 25 (2010) 1376–1381.

[59] J. Yakovleva, R. Davidsson, M. Bengtsson, T. Laurell, J. Emneus, Microfluidic enzyme immunosensors with immobilised protein A and G using chemiluminescence detection, Biosens. Bioelectron. 19 (2003) 21–34.

[60] N. Yamaguchi, Y. Fujii, Rapid on-site monitoring of bacteria in freshwater environments using a portable microfluidic counting system, Biol. Pharm. Bull. 43 (2020) 87–92.

[61] A. Donohoe, G. Lacour, P. McCluskey, D. Diamond, M. McCaul, Development of a cost-effective sensing platform for monitoring phosphate in natural waters, Chemosensors 6 (2018) 2–13.

[62] B.M. Jayawardane, I.D. McKelvie, S.D. Kolev, A paper-based device for measurement of reactive phosphate in water, Talanta 100 (2012) 454–460.

[63] M. Kim, W. Choi, H. Lim, S. Yang, Integrated microfluidic-based sensor module for real-time measurement of temperature, conductivity, and salinity to monitor reverse osmosis, Desalination 317 (2013) 166–174.

[64] Z. Zou, E. MacKnight, A. Jang, P. Wu, J. Do, P.L. Bishop, C.H. Ahn, On-site heavy metal analyzer with polymer lab chip array for automatic continuous sampling and monitoring, Int. Conf. Miniaturized Syst. Chem. Life Sci. Proc. MicroTAS Conf. (2008) 1251–1253.

[65] A.D. Beaton, V.J. Sieben, C.F.A. Floquet, E.M. Waugh, S. Abi Kaed Bey, I.R.G. Ogilvie, M.C. Mowlem, H. Morgan, An automated microfluidic colourimetric sensor applied in situ to determine nitrite concentration, Sensor. Actuator. B Chem. 156 (2011) 1009–1014.

[66] A.D. Beaton, C.L. Cardwell, R.S. Thomas, V.J. Sieben, F. Legiret, E.M. Waugh, P.J. Statham, M.C. Mowlem, H. Morgan, Lab-on-chip measurement of nitrate and nitrite for in situ analysis of natural waters, Environ. Sci. Technol. 46 (2012) 9548–9556.

[67] Q. Zhang, X. Zhang, X. Zhang, L. Jiang, J. Yin, P. Zhang, S. Han, Y. Wang, G. Zheng, A feedback-controlling digital microfluidic fluorimetric sensor device for simple and rapid detection of mercury (II) in costal seawater, Mar. Pollut. Bull. 144 (2019) 20–27.

[68] S. Han, X. Liu, L. Wang, Y. Wang, G. Zheng, An efficient protocol to use feedback-controlling digital microfluidic fluorimetric sensor for detection of mercury (II) in coastal seawaters, Methods 6 (2019) 1443–1453.

[69] H. Hwang, Y. Kim, J. Cho, J.Y. Lee, M.S. Choi, Y.K. Cho, Lab-on-a-disc for

simultaneous determination of nutrients in water, Anal. Chem. 85 (2013) 2954–2960.

[70] X. Cao, S.W. Zhang, D.Z. Chu, N. Wu, H.K. Ma, Y. Liu, A design of spectro-photometric microfluidic chip sensor for analyzing silicate in seawater, IOP Earth Environ. Sci. 82 (2017), 012080.

[71] M.M. Grand, G. Clinton-Bailey, A.D. Beaton, A.M. Schaap, T.H. Johengen, M.N. Tamburri, D.P. Connelly, M.C. Mowlem, E.P. Achterberg, A lab-on-chip phosphate analyzer for long-term in situ monitoring at fixed observatories: optimization and performance evaluation in estuarine and oligotrophic coastal waters, Front. Mar. Sci. 4 (2017) 255.

[72] V.C. Pinto, C.F. Araújo, P.J. Sousa, L.M. Gonçalves, G. Minas, A low-cost lab-on-a-chip device for marine pH quantification by colorimetry, Sensor. Actuator. B Chem. 290 (2019) 285–292.

[73] W. Huang, L. Yang, G. Yang, F. Li, Microfluidic multi-angle laser scattering system for rapid and label-free detection of waterborne parasites, Biomed. Optic Express 9 (2018) 1520–1530.

[74] L. Diéguez, M. Winter, S. Molan, P. Monis, B. King, B. Thierry, Disposable microfluidic micromixers for effective capture of Cryptosporidium parvum oocysts from water samples, J. Bioeng. 12 (2018) 1–8.

[75] E. Tyrrell, C. Gibson, B.D. MacCraith, D. Gray, P. Byrne, N. Kent, C. Burke, B. Paull, Development of a micro-fluidic manifold for copper monitoring utilising chemiluminescence detection, Lab Chip 4 (2004) 384–390.

[76] J. Chen, S. Xiao, X. Wu, K. Fang, W. Liu, Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction, Talanta 67 (2005) 992–996.

[77] M.J. Shiddiky, M.S. Won, Y.B. Shim, Simultaneous analysis of nitrate and nitrite in a microfluidic device with a Cu-complex-modified electrode, Electrophoresis 27 (2006) 4545–4554.

[78] A. Fonseca, I.M. Raimundo Jr., J.J. Rohwedder, R.S. Lima, M.C. Araujo, A microfluidic device with integrated fluorimetric detection for flow injection analysis, Anal. Bioanal. Chem. 396 (2010) 715–723.

[79] R. Olivé-Monllau, C.S. Martínez-Cisneros, J. Bartrolí, M. Baeza, F. Céspedes, Integration of a sensitive carbon nanotube composite electrode in a ceramic microanalyzer for the amperometric determination of free chlorine, Sensor. Actuator. B Chem. 151 (2011) 416–422.

[80] M. Sierra-Rodero, J.M. Fernández-Romero, A. Gómez-Hens, Determination of aminoglycoside antibiotics using an on-chip microfluidic device with chemiluminescence detection, Microchim.Acta 179 (2012) 185–192.

[81] A. Bonyár, P. Nagy, V. Mayer, A. Vitéz, A. Gerecs, H. Sántha, G. Harsányi, A colorimetry based, semi-automated portable sensor device for the detection of arsenic in drinking water, Sensor. Actuator. B Chem. 251 (2017) 1042–1049.

[82] M.F. Khanfar, W. Al-Faqheri, A. Al-Halhouli, Low cost lab on chip for the colorimetric detection of nitrate in mineral water products, Sensors 17 (2017) 2345.

[83] P. Inpota, K. Strzelak, R. Koncki, W. Sripumkhai, W. Jeamsaksiri, N. Ratanawimarnwong, P. Wilairat, N. Choengchan, R. Chantiwas, D. Nacapricha, Microfluidic analysis with front-face fluorometric detection for the determination of total inorganic iodine in drinking water, Anal. Sci. 34 (2018) 161–167.

[84] G.C. Bandara, C.A. Heist, V.T. Remcho, Chromatographic separation and visual detection on wicking microfluidic devices: quantitation of Cu2+ in surface, ground, and drinking water, Anal. Chem. 90 (2018) 2594–2600.

[85] J.S. McGrath, J. Quist, J.R.T. Seddon, S.C.S. Lai, S.G. Lemay, H.L. Bridle, Deformability assessment of waterborne protozoa using a microfluidic-enabled force microscopy probe, PloS One 11 (2016) 1–12.

[86] C. Sakamoto, N. Yamaguchi, M. Yamada, H. Nagase, M. Seki, M. Nasu, Rapid quantification of bacterial cells in potable water using a simplified microfluidic device, J. Microbiol. Methods 68 (2007) 643–647.

[87] F.R. Caetano, E.A. Carneiro, D. Agustini, L. Figueiredo-Filho, C.E. Banks, M.F. Bergamini, L. Marcolino-Junior, Combination of electrochemical biosensor and textile threads: a microfluidic device for phenol determination in tap water, Biosens. Bioelectron. 99 (2018) 382–388.

[88] C. Páez-Avilés, E. Juanola-Feliu, J. Punter-Villagrasa, B. Del Moral Zamora, A. Homs-Corbera, J. Colomer-Farrarons, P.L. Miribel-Català, J. Samitier, Combined dielectrophoresis and impedance systems for bacteria analysis in microfluidic on-chip platforms, Sensors 16 (2016) 1514.

[89] D.A. Larsen, K.R. Wigginton, Tracking COVID-19 with wastewater, Nat. Biotechnol. 38 (2020) 1151–1153.

[90] K. Lancaster, T. Rhodes, Wastewater monitoring of SARS-CoV-2: lessons from illicit drug policy, the lancet, Gastroenterol. Hepatol. 5 (2020) 641–642.

[91] K. Piaskowski, R. Świderska-Dąbrowska, A. Kaleniecka, P.K. Zarzycki, Advances in the analysis of water and wastewater samples using various sensing protocols and microfluidic devices based on PAD and µTAS systems, J. AOAC Int. 100 (2019) 962–970.

[92] T.H. Nguyen, B. Helm, H. Hettiarachchi, S. Caucci, P. Krebs, The selection of design methods for river water quality monitoring networks: a review, Environ. Earth Sci. 78 (2019) 96.

[93] D. Cogan, C. Fay, D. Boyle, C. Osborne, N. Kent, J. Cleary, D. Diamond, Development of a low cost microfluidic sensor for the direct determination of nitrate using chromotropic acid in natural waters, Anal. Meth. 7 (2015) 5396–5405.

[94] M. Czugala, C. Fay, N.E. O'Connor, B. Corcoran, F. Benito-Lopez, D. Diamond, Portable integrated microfluidic analytical platform for the monitoring and detection of nitrite, Talanta 116 (2013) 997–1004.

[95] M. Yücel, A.D. Beaton, M. Dengler, M.C. Mowlem, F. Sohl, S. Sommer, Nitrate and nitrite variability at the seafloor of an oxygen minimum zone revealed by a novel microfluidic in-situ chemical sensor, PloS One 10 (2015) 1–10.

[96] I. Apsite, A. Biswas, Y. Li, L. Ionov, Microfabrication using shape-transforming soft materials, Adv. Funct. Mater. 30 (2020) 1908028.

[97] L. Zhang, P. Naumov, X. Du, Z. Hu, J. Wang, Vapomechanically responsive motion of microchannel-programmed actuators, Adv. Mater. 29 (2017) 1702231.

[98] A.A. Adedoyin, A.K. Ekenseair, Biomedical applications of magneto-responsive scaffolds, Nano Res 11 (2018) 5049–5064.

[99] K. Asaka, M. Hashimoto, Electrical properties and electromechanical modeling of plasticized PVC gel actuators, Sensor. Actuator. B Chem. 273 (2018) 1246–1256.

[100] Z. Huang, X. Feng, T. Zhang, Z. Liu, B. Zhu, Y. Xie, Highly stretchable hydrogels for sensitive pressure sensor and programmable surface patterning by thermal bubble inkjet technology, J. Appl. Polym. Sci. 137 (2020) 49146.

[101] H. Zeng, O.M. Wani, P. Wasylczyk, A. Priimagi, Light-Driven, caterpillar-inspired miniature inching robot, Macromol. Rapid Commun. 39 (2018) 1700224.

[102] W. Yan, T. Rudolph, U. Noechel, O. Gould, M. Behl, K. Kratz, A. Lendlein, Reversible actuation of thermoplastic multiblock copolymers with over-lapping thermal transitions of crystalline and glassy domains, Macromolecules 51 (2018) 4624–4632.

[103] S. Agarwal, S. Jiang, Y. Chen, Progress in the field of water- and/or temperature-triggered polymer actuators, Macromol. Mater. Eng. 304 (2019) 1800548.

[104] A.M. Sanjuan, J.A. Reglero Ruiz, F.C. Garcia, J.M. Garcia, Recent developments in sensing devices based on polymeric systems, React. Funct. Polym. 133 (2018) 103–125.

[105] S. Coleman, A.B. Azouz, J.T. Schiphorst, J. Saez, J. Whyte, P. McCluskey, N. Kent, F. Benito-Lopez, A. Schenning, D. Diamond, Next generation, in-situ microfluidic flow control using stimuli responsive materials for biomemetic microfluicic platforms, in: 10th International Conference on Miniaturized Systems for Chemistry and Life Sciences, Micro Total Analysis Systems µ-TAS-2016, 2016, pp. 1126–1127.

[106] J. Kim, J.W. Kim, H.C. Kim, L. Zhai, H. Ko, R.M. Muthoka, Review of soft actuator materials, Int. J. Precis. Eng. Manuf. 20 (2019) 2221–2241.

[107] R. Byrne, F. Benito-Lopez, D. Diamond, Materials science and the sensor revolution, Mater. Today 13 (2010) 16–23.

[108] C. Boller, Composites for sensors and actuators, in: Encyclopedia of Materials: Science and Technology, Elsevier Science Ltd., 2001, pp. 1376–1382.

[109] Z.G. Wei, R. Sandstroram, S. Miyazaki, Shape-memory materials and hybrid composites for smart systems: Part I Shape-memory materials, J. Mater. Sci. 33 (1998) 3743–3762.

[110] C. Moran, C. Cabrera, A. Moran, A. Garcia, M. Gonzalez, Magnetic sensors based on amorphous ferromagnetic materials: a review, Sensors 15 (2015) 28340–28366.

[111] S. Argentiere, G. Gigli, M. Mortato, Irini Gerges, L. Blasi, in: R.T. Kelly (Ed.), Advances in Microfluidics, InTech, 2012, pp. 127–154.

[112] X. Wang, N. Jiao, S. Tung, L. Liu, Photoresponsive graphene composite bilayer actuator for soft robots, ACS Appl. Mater. Interfaces 11 (2019) 30290–30299.

[113] S. Zahn, F. Uhlig, J. Thar, C. Spickermann, B. Kirchner, Intermolecular forces in an ionic liquid ([Mmim][Cl]) versus those in a typical salt (NaCl), Angew. Chem. Int. Ed. 47 (2008) 3639–3641.

[114] N. Mohmeyer, D. Kuang, P. Wang, H. Schmidt, S.M. Zakeeruddin, M. Grätzel, An efficient organogelator for ionic liquids to prepare stable quasi-solid-state dye-sensitized solar cells, J. Mater. Chem. 16 (2006) 2978–2983.

[115] L. Viau, C. Tourné-Péteilh, J. Devoisselle, A. Vioux, Ionogels as drug delivery system: one-step sol-gel synthesis using imidazolium ibuprofenate ionic liquid, Chem. Commun. (J. Chem. Soc. Sect. D) 46 (2010) 228–230.

[116] F. Gayet, L. Viau, F. Leroux, F. Mabille, S. Monge, J. Robin, A. Vioux, Unique combination of mechanical strength, thermal stability, and high ion conduction in PMMA - silica nanocomposites containing high loadings of ionic liquid, Chem. Mater. 21 (2009) 5575–5577.

[117] J. Le Bideau, L. Viau, A. Vioux, Ionogels, Ionic liquid based hybrid materials, Chem. Soc. Rev. 40 (2011) 907–925.

[118] S. Gallagher, A. Kavanagh, L. Florea, D.R. MacFarlane, K.J. Fraser, D. Diamond, Temperature and pH triggered release characteristics of water/fluorescein from 1-ethyl-3-methylimidazolium ethylsulfate based ionogels, Chem. Commun. (J. Chem. Soc. Sect. D) 49 (2013) 4613–4615.

[119] C. Zuliani, G. Matzeu, D. Diamond, A liquid-junction-free reference electrode based on a PEDOT solid-contact and ionogel capping membrane, Talanta 125 (2014) 58–64.

[120] S. Wang, B. Hsia, J.P. Alper, C. Carraro, Z. Wang, R. Maboudian, Comparative studies on electrochemical cycling behavior of two different silica-based ionogels, J. Power Sources 301 (2016) 299–305.

[121] N. Gil-González, T. Akyazi, E. Castaño, F. Benito-Lopez, M.C. Morant-Miñana, Elucidating the role of the ionic liquid in the actuation behavior of thermo-responsive ionogels, Sensor. Actuator. B Chem. 260 (2018) 380–387.

[122] D. Khodagholy, V.F. Curto, K.J. Fraser, M. Gurfinkel, R. Byrne, D. Diamond, G.G. Malliaras, F. Benito-Lopez, R.M. Owens, Organic electrochemical transistor incorporating an ionogel as a solid state electrolyte for lactate sensing, J. Mater. Chem. 22 (2012) 4440–4443.

[123] M. Tijero, R. Díez-Ahedo, F. Benito-Lopez, L. Basabe-Desmonts, V. Castro-López, A. Valero, Biomolecule storage on non-modified thermoplastic

microfluidic chip by ink-jet printing of ionogels, Biomicrofluidics 9 (2015), 044124.

[124] B. Ziólkowski, L. Florea, J. Theobald, F. Benito-Lopez, D. Diamond, Self-protonating spiropyran-co-NIPAM-co-acrylic acid hydrogel photoactuators, Soft Matter 9 (2013) 8754–8760.

[125] J. ter Schiphorst, S. Coleman, J.E. Stumpel, A. Ben Azouz, D. Diamond, A.P.H.J. Schenning, Molecular design of light-responsive hydrogels, for in situ generation of fast and reversible valves for microfluidic applications, Chem. Mater. 27 (2015) 5925–5931.

[126] S. Coleman, J. ter Schiphorst, A. Azouz, S. Ben Bakker, A.P.H.J. Schenning, D. Diamond, Tuning microfluidic flow by pulsed light oscillating spiropyran-based polymer hydrogel valves, Sensor. Actuator. B Chem. 245 (2017) 81–86.

[127] J. ter Schiphorst, G.G. Melpignano, H.E. Amirabadi, M.H.J.M. Houben, S. Bakker, den Toonder, M.J. Jaap, A.P.H.J. Schenning, Photoresponsive passive micromixers based on spiropyran size-tunable hydrogels, Macromol. Rapid Commun. 39 (2018) 1700086.

[128] B. Ziólkowski, D. Diamond, Thermoresponsive poly(ionic liquid) hydrogels, Chem. Commun. (J. Chem. Soc. Sect. D) 49 (2013) 10308–10310.

[129] S. Gallagher, L. Florea, K.J. Fraser, D. Diamond, Swelling and shrinking properties of thermo-responsive polymeric ionic liquid hydrogels with embedded linear pNIPAAM, Int. J. Mol. Sci. 15 (2014) 5337–5349.

[130] N. Sun, P. Sun, A. Wu, X. Qiao, F. Lu, L. Zheng, Facile fabrication of thermo/redox responsive hydrogels based on a dual crosslinked matrix for a smart on-off switch, Soft Matter 14 (2018) 4327–4334.

[131] K. Manojkumar, D. Mecerreyes, D. Taton, Y. Gnanou, K. Vijayakrishna, Self-assembly of poly(ionic liquid) (PIL)-based amphiphilic homopolymers into vesicles and supramolecular structures with dyes and silver nanoparticles, Polym. Chem. 8 (2017) 3497–3503.

[132] L. Miao, H. Duan, M. Liu, W. Lu, D. Zhu, T. Chen, L. Li, L. Gan, Poly(ionic liquid)-derived, N, S-codoped ultramicroporous carbon nanoparticles for supercapacitors, Chem. Eng. J. 317 (2017) 651–659.

[133] W. Wu, J. Li, S. Zou, J. Guo, H. Zhou, Construction of Au@Pt core-satellite nanoparticles based on in-situ reduction of polymeric ionic liquid protected gold nanoparticles, Front. Mater. Sci. 11 (2017) 42–50.

[134] M.G. Cowan, D.L. Gin, R.D. Noble, Poly(ionic liquid)/ionic liquid ion-gels with high "free" ionic liquid content: platform membrane materials for CO2/light gas separations, Acc. Chem. Res. 49 (2016) 724–732.

[135] B. Yu, F. Zhou, C. Wang, W. Liu, A novel gel polymer electrolyte based on poly ionic liquid 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium iodide, Eur. Polym. J. 43 (2007) 2699–2707.

[136] C. Yuan, J. Guo, F. Yan, Shape memory poly(ionic liquid) gels controlled by host–guest interaction with β-cyclodextrin, Polymers 55 (2014) 3431–3435.

[137] A. Tudor, J. Saez, L. Florea, F. Benito-Lopez, D. Diamond, Poly(ionic liquid) thermo-responsive hydrogel microfluidic actuators, Sensor. Actuator. B Chem. 247 (2017) 749–755.

[138] Q. Zhao, J.W.C. Dunlop, X. Qiu, F. Huang, Z. Zhang, J. Heyda, J. Dzubiella, M. Antonietti, J. Yuan, An instant multi-responsive porous polymer actuator driven by solvent molecule sorption, Nat. Commun. 5 (2014) 4293.

[139] Q. Zhao, J. Heyda, J. Dzubiella, K. Täuber, J.W.C. Dunlop, J. Yuan, Sensing solvents with ultrasensitive porous poly(ionic liquid) actuators, Adv. Math. 27 (2015) 2913–2917.

[140] C.B. Goy, R.E. Chaile, R.E. Madrid, Microfluidics and hydrogel: a powerful combination, React. Funct. Polym. 145 (2019) 104314.

[141] L. Liang, X. Feng, J. Liu, P.C. Rieke, G.E. Fryxell, Reversible surface properties of glass plate and capillary tube grafted by photopolymerization of N-isopropylacrylamide, Macromolecules 31 (1998) 7845–7850.

[142] P. Salvo, B. Melai, N. Calisi, C. Paoletti, F. Bellagambi, A. Kirchhain, M.G. Trivella, R. Fuoco, F. Di Francesco, Graphene-based devices for measuring pH, Sensor. Actuator. B Chem. 256 (2018) 976–991.

[143] E.M. Frazar, R.A. Shah, T.D. Dziubla, J.Z. Hilt, Multifunctional temperature-responsive polymers as advanced biomaterials and beyond, J. Appl. Polym. Sci. 137 (2020) 48770.

[144] M.E. Harmon, M. Tang, C.W. Frank, A microfluidic actuator based on thermoresponsive hydrogels, Polymers 44 (2003) 4547–4556.

[145] A. Richter, S. Klatt, G. Paschew, C. Klenke, Micropumps operated by swelling and shrinking of temperature-sensitive hydrogels, Lab Chip 9 (2009) 613–618.

[146] S. Lin, W. Wang, X. Ju, R. Xie, L. Chu, A simple strategy for in situ fabrication of a smart hydrogel microvalve within microchannels for thermostatic control, Lab Chip 14 (2014) 2626–2634.

[147] M.A. Haq, Y. Su, D. Wang, Mechanical properties of PNIPAM based hydrogels: a review, Mater. Sci. Eng. C 70 (2017) 842–855.

[148] A. Li, A. Khosla, C. Drewbrook, B.L. Gray, Fabrication and testing of thermally responsive hydrogel-based actuators using polymer heater elements for flexible microvalves, Proceedings of SPIE - Inter. Soc. Opt. Eng. (2011) 7929.

[149] F. Benito-Lopez, M. Antoñana-Díez, V.F. Curto, D. Diamond, V. Castro-López, Modular microfluidic valve structures based on reversible thermoresponsive ionogel actuators, Lab Chip 14 (2014) 3530–3538.

[150] M. Rahman, Y. Nahar, W. Ullah, A. Elaissari, H. Ahmad, Incorporation of iron

oxide nanoparticles into temperature-responsive poly (N-isopropylacrylamide-co-acrylic acid) P (NIPAAm-AA) polymer hydrogel, J. Polym. Res. 22 (2015) 1–9.

[151] X. Lin, R. Huang, M. Ulbricht, Novel magneto-responsive membrane for remote control switchable molecular sieving, J. Mater. Chem. B 4 (2016) 867–879.

[152] W. Jeong, S. Kim, S. Yang, Photothermal control of membrane permeability of microcapsules for on-demand release, ACS Appl. Mater. Interfaces 6 (2014) 826–832.

[153] L. Breuer, M. Raue, M. Kirschbaum, T. Mang, M.J. Schöning, T. Thoelen, T. Wagner, Light-controllable polymeric material based on temperature-sensitive hydrogels with incorporated graphene oxide, Phys. Status Solidi 212 (2015) 1368–1374.

[154] N. Sharma, H. Keshmiri, X. Zhou, T.I. Wong, C. Petri, U. Jonas, B. Liedberg, J. Dostalek, Tunable plasmonic nanohole arrays actuated by a thermoresponsive hydrogel cushion, J. Phys. Chem. C 120 (2016) 561–568.

[155] M. Mariam, M.N. Ali, A. Umar, J. Smith Patrick, Z. Amber, Q. Faisal, A. Sabtain, Aqua-gel pH sensor: intelligent engineering and evaluation of pH sensor based on multi-factorial testing regimes, Sens. Rev. 39 (2019) 178–189.

[156] M. Bäcker, M. Raue, S. Schusser, C. Jeitner, L. Breuer, P. Wagner, A. Poghossian, A. Förster, T. Mang, M.J. Schöning, Microfluidic chip with integrated microvalves based on temperature- and pH-responsive hydrogel thin films, Phys. Status Solidi 209 (2012) 839–845.

[157] G. Paschew, J. Schreiter, A. Voigt, C. Pini, J.P. Chávez, M. Allerdiben, U. Marschner, S. Siegmund, R. Schüffny, F. Jülicher, A. Richter, Autonomous chemical oscillator circuit based on bidirectional chemical-microfluidic coupling, Adv.Mater.Technol. 1 (2016) 1600005.

[158] J. Saez, J. Etxebarria, M. Antoñana-Diez, F. Benito-Lopez, On-demand generation and removal of alginate biocompatible microvalves for flow control in microfluidics, Sensor. Actuator. B Chem. 234 (2016) 1–7.

[159] S. Gallagher, A. Kavanagh, B. Ziólkowski, L. Florea, D.R. Macfarlane, K. Fraser, D. Diamond, Ionic liquid modulation of swelling and LCST behavior of N-isopropylacrylamide polymer gels, Phys. Chem. Chem. Phys. 16 (2014) 3610–3616.

[160] T. Akyazi, J. Saez, J. Elizalde, F. Benito-Lopez, Fluidic flow delay by ionogel passive pumps in microfluidic paper-based analytical devices, Sensor. Actuator. B Chem. 233 (2016) 402–408.

[161] J. Ter Schiphorst, J. Saez, D. Diamond, F. Benito-Lopez, A.P.H.J. Schenning, Light-responsive polymers for microfluidic applications, Lab Chip 18 (2018) 699–709.

[162] J. Saez, T. Glennon, M. Czugala, A. Tudor, J. Ducreé, D. Diamond, L. Florea, F. Benito-Lopez, Reusable ionogel-based photo-actuators in a lab-on-a-disc, Sensor. Actuator. B Chem. 257 (2018) 963–970.

[163] Y. Qin, H. Kwon, M.M.R. Howlader, M.J. Deen, Microfabricated electrochemical pH and free chlorine for water quality monitoring: recent advances and research challenges, RSC Adv. 5 (2015) 69086–69109.

[164] M. Torres-Mapa, M. Singh, O. Simon, J.L. Mapa, M. Machida, A. Günther, B. Roth, D. Heinemann, M. Terakawa, A. Heisterkamp, Fabrication of a monolithic lab-on-a-chip platform with integrated hydrogel waveguides for chemical sensing, Sensors 19 (2019) 4333.

[165] S. Herber, J. Bomer, W. Olthuis, P. Bergveld, A. Berg, A miniaturized carbon dioxide gas sensor based on sensing of pH-sensitive hydrogel swelling with a pressure sensor, Biomed. Microdevices 7 (2005) 197–204.

[166] R.J. Russell, M.V. Pishko, C.C. Gefrides, M.J. McShane, G.L. Coté, A fluorescence-based glucose biosensor using concanavalin A and dextran encapsulated in a poly(ethylene glycol) hydrogel, Anal. Chem. 71 (1999) 3126–3132.

[167] van der Linden, J. Heiko, S. Herber, W. Olthuis, P. Bergveld, Stimulus-sensitive hydrogels and their applications in chemical (micro)analysis, Analyst 128 (2003) 325–331.

[168] O. Czakkel, B. Berke, K. László, Effect of graphene-derivatives on the responsivity of PNIPAM-based thermosensitive nanocomposites — a review, Eur. Polym. J. 116 (2019) 106–116.

[169] Y. Zhan, Y. Zeng, L. Li, F. Luo, B. Qiu, Z. Lin, L. Guo, Ratiometric fluorescent hydrogel test kit for on-spot visual detection of nitrite, ACS Sens. 4 (2019) 1252–1260.

[170] V.F. Curto, C. Fay, S. Coyle, R. Byrne, C. O'Toole, C. Barry, S. Hughes, N. Moyna, D. Diamond, F. Benito-Lopez, Real-time sweat pH monitoring based on a wearable chemical barcode micro-fluidic platform incorporating ionic liquids, Sensor. Actuator. B Chem. 171 (2012) 1327–1334.

[171] B. Chen, J. Dong, B. Li, C. Xue, P.A. Tetteh, D. Li, K. Gao, X. Deng, Using a freshwater green alga Chlorella pyrenoidosa to evaluate the biotoxicity of ionic liquids with different cations and anions, Ecotoxicol. Environ. Saf. 198 (2020) 110604.

[172] T.R. Ray, J. Choi, A.J. Bandodkar, S. Krishnan, P. Gutruf, L. Tian, R. Ghaffari, J.A. Rogers, Bio-integrated wearable systems: a comprehensive review, Chem. Rev. 119 (2019) 5461–5533.

[173] J. Saez, F. Benito-Lopez, G. Arana, L.A. Fernandez-Cuadrado, Ionogel-based nitrate sensor device, Proceed. IEEE Sensors. (2017) 16614612.

[174] P. Cui, S. Wang, Application of microfluidic chip technology in pharmaceutical analysis: a review, J. Pharm. Anal. 9 (2019) 238–247.

Janire Saez is a Marie Curie Fellow and Research Associate in the Bioelectronic Systems and Technology group at the University of Cambridge working on bioelectronics and microfluidics. She has a degree in Chemistry and a Master's degree in Pharmacology from the University of the Basque Country (UPV/EHU). In 2017, she obtained her PhD in Environment and Marine Resources from the same university. During this time, she studied the integration of smart materials into microfluidic devices for environmental water monitoring, fluidic handling and sensing.

Raquel Catalán-Carrio studied Chemistry in the University of Valencia and completed her master studies in Electrochemistry in the Department of Physical Chemistry in 2014. Then, she worked in the Polytechnic University of Valencia (UPV) studying the corrosion of hip prosthesis, for six months. In 2018 she finished another master degree in Environmental Contamination and Toxicology at the Basque Country University (UPV/EHU) on microfluidics for the detection of nitrite and nitrate in water. Now, she's doing her PhD in the generation of innovative detection systems based on microfluidics and optical fibers to monitor water analytes at the point of need.

Róisín M. Owens is a University Lecturer at the Dept. of Chemical Engineering and Biotechnology in the University of Cambridge and a Fellow of Newnham College. She received her BA in Natural Sciences (Mod. Biochemistry) at Trinity College Dublin, and her PhD in Biochemistry and Molecular Biology at Southampton University. From 2009 to 2017 she was a group leader in the dept. of bio-electronics at Ecole des Mines de St. Etienne, on the microelectronics campus in Provence. Her current research centers on application of organic electronic materials for monitoring biological systems in vitro, with a specific interest in enhancing the biological complexity and adapting

the electronics to be fit for purpose. She currently serves as co-I and co-director for the EPSRC CDT in Sensor Technologies, renewed in 2019. She is a 2019 laureate of the Suffrage Science award. From 2014 to 2020, she was principle editor for biomaterials for MRS communications (Cambridge University Press), and she serves on the advisory board of Advanced BioSystems and Journal of Applied Polymer Science (Wiley). In 2020 she became Scientific Editor for Materials Horizons (RSC). She is author of 80+ publications and 2 patents and her work has been cited more than 4000 times.

Lourdes Basabe-Desmonts is an IKERBASQUE Research Professor and the group leader of BIOMICS microfluidics Research Group at the University of the Basque Country (UPV/EHU). Her team is focused on the development of microtechnologies for lab-on-a-chip applications for biology and medicine, comprising areas such as chemistry, micro and nano engineering of surfaces, optical sensing, microfluidics, microsystems for single cell studies and point of care diagnostics. She is co-founder of the Microfluidics Cluster UPV/EHU. Lourdes studied Chemistry at the Universidad Autónoma de Madrid, then she did a PhD at the University of Twente in Supramolecular Chemistry and Nanotechnology. Following she joined the Biomedical Diagnostics Institute in Dublin where after a postdoc in polymer microfluidics she became a team leader on "microtechnologies for platelet biology". In June 2012 she was appointed Research Professor by IKERBASQUE the Basque Foundation of Spain in Spain.

Fernando Benito-Lopez studied chemistry at the Universidad Autonoma de Madrid and completed his master studies in the Department of Inorganic Chemistry in 2002. He obtained his PhD at the University of Twente, The Netherlands in 2007. He carried out his postdoctoral research in the group of Prof. Dermot Diamond at Dublin City University, Dublin, where in 2010, he became Team Leader in polymer microfluidics. In 2012 he moved to CIC microGUNE a Research Center working in Microtechnology in Spain. In 2015 he became Ramón y Cajal Fellow at the University of the Basque Country, Spain. He is currently Assoc. Prof. of the Microfluidics Cluster UPV/EHU at the University of the Basque Country.