The Water Pathway and Microfluidics: A Potential Solution to the Global Water Crisis

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Abstract. How can we ensure the access to water, a basic resource, for the global population? Among the several challenges related to water, we can highlight the reduction of water availability inherent from the climate changes, fountain contamination due to the low sanitation levels and the losses related to leaking in the distribution systems. In the present paper was presented a script for the cycle of use/reuse of water in human activities, “The Water Pathway”, and the use of Microfluidics as a technology capable to be used along this cycle. Our main goal was to identify fundamental stages along the different steps of the use/reuse water cycle in distinct human activities. Also, a generic flowchart was proposed to aid the identification of required knowledge and skills in the stages of the cycle. Then, some applications of Microfluidics in the Water Pathway were highlighted.

1. Introduction

According to the World Bank, about 45 million of cubic meters of water were wasted daily in developing countries, spending more than US$ 3 billion per year [1]. Therefore, how can we ensure the access to this basic resource for the global population? In this context, the United Nations proposed the SGD6 to guarantee the availability and a sustainable management of water and sanitation for everyone [2]. Among the several challenges related to water, we can highlight the reduction of water availability due to the climate changes, fountain contamination due to the low sanitation levels and the losses related to leaking in the distribution system piping [2]. Accordingly, which knowledge and skills could be useful to achieve the SDG6? In the present paper is presented a script for the cycle of use/reuse of water in human activities, named as “The Water Pathway” that integrates the natural hydric cycle and the use of Microfluidics as a technology capable to be used along this cycle. Our main goal was to identify fundamental stages along the different steps of the use/reuse water cycle for distinct human activities. Also a generic flowchart was proposed to aid the identification of required knowledge and skills in the several stages of the cycle. The following stages were identified: withdraw, treatment, analysis, use/reuse and discharge and it was organized according to flowchart provided in Figure 1.
2. Use/Reuse Cycle: The Water Pathway

The starting point is the water withdraw that is basically performed by dealership companies (private or public), surface fountains (rivers, lakes or dams), underground aquifer, rain or atmospheric vapor. Over the hydrological cycle, water can be stored in distinct reservoirs: oceans, polar caps and glaciers, surface water (rivers and lakes), underground sources and as atmospheric vapor. About 97% of available water in Earth is salt water (oceans and seas), and only 3% is fresh water. From these 3%, only 1% (or 0.03% of the total water) is from surface sources, while about 20% of fresh water (or 0.6% of total water) is found in the subsoil. Therefore, there is about 20 times more fresh water in the underground than in the surface! This information already highlights the importance of hydrogeology knowledge for the sustainable use of underground water [3]. Furthermore, it is fundamental to consider the climate change effects in the pluviometric regimes, affecting the hydric availability of surface and underground water sources [4]. After the withdraw stage, we can observe the analysis step. This stage is repeated several times from withdraw to discharge. The analysis can refer to two attribution types: quantity and quality, both essential to define the availability concept. Here, we shall define two universal quality criteria:

1) Quality criteria related to human consumption (potability)
2) Quality criteria to effluent discharge (urban or industrial) in a water body (rivers, lakes and seas).

In the Brazilian legislation, there is groups of parameters regulating the potability standards of water for human consumption that establish thresholds for a total of 91 parameters, such as microbiological, inorganic, organic, pesticides, disinfectants and derivatives, cyanotoxins, radioactivity and organoleptic. However, due to the technical and costs limitations, not all of these parameters are monitored in the recommended frequency. Furthermore, the lack of well-established models of dose-response impedes a realistic description of how the pollution affects economy and health. Organizations such as WHO and EPA determine safety levels of concentration for several common pollutants. Despite these concentration levels are partially based on recent scientific reports, there is still uncertainties about the real safer thresholds.

After the analysis step, the treatment stage also is repeated in different stages over the cycle. Distinct treatment technologies aim to adjust the water to the different quality standards related to the specific usage. In this context, there are limits for physical, physicochemical, chemical and biological properties. The water treatment could be divided in three main categories:

1. Purification for domestic use/reuse
2. Treatment for specific industrial use/reuse
3. Treatment of effluents, domestic and industrial sewage, for discharge or reutilization
Accordingly, in the face of diversity usage of water we can conclude that there is no single better treatment. A better treatment would be defined as that capable to achieve the quality standards considering the water source and the destination usage with the lower cost (direct and indirect).

The water for human or animal consumption must be disinfected to eliminate pathogenic microorganisms, however can contain considerable levels of calcium and magnesium (hardness of water). In contrast, water used in boilers for steam generation can contain bacteria, but must be softening (removal of calcium and magnesium salts) to avoid incrustation inside the equipment. In this context, water passes by different treatment stages for human consumption (potability) and for effluent discharge (urban and industrial) in water bodies (rivers, lakes and seas). Firstly, we shall consider the treatment focused in human consumption. The water is initially withdrawn from a source (well, spring, river or lake) and undergoes a railing step to remove large residues, such as leaves, branches, packing, etc. Most part of solid material remains in suspension and requires the addition of coagulants, such as the iron (III) chloride or aluminum sulfate, generating a gelatinous precipitate. The suspended particles are adsorbed in this gelatinous precipitate and then sediment in a decantation tank. Following, a filtration stage is performed in a sand or activated carbon filter. Finally, the addition of chloride and fluoride and the final pH correction by addition of lime are performed. Two great challenges in water treatment for human consumption are:

- The suitable destination for large volumes of sludge from water treatment stations [5]
- The inability of conventional treatment systems to remove the emerging contaminants [6]

So, what about the effluent discharge? The investments on effluent treatment are justified by the simple fact that lower overload levels in natural depuration systems, results in the disposal of effluents with lower organic concentrations in the water bodies. Accordingly, it will result in better quality water in the withdraw points, requiring simpler and cheaper treatment to achieve potable water. The main steps in effluent treatment are: pre-treatment, primary, secondary and tertiary treatment stages. Pre-treatment aims to protect the equipment of the treatment station, with little effect on organic concentration reduction. This stage implies only on the suspended solid reduction and storage of effluent for the posterior stages. The pre-treatment stage can include: railing, sieving, trituration, desarenation and equalization.

Primary treatment promotes the removal of dissolved solids, suspended solids and wax and oils from effluents. About 50-60% of suspended solids are removed in this stage and also about 35% of biochemical oxygen demand (BOD), depending on the used process. The most frequently employed unit operations are sedimentation and flotation (with coagulation and flocculation). It is important to keep in mind that all sedimented or floated material in the sludge form is a waste requiring specific treatment. The secondary treatment encompasses all biological treatments including aerobic and anaerobic processing. The main goal is to convert organic matter (e.g. waxes, proteins and sugars) contained in the effluent into inorganic matter (e.g. carbonates, sulfates, phosphates, etc.) and sedimentable biological material (bacterial flakes) that can be removed in decantation tanks. The technologies employed in the tertiary stage started to be adopted as a consequence of increase on water reuse projects due to the reduction on water availability and increment on water demand.

Among the tertiary treatment technologies, we can highlight: Maturation Ponds; Adsorption in Activated Carbon; Ion Exchange Resins; Removal of Nutrients - Nitrogen and Phosphorus; Advanced Oxidative Processes (AOPs); Separation Processes by Semipermeable Membranes (Reverse Osmosis; Electrodialysis and Membrane Bioreactors). Still, none of treatment technologies is capable to carry out “alone” the demand from distinct uses. For example, the association of a tertiary treatment (e.g. AOP), as a pre-treatment (or even, post-treatment), jointly with a secondary treatment (biological processing) is, from the economic and environmental point of view, an important alternative to make feasible reuse projects or even to control the chronic toxicity of the effluent.

Based on the aforementioned, we can conclude that to achieve water availability and sustainable management of water and sanitation for everyone it is required a large process chain dependent from the hydrological cycle to the treatment, analysis and quality evaluation stages. Accordingly, it is necessary to develop technologies that could facilitate and democratize the access of water to everyone.
In this context, the Microfluidics appears as a new technology that can greatly contribute in the use/reuse cycle of water.

3. Microfluidics

Defined as the science and technology that employs structured channels with dimensions ranging from tens to hundreds of micrometers, the Microfluidics presents a major potential in the project, development and optimization of chemical process [7]. Micrometric systems, also called microdevices, allow the handling of low amounts of reactants and samples, also provides superior reaction performance with shorter residence times and better control of chemical species concentration and high rates of heat and mass transfer due to elevate surface area-to-volume ratio (A/V, about 20000 m² m⁻³) [8]. Some successful applications of Microfluidics include: Healthcare Diagnostics, Analytical Devices, Pharma & Life Sciences research, Microreactors – Flow Chemistry, among others [9]. For this wide range of applications, researches and professionals working with Microfluidics must have easy access to the microfluidic devices. These devices can be manufactured by photolithography, micromolding, micromachining and 3D printing, using materials like glass, polymers, ceramic, metals and others. Such characteristics provide an easy access for the development and fabrication of the devices, also providing the required mechanical and chemical resistance for the specific process application. Furthermore, microscale process can achieve higher throughputs by the application of numbering-up concept. This can be defined as a modular scale-up procedure, using several units of the optimized microdevice in a parallel arrangement, resulting in a continuous process with higher flow rate capacity and also providing more flexible operation and maintenance. The numbering-up concept yields smart time-to-market results, allowing the development of new products and processes [7]. This is a fundamental key to increase the product and process variety, being one of the greatest advantages of Microfluidics usage by professionals to overcome the challenges from the use and reuse cycle of water. Accordingly, in the next section some applications of Microfluidics in the Water Pathway are highlighted.

4. Microfluidics Technologies Applied to Use and Reuse of Water

The Microfluidics has received great attention in water and effluent treatment. Microdevices can be used for analytical tasks, such as the Lab-on-a-Chip (LOC) and the micro total analysis systems (μTAS). Such devices integrate and automate multiple laboratory tasks into a small chip, allowing in-situ measuring and monitoring of water quality parameters. Also, microdevices can be employed in secondary and tertiary stages of water treatment. The concept of numbering-up can be applied to achieve the desired throughput. Accordingly, efforts have been spent to develop specific microreactors, since chemical treatment presents major advantages over physical. Chemical processing performs the destruction of harmful compounds in innocuous species, thus, do not require further treatment. In this context, the state-of-art of electrochemical and photocatalyst microreactor technologies are presented below. Also, the reader can find a comprehensive review about Microfluidic devices on water quality monitoring sensors as provided by Jaywant and Arif [10].

Electrochemical technologies appear as one of most promising techniques for water and effluent treatment. In general, the fluid to be treated must flow between two electrodes. The electrode plates can be arranged in parallel with fluid flow, the Flow-By (FB) configuration or the fluid can flow through the electrode, the Flow-Through (FT) design, as for example 3D meshed/porous electrodes. Further details about these configurations, as well, about electrochemical oxidation of pollutants are provided by Santana et al. [11]. The key-factor for the development of an electrochemical reactor is the energy consumption, directly related to the ohmic drop. Higher consumption of energy occurs especially in the purification of low-conductive water. The ohmic drop is inherent from the energy dissipation directly due to the inter-electrode spacing, the IE gap. One strategy to improve electrolyte conductivity is to increase the electrolyte concentration. In contrast, this leads to secondary pollution, once higher concentration of inorganic compounds will be carried out in effluent, increasing operational costs [12,13]. Microfluidic devices allow small IE gaps (below 1000 μm) and also present
higher oxidation rates due to the mass transfer enhancement [13]. Scialdone et al. [13] listed some advantages of microdevices over traditional reactors: easier scale-up procedure using parallelization (numbering-up), faster optimization of operating conditions inherent from small IE gaps and shorter residence times and the potential use of multistage electrochemical cells, arranged in series to operate under optimal current densities. Scialdone et al. [14] also proposed a micro-electrochemical cell with IE gaps ranging from 50 to 75 μm. The oxidation of formic acid was evaluated. Superior performance was noticed at longer residence times and higher current densities. 99% of formic acid was abated at 0.05 mL min⁻¹ and IE gap of 50 μm. Scialdone et al. [13] compared macro- and micro-fluidic electrochemical cells for the abatement of chloroacetic acid (CAA) by direct and indirect oxidation pathways. The authors compared a stirred batch glass cell (system I) with IE gap of 1 cm and electrodes plates of 3 cm² with a filter-press reactor (system II) with IE gap of 4 cm and electrodes plates of 10 cm² and with a single-pass microreactor (system III) with IE gap ranging from 50-100 μm and electrodes plates of 5 cm². The system III exhibited superior performance also without the use of supporting electrode, an essential element in traditional macro reactors. Abatement over 90% of CAA was observed for the microreactor under low current densities with a IE gap of 100 μm. Perez et al. [10] proposed a flow-through microreactor (FTMR) using meshed electrodes. These characteristics resulted in higher electrode surface area (52.8 cm² for the cathode and 49.5 cm² for the anode). The microreactor performance was assessed for IE gaps of 6,000-1,000 and 400 μm by comparing the mineralization of clopyralid with a stirred tank reactor (STR) with IE gaps of 25,000-6,000 and 1,000 μm. The FTMR exhibited lower energy consumption (6-15 times) and electric charge (4-10 times) regarding the STR. The estimated mass transfer coefficient was 70% higher than in the STR and the ohmic resistances was about 6 times lower for an IE gap of 1,000 μm. Seymour et al. [15] proposed a microdevice using solid state interdigitated electrodes to perform in-situ pH control simultaneously detecting free-chlorine, a measurement that requires buffering of samples. The authors reported effective chlorine detection for tap water samples. The proposed micro-analytical platform presents a potential of a reagent-free approach for in-line chlorine measurements and could be used in water distribution networks. Arena et al. [16] manufactured a 3D-printed, highly ordered porous electrode. The 3D meshed electrode presented good catalytic activity, active surface area and mass transfer. The authors highlighted the versatile fabrication of specific designed electrochemical reactors. The advancement of 3D printing techniques and the superior performance of FT electrochemical reactors in the scale-up depicts the great potential of a synergetic application between additive manufacture and Microfluidics. Furthermore, Computational Fluid Dynamics (CFD) can be a powerful tool for Research and Designs of such electrochemical microreactors.

Photocatalytic processes also received great attention in the fields of water treatment using Microfluidics. Photocatalysis is a sequence of oxidation-reduction reactions, driven by photo-excited electron activated by photon absorption that carries an amount of energy equal, or higher than, the catalyst band-gap energy [17]. Photocatalytic reactors appear as promising tools to effectively decompose a wide range of organic compounds into innocuous species by the use of irradiation sources, commonly from sunlight or ultraviolet (UV) [17]. Usually, titanium dioxide (TiO₂) is used as photocatalyst due to its high efficiency and stability and safety. Also, it is nontoxic and chemically and biologically inert [18]. The performance of photocatalytic reactors depends on three main limiting factors: mass transfer – directly related to the surface area-to-volume ratio (A/V); photon transfer – related to the uniform radiation of the catalytic surface; and the available dissolved oxygen – related to the oxidation reaction pathway, also correlated with mass transfer. The combination of microfluidic devices with photocatalytic technology resulted in the Optofluidics, an emerging field aiming the synergetic development of Microfluidics, Optics and Photonics. Traditional photocatalytic reactors, or bulk reactors, can be classified in two groups: slurry reactors (SR) and immobilized reactors (IR). The SR consists in photocatalyst particles suspended in the liquid media. This configuration results in large A/V and good mass transfer rates, contrasting with limitations of light scattering and light absorption by the suspended particles. Also, SR requires an additional filtration operation, to remove the particles from the effluent. IR consists in the coating of photocatalyst on substrates. Low A/V and mass transfer
rates are the major drawbacks of IR. Good photon transfer is the major advantage of such design. Some variations of bulk reactors were also proposed, however, no single configuration was capable to overcome the three major limiting factors yet. Photocatalytic microreactors (PCMRs) present some advantages over traditional reactors: larger surface area-to-volume ratio (A/V), short and uniform residence time, diffusion path reduction and uniform irradiation. As previously stated, the A/V is usually over 20,000 m$^2$m$^{-3}$ [8] and can reach about 300,000 m$^2$m$^{-3}$ in PCMR, against about < 600 m$^2$m$^{-3}$ of traditional bulk reactors [19]. Higher abatement of pollutants (> 90%) were noticed for very short residence times (about tens of seconds) against several hours observed in traditional reactors [19, 20]. In general, PCMR presents coated photocatalyst and the fluid to be treated flows over this layer. Due to the micrometric size scale, uniform irradiation and high illumination efficiency are obtained. Also, optimal microdevices are capable to treat most of pollutants in one single run, without requiring multiple passes, a common strategy necessary in bulk reactors [17]. Lei et al. [20] proposed a planar microreactor (PMR) using solar radiation and three setups to deteriorate methylene blue. The reaction rate constant increased over 100 times concerning bulk reactors. The observed degradation was 94% for a residence time of 36 s. Meng et al. [21] proposed PCMR using nanofibrous TiO$_2$, providing shorter diffusion path, higher photocatalytic activity due the higher A/V of nanofibers. Superior degradation of methylene blue (> 99%) was observed for the nanofiber PCMR against 40% from a traditional wall-coated film PCMR, both at residence time of 53 s. Leblebici et al. [22] evaluated the performance of 12 photocatalytic reactor designs including a microreactor. The authors evaluate the photocatalytic space-time yield (PSTY, in m$^3$ water day$^{-1}$ m$^{-3}$ reactor kW$^{-1}$ lamp), a benchmark correlating the key operating parameters of: flow rate of wastewater processed, reactor volume, apparent reaction rate and lamp power. The overall superior PSTY was 0.72 obtained for a tubular slurry reactor. The microreactor scored PSTY = 0.0108, however the authors emphasized that the microreactor PSTY could increase up to 13 with a lamp power optimization, as for example, using LED arrays. Another feature highlighting the potential usage of photocatalytic microreactors was the reaction constant rate with a magnitude order about 10$^6$ day$^{-1}$ against 10$^1$ to 10$^2$ day$^{-1}$ from other reactor designs. Azzouz et al. [23] proposed a tree-branched microfluidic photocatalytic reactor using zinc oxide nanowires (ZnO NWs). High abatement efficiency of 95% of a BTEX mixture (VOCs: benzene, toluene, m–p Xylenes; and o-Xylene) was observed for a single pass and short residence times < 5s. The authors reported the potential application of the microdevice in a realistic throughput of 400 mL day$^{-1}$. The estimation was made based on the degradation efficiency and the stable photocatalytic activity by ZnO NWs. Optimized PCMR must cover intensification of mass and photon transfer, efficient oxygen supply and high efficiency irradiation. Numbering-up is a smart strategy to achieve the desired throughputs, therefore, uniform distribution of flow and irradiation must be considered in the design stage. Also, advances in Material Science and Nanotechnology appear as very promising fields to aid the photocatalytic microreactors development and optimization.

5. Conclusion
In this article we show “The Water Pathway”, a use and reuse of water that integrates the natural hydric cycle and technologies. We identified the fundamental stages for the water use/reuse cycle in different human activities. After discussing "The Water Pathway" we show the application of Microfluidics as a possible solution to the problems that were identified in the use/reuse cycle. Using these two concepts we think that it is possible to ensure water for the entire global population.

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