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Water treatment chemicals: Trends and challenges

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ABSTRACT

The addition of water treatment chemicals has always been considered as a standard operation in water and wastewater treatment. The concentration of chemicals was usually kept to the minimum necessary to achieve a good quality of potable or otherwise treated water. A significant interruption to the status-quo occurred more than 20 years ago after a severe and highly publicized outbreak of *Cryptosporidium parvum* oocysts. The strategic planning after the outbreak was to shift from physical-chemical to physical treatment methods, such as membrane filtration and UV disinfection. As such, the new procedures were supposed to eliminate the threat of water contamination through a minor addition of chemicals. Such was the mistrust and disappointment with water treatment chemicals themselves.

Indeed, water treatment technologies are now using novel physical treatment methods. Membranes largely replaced granular filtration, and UV is paving the way towards minimization or elimination of the use of classic disinfection chemicals, such as chlorine and its derivatives. Yet, far from the "high-tech" revolution in water treatment technologies actually reducing the use of chemicals, the latter has in fact been significantly increased. The "conventional" chemicals used for pre-treatment, disinfection, corrosion prevention, softening and algae bloom depression are all still in place. Furthermore, new groups of chemicals such as biocides, chelating agents and fouling cleaners are currently used to supplement them. These latter are the chemicals needed to protect the high-tech equipment, to optimize the treatment, and to clean the equipment between uses.

The health effects of the new chemicals introduced into water are yet to be fully established. Typically, a higher treatment efficiency requires effective chemicals, yet these are not always environmentally friendly. It seems obvious that the "high-tech" revolution currently affects the sustainability of water resources, and certainly not in a completely positive way. In short, the adverse effects of the introduction of such a significant amount of treatment chemicals into our sources of water are yet to be evaluated.

1. Water treatment processes

For the last century, industrial water treatment has evolved from an optional and voluntary approach into a must-have multistage operation, which is applied to substantially improve the quality of potable water. After many trials and failures, the technology has established a set of well-defined treatment processes that are widely applied to various water feeds.

A typical separation process is based on the characteristics of the feed mixture. Water treatment has a pre-set combination of separation processes applicable to water of almost every possible origin. This combination is a sequence of several robust processes, selected from a rather limited list of about twenty processes in total. The processes are applied in sequence, each in a separate reactor. For example, a typical process setup for the treatment of surface feed water to the potable level comprises the stages of initial screening, coagulation, flocculation, sedimentation, filtration and disinfection. Whilst in the past some of these methods were used individually, current water treatment practices a multi-barrier approach. The term was coined by the US EPA some 40 years ago and means that no single treatment process is relied upon to ensure the required potable water quality for at least 95% of the treatment time. A sequence of several methods in series not only has a synergistic effect, it also ensures that the system as a whole will still be capable of treating the water when one stage fails and during the subsequent failure discovery and repair. A second benefit of the multi-barrier approach is the must-have coexistence of chemical and physical treatment methods. Chemical and physical methods have been used to back each other up for many years, and that trend will continue for the near future.

Coagulation and disinfection are the two stages in the water treatment process that are based principally on the introduction of chemicals into the feed water. In a coagulation process, the introduction of

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chemicals followed by hydrodynamic shear results in the subsequent formation of particle-particle agglomerates (for which the particles are often colloidal or macromolecular), known as flocs [1,2]. This floc formation process, named flocculation, is followed by the physical retention of flocs. This retention exploits the increased floc density and larger dimensions relative to the constituent particles. Dense, large flocs settle down quickly from a feed mixture by a process called sedimentation. Alternatively, these flocs are attached to air bubbles and floated away in the 'Dissolved Air Flotation' process. Small, less-dense flocs or unflocculated particles are removed by filtration [3].

The process of chemical disinfection is based on the introduction of free chlorine or other oxidizing agents in a gaseous, liquid or powdered form. Chlorine disinfection has been established for more than a century as a cost-effective and robust disinfection process, and it is likely to remain as such. The biggest undesired side effect of the introduction of chlorine into water is the formation of trihalomethanes. These compounds arise from the reaction of free chlorine with organic matter present in the feed water [4]. Typical concentrations of free chlorine in water are therefore limited to avoid the formation of trihalomethanes, and are consequently less successful in the disinfection of some modern pathogens [5,6].

Both coagulation and chemical disinfection depend upon the feed water quality and the use of adjustable chemical doses. Despite the fact that dosage adjustment is often performed by qualified personal at centralized water treatment facilities, the resulting water quality is not always satisfactory. If we add to this the need for the addition of many different chemicals into the water and the requirement for appropriately qualified personnel at centralized treatment facilities, the incentive to replace existing chemical water treatment methods is clear.

The need to develop robust water treatment methods using a minimum amount of chemicals became even more pressing after the occurrence of several severe outbreaks of waterborne pathogens through water treatment systems. A massive and heavily documented outbreak of *Cryptosporidium parvum* occurred in Milwaukee (Wisconsin), USA. The Milwaukee water treatment plant included all the stages that were considered to be perfectly adequate for a solid water treatment operation; coagulation, flocculation, sedimentation, sand filtration, and chlorination units operated in series represented the most tried and tested process to date employed around the world, and as such was considered at the time to be the most effective and dependable. However, a double failure of chemical treatment methods occurred when the coagulant dosing pump failed to operate and the chlorine dose was simply tuned to meet the WHO recommendations [7]. A subsequent investigation revealed that there was a close distance between the water intake and the filter backwash discharge. This resulted in a closed loop, whereby oocysts that had been washed out from the filter eventually appeared in the feed. The concentration of cysts constantly increased until a breakthrough occurred across the filter during a filter run; this was compounded by the double chemical failure.

The Milwaukee event revealed the weakness of the usual "conventional" approach and was a clear trigger to search for better alternatives. Along with a thorough investigation of the reasons and consequences of the outbreak, the US EPA lunched a large program of investigation that was aimed at looking for alternatives to the chemical treatment processes. The significant funding by the EPA boosted the development of several methods that already existed on the market. Among these, membrane filtration was supposed to replace all types of coagulation-flocculation-sedimentation-filtration stages, and UV light was supposed to replace the chemical disinfection albeit with the need for small amounts of secondary disinfectant [8]. Both methods are strictly physical and *per se* do not require any chemicals. A blooming development of ultrafiltration (UF) and UV processes was supposed to gradually decrease dependence on the addition of chemicals and thereby to increase the sustainability of water treatment processes.

Since the Milwaukee plant was unable to prevent the penetration of the pathogens, the US EPA started to consider other options. True, if an outbreak of such size should have occured outside the US, we might have seen no changes. But there we saw a massive allocation of taxpayer's money to develop and implement several new technologies, such as UV disinfection and low-pressure membranes, for surface water treatment.

The expected paradigm shift was partially realised. We are witnessing a boost in both UV and UF technologies on the water treatment market. During the last decade alone, the average sales of UF processes and membrane processes in general has more than doubled, with the compound annual growth rate (CAGR) at around 10% and with $15 billion annual revenues worldwide. The UV technologies do not lag far behind, with a stable 6% GAGR.

For industry, the water treatment market became increasingly attractive with a stable growth and significant revenues, and many companies that were not initially involved in the market moved in. For example, in 2011, the German chemical giant BASF purchased a membrane company Inge AG and became immediately engaged in a large $125 million membrane installation process. Another large German company Lanxcess, which was initially in the resin market, found the resins increasingly attractive in water treatment for the retention of ions and non-polar molecules. The company currently offers not only ion exchange resins but also membrane polymers and the membranes themselves. In-line with a current comprehensive approach, the companies offer a complex solution for treating water from feed up to tap quality. And what is more logical for a chemical company than to offer a combined chemical-physical treatment that once again includes the use of chemicals?

2. Water treatment chemicals – the full picture

Water treatment chemicals are the solid core of water treatment processes. They became essential about a hundred years ago, after an expert panel discussion on the chlorination of potable water as a means of preventing waterborne diseases [9]. They became even more essential after the introduction of coagulants and the intensification of filtration processes [10]. They are and will remain essential in corrosion prevention, the softening of hard water, the depression of algal blooms and many other important applications. They should be added to treat water, for which there is no question. What is debatable is which chemicals should be added to the water, and in what precise amount. Table 1 presents the chemicals used world-wide in water treatment in 1981, and the quantities consumed.

Table 1
Water Treatment Chemicals used in 1981.

Group	Chemical	Total weight, tons
Coagulants and flocculants	Alum	152 801
	Ferric chloride	15 583
	Ferric sulphate	6 196
	Polyelectrolytes	4 280
	Sodium aluminate	2 650
	Ferrous sulphate	1 912
Disinfectants and oxidizers	Hypochlorite	440 222
	Chlorine	104 477
	Sodium chlorite	6 369
	Ammonia	2 497
Precipitation and softening	Calcium oxide	349 312
	Hydrated lime	86 313
	Sodium hydroxide	49 093
	Carbon dioxide	18 604
	Soda ash	15 805
	Sodium chloride	6 369
Algaecides	Copper sulphate	1 051
Corrosion inhibitors	Phosphates	8 891
Others	Fluoride compounds	37 327
	Activated carbon	9 287