Water purification: from ancient civilization to the XXI Century

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Abstract
Ancient civilization valued the vital role of water in human life. As reflected in the literature, environmental awareness led to early water treatments and these are briefly described in this paper. Thus the period prior to 500 BC to 1000 AD saw the use of naturally occurring materials for water purification, the building of aqueducts, and the introduction of the distillation process. This was followed by a dormant period of five centuries in which hardly any progress was made in water purification methodology. From the 17th to the 19th century, progress was made on filtration processes and the introduction of the microscope. In addition chemical methods for water disinfection by the use of chlorine and ozone were reported. These methods and their combination progressed significantly through the 20th century. However the problems associated with chemical contamination of ground water, from which, drinking water is mainly generated remained practically ignored for about five decades. It was in the late seventies that this was brought to light. Since then technologies for groundwater purification started to emerge but a lot remains to be done in this area of research. The crucial role of suitable analytical tools for any technological development which aim to remove toxic pollutants from water is acknowledged. Thus the need of re-visiting old methodology making use of the advantages resulting from the availability of advanced analytical techniques and the possibility of enriching naturally occurring materials by the introduction of supramolecular receptors for water decontamination purposes are emphasized.

Keywords
Hippocrates filter; natural attenuation; supramolecular chemistry; water purification

Introduction
Water is a chemical substance essential to life to an extent that we cannot live without it. As such, water is closely tied to the history of civilisation. Although scientific achievements have contributed significantly to our present understanding of the role of water in every day life, there is a great deal to be investigated on its unique physico-chemical properties (Clementi, 1976; Eisenberg and Kauzmann, 2005).

In the last few decades the concept of Supramolecular Chemistry has been introduced by Lehn (Lehn, 1995; Steed and Atwood, 2000). Unlike Molecular Chemistry (covalent bonds between atoms to give molecules), Supramolecular Chemistry is concerned with the association between two or more chemical species to give the ‘supermolecule’ through weaker interactions (electrostatic forces, hydrogen bonding, van der Waals, etc) than those involved in Molecular Chemistry (Cox and Schneider, 1992). Within Supramolecular Chemistry the concept of ‘self assembly’ has been extensively discussed (Voet and Voet, 1995) in recent years. In fact, water, the most known chemical substance, shows self-assembly behaviour. Considering its use, water boils at relatively high temperature while its freezing point is much higher than expected (Clementi, 1976; Eisenberg and Kauzmann, 2005). This is attributed to the self-assembly behaviour of water through hydrogen bond formation (Figure 1), regarded by Steed and Atwood as the master key interaction in Supramolecular Chemistry.
Being water such an essential component of life, the search for clean water was already a subject of priority concern in Ancient Civilisations (Hall and Dietrich, 2000). This paper aims to give an account on the main developments in water purification from ancient civilizations up to modern times and how chemistry has contributed to these developments.

**Historical developments**

For the purposes of this paper, it seems relevant to define the areas covered in Ancient Civilizations. According to the literature Ancient Civilisation of the old World covers parts of Africa, Southern Europe, the Middle East and Asia to India. Thus prior to 500 BC there was already concern about the quality of drinking water (Feig, 2006). Thus the lack of awareness about the fact that toxic and tasteless substances may be present in clear water led Ancient Civilization to believe that the clarity and taste of water as assessed by visual observation was an indication of its suitability for drinking purposes.

However the use of chemicals to purify water, mainly to improve its appearance and taste dates back to the 500 BC period. Indeed the Egyptians used iron sulphate or aluminium sulphate or a mixture of the two to extract suspended solids from water. These were known in ancient times as alum and differs from the variety of alums derived from clays, bauxite or alum from alunite known today (potassium alum \[K_2SO_4Al_2(SO_4)_3\cdot24H_2O\]; sodium alum \[Na_2SO_4Al_2(SO_4)_3\cdot24H_2O\]; chrome alum \[K_2SO_4Cr_2(SO_4)_3\cdot24H_2O\]; ammonium alum, \(NH_4Al(SO_4)_2\cdot12H_2O\)). There are representative examples that coagulants were already used in the early stages of civilisation. These coagulants are still used nowadays. Of course parameters such as doses of coagulants, pH and colloid concentrations are now considered (Jeperson, 1996; Barthi, 2000).

Water conservation and properties were already a matter of concern in Ancient India. Thus awareness regarding the presence of minerals in drinking water as well as its acid-base pH balance were among the properties required for pure water besides temperature (cold to touch), cleanliness and transparency. As far as water purification methods are concerned those involving naturally occurring substances such as mixtures of herbs (Jeperson, 1996; Barthi, 2000), including Amla (known today as an antioxidant with the richest source of vitamin C) and Khus (Vetiver, known as oil of tranquillity) among others were...
used. These herbs were introduced to water in wells for purification purposes. Others
methods used for water purification, based on herbs and naturally occurring products and
materials are Nirmali seeds (*Strychnos potatorum*, found now to be useful in obstetrics),
roots of Kanal (lotus/ water lily), rhizomes of algae and different types of stones such as
quartz crystals, garnet and pearls.

Treatment of water with iron or sand (hot) or exposure to sunlight was used. For disin-
fection, boiling followed by exposure of water to sunlight or the introduction of iron, copper
or sand (hot) in water were recommended. It is now well established that copper
interferes with the life cycle of bacteria (*Saeki et al.*, 2002; *Boivin et al.*, 2005). In fact
the use of brass containers to store water was already common practice in Ancient Indian
Civilization. Achievements in water purification methods in the 500 BC to 1500 AD
period are noted by Hippocrates, a Greek philosopher of the classical period (*ca.
460–360 BC*) (*Hall and Dietrich, 2000*). In his article on Airs, Waters and Places he
emphasized the importance of considering the qualities of water and gave a detailed
account through the different parts of his article, on the implications arising from drinking
different types of water on the human body and general health. He is acknowledged
for introducing the conical water filter known as Hippocrates filter.

Numerous aqueducts (about eleven) were built in Ancient Rome in the period 312
BC–AD 226. These were essentially artificial channels for the transport of water to the
city powered by gravity. The fact that the availability of water per inhabitant was around
1 m$^3$/day gives a clear indication that water scarcity was not a problem at the time for a
population of over a million people in the city.

Geber-Jabir Ibn Hayyan (721–815 AD) (*Hilti, 1959; Columbia Encyclopaedia, 2004*)
belonged to the current of Alchemists of Ancient Civilization. He declared that ‘The first
essential in Chemistry is that you should perform practical work and conduct exper-
iments, for he who performs not practical work nor makes experiments will never obtain
the least degree of mastery’. Among his many contributions to Chemistry and Alchemy,
he introduced the distillation process for water purification.

Avicenna (Ibn-Sina) (*Gutas, 1988*) considered boiling as a water purification process
by which the impurities are left in the mineral residue (*Gruner, 1930*). Purification of
water by passing it through a wick of sheep’s wood was also suggested. However the fall
of these civilizations for different reasons interrupted the developments of methodologies
for water purification during the AD 1000–1500 period. Indeed there are no records of
any significant development during this period. It was in the 17th century (1627)
that following a compilation of Natural History over ten centuries Sir Francis Bacon,
philosopher and scientist, introduced his thoughts about desalination, an area of research
which is still in progress today. However his idea that the passage of water through sand
by making a hole close to the sea shore would lead to the removal of salt from water did
not work. Other important developments during the 17th century were the following.

(a) The invention of the microscope (*Wilson, 1995*). Although this is currently attributed
to van Leewenhoek (Dutch) (1632–1723), it is likely that the invention took place earlier.
Indeed several names have been mentioned in the literature. Among them
are Hooke (English) and Suammerdam (Dutch). However there is no doubt that
van Leewenhoek was able to enhance significantly the magnification power of the
lens for practical use and his contributions are documented in a series of letters
addressed to the Royal Society (London). Having stated it, the realization that the
placement of lens in a tube leads to the magnification of objects has been attributed
to Z and H. Janssen (1590) and Hans Lippershey. It was on this basis that the micro-
scope was invented (*Ford, 1991; Croft, 2000*).

(b) The design of the multiple filter by the Italian physician Lu Antonio Porzio.
These two developments were undoubtedly essential tools in biology and water analysis and treatment. Indeed it was the microscope which allowed scientists to visualize living organisms in water to the extent that in 1850 (London) it was this instrument and its improved version which allowed the detection of the cholera bacteria while filtration of water through sand filters significantly reduced the outbreak of cholera (Baker and Taras, 1981). In fact, a British scientist John Snow found a link between cholera and poor water quality.

Prior to this incident during the 18th century, concern about the implications of poor quality water on human health grew significantly. This was mainly motivated by philosophers (16th–18th centuries) who were strongly of the view that pure water was one of the rights of the human race. This statement is based on the fact that the French scientist La Hire put forward a proposal by which sand water filters should be installed in all French households. Two patents were granted in the 18th century, the first one to the French man Joseph Army for designing a filter consisting of sponge and sand while a second one was granted to a British architect, James Peacock in 1791 on the design of a three-tank, upward-flow backward filter (Baker and Taras, 1981; Jeperson, 1996; Hall and Dietrich, 2000).

A century later following La Hire’s suggestion, the first municipal water treatment plant was installed in Scotland as recorded by Baker and Taras. The aim was to provide filtered water to every household. Filters used were those designed by Thorn and later on by Simpson. However two main drawbacks were encountered in that these filters were slow and their size were too large. Consequently their cleaning was a time consuming exercise. These problems were overcome by the development of fast water sand filters in the USA (Hilti, 1959) which were easily cleaned by extensive jet streams of water.

However the ceramic revolution started in 1827 (Survival Unlimited, 2006), when Henry Doulton introduced the ceramic filter to remove bacteria from drinking water using earth and clay materials. In 1835 at the request of Queen Victoria, Doulton produced a water filter which was considered a mixture of art and ceramic technology. Indeed the container was a combination of hand-craft with ceramic filter technology. This development had a considerable impact on sanitation. Almost simultaneously with Pasteur’s discoveries on micro-organisms, Doulton designed in 1862 filters for micro-organisms and subsequently microporous ceramics (diatomaceous earth) capable of removing bacteria with a high degree of efficiency (higher than 99%). These developments had worldwide impact.

The progress made on ensuring water quality in the USA led to the foundation of the American Water Works Company followed by initiatives aiming to standardise bacteriological tests (Hall and Dietrich, 2000). Filtration methodology expanded significantly in the last two decades of the 19th century and thereafter. At present, whole house filtration systems are claimed to be the most up to date water filtration technology. Placed in individual houses, water is filtered as soon as it reaches the house’s plumbing system to remove toxic substances from it.

The effect of the Industrial Revolution was strongly felt. Thus at the end of 19th century chemical methods for tackling water infection were introduced. The aim was to liberate water from harmful bacteria and viruses using either ozone or chlorine for this purpose. The scope and limitations of these two methods as well as other recent approaches for water disinfection have been discussed in the literature (Baird and Cann, 2005).

The Industrial Revolution in the 18th century brought about the exploitation of natural resources and labour with the consequent increase in population and human activities. The developments led to a negative impact on our ecosystem. Chemical contamination started to be a matter of concern. However this concern was mainly centred on surface waters of rivers and lakes. As far as groundwater is concerned, from which drinking
water is mainly generated, the issue of chemical pollution remained dormant for about half a century. It was assumed that Nature through the filtration properties of soil offered a suitable purification method to liberate groundwater from chemical pollutants. It was in the 1970s when chemical contamination of groundwater began to be and still is a matter of serious concern (Baird and Cann, 2005).

By then, very well established methods of chemical analysis were available and new methods were appearing. These are essential tools for the detection (qualitative and quantitative) of contaminants in water as well as for the development of new technological approaches for the removal of pollutants from water. Thus the invention of the hollow cathode lamp by Welsh in 1955 has made absorption atomic spectroscopy one of the most popular analytical techniques in water analysis (Braun, 1987). The introduction of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the eighties (Date and Gray, 1981, 1983a, 1983b) added a very powerful tool for the detection of trace (ppb-ppt) and ultra (ppq-ppb) elemental analysis. Among electrochemical techniques, particular mention should be made about voltammetry and potentiometry. The latter has a wide range of applications due to the development of ion selective electrodes, which are currently used for water quality monitoring (ammonium and nitrates in groundwater, cyanide, mercury, cadmium, copper etc) (Braun, 1987; Rundle, 2006).

A wide variety of chemical pollutants can be found in water. Among these are organic compounds (hydrocarbons, oxygenated hydrocarbons, halogenated aliphatic and aromatic compounds, metal cations (cadmium, mercury, copper, lead, chromium), non-metallic species (arsenic and selenium) and oxy-anions (nitrates and perchlorates)(Baird and Cann, 2005) and common anions such as fluoride (Danil de Namor and Abbas, 2006). As a result several technological approaches have been developed to tackle the problem of ground water contamination by chemicals. Among these are the conventional ones, natural attenuation, free product recovery (non-halogenated, semi-volatiles and hydrocarbons), air stripping (volatiles), carbon adsorption (semi-volatiles) and slurry walls (all contaminants) (Baird and Cann, 2005; Environment Canada, 2006). Advantages and disadvantages of these approaches can be found in the literature. Some innovative approaches have been reported. Of particular interest are those using permeable reactive barriers (Simon and Meggyes, 2000) which have been successfully used for the removal of halogenated hydrocarbons, aromatic and nitro aromatic compounds as well for inorganic pollutants such as lead, chromium, uranium and arsenic. Among the materials used in the barriers are those of high sorption capacity. To the writer’s knowledge highly selective materials based on supramolecular systems have not yet being investigated in these systems. It seems appropriate to emphasise that Supramolecular Chemistry is one of the most active areas of chemical research at present and has already shown promise in the development of selective decontaminating agents which can form the backbone of new technological approaches (Danil de Namor and Abbas, 2006).

Conclusions

From the above discussion it follows that:

(a) Ancient Civilization has provided the basis for many technological approaches that are in current use. In fact, the ancient treatment of filtering water through sand and charcoal filters has gone a long way to the extent that whole house filtration systems are claimed to be the most efficient technology for the removal of chlorine by-products and organic pollutants.

(b) The idea of using naturally occurring materials such as clays and plants introduced in early civilisation for water purification is still a research area of considerable interest particularly if these can be enriched by receptors able to interact selectively with
heavy metal cations such as mercury speciation, lead, cadmium and many other polluting agents. These still pose a serious threat to the environment and to human health.

(c) The field of Supramolecular Chemistry should be further explored for the design of decontaminating agents for the removal of pollutants from water. Attachments of these receptors to solid supports are likely to provide new tools for the development of new technological approaches for water purification.

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