The Lethal Water Tri-Therapy: Chlorine, Alum, and Polyelectrolyte

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Abstract: There is no doubt that the chemical water treatment has resolved the problem of drinking water supply for several decades to humankind especially in terms of pathogen microorganisms and turbidity removal. However, due to chemicals used through this treatment and increasing quantities of pollutants discharged into nature, numerous health problems have been largely more and more proved and reported. This review discusses the toxicity of chlorine, alum, and polyelectrolyte which are widely employed through the world. The main addressed question here is: When the true and radical water treatment technology will be really and definitely applied? There is no water treatment technique but only distillation process which is successfully applied at the largest scale in nature by God. At least, physical processes such as membrane processes should be more and more applied through water treatment plants for reducing chemicals use. Most of chlorination disadvantages may be avoided through a better understanding of the mutual actions conducting to the generation of chlorine by-products and the use of more sophisticated procedures to assess toxicity capacity of such chemicals. Finally, this study arrives at its time since the Environmental Engineers and the Green Chemistry specialists have largely opened the discussion about polluting industry and preserving nature. Returning Man to its initial and noble Mission on Earth is reflected through this research to preserve both humankind and nature.

Keywords: Water Treatment, Chlorine, Alum, Polyelectrolyte, Chemicals Toxicity, Potable Water

1. Introduction

Water is more than vital for life; however, it is frequently contaminated with chemicals [1, 2]. Even during its proper treatment for potabilization purpose, additional chemicals are injected into water such as chlorine, alum, and polyelectrolyte. These harmful products are added to water during its purification technique, despite its known and established inherent toxicities.

There are several reasons of tap water pollution, extending from agricultural runoff, to inappropriate usage of household chemicals, and everything in between. Rarely the magnitude or effects of these low level synthetic chemicals used in the water are assessed. At the same time as the normal usage nowadays of more than 80,000 various artificial chemicals has given more convenience and productivity to our existences, it has as well arrived at a high cost [2].

It is not a secret that any chemical product employed will in the end finish in water supplies. In fact, there is no "novel" water. During its hydrologic cycle, Earth re-uses the same water over and over. Moreover, since employing synthetic organic chemicals (SOCs) augments, the poisoning of water increases. Planet's proper filtration technique becomes not efficient at reducing such harmful SOCs nor is municipal
water treatment. Other factors such as industry, agriculture, and humans all participate to the disaster. Several of the pollutants detected in water may be traced back to inappropriate or immoderate usage of usual compounds, like lawn chemicals, gasoline, dry cleaning solvents, and cleaning products [2].

As mentioned above, considering the fact that all water that goes down the drain in the end finishes in the potable water, water supplies are highly exposed to pollution [3, 4]. On the other hand, municipal water treatment plants do not eliminate SOCs and usually comprise only coagulation, sand bed filtration, and disinfection. In other words, mostly water treatment plants nowadays are practically remaining as they were at the turn of the century; the rule focuses on filtering out the visible particles and adding bleach. Employing pesticides and herbicides is now so imprudent that they are now detected more frequently in household tap water and bottled water [2, 5].

This review aims to attract attention to the poisoning of chlorine, alum, and polyelectrolyte which are largely used through the world. The principal addressed question here is: When the true and radical water treatment technology will be really and definitely applied?

2. Chlorine Toxicity

Certainly chlorination has been successfully employed for the monitoring of water borne infection diseases for more than a century [1, 6-8]. Nevertheless, discovery of chlorination by-products [9] and occurrences of elevated health risks generated a main problem on the balancing of the toxicodynamics of the chemical species and hazard from pathogenic microbes in the supply of potable water (Figure 1) [10, 11]. There have been epidemiological confirmations of solid link among its subjection and harmful net results especially the cancers of vital organs in humans. Halogenated trihalomethanes (THMs) and haloacetic acids are two main groups of disinfection by-products (DBPs) frequently observed in waters disinfected using chlorine [12-14]. The global amount of THMs and the generation of single THM species in chlorinated water greatly depend on the constitution of the raw water, on working factors and on the existence of remaining chlorine [15] in the distribution system. Different techniques have been proposed which comprise adsorption on activated carbons, coagulation [16, 17] with polymer, alum, lime or iron, sulfates, ion exchange and membrane process for the elimination of DBPs. Therefore, with view to decrease the public health hazard from such poisonous chemicals regulation [18] must be coerced for the application of guideline levels to diminish the allowable concentrations or exposure [8].

Selcuk et al. [19] employed alum and polyaluminum chloride in coagulation of various origin water (Buyukcekmece, BC and Omerli, OM in Istanbul, Turkey and Carmine, CR in Salerno, Italy). They studied the impact of pre-ozonation single and integrated with coagulation on natural organic matter reduction which was identified by total organic carbon (TOC) and UV. They also determined DBPs formation and acute toxicity on Daphnia magna of chlorinated raw and treated samples. Optimum alum dose for TOC removal was observed to be 40 mg/L for OM while 80 mg/L of alum presented the lowest total THM formation potential. Pre-ozonation improved the reduction of TOC and decrease of total THM formation potential when it was employed in fusion with both coagulants. Raw and treated samples mentioned acute toxicity on Daphnia magna in various fashion and practically “no dose-response behavior” was detected.

With a view to monitor the ecological hazard of microcystin-LR disinfection by-products (MCLR-DBPs), Zong et al. [10] assessed their productive procedures and biological poisoning. Exposed to chlorination [20], MCLR was completely modified during 45 min and formed 5 types of MCLR-DBPs. However, poisoning experiment proved the poisoning of MCLR-DBPs on protein phosphatase 1 diminished with the prolongation of disinfection by and large, such DBPs still possessed certain biological poisoning [10, 21].

Shi et al. [22] assessed the in vitro poisoning of extracts of Hanjiang water disinfected by different sequential treatments. They disinfected Hanjiang water employing ozone, chloride dioxide or chlorine as the main disinfectant followed by chlorine as the secondary disinfectant. HepG2 cells were subjected to extracts corresponding to concentrations of 0.2, 1, 5, 25 and 125 mL water/mL medium. Compared with control, HepG2 cells subjected to extracts of raw water and all disinfected water for 24 h augmented oxidative stress degree, DNA damage and micronuclei frequency, and diminished cell viability. Water disinfected by C12 + C12 had the highest DNA double-strand breaks. All disinfected water and raw water augmented micronuclei frequency via elastogenic and aneugenic effects. Oxidative stress generated DNA strand breaks and micronuclei frequency and thus decreased cell
viability either in disinfected water or raw water. Compared with raw water, water after disinfection augmented DNA strand breaks, diminished cell viability and modified oxidative stress capacity. Compared with chlorination, sequential treatment employing O₃ or ClO₂ as main disinfectant followed by chlorine disinfection decreased chlorinated by-products, DNA double-strand breaks and cell viability, but did not reduce micronuclei frequency and other DNA damage like DNA single-strand break, alkali liable sites and incomplete excision sites. Sequential treatments did not importantly decrease in vivo poisoning of disinfected Hanjiang water.

2.1. THMs Are Only the Tip of the Iceberg

Scientists have proven that there are more than 600 undesirable chemicals formed through the mutual action of water treatment disinfectants and contaminants in source water [23, 24]. The main part of these water treatment pollutants have not been examined comprehensively and thoroughly. Among them: haloacetonitriles, haloaldehydes, haloketones, halohydroxyfuranones, haloquinones, aldehydes, haloacetamides, halonitriles, halonitromethanes, nitrosamines, organic N-chloramines, iodooacids, ketones and carboxylic acids [25]. Some of these compounds are suspected carcinogens [26]. Remarkably, researchers believe that hundreds more water treatment pollutants exist but have not until now been recognized [23, 24].

2.2. A Chlorine Surrogate that Complicated the Situation

Recently, several water plants have attempted to decrease pollution provoked by water treatment through moving from free chlorine to chloramines, chemicals formed from chlorine and ammonia gases [23].

Chloramines are more steady than chlorine and do not form as many THMs and haloacetic acids. The United States Environmental Protection Agency (EPA) has given an account that when Washington Aqueduct, a U.S. Corps of Engineers facility that treats potable water for Washington D.C., changed to chloramines, the evaluated average of the regulated water treatment pollutants in these two facilities dropped by 47 percent [23].

Until now, moving to chloramines has not found a solution to the dilemma but rather displaced the issue – and may have made it more difficult. Chloramines are poisonous to kidney dialysis patients and very harmful to fish [23].

3. Aluminum Toxicity

Following the World Health Organization (WHO), oral consumption of aluminum added ingredients is the major type of aluminum subjection for the human beings [27-29]. Aluminum salts are introduced into a variety of commercially-prepared foods and beverages: to clarify drinking water, make salt free-pouring, color snack/dessert foods, and make baked goods rise [27].

Gauthier et al. [30] evaluated the link among long-term subjection to various aluminum (Al) forms in potable water and Alzheimer’s disease (AD). They chose participants from a arbitrary specimen of the elderly population (≥ 70 years of age) of the Saguenay-Lac-Saint-Jean region (Quebec). Following established standards, sixty-eight cases of AD identified were coordinated with age (+2 years) and sex with non-demented controls. Aluminum speciation was evaluated employing recognized criteria analytical methods with quality monitoring techniques. Subjection to Al species (total Al, total dissolved Al, monomeric organic Al, monomeric inorganic Al, polymeric Al, Al³⁺, AIOH, AlF, AlH₂SiO₄³⁻, Al₂SiO₅⁴⁰⁻) in potable water was determined through comparing the subject’s residential history with the physicochemical data of the municipalities. The markers of long-term subjections (1945 to onset) to Al species in potable water were not importantly linked to AD. Further, after adaptation for education degree, presence of family cases, and APOE ε4 allele, subjection to organic monomeric aluminum evaluated at the onset of the disease was related to AD. In a general manner, the subjection evaluated at the onset had been stable for 44 years. Gauthier et al. [30]’s findings proved the significance of determination of Al speciation and account of genetic features in the evaluation of the link among aluminum subjection and AD.

In order to give penetration into aluminum speciation in raw and in treated water and to examine the parameters that may influence it, Schintu et al. [31] isolated and analyzed aluminum fractions in water samples from three potable water reservoirs in Sardinia (Italy) and at the outlet of their treatment plants. All water treatment plants used polyaluminum chloride as coagulant. Their findings established that the treatment of raw water with the aluminum-based coagulant did not augment the amount of the metal in the treated water. Aluminum portions were totally distinct in raw water and in treated water. More than 80% of the aluminum in raw water was in the particulate form. In the dissolved portion, organic forms were existent at higher levels in the raw water, while after water treatment (coagulation, flocculation [32-34], and filtration) most of the aluminum was in the inorganic form. Most of the dissolved Al in raw water was hardly linked or polymeric colloidal, at the same time fractions of monomeric Al varying from 40 to 62% were existent in the treated water.

Lévesque et al. [35] investigated aluminum consumption in both neuronal and astroglial cells as well as the contribution of metal speciation. The relative accumulation of four aluminum salts, aluminum maltolate, aluminum lactate, aluminum chloride and aluminum fluoride, was examined and linked with cell viability and intracellular distribution as determined by morin staining. Important differences in aluminum uptake and poisoning were detected in both neuronal and glia cells with the largest impacts shown by the maltol species. This was accompanied by a nuclear accumulation in the neuronal cell line that was contrasted by the perinuclear, vesicular distribution in astrocytes that partially co-localized with cathepsin D, a lysosomal marker. These results prove variations in aluminum species and mention the significance of these parameters in modulating
the lethal impact of aluminum. Inflammatory and oxidative occurrences are up-regulated in the brain of AD patients. It has been mentioned that in animal models of AD, subjection to aluminum (Al) or copper (Cu) improved oxidative occurrences and accumulation of amyloid beta peptides [36].

4. Polyelectrolyte Toxicity

The anionic charge bring by aquatic humic substances (HSs) has a significant contribution in their mutual action with metal ions and other cationic species [37-40]. Eliminating these substances by coagulation/flocculation [41-45] may be at a certain level controlled through charge neutralization mechanism [46]. Kam and Gregory [47] examined the charge densities of a commercial humic acid (HA) [48, 49] and an aquatic humic extract through observing their mutual actions with a series of synthetic cationic polyelectrolytes including a collection of charge densities and molecular weights. With small charge density polyelectrolytes, the apparent anionic charge of the HSs was observed to be small. With higher polyelectrolyte charge densities, the apparent HS charge density augments and attains a restricting level when the polyelectrolyte charge is bigger than ~ 3 meq/g. This shows a non-stoichiometric mutual action among the anionic sites of the HSs and the cationic charges of the low-charge polyelectrolytes. Optimum flocculation of humics happened with less cationic charge in the case of low-charge polyelectrolytes than those with higher charge density. Nevertheless, the level of reduction was significantly better in the latter case. In a general manner, the molecular weight of the cationic polyelectrolytes (over a range from about 50,000 to 15 million) seemed to possess no influence on the efficiencies.

Bolto and Gregory [50] re-examined the usage of polymers in the treatment of potable water focusing on the features of the pollutants to be eliminated, the mechanisms of coagulation and flocculation, and the kinds of polymers frequently useable. They also focused on polymer toxicity, and the existence of residual polymer in the final potable water. They as well discussed the interrogations of polymer decomposition and the generation of DBPs.

In a general manner, the usually employed anionic and non-ionic polymers are of low poisoning; however, cationic types are more poisonous, particularly to aquatic organisms [50, 51]. The health importance of likely pollutants has been discussed by Letterman and Pero [52]. The monomers are more poisonous than the polymers [53]. Maximums on the quantity of monomer are severely checked, particularly with acrylamide products, where the maximum allowable amount of free acrylamide is frequently 0.025%, and the residue in potable water is restricted to 0.5 mg/L. For polydiallyldimethyl-ammonium chloride (PDADMAC), the monomer amount limit is 0.5% in Europe and 2% in the USA [54, 55]. For potable water treatment [56-59], the National Sanitation Foundation has suggested limit injections for usually employed commercial polymers in the USA. The maximums are frequently < 50 mg/L for PDADMAC, < 20 mg/L for epichlorohydrin and dimethylamine (ECH/DMA) polymers and < 1 mg/L for polyacrylamides (PAMs), irrespective of the PAM charge kind [50].

In evaluating the poisoning of polymers to aquatic species there are various factors comparatively with non-polymeric additives [60]. Artificial polymers have tendency not to be easily taken by organisms, and their poisoning may be significantly modified by fundamental aquatic components [61]. Cationic polymers are classified at moderate to elevated poisoning, and are significantly more lethal to aquatic organisms than anionic or non-ionic polymers [61]. The cationic types are harmful to fish due to mechanical gill blockage that provokes suffocation [62, 63]. This is importantly diminished through introducing solids like clays that are usually existent in different forms in receiving waters and sediments, where they may powerfully adsorb the cationic polyelectrolyte [64, 65]. HAs as well influence the poisoning, decreasing it by an order of magnitude at HA levels of 5 mg/L [50, 66].

5. Avoiding Chemicals Use in Water Treatment

According to the EPA, the most crucial hazard to both human, animal and plant life on earth resides in the impacts of toxic chemicals [67]. Hundreds of thousands of chemicals have been formed through the world in the past two hundred years, particularly, usually with little comprehension and monitoring of their poisoning - until a disaster appears [68]. Thus, avoiding chemicals in water treatment is vital.

Natural spring water is often the best drinking water [6, 67]. Spring water in the United States is regulated by the government, and most of it excellent [67]. In the United States, the second best drinking water is usually carbon-only filtered or sand-filtered tap water. This may be considered bizarre since tap water holds some chlorine, and usually some aluminum and maybe additional chemicals. In some other countries, tap water may not be safe to drink [67].

In 2013, we have [6] proposed the idea of the best available technology of water/wastewater treatment and seawater desalination which is really a simulation of the seawater distillation at the open sky: coagulation in salty water aerated basin/coagulation using seawater as coagulant solution with distillation using stored solar energy followed by waterfall on a natural mountain. This natural, green, and technico-economical technology is constituted of three steps: the first one is coagulation which may be achieved: 1) in salty water aerated basin (air stripping, AS; dissolved air flotation, DAF) where the raw water is “diluted” in seawater; or 2) in “conventional” coagulation using seawater as coagulant solution instead of alum/ferric salts. The first option seems to be more natural as it simulates river water dilution in seawater and the second one is more practical for “rapid” water consummation. For colloids and microorganisms’ removal,
double layer compression and charge neutralization, as main coagulation and disinfection mechanisms, would be involved in the first and second options, respectively. Aerated basin (AS/DAF) reproduces the natural aeration to simulate healthy natural water basin. Using stored solar energy, distillation as the best liquid-solid/liquid-liquid separation process provides the removal of dissolved pollutants. For well-balanced calco-carbonic equilibrium, the last step of this green treatment is the waterfall on a natural mountain providing useful gases, dissolved oxygen and carbon dioxide, and mineral salts to the water.

Finally, this study arrives at its time since the Environmental Engineers and the Green Chemistry specialists have largely opened the discussion about polluting industry (especially chemistry) and preserving nature. Returning Man to its initial and noble Mission on Earth is reflected through this research to preserve both humankind and nature [1].

6. Conclusion

1. Aluminum remains the most abundant metallic element, and the third constituent of the earth’s crust. Aluminum is found everywhere in the nature, as salts and oxides. Due to its physical and chemical properties, aluminum metal and compounds possess a large diversity of usages: building, transportation, food packaging, beverage cans, cooking utensils, food additives, medicines, surgery materials, cosmetics, water purification. Aluminum evaluation is not simple, and even if toxicity estimation to a certain degree is function of speciation, only total aluminum is frequently assessed in environmental and biological samples. Poisonous impacts of aluminum chronic subjection are mostly neurological impacts (encephalopathy, cognitive and motors disorders), bone disease (vitamin D resistant osteomalacia), and blood effects (microcytic anaemia). Aluminum as well provokes immune and allergic effects. Other suspected effects remain to be proved, in particular AD.

2. It is established that chlorination is not the best possible ultimate disinfection technique before water distribution. Nevertheless, most of its disadvantages may be avoided through a better understanding of the mutual actions conducting to the generation of DBPs and the use of more sophisticated procedures to assess toxicity capacity of such chemicals. This is a fundamental question when taking into account existing health troubles linked to inconveniently disinfected or not disinfected waters that are distributed.

3. Discussing the poisoning of polymers to freshwater organisms shows that fish are more sensitive to cationic polymers; however, algae are sensitive to anionic polymers due to the chelation of nutrient metal cations. This impact may be counterbalanced upon injecting Ca\(^{++}\). The existence of HSSs or clays may greatly decrease the bioavailability and consequently toxicity of the polymers and this must be considered in any risk evaluation of environmental harm resulting from the existence of polymer in surface waters.

4. God has successfully applied at the largest scale in nature distillation process to provide humans, animals, and plants safe water. At least, physical processes such as membrane processes should be more applied through water treatment plants for reducing chemicals use.

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Abbreviations

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<th>Acronym</th>
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<tr>
<td>DBPs</td>
<td>Disinfection by-products</td>
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<td>HA</td>
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<td>HSSs</td>
<td>Humic substances</td>
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<td>MCLR</td>
<td>Microcystin-LR</td>
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<td>SOCs</td>
<td>Synthetic organic chemicals</td>
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<td>THMs</td>
<td>Trihalomethanes</td>
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<td>TOC</td>
<td>Total organic carbon</td>
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References


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