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Resumen

El agua es una necesidad universal que ha sido reportada por las Naciones Unidas (ONU) y la Organización Mundial de la Salud (OMS) como una prioridad. Existe una necesidad apremiante de acceso gratuito al agua potable para las poblaciones de los países en desarrollo. Además, las fuentes de agua de los países desarrollados también requieren atención debido a la presencia de un alto nivel de contaminantes emergentes. Por lo tanto, la nanotecnología parece ser una herramienta poderosa que podría usarse como sensores, filtros, superficies antibacterianas y nanoantimicrobianos. En esta revisión, hemos discutido la aplicación de las nanopartículas y los nanocompuestos para el tratamiento de aguas y aguas residuales. Además, el impacto de las nanopartículas libres como contaminantes emergentes en las plantas de tratamiento de agua, así como en las aguas subterráneas, merece más estudios.

Palabras clave: Contaminantes del agua, nanotecnología, sensores, filtros, superficies antibacterianas, nanopartículas, nanocompuestos.

Abstract

The water is a universal need that has been reported by the United Nations (UN) and World Health Organization (WHO) as a priority. There is a pressing need for free access to drinking water for populations from developing countries. Furthermore, the water sources of developed countries also require attention due to the presence of a high level of emergent contaminants. Therefore, nanotechnology appears to be a powerful tool that could be used as sensors, filters, antibacterial surfaces, and nanoantimicrobials. In this review, we have discussed the application of nanoparticles and nanocomposites for water and wastewater treatment. Moreover, the impact of free-nanoparticles as emergent contaminants in water treatment plants as well as groundwater warrants further studies.

Keywords: Water contaminants, nanotechnology, sensors, filters, antibacterial surfaces, nanoparticles, nanocomposites.

1. Introduction

Water is one of the most important compounds that greatly influence life (1). Groundwater is used for domestic, industrial, and also for irrigation purposes, all over the world. Water also plays an important role in shaping the land and regulating the climate. During the last few decades, there has been a tremendous increase in the global demand for freshwater as well as sewage treatment due to the rapid growth of population and the accelerated pace of industrialization (2). Those demands also shed light on waterborne diseases that can rapidly spread and affect several countries, as an example of last cholera outbreak(3). According to the report of WHO, about 80% of all the diseases in human beings are caused by waterborne pathogens. Considering that, once the groundwater is contaminated, its quality cannot be restored easily(4).

The water quality index is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policymakers. Hence, analysis of the water quality is very important to protect citizen's health, as well as to preserve the natural ecosystems of each country(5). Besides that, reports from various agencies such as the United Nations (UN) and its other divisions (UNESCO, and FAO) provide the data on water consumption in the world. According to their reports, the distribution of available water worldwide can be 70% for agriculture, 20% for industry, and 10% for domestic use. Providing high-quality water for agricultural use has been the major challenge due to the increased production of industrial waste and chemicals released into the water bodies (6). It was reported that in developed countries having huge industrialization, more than half of the water available for human use is

consumed by the industries. From UNESCO's report, it is clear that the withdrawal of freshwater was three times more in the last 50 years because the demand for freshwater is increasing by 64 billion cubic meters a year (7). The possible reasons for an increase in global demand of freshwater are as follows: (i) the world's population is growing by roughly 80 million people each year (ii) modifications in lifestyles and eating habits in recent years need more water consumption per capita (iii) the production of biofuels has also augmented abruptly in recent years, with substantial impact on water demand. Between 1,000 and 4,000 liters of water are required to produce a single liter of biofuel, and (iv) energy demand is also accelerating, with corresponding implications for water demand (6).

Considering the water and wastewater treatment problems, nanotechnology appears as an important tool to improve water quality, quick detection of pollutants, as well as to the removal of recalcitrant/emergent contaminants from water and wastewater. Nanoparticles present unique properties that allow their application in several areas. Along with this, we will discuss nanotechnological solutions for water and wastewater treatment, as well as some concerns related to the toxicity of nanoparticles. To understand the main problems regarding water and wastewater pollutants, this review also discusses the source, environmental effects, and traditional mechanisms for treatment and removal of aquatic pollutants.

2. Main contaminants of water

Clean potable water is one of the important fundamental requirements for a healthy human population. However, nowadays, the contamination of water resources represents one of the major concerns of the modern world. The huge industrialization, excessive use of chemicals in various applications as well as scientific and technical development are collectively responsible for the generation of numerous unwanted contaminants (organic, inorganic, and pathogens) which has ultimately increased the burden of pollutants in drinking water in developing and developed countries (8–11). As mentioned above, organic and inorganic contaminants are the major class of the pollutants of water resources, along with microbial pathogens, which are briefly discussed here (see Figure 1).

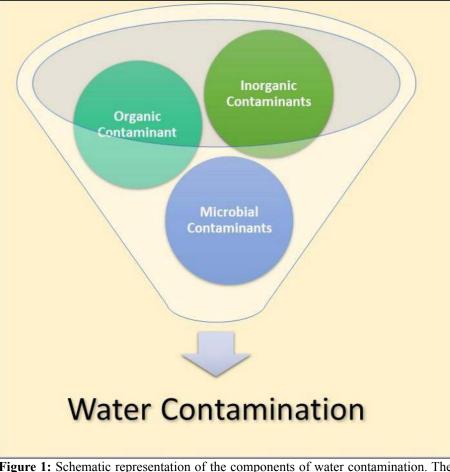


Figure 1: Schematic representation of the components of water contamination. The organic, inorganic, and microbial contaminants together lead to contamination of water.

2.1. Organic contaminants

A variety of organic contaminants generated from various sources are also responsible for the contamination of water. Among the organic contaminants, the wastewater generated from dye industries poses major problems because generally, it contains acids and bases, dissolved organic solids, toxic chemicals, and also dyes. Coloured chemicals can be easily recognized as they are visible, whereas, other contaminants are difficult to identify. Moreover, it was demonstrated that the removal of many textile dyes by traditional treatment methods from the waste is very challenging as they showed stability towards light and resistance to oxidizing agents as well as aerobic digestion (12,13). Phenolic compounds, such as nitrophenols and chlorophenols are other important contaminants of water resources that originated from various industries. Phenolic compounds can create serious health problems when entered into the food chain as water pollutants. It is also reported to affect the taste and odour of fish and drinking water at a very low concentration (14). Karakoyun et al (15) developed different biochars, which can be used for the removal of aqueous phenols from the wastewater. Pesticide and polycyclic aromatic hydrocarbons (PAH) have attracted great attention as they are responsible for serious health issues. These compounds are mostly used in agriculture for the control of pests and therefore, easily get entered into the water resources like wells, ponds, etc. Khim et al(16) analyzed 32 water and sediment samples collected from different locations in Ulsan

Bay of South Korea and adjacent inland areas for the presence of various organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), nonylphenol (NP), octylphenol (OP), bisphenol A (BPA), organochlorine (OC), various pesticides, and polychlorinated biphenyls (PCBs). The results showed that the presence of all the above-mentioned pollutants in varying concentrations. The concentration reported for PAHs was about 17 to 3,100 ng/g on a dry weight basis (DW). Whereas, the concentrations of NP, OP, and BPA in sediments were found to be 1040, 120, and 54 ng/g (DW), respectively. Besides, some other important pesticides include organophosphorus, organochlorine, carbamate, triazine, and chlorophenoxy acid compounds which were reported in the samples. Therefore, in nutshell, it can be said that if such contaminated water is used either for drinking or daily household purpose then it is hazardous for human health. Moreover, if such water is released into any kind of water bodies then it will cause harmful effects to the flora and fauna thereby affecting the complete ecosystem.

Another compound, dibromochloropropane, a soil fumigant used to control nematodes has been commonly reported in water resources (17). These chemicals usually possess the potential for bio-magnification and bioaccumulation. In both cases, such chemicals can have a tremendously hazardous effect on humans and the environment. Lindane, or γ -HCH (hexachlorocyclohexane), an organochlorine pesticide (gamma isomer of 1,2,3,4,5,6-HCH), is used all over the world for controlling various agricultural pests. However, this compound is known to be bioaccumulated, causing cancer and disturbing the homeostasis of the endocrinal system (18). However, Maes et al proposed solutions like metal-organic frameworks (MOFs) for the extraction of phenol and p-cresol from contaminated water based on the isotherm for phenol uptake from the liquid phase mechanism to minimize the adverse effects caused due to such organic contaminants (19). Chemical pesticides used for agricultural purposes are always threat to the ecosystem. Generally, it is observed that they either get wash away with the rainwater so that they will reach the rivers and large water bodies thereby making it nonhabitable for the aquatic animals and plants. Secondly, such pesticides can also get percolated and contaminate the groundwater. Such contamination will make the groundwater non-potable / non-drinkable. Overall, the overuse of pesticides for agricultural purposes can result in the contamination of all water bodies.

2.2. Inorganic contaminants

Heavy metals pose serious health threats even at very low concentrations. Some are cumulative poisons, capable of assimilation, storage, and concentration by organisms exposed long periods to low concentrations. Eventual metal built-up in tissues can cause harmful physiological effects. The heavy metals appear to be the main pollutants in this century (20). Discharged heavy metals are responsible for a serious threat to human, animal, and plant health and natural water. According to Järup (21), various heavy metals like lead, cadmium, mercury, arsenic, and many others have been extensively used by humans for thousands of years. Different studies carried out all over the world including WHO, United States Environment Protection Agency (US-EPA) demonstrated the presence of heavy metals such as arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, zinc, etc. in water resources which are found to be toxic (10,22,23).

Many studies reported that diverse functions of wetlands and other water resources are being adversely affected by human activities. For example, Harike wetland, Punjab, India is one of the important wetlands as it provides a significant site for diverse flora and fauna. Brraich and Jangu studied the intensity of heavy metal pollution particularly toxic metals in Harike wetland that occurred due to discharge from various industries (24). The report suggested that this wetland is highly polluted due to the rapid industrialization, urbanization, and dumping of solid wastes. Further analysis showed the presence of lead, chromium, iron, copper, nickel, zinc, and cadmium which have drastically deteriorated the quality of water. Among these, the concentration of many metals was found to be higher than the international standards. As mentioned earlier, such a quality of water is not safe for various aquatic life and is even unfit for human drinking and irrigation purposes. Moreover, many other recent studies carried out worldwide reported the contamination of water resources by heavy metals (25-29).

2.3. Microbial contamination

Microbial contamination of water continues to be a general problem across countries and is one of the main causes of illness and deaths with 37,7 million affected by waterborne diseases yearly. Ashbolt reviewed that poor quality drinking water, sanitation and hygiene are collectively responsible for about 1,7 million deaths per year worldwide mainly due to the infectious diarrhoea (31,32). Most important is, 90% of deaths are in chilRevista de la Asociación Colombiana de Ciencias Biológicas issn impreso 0120-4173, issn en línea 2500-7459

dren and virtually all of the deaths are in developing countries. Major enteric pathogens in children include Rotavirus, Poliovirus, *Campylobacter jejuni*, *Escherichia coli, Shigella* spp., *Vibrio cholerae*, *Aeromonas* spp. *Clostridium difficile* and *Cryptosporidium parvum*. Also, microbes like *Helicobacter pylori* and *Burkholderia pseudomallei*, are prominent in some regions. Whereas, in adults, *Entamoeba histolytica*, *Giardia lamblia*, Hepatitis viruses, C. *jejuni* as well as *H. pylori* and hookworm (*Ancylostoma duodenale*) are the emerging waterborne pathogens.

A study carried out for the determination of bacterial contamination in rural areas of Beijing, China demonstrated the bacterial contamination in drinking water. The analysis was carried out to determine the total bacterial count, total coliforms, and E. coli and the results obtained showed the presence of 88,000 CFU/mL, 1,600 MPN/100 mL, and 1,600 MPN/100 mL count respectively, which explains the quality of water (33). Moreover, the results of many other studies revealed the severity of water contamination by various microbial pathogens and their hazards to all forms of life (34–38). Problems in drinking water quality include the presence of organic, inorganic, and microbial contaminants in excess concentrations, which are the cause of various water-borne diseases. Since it is very difficult to prevent these contaminants from draining into the drinking water sources, the only way to maintain safer water bodies is to develop efficient purifying technologies. To date, many technologies have been developed for purifying the water. Some of them are traditional methods which are efficient up to some extent and others are recent techniques which have certain advancement to the traditional techniques overcoming their lacunae.

3. Traditional methods of water and wastewater treatment

The prime objective of water treatment is to get safe and potable water. An adequate supply of pure water is essential to human existence. The available raw water must be treated and purified before it is supplied to the general public for their domestic, agricultural, industrial, or any other use. To purify water, a series of treatment processes such as coagulation, sedimentation, filtration, and disinfection are used. Furthermore, there are some other techniques such as activated carbon, alum, and chlorine treatments. Briefly, activated carbon acts as adsorbent useful for the removal of toxic organic and volatile compounds and those responsible for unpleasant taste and odour in the water, as well. (39). Moreover, selective removal of radioactive materials like uranium can also be efficiently achieved using this technique (40). In another hand, alum is generally used as a flocculant to remove unwanted colour and turbidity from water supplies. Along with those treatments, chlorination is used for water disinfection. It is generally carried out by adding chlorine (Cl_2) or hypochlorite to water. As the chlorine is strong oxidizing agent chlorine treatment is highly effective against almost all waterborne pathogens, with some exceptions like *Cryptosporidium parvum oocysts* and mycobacteria species (41,42). Ultimately, chlorination of water helps to control the spread of waterborne diseases such as cholera, diarrhea, typhoid, etc.

Considering the overall limitations of traditional methods, scientists are trying to develop novel, efficient, and economically viable procedures for the treatment of water which should achieve a high degree of purity in less time. Nowadays, nanotechnology is emerging with great impact and has been used for the treatment of water by using various nanomaterials.

4.Nanotechnology for water and wastewater treatment

A wide range of applications connected with nanotechnology in nearly all fields, make it a very important and emerging technology. Therefore, the application of nanotechnology in water and wastewater treatment is gaining ground in both developing and developed countries. Studies carried out proved that the metal nanoparticles like silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), etc. and other nano-based materials such as nanomembranes / nanofilters would be helpful for the development of new water treatment technologies, which can be used to mitigate water-related problems such as waterborne pathogens, biofilm formation, as well as the removal of toxic heavy metals, etc.(43).

4.1. Nanoparticles and nanocomposites as adsorbents for removal of contaminants

Adsorption is employed to remove organic and inorganic pollutants from water and wastewater. This process is dependent on materials' surface area as well as its active centers that will determine the type of contaminants in which those materials will interact. Nanoadsorbents have the advantage to provide high specific surface area, strong sorption, as well as high reactivity and short intra-particle diffusion distance. NPs can also remove recalcitrant pollutants from water. Carbon nanostructures (CNS) are important materials to interact with organic or hydrophobic pollutants (44,45). In this regard, carbon nanotubes (CNTs) were one of the first CNS used for the adsorption of pollutants (46). Indeed, the high surface area provides potential to adsorb contaminants such as complexes of benzene, toluene, and xylene (BTX) (47) and trihalomethanes (THMs)(48, 49). However, in the aqueous medium, CNTs form bundle (50) that decreases its effective surface area, and as a consequence, could affect its adsorption capacity (51). Nevertheless, those aggregates present high adsorption energy sites through its interstitial spaces and groves created during this aggregation process. CNTs are more efficient adsorbent than activated carbon (AC) in the same condition and same surface area (52).

Another advantage of CNTs is its functionalization that generates new functional groups at the external surface. These groups can also promote better dispersion at the water, as well as, creation of hydrogen bonds with hydrophilic pollutants, such as antibiotics (53), hormones (54), and cations of heavy metals (55), among others. Despite its great adsorption capacity, CNTs need an immobilizing matrix (56) to avoid its spreading at potable water or wastewater with the potential production of secondary contaminants by interaction with the recalcitrant pollutant. Thus, functionalization of CNTs with specific functional groups (e.g. carboxylic acids, amides, amines, phenols, etc.) with the creation of composites, allows targeting of special contaminants (e.g. pesticides) as well as its use into sensors (28,57) or photocatalytic materials (58). In as much, those applications need a small quantity of CNTs for high efficiency.

Compared to CNTs, graphene oxide (GO) and reduced graphene oxide (RGO) have demonstrated exceptional adsorbent capacity (59,60) Their advantage over CNTs consists of generation of self-supported materials (61) as well as, in the case of GO also has shown the natural presence of functional groups at its surface (62). In this regard, Yang et al (63) interacted GO with solutions of CuCl₂ and observed its immediate aggregation confirmed by UV-Vis spectra, which showed a peak at 800 nm that corresponds to Cu^{2+} Likewise, a complementary experiment for the interaction of GO with Na⁺ was performed (with equivalent ion strength) that showed electrostatic interaction instead of aggregation; indicating that, GO could be useful for selective removal of Cu^{2+} .

Mishra and Ramaprabhu applied hydrogen inducted

exfoliation to synthesize graphene sheets which are similar to the common water filters (64). Those materials were used for simultaneous removal of species of arsenic and sodium from aqueous solution. Additionally, the membranes were used for desalination of seawater (Na⁺, Mg²⁺, Ca²⁺, K⁺). Both applications were successful for the removal of almost 60% of all studied cations. These preliminary data encourage the application of CNS into the pre-concentration of metals, as well as obtainment of multifunctional nanocomposites.

CNS application into water and wastewater treatment is not limited to the adsorption of heavy metals or desalination. CNSs have been used to adsorb dyes, antibiotics, among others from water (65). Thus, anthraquinone dye, Reactive blue 29 (RB29), were removed from water by advanced oxidation process that also results in a sub-product with high interaction in CNT's curvature zone (66) known as a region of high energy at CNTs. Furthermore, Fan et al (67) removed methylene blue from water combining chitosan with GO.

Inorganic nanoparticles (e.g. iron oxide, titanium dioxide, among others) also play an important role in the adsorption of contaminants from water because of its low-cost production and high interaction with cations of heavy metals. Magnetic iron oxide nanoparticles (magnetite) are gaining considerable attention from the scientific community regarding its application into water and wastewater treatment as a result of its high biocompatibility and safe degradation by environment (68,69). Therefore, those NPs have been used for arsenic removal from water (70). Thus, by controlling its size it was also possible to increase the adsorption capacity of arsenic up to 100 times. Such adsorption was also attributed to the "nanoscale effect" which change nanoparticles surface creating new sites for adsorption. For instance, Fe-S nanocomposite was shown to remove cadmium up to a greater extent as compared to the pure adsorbents. In this case, the adsorption rate reached over 98.5% at pH 7, resulting in the fast removal of cadmium from water (71). Moreover, by dramatically size decreasing (below ~40 nm), magnetite can turn from magnetic to supermagnetic nanoparticles having high magnetic susceptibility. Superparamagnetic iron oxide nanoparticles (SPIONS) have been used to adsorb ions of heavy metals,(72), as well as other inorganic pollutants (73). However, the main application of SPIONS into water treatment depends upon functionalization at its surface. Indeed, silica core-shell SPIONS are an interesting platform for trapping complexes or emergent

contaminants (74).

Although each nanostructure described above shows exceptional properties for adsorption of several types of contaminants from water and wastewater, they also show limitations that involve cost of production, low dispensability at water, need of physical support for water filtration or pollutant aggregation. In this regard, nanocomposites are important since they combine properties from NPs with other materials or from two or more nanoparticles. Thereafter, the application of nanocomposites into water decontamination has been extensively reported. Thus, Qin et al reported adsorption of rhodamine B (RhB), a traditional dye, by using nanocomposites made of reduced graphene oxide (RGO) and SPIONS (75). This nanocomposite was obtained by in situ technique that GO was added into SPIONS' synthesis medium. In the same environment, GO was reduced by the addition of ammonium hydroxide. These nanocomposites were efficient to adsorb RhB, and for its re-utilization after regeneration by methanol washing. These data suggest the application of SPIONS@RGO nanocomposites into pre-concentration of RhB. Herein, SPIONS also have been coated with polystyrene (PS) to remove oil spills from water (76). In this case, it was taken advantage of the high hydrophobicity of those nanocomposites aiming oil adsorption with subsequent removal by aggregation under the action of a magnetic field.

The application of cited nanocomposites depends on secondary steps for water cleaning, that means, use of centrifugation, aggregation by a magnetic field, or filtration of the mixture (water/nanocomposites) through water filtration membrane. Furthermore, those nanocomposites are specific for some organic contaminants or unique cations of heavy metals, which also increase the cost of water treatment. In this context, Alves et al (77) developed self-supported nanocomposites made of cerium hydrogen - phosphate (CeP) and functionalized CNTs and GO. These nanocomposites were capable to remove several cations of heavy metal from water, even when they were into a mixture as well as at different pH. The advantage of such nanocomposites includes a self-supported character that avoids additional steps for water decontamination. Indeed, decontamination occurs by filtering the water or wastewater through the

composite which exhibited similarity with filter papers.

4.2. Nanoparticles with photocatalytic activity for water and wastewater decontamination

Alternatively, to adsorb contaminants from water and wastewater, NPs have been used as photocatalyst materials to degrade contaminants. It is observed that the extracellular polymeric substance of bacterial cells is responsible for the development of resistance against the antimicrobial activity of catalyst through the bactericidal activity of photocatalyst. Hence, during wastewater treatment, removal of such extracellular material from bacterial biofilm could help the antimicrobial activity of photocatalysts (78). In this regard, nano - titanium dioxide (TiO2) is commonly deposited on surfaces aiming photodegradation of compounds such as phenols (79), volatile compounds (VOCs) (80), dyes,(81).

Furthermore, Chong et al (82) used TiO_2 and nano - titanium dioxide in photocatalytic membranes for large - scale water decontamination. Other NPs such as ZnONPs (83) and AuNPs (84) have been also applied to photocatalysis; however, their cost of production still elevates.

4.3. Nanoparticles and nanocomposites as sensors for contaminant monitoring

An important step of water and wastewater treatment consists of pollutant detection. Several techniques (85) and sensors (86,87) have been used with this aim. Nevertheless, NPs are changing the way of pollutant detection. AuNPs have been extensively used to detect ions of heavy metals from water and wastewater. In this regard, Ding et al (88) developed a new method for visual detection of Hg²⁺ by anti-aggregation of AuNPs. That means Hg²⁺ acts as a competitor to interact with the aggregating agent (cysteine) of AuNPs. This technique could be useful for qualitative assays for field identification of Hg^{2+} into water. Similarly, Li et al (89) developed a colorimetric technique for Hg²⁺ detection from water, using the anti-aggregation of AuNPs by the interaction of Hg²⁺ with O-phenylenediamine (OPD); a known aggregation agent of AuNPs. Briefly, citratestabilized AuNPs get aggregated in presence of OPD; however, when the water is contaminated with Hg²⁺, such aggregation doesn't occur (Figure 2-a) and the colour of the solution turns into pink (Figure 2-b).

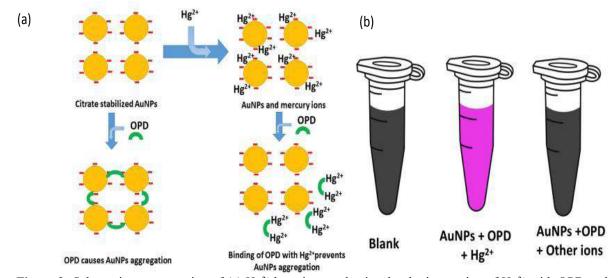


Figure 2: Schematic representation of (a) Hg^{2+} detection mechanism by the interaction of Hg^{2+} with OPD and non-aggregation of AuNPs; (b) detection system (AuNPs / OPD) in presence of several ions, showing the high specificity of OPD by Hg^{2+} .

Due to its high toxicity, the detection of Hg^{2+} was also the aim of research teams that study the application of AgNPs for water treatment. They can be used as a selective colorimetric sensor for the detection of Hg^{2+} by adding a solution at AgNPs dispersion followed by incubation at room temperature. Indeed, the presence of Hg^{2+} at water would destroy AgNPs and release Ag⁺, which is visually detected (90). The same approach was tested for other cations, however, the visual colour changing occurred only by Hg^{2+} action. Although this approach is free from complex and expensive equipment and techniques; it is also limited by potential interference from other cations during Hg^{2+} detection. Besides that, Ag+ released in water is also considered harmful for the environment as well as for human health.

AgNPs were also applied as dual colorimetric sensors either for Hg^{2+} detection as well as for hydrogen peroxide degradation by taking advantage of catalytic reduction properties of AgNPs (91). Similarly, Li et al (89) and Wang et al (91) used citrate to stabilize AuNPs and AgNPs, respectively, during Hg^{2+} detection. Indeed, H_2O_2 was used as a catalytic agent for Hg^{2+} detection. The advantage of this technique compared with that described above is the increased sensitivity towards Hg^{2+} concentrations in water, as well as progressive colour change from light- yellow to purple, which is due to an increase in Hg^{2+} concentration.

Other cations have been equally detected by AgNPs or AuNPs. Hereof, Alizadeh et al applied pyridines-functionalized AuNPs for Cu^{2+} detection in water.

Certainly, the detection occurs by Cu^{2+} quelation with chelidamate chains from AuNPs. Due to quelation process, the colour of the AuNPs suspension changes from brown to blue (presence of free - Cu^{2+}), and later to colourless which indicates the total complexation of Cu^{2+} . Apart from that, a precipitate also appears at the vial's bottom (92). Likewise, Xin et al (93) developed an electrode made with core-shell multiwalled carbon nanotubes / GO nanoribbons also coated with chitosan (CS), for bisphenol A (BPA) identification at the water. The electrode was sensitive to BPA even in presence of several ions such as K⁺, Na⁺, Ca²⁺, Mg²⁺, Al³⁺, Zn²⁺, Cu²⁺, indicating that technique is robust and could be applied at the field.

4.4. Nanoparticles with antibacterial properties for water decontamination

Waterborne bacterial infections are a worldwide dilemma, especially because many types of microbes and their spores occur in water, sewage, and wastewater (94). Therefore, water disinfection is an important issue even as its contaminant detection and degradation. Due to the indiscriminate use of antibiotics, bacteria became more resistant. Moreover, traditional techniques for water disinfection such as ultraviolet irradiation and ozonation, promote local disinfection by a short time.

Several NPs have been highlighted for water disinfection including quantum dots, AgNPs, AuNPs, and CNSs which are efficient NPs to kill or immobilize bacteria and a few viruses (95). In this regard, Adams et al (96) investigated the antimicrobial activity of metal oxi-

de NPs (ZnO, TiO₂ and SiO₂) against Gram-positive Bacillus and Gram-negative E. coli present in water. Comparatively, antibacterial activity for demonstrated NPs is ZnO>TiO₂>SiO₂ Also, the penetration into the cell leads to disarranging the bacterial membrane upon contact with these NPs. Apart from that, all tested NPs showed efficient inhibition of bacterial growth (97),. Biogenic AgNPs were shown to be more advantageous for such use. They were shown to possess the size and phytochemical dependant antibacterial activity against E. coli and other bacteria. Furthermore, they were also reported to have high catalytic activity for the degradation of toxic contaminants such as 4-nitrophenol and methyl orange. Both antibacterial and catalytic activities of biogenic AgNPs suggest its application in the effective treatment of wastewater.

Developing countries have difficulties in managing their sewage, which is directly released at potable water sources; consequently, they are more vulnerable at epidemics of cholera, bacillary dysentery, among others. Thus, in order to offer an alternative for people from those countries, green synthesized AgNPs and ZnONPs against *V. cholerae* and enterotoxic *E. coli* can be used (99). Both, AgNPs and ZnONPs, showed considerable antibacterial activity against the tested strains. However, the application of those NPs was done in infected animal models for the development of potential emergency treatment for cholera and dysentery; unfortunately, the action of those NPs at living animals remains unknown.

Although, some research groups applied isolated NPs coated TiO_2 anatase with AgNPs to obtain photocatalytic activity and bactericidal activity against strains of enterohemorrhagic *E. coli* and *Listeria monocytogenes*. Furthermore, those nanocomposites showed strong activity against deadly spores of *C. perfringens*, responsible for human gas gangrene, which regularly spread by water or sewage (100).

4.5. Other applications of nanoparticles for water treatment or remediation

Nowadays, emergent and complex pollutants are the most challenging problem faced by governments worldwide, due to lack of knowledge concerning the dynamics of those contaminants in environment (101), and their interaction with living organisms (102,103) or its spreading at food chain (104). While a majority of developing countries still struggle to offer potable water for their people by improving water treatment systems

(105); antibiotics (106,107), hormones (108,109), dioxins (110,111), surfactants (112,113), pesticides (114,115) which appear as emergent water contaminants (116), urging for new materials or techniques applicable for their detection and removal from water (117,118). Considerable progress has been made in the field of water and wastewater decontamination (119), however, a key-point remains unsolved regarding the safe application of NPs and the control or disinfection of toxic by-products (DBPs) 120 that are carcinogenic or show deleterious effects (121,122).

GO has been used to adsorb pharmaceutical compounds such as tetracyclines. Its adsorption occurred by π - π interaction and cation - π bonding either between GO electronic network and π electrons from the aromatic chain or cations from tetracycline. In fact, several research groups have taken advantage of π - π interactions to adsorb dioxins as well as hormones at GO surface (123). The functional groups from GO are useful for adsorption of some types of DBPs (e.g. trihalomethanes, brominated haloacetonitriles - HANs) (59,124). Those functional groups are also important to combine GO with other materials and promote the detection of hormones such as estradiol (125,126).

Considering that nonylphenols are potential disruptors and xenostrogen due to its estrogen-like activity; its early detection in water and wastewater is necessary (127,128). Thus, GO was used into gold electrodes to detect nonylphenols (129), as DBPs from nonylphenolethoxylates. Such application was viable by functionalization of GO with β - cyclodextrins. However, detection and removal of DBPs from drinking water by new technologies is the need of the hour.

From all of the above discussion, it is imperative that nanomaterial-based technology is proving to be the boon for the effective treatment and/or purification of various types of water bodies contaminated with various types of polluters. It has upper hand over various conventional methods of purification and/or treatment of water. Various studies performed to date make a point that this technology has huge potential to revolutionise water treatment technology in the 21st century.

5. Toxicity of nanoparticles

Although nanoparticles have shown various applications, there are a number of reports stating that they could be harmful to humans and the environment. The nanoparticles are released into water bodies through sewage effluent, and therefore, the contamination of the environment is unavoidable (130–133), and the sewage contamination by nanoparticles has been also observed through various reports (134–137). Therefore, as compared to the other contaminants, nanoparticles are also important contaminants for nanotechnologists. Various parameters are affecting their properties including size, shape, and most importantly the surface coating (138,139). Therefore, it is inevitable that nanomaterials are under the scanner of the U.S. Environmental Protection Agency. There are various initiatives undertaken by scientists across the globe dealing with the study of the fate of nanomaterials in the ecosystem especially in aquatic systems (140).

According to a report, after 21 day exposure of citric acid coated silver nanoparticles on Daphnia magna, the reproductive toxicity at the concentrations of 10 μ g Ag/L (141) was demonstrated. Similar results were also found after the exposure of sulfidized AgNPs on Caenorhabditis elegans (142). Interestingly, silver nanoparticles were found to be more toxic to the algal (Pseudokirchneriella subcapitata) growth than platinum nanoparticles (143). Gold nanoparticles also reported to induce the reactive oxygen species (ROS), expression of genes involved in oxidative and general cellular stress such as glutathione S-transferase (GST), catalase (CAT), heat shock protein 70 (HSP70), and metallothionein1 (MT1) (144). All of these studies indicate that though nanoparticles can help us in the treatment of water, they can also be harmful after their accumulation or release in the aquatic environment.

5.1. Interaction of nanoparticles with surfactants and organic compound in water and wastewater

Many times researchers use surfactants for either stabilizing or modifying nanoparticles (145–148) and therefore, surfactants exist with nanoparticles. Surfactants are mostly chemicals, and hence they add to the properties of nanoparticles. In summary, they will certainly affect the environment. Adsorption of surfactant on the surface of nanoparticles is a critical step for the application of nanoparticles as a superior sorbent in the treatment of wastewater (131,149). They also play a role in deciding the hazard associated with their use along with nanomaterials to which they are bound (131,150–152).

Surfactants have been used as antibacterial agents for a long time (153). It has been demonstrated that the bacterial surface is negatively charged due to the hydrolysis of the surface groups (154); thus, the cationic sur-

factant dodecyl-trimethylammonium chloride (DTAC) with positively charged groups can combine with the bacterial surface through electrostatic interactions and consequently cause an antibacterial effect. Brayner et al (97) studied the effect of ZnO nanoparticles on bacterial growth. They used the SDS surfactant for regulating the shape of ZnO nanoparticles. Furthermore, they observed that the SDS surfactant used was contributing to the toxicity. The observed toxicity might be due to the denaturation of bacterial protein by SDS. By composition Tween 20 does not have any charged group and therefore, does not affect the ZnO toxicity. The combined effect of ZnO NPs with adsorbed Tween 20 is additive. The additive effect might be due to the dissolved Zn ions and the surfactant (155).

According to the study performed by Sayes et al (156), surfactants were shown to decrease the toxicity of single-walled carbon nanotube. The mechanism lying behind such observation might be in the surface adsorption of surfactant on the nanoparticle surface thereby conditioning the nanoparticle surface, finally affecting the cytotoxicity (157). The reason behind this output might include the interaction between nanoparticles and bacteria through steric hindrance and charge repulsion thereby decreasing the toxicity of nanoparticles (158). Furthermore, through attachment to the nanoparticle surface, the surfactant modifies the surface charge of the nanoparticles, resulting in the alterations in their properties and toxicity (159,160). Additionally, humic acid has also been reported to markedly reduce the toxicity of nanoparticles (161–163). On the other hand, it has been reported to increase nanoparticle toxicity (164). A recent study by Wang et al (165) also found the similar results suggesting the alleviative property of humic acid on PVP-coated AgNP, in an alga (Raphidocelissub *capitata*), a cladoceran species (*Chydorus sphaericus*), and a freshwater fish larva (Danio rerio). Bisphenol A (BPA), an organic compound, mimics the hormone estrogen thereby disrupting the endocrine system. Therefore, it could show a harmful effect on human health (166,167). It can also be found in water bodies as a contaminant. However, the BPA may interact with TiO₂NP when it could be used as a drug carrier. Furthermore, Shi et al(168) investigated the activity of both TiO_2NP and BPA, both independently and in combination with L-02 cells, human embryo hepatocytes. The authors observed that both TiO₂NP and BPA alone did not show significant damage to DNA and chromosome. However, a combination of both of them induced much rise in oxidative stress, double-strand breaks in DNA, and forRevista de la Asociación Colombiana de Ciencias Biológicas issn impreso 0120-4173, issn en línea 2500-7459

mation of micronuclei. The reason behind such activity was claimed to be the increased intracellular binding of BPA to TiO₂NP.

Dichloro diphenyl trichloroethane (p,p'-DDT) was widely used as an efficient insecticide. It was shown to possess a genotoxic and endocrine disruptive effect on humans and other organisms (169–171). Therefore, to avoid its harmful effect its removal from the environment is essential. TiO₂NP has been shown to degrade it. But surprisingly it has been observed that the combined action of TiO₂NP and p,p'-DDT synergistically increased genotoxicity, oxidative stress, DNA, and chromosomal damage in L-02 cells (168). Such interaction thus poses an environmental threat. However, the literature on the effect of surfactants in combination with nanoparticles is inadequate. Therefore, there is a need to highly explore this aspect.

5.2. Interaction of nanoparticles with ions and inorganic compounds

The interaction of nanoparticles with various metal ions and toxic inorganic compounds can both increase and decrease their toxicity. Sodium fluoride (NaF) and TiO₂NPs are additive materials used in toothpaste (172,173). Nevertheless, Xie et al (174) studied the combined effects of both of them on 16-HBE, the human bronchial epithelial cells. After exposure, the lysozymes are adsorbed on the surface of TiO₂NPs. The adsorption might be due to the electrostatic attraction and hydrogen bonds between the lysozymes and the nanoparticles. It implies that such interaction could give rise to harmful effects on the exposed cells.

6. Generation of complex pollutants

Through various usage, nanoparticles are reaching to water bodies and thus affecting the aquatic environments. As discussed, ultimately these nanoparticles certainly mix and interact with the other water pollutant and form the complex compounds, which might be more toxic than nanoparticles and the pollutant alone (175). It is a well-known fact that copper is essential for the normal functioning of our homeostasis. At lower doses, it is harmless to the human body. Whereas, at a high dose, copper could be toxic to humans. At high doses, it has demonstrated to cause immunotoxicity in mice (176). However, TiO₂NPs with copper have increased bioaccumulation of copper in freshwater *D. magna*

(water flea), resulting in toxicity (177). Furthermore, TiO_2 NPs when mixed with lead acetate (PbAC) was reported to increase the generation of reactive oxygen species (ROS), intracellular superoxide dismutase, glutathione, and cytotoxicity in human embryo hepatocyte cells (178). These observations suggested an increased oxidative stress due to the interaction of TiO_2 NP with PbAC.

Arsenic is also a water pollutant. Exposure to arsenic can result in various ailments such as cancer, cardiovascular and metabolic diseases (179). TiO₂NP can be used to reduce the arsenic level from water because it acts as photocatalytic oxidant and absorbent for As (180). Through a study, Wang et al (181) demonstrated that TiO₂NP and As were nontoxic to Ceriodaphnia dubia (water flea) at 400 mg/L and 3.68±0.22 mg/L respectively after their independent exposure. Exposure of both materials in combination increased the toxicity at the lower concentration of 50 mg/L TiO₂NPs and 1.43 mg/L As. Similarly, TiO, with humic acid also affects the accumulation of Cadmium in zebrafish. TiO₂NP of 21nm in diameter at the concentration of 5-20 mg/L in humic acid-containing water has been reported to alter the Cd uptake(182).

Polyacryl coated TiO₂NP can also be used to remove Cd from water. The coated TiO₂NPs are much safer than the uncoated, as mentioned above. This is because it is found that Cd absorbs quickly on polyacryl coated TiO₂NP thereby removing them from the aquatic environment and thus reducing the incidence of Cd toxicity. Additionally, as per the experiment performed on Chlamydomonas reinhardtii the electrostatic and steric repulsion between algal cells and TiO₂NP minimizes the chances of cell - nanoparticle interaction, ultimately reducing the chances of nanoparticle toxicity (183). Various studies are reporting the combined toxicity of a nanoparticle with a pollutant, there is also a need to study the combined toxicity of one type of nanoparticle with another type of nanoparticle in the aquatic environment. It will open up a new avenue as a water body including sewage water and/or drinking water might possess more than one type of nanoparticles. Therefore, there are possibilities to have altered toxicity of various nanoparticles in combination with aquatic life. Figure 3 is the summary of the comparative activity and result of nanoparticles and pollutants alone and in combination.

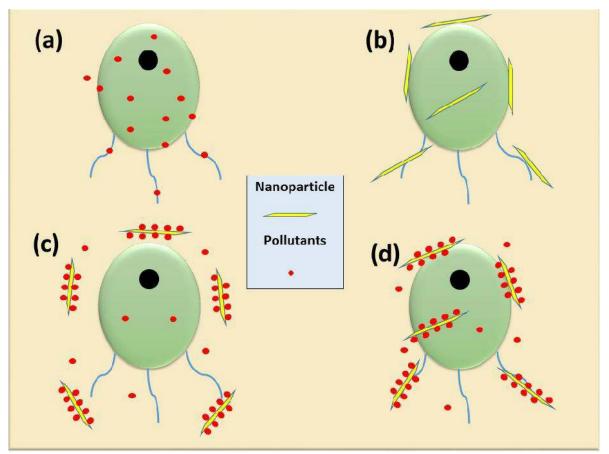


Figure 3: Scheme of the interactions of pollutants, NP, and organisms (algae as an example). (a) Adsorption and uptake of pollutants, (b) adsorption and uptake of nanoparticles, (c) adsorption (or absorption) of pollutants onto NP and reduction in pollutant uptake by organisms and (d) adsorption of NP with adsorbed (or absorbed) pollutant and possible uptake of pollutant-NP (131).

7. Solutions to avoid toxicity

As seen in the earlier section nanoparticles might show the hazardous effect. Therefore, there is a need of finding the ways by which the nanotoxicity can be avoided and/or reduced. For instance, gold from the soil can be absorbed by the plants. Gardea-Torresdey (184) has shown that the alfalfa plants can absorb the elemental gold from the soil. They have further demonstrated the formation of gold nanoparticles inside the live plants. This approach has the potential to remove the metallic compounds from the environment, especially from the water bodies. Secondly, Kiser et al (137) explored the use of removal of different nanoparticles from contaminated wastewater. The group has used natural organic matter (NOM), extracellular polymeric substances (EPS) to adsorb nanoparticles from wastewater. The study claimed that the NOM and EPS to be more significant in biosorption of fullerenes. Furthermore, the authors also added that this approach led to the removal of 97% AgNPs, 88% of aqueous fullerene, 39% of functionalized AgNPs, 23% of TiO2NPs, and 13% fullerenes.

More rigorous studies are needed in such a novel approach. In the future, such studies will be very helpful for efficiently removing nanoparticles from contaminated sewage. Moreover, there is also a need to prevent the potential release of nanomaterials in the environment. This can be achieved by using the nanomaterials at the required concentrations/level. The overexploitation of nanomaterials could lead to bioaccumulation in the aquatic flora and fauna thereby disturbing the aquatic life system.

8. Conclusion

The availability of safe drinking water has become very difficult in many parts of the world due to their contamination by means of increasing population and many others. Many laboratories around the globe including developed and developing countries are engaged in the development of cheaper and efficient methods for water and wastewater treatments. Although various traditional approaches are available for the treatment of water, those have their own limitations. Therefore, the fabrication of nano-products and/or approaches for purification and treatment of water would be the hope. Some of the studies mentioned in this review shown the effective use of nanomaterial-based products for the purification of water. Moreover, these purification approaches also meet the WHO guidelines for drinking water. Collectively, from the present review, it is confirmed that water/wastewater treatment using nanomaterials is a promising field for current and future research. While, considering the toxicological concerns of nanomaterials, more work is required to explore actual risks associated with humans and the environment. It can be predicted that, in the coming decade, we will see nanotechnology playing a very significant role all over the world.

Referencias

- 1. Gorde, S.P. and Jadhav, V.M. (2013) Assessment of water quality parameters: a review. *Int J Eng Res Appl 3*, 2029–2035.
- 2. Bouabid, A. and Louis, G.E. (2015) Capacity factor analysis for evaluating water and sanitation infrastructure choices for developing communities *J Environ Manage*, 161, 335–343.
- World Health Organization. Cholera, Number of Reported Cases (data by Country)." (2016) Global Health Observatory Data Repository, https://www.who.int/gho/ epidemic_diseases/cholera/en/
- 4. World Health Organization (2008) Guidelines for drinking water quality., 3rd ed. Geneva. https://www.who.int/water_sanitation_health/publications/gdwq3rev/en/
- 5. Dohare, D., Deshpande, S. and Kotiya, A. (2014) Analysis of ground water quality parameters: a review. *Res J Eng Sci* 3, 26–31.
- 6. Ahmad, T., Aadil, R., Ahmed, H., Rahman, U., Soares, B., Souza, S. et al (2019) Treatment and utilization of dairy industrial waste: a review. *Trends Food Sci Tech*, 88, 361-372
- WWAP (United Nations World Water Assessment Programme) (2015) The United Nations World Water Development Report 2015: Water for a Sustainable World. Paris, UNESCO.http://www.unesco. org/new/en/natural-sciences/environment/water/wwap/ wwdr/2015-water-for-a-sustainable-world/
- 8. Mehndiratta, P., Jain, A., Srivastava, S. and Gupta, N. (2013) Environmental pollution and nanotechnology. *Environ Pollut*, 2(2), 49-58
- Kumar, S., Ahlawat, W., Kumar, R. and Dilbaghi, N. (2015) Graphene, carbon nanotubes, zinc oxide and gold as elite nanomaterials for fabrication of biosensors for healthcare. *Biosens Bioelectron* 70, 498–503.
- Borah, P., Kumar, M. and Devi P. (2020) Types of inorganic pollutants: metals/metalloids, acids and organic forms. *In 'Inorganic Pollutants in Water*', Eds. Devi, P., Singh, P. and Kansal S.K., Elsevier, Amsterdam, Netherlands, 2020, pp- 17-31.
- Srinivasan, R. (2011) Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. *Adv Mater Sci Eng*, Article ID 872531, doi:10.1155/2011/872531
- 12. Qiu, Y., Zheng, Z., Zhou, Z. and Sheng, G.D. (2009) Effectiveness and mechanisms of dye adsorption on a straw-based biochar. *Bioresour Technol* 100, 5348–5351.
- 13. Xu, R-kou, Xiao, S-cheng, Yuan, J-hua, Zhao, A-zhen, (2011) Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. *Bioresour Technol*, 102, 10293–10298.
- 14. Mohan, D., Sarswat, A., Ok, Y.S. and Pittman, C.U. (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent--a critical review. *Bioresour Technol*, 160, 191–202.
- Karakoyun, N., Kubilay, S., Aktas, N., Turhan, O., Kasimoglu, M., Yilmaz, S. et al. (2011) Hydrogel– biochar composites for effective organic contaminant removal from aqueous media. *Desalination*, 280, 319–325.
- Khim, J.S., Lee, K.T., Kannan, K., Villeneuve, D.L., Giesy, J.P. and Koh, C.H. (2001) Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity. *Korea Arch Environ Contam Toxicol*, 40, 141–150.
- 17. Klasson, K.T., Ledbetter, C.A., Uchimiya, M. and Lima, I.M. (2013) Activated biochar removes 100 % dibromochloropropane from field well water. *Environ Chem Lett*, 11, 271–275.
- 18. Vijgen, J, Abhilash, P.C., Li, Y., Lal, R., Forter, M., Torres, J., et al (2011) Hexachlorocyclohexane

(HCH) as new Stockholm Convention POPs—a global perspective on the management of Lindane and its waste isomers. *Environ Sci Pollut Res* 18, 152–162.

- 19. Maes, M., Schouteden, S., Alaerts, L., Depla, D. and De Vos, D.E. (2011) Extracting organic contaminants from water using the metal-organic framework CrIII(OH)[middle dot]{O2C-C6H4-CO2}. *Phys Chem Chem Phys*, 13, 5587–5589.
- 20. Davydova, S.L. (1998) Heavy metals as main pollutants of the next century. *Crit Rev Anal Chem*, 28, 377–381.
- 21. Järup, L. (2003) Hazards of heavy metal contamination. Br Med Bull 68, 167–182.
- Zhaoyong, Z., Abuduwaili, J. and Fengqing, J. (2015) Heavy metal contamination, sources, and pollution assessment of surface water in the Tianshan Mountains of China. *Environ Monit Assess*, 187, 1–13.
- 23. Gul, N., Shah, M.T., Khan, S., Khattak, N.U. and Muhammad, S. (2015) Arsenic and heavy metals contamination, risk assessment and their source in drinking water of the Mardan District, Khyber Pakhtunkhwa, Pakistan. *J Water Health*, 13(4):1073-1084.
- 24. Brraich, O.S. and Jangu, S. (2015) Evaluation of water quality pollution indices for heavy metal contamination monitoring in the water of Harike Wetland (Ramsar Site), India. *Intl J Sci Res Publ*, 5, 1–6.
- D. Paul (2017) Research on heavy metal pollution of river Ganga: a review Ann. Agrar. Sci, 15(2):278-286
- 26. L. Joseph, B-M Jun, J Flora, C.Park, Y.Yoon (2019) Removal of heavy metals from water sources in the developing world using low-cost materials: a review. *Chemosphere*, 229: 142-159
- Rathoure, A. (2020) Heavy metal pollution and its management: bioremediation of heavy metal. *In* 'Waste management: concepts, methodologies, tools, and applications', Eds Rathoure A., IGI Global, pp1013-1036.
- Dixit, R., Wasiullah, Malaviya, D., Pandiyan, K., Singh, U.B., Sahu, A., et al (2015) Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes. *Sustainability*, 7(2), 2189-2212
- 29. Hu, C., Deng, Z., Xie, Y., Chen, X. and Li, F. (2015) The risk assessment of sediment heavy metal pollution in the East Dongting Lake Wetland. *J Chem* 2015, 1–8.
- Khurana, I. and Sen, R. (2007) Drinking water quality in rural India: Issues and approaches. Water Aid. https://www.indiawaterportal.org/sites/indiawaterportal.org/files/Drinking%20Water%20Quality%20 in%20Rural%20India_Issues%20and%20Approaches_WaterAid_2008.pdf
- Ashbolt, N.J. (2004) Microbial contamination of drinking water and disease outcomes in developing regions. *Toxicology*198(1–3), 229–238.
- 32. Ashbolt, N.J. (2015) Microbial aontamination of drinking water and human health from community water systems. *Curr Environ Heal reports*, 2, 95–106.
- Ye, B., Yang, L., Li, Y., Wang, W. and Li, H., (2013) Water sources and their protection from the impact of microbial contamination in rural areas of Beijing, *China Intl J Environ Res Public Health*, 10, 879–891.
- 34. Singh,A., Das,S., Singh,S., Pradhan,N., Gajamer,V., Kumar, S. et al (2019) Physicochemical parameters and alarming coliform count of the potable water of Eastern Himalayan State Sikkim: an indication of severe fecal contamination and immediate health risk. *Front Public Health*, 7:174.
- Jung, A.V., Cann, P. Le, Roig, B., Thomas, O., Baurès, E. and Thomas, M.F. (2014) Microbial contamination detection in water resources: Interest of current optical methods, trends and needs in the context of climate change. *Intl J Environ Res Public Health*, 11(4), 4292-4310.
- 36. Daley, R., Jamieson, D., Rainham, D. and Hansen, L.T. (2018) Wastewater treatment and public health in Nunavut: a microbial risk assessment framework for the Canadian Arctic. *Environ Sci Pollut Res*, 25:32860–32872.
- Kilungo, A.P., Carlton-Carew, N. and Powers, L.S. (2013) Continuous real-time detection of microbial contamination in water using intrinsic fluorescence. *J Biosens Bioelectron*, S12:002. doi:10.4172/2155-6210.S12-002
- Lavanya, V. and Ravichandran, S. (2013) Microbial contamination of drinking water at the source and household storage level in the peri-urban area of southern Chennai and its implication on health, India. *J Public Heal*, 21, 481–488.
- 39. Li, L., Sun, Z., Li, H. and Keener, T.C. (2012) Effects of activated carbon surface properties on the

adsorption of volatile organic compounds. J Air Waste Manage Assoc, 62, 1196–1202.

- 40. Kütahyalı, C. and Eral, M. (2004) Selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation. *Sep Purif Technol*, 40(2), 109-114
- 41. UNICEF, 2008. Promotion of household wa ter treatment and safe storage in unicef wash programmes. https://www.unicef.org/wash/files/Scaling_up_HWTS_Jan_25th_with_comments.pdf
- 42. Agrawal, V.K. and Bhalwar, R. (2009) Household water purification: low-cost interventions. *Med J Armed Forces India*, 65(3): 260–263.
- 43. Ahmed, T., Imdad, S., Yaldram, K., Butt, N.M. and Pervez, A. (2013) Emerging nanotechnology-based methods for water purification: a review. *Desalin Water Treat* 52, 4089–4101.
- 44. S. Kumar, W. Ahlawat, R. Kumar and N. Dilbaghi. Graphene, carbon nanotubes, zinc oxide and gold as elite nanomaterials for fabrication of biosensors for healthcare. *Biosens Bioelectron*, 2015, 70, 498–503.
- 45. Sun, H., Kwan, C., Suvorova, A., Ang, H.M., Tadé, M.O.and Wang, S. (2014) Catalytic oxidation of organic pollutants on pristine and surface nitrogen-modified carbon nanotubes with sulfate radicals. *Appl Catal B Environ*, 154-155, 134–141.
- 46. Pan, B. and Xing, B. (2008) Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environ Sci Techno*, 142(24), 9005–9013.
- 47. Ndiaye, A., Bonnet, P., Pauly, A., Dubois, M., Brunet, J., Varenne, C., et al (2013) Noncovalent functionalization of single-wall carbon nanotubes for the elaboration of gas sensor dedicated to BTX type gases: the case of toluene. *J Phys Chem C* 117, 20217–20228.
- 48. Lu, C., Chung, Y.-L. and Chang, K.-F. (2005) Adsorption of trihalomethanes from water with carbon nanotubes. *Water Res*, 39, 1183–1189.
- 49. Azamat, J., Khataee, A., Joo, S.W. and Yin, B. (2015) Removal of trihalomethanes from aqueous solution through armchair carbon nanotubes: a molecular dynamics study. *J Mol Graph Model*, 57, 70–75.
- Dresselhaus, M.S., Dresselhaus, G., Saito, R. and Jorio, A. (2005) Raman spectroscopy of carbon nanotubes. *Phys Rep*, 409, 47–99.
- 51. Koh, B. and Cheng, W. (2014) Mechanisms of carbon nanotube aggregation and the reversion of carbon nanotube aggregates in aqueous medium. *Langmuir*, 30, 10899–10909.
- 52. Ji, L., Chen, W., Duan, L. and Zhu, D, (2009) Mechanisms for strong adsorption of tetracycline to carbon nanotubes: a comparative study using activated carbon and graphite as adsorbents. *Environ Sci Technol*, 43, 2322–2327.
- Kim, B., Lim, D., Jin, H.J., Lee, H.Y., Namgung, S., Ko, Y., et al (2012) Family-selective detection of antibiotics using antibody-functionalized carbon nanotube sensors. *Sensors Actuators B Chem*, 166-167, 193–199.
- 54. Song, X.-Y., Ha, W., Chen, J. and Shi, Y.-P. (2014) Application of β-cyclodextrin-modified, carbon nanotube-reinforced hollow fiber to solid-phase microextraction of plant hormones. *J Chromatogr*, *A* 1374, 23–30.
- 55. Dai, B., Cao, M., Fang, G., Liu, B., Dong, X., Pan, M., et al (2012) Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS. *J Hazard Mater*, 219-220, 103–110.
- 56. Tian, Y., Gao, B., Morales, V.L., Wu, L., Wang, Y., Muñoz-Carpena, R., et al (2012) Methods of using carbon nanotubes as filter media to remove aqueous heavy metals. *Chem Eng J*, 210, 557–563.
- Mazloum-Ardakani, M. and Khoshroo, A. (2014) High sensitive sensor based on functionalized carbon nanotube/ionic liquid nanocomposite for simultaneous determination of norepinephrine and serotonin. *J Electroanal Chem*, 717-718, 17–23.
- 58. Neelgund, G.M. and Oki, A. (2011) Photocatalytic activity of CdS and Ag(2)S quantum dots deposited on poly(amidoamine) functionalized carbon nanotubes. *Appl Catal B*, 110, 99–107.
- 59. Liu, Q., Zhou, Q. and Jiang, G. (2014) Nanomaterials for analysis and monitoring of emerging chemical pollutants. *TrAC Trends Anal Chem*, 58, 10–22.
- 60. Tonucci, M.C., Gurgel, L.V.A. and Aquino, S.F. de (2015) Activated carbons from agricultural byproducts (pine tree and coconut shell), coal, and carbon nanotubes as adsorbents for removal of sulfamethoxazole from spiked aqueous solutions: Kinetic and thermodynamic studies. *Ind Crops Prod*, 74, 111–121.
- 61. Duran, A., Tuzen, M. and Soylak, M. (2009) Preconcentration of some trace elements via using multiwalled carbon nanotubes as solid phase extraction adsorbent. *J Hazard Mater*, 169, 466–471.

- 62. Yao, W., Ni, T., Chen, S., Li, H. and Lu, Y. (2014) Graphene/Fe₃O₄@polypyrrole nanocomposites as a synergistic adsorbent for Cr(VI) ion removal. *Compos Sci Technol*, 99, 15–22.
- 63. Yang, K. and Xing, B. (2010) Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chem Rev*, 110, 5989–6008.
- Mishra, A.K. and Ramaprabhu, S. (2011) Functionalized graphene sheets for arsenic removal and desalination of sea water. *Desalination*, 282, 39–45.
- Jung, C., Son, A., Her, N., Zoh, K.-D., Cho, J. and Yoon, Y. (2015) Removal of endocrine disrupting compounds, pharmaceuticals, and personal care products in water using carbon nanotubes: a review. J Ind Eng Chem, 27, 1–11.
- 66. Jahangiri-Rad, M., Nadafi, K., Mesdaghinia, A., Nabizadeh, R., Younesian, M. and Rafiee, M. (2013) Sequential study on reactive blue 29 dye removal from aqueous solution by peroxy acid and single wall carbon nanotubes: experiment and theory. *Iranian J Environ Health Sci Eng* 10, 5.
- Fan, L., Luo, C., Li, X., Lu, F., Qiu, H. and Sun, M. (2012) Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue. *J Hazard Mater*, 215-216, 272–279.
- Mahmoudi, M., Sant, S., Wang, B., Laurent, S.and Sen, T. (2011) Superparamagnetic iron oxide nanoparticles (SPIONs): development, surface modification and applications in chemotherapy. *Adv Drug Deliv Rev*, 63, 24–46.
- 69. Petri-Fink, A., Steitz, B., Finka, A., Salaklang, J. and Hofmann, H. (2008) Effect of cell media on polymer coated superparamagnetic iron oxide nanoparticles (SPIONs): colloidal stability, cytotoxicity, and cellular uptake studies. *Eur J Pharm Biopharm*, 68, 129–137.
- 70. Yean, S., Cong, L., Yavuz, C.T., Mayo, J.T., Yu, W.W., Kan, A.T., et al (2005) Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate. *J Mater Res*, 20, 3255–3264.
- Shahryari, T., Mostafavi, A., Afzali, D. and Rahmati, M. (2019) Enhancing cadmium removal by lowcost nanocomposite adsorbents from aqueous solutions; a continuous system. *Comp Part B: Eng*, 173, 106963.
- 72. Burks, T., Avila, M., Akhtar, F., Göthelid, M., Lansåker, P.C., Toprak, M.S. et al (2014) Studies on the adsorption of chromium(VI) onto 3-Mercaptopropionic acid coated superparamagnetic iron oxide nanoparticles. *J Colloid Interface Sci*, 425, 36–43.
- 73. Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H. et al (2012) Use of iron oxide nanomaterials in wastewater treatment: a review. *Sci Total Environ*, 424, 1–10.
- Zhang, S., Jiao, Z. and Yao, W. (2014) A simple solvothermal process for fabrication of a metal-organic framework with an iron oxide enclosure for the determination of organophosphorus pesticides in biological samples. *J Chromatogr A*, 1371, 74–81.
- Qin, Y., Long, M., Tan, B. and Zhou, B. (2014) RhB adsorption performance of magnetic adsorbent Fe₃O₄/RGO composite and its regeneration through a Fenton-like reaction. *Nano-Micro Lett*, 6, 125– 135.
- Chen, M., Jiang, W., Wang, F., Shen, P., Ma, P., Gu, J. et al (2013) Synthesis of highly hydrophobic floating magnetic polymer nanocomposites for the removal of oils from water surface. *Appl Surf Sci*, 286, 249–256.
- 77. Alves, O.L., Nascimento, R.O. do, Martinez, D.S.T., Rodrigues, O.E.D. and Moraes, A.C.M. (2013) Processo de obtenção de nanocompósitos auto-suportados de fosfato de cério fibroso (CeP) e nanotubos de carbono funcionalizados (NTC-FUNC), os nanocompósitos obtidos pelo dito processo e uso dos mesmos. BR 10 2013 010433 7.
- 78. Sahu, J.N., Karri, R.R., Zabed, H.M., Shams, S., Qi, X. (2019). Current perspectives and future prospects of nano-biotechnology in wastewater treatment. *Sep Purf Rev*, 0, 1–20.
- Dougna, A.A., Gombert, B., Kodom, T., Djaneye-Boundjou, G., Boukari, S.O.B., Leitner, N.K.V. et al (2015) Photocatalytic removal of phenol using titanium dioxide deposited on different substrates: effect of inorganic oxidants. *J Photochem Photobiol A Chem*, 305, 67–77.
- Tsoukleris, D.S., Maggos, T., Vassilakos, C. and Falaras, P. (2007) Photocatalytic degradation of volatile organics on TiO, embedded glass spherules. *Catal Today*, 129, 96–101.
- Fotiou, T., Triantis, T.M., Kaloudis, T., Papaconstantinou, E. and Hiskia, A. (2014) Photocatalytic degradation of water taste and odour compounds in the presence of polyoxometalates and TiO₂: Intermediates and degradation pathways. *J Photochem Photobiol A Chem*, 286, 1–9.
- 82. Chong, M.N., Jin, B., Chow, C.W.K. and Saint, C. (2010) Recent developments in photocatalytic water

treatment technology: a review. Water Res, 44, 2997-3027.

- 83. Wahab, R., Hwang, I.H., Kim, Y.-S., Musarrat, J., Siddiqui, M.A., Seo, H.-K. et al (2011) Non-hydrolytic synthesis and photo-catalytic studies of ZnO nanoparticles. *Chem Eng J*, 175, 450–457.
- 84. Kaur, R. and Pal, B. (2012) Size and shape dependent attachments of Au nanostructures to TiO₂ for optimum reactivity of Au–TiO₂ photocatalysis. *J Mol Catal A Chem*, 355, 39–43.
- 85. Prabhakaran, D., Nanjo, H. and Matsunaga, H. (2007) Naked eye sensor on polyvinyl chloride platform of chromo-ionophore molecular assemblies: a smart way for the colorimetric sensing of toxic metal ions. *Anal Chim Acta*, 601, 108–117.
- 86. Elad, T. and Belkin, S. (2013) Broad spectrum detection and "barcoding" of water pollutants by a genome-wide bacterial sensor array. *Water Res*, 47, 3782–90.
- Guijarro, C., Fuchs, K., Bohrn, U., Stütz, E. and Wölfl, S. (2015) Simultaneous detection of multiple bioactive pollutants using a multiparametric biochip for water quality monitoring *Biosens Bioelectron*, 72, 71–79.
- Ding, N., Zhao, H., Peng, W., He, Y., Zhou, Y., Yuan, L. et al (2012) A simple colorimetric sensor based on anti-aggregation of gold nanoparticles for Hg²⁺ detection. *Colloids Surfaces A Physicochem Eng Asp*, 395,161-167.
- Li, Y.L., Leng, Y.M., Zhang, Y.J., Li, T.H., Shen, Z.Y. and Wu, A.G. (2014) A new simple and reliable Hg²⁺ detection system based on anti-aggregation of unmodified gold nanoparticles in the presence of O-phenylenediamine *Sensors Actuators B Chem*, 200, 140-146.
- Farhadi, K., Forough, M., Molaei, R., Hajizadeh, S. and Rafipour, A. (2012) Highly selective Hg²⁺ colorimetric sensor using green synthesized and unmodified silver nanoparticles. *Sensors Actuators B Chem*, 161, 880–885.
- Wang, G.-L., Zhu, X.-Y., Jiao, H.-J., Dong, Y.-M. and Li, Z.-J. (2012) Ultrasensitive and dual functional colorimetric sensors for mercury (II) ions and hydrogen peroxide based on catalytic reduction property of silver nanoparticles. *Biosens Bioelectron*, 31, 337–342.
- Alizadeh, A., Khodaei, M.M., Hamidi, Z. and Shamsuddin, M. bin (2014) Naked-eye colorimetric detection of Cu²⁺ and Ag⁺ ions based on close-packed aggregation of pyridines-functionalized gold nanoparticles. *Sensors Actuators B Chem*, 190, 782–791.
- Xin, X., Sun, S., Li, H., Wang, M. and Jia, R. (2015) Electrochemical bisphenol A sensor based on core-shell multiwalled carbon nanotubes/graphene oxide nanoribbons. *Sensors Actuators B Chem*, 209, 275–280.
- 94. Cabral, J.P.S. (2010) Water microbiology. Bacterial pathogens and water. Int J Environ Res Public Health, 7, 3657–3703.
- 95. Bindhu, M.R. and Umadevi, M. (2014) Silver and gold nanoparticles for sensor and antibacterial applications. Spectrochim. *Acta A Mol Biomol Spectrosc*, 128, 37–45.
- 96. Adams, L.K., Lyon, D.Y. and Alvarez, P.J.J. (2006) Comparative eco-toxicity of nanoscale TiO₂, SiO₂, and ZnO water suspensions. *Water Res*, 40, 3527–32.
- Brayner, R., Ferrari-Iliou, R., Brivois, N., Djediat, S., Benedetti, M.F. and Fiévet, F. (2006) Toxicological impact studies based on *Escherichia coli* bacteria in ultrafine ZnO nanoparticles colloidal medium. *Nano Lett*, 6, 866–870.
- Nguyen, T., Huynh, T., Dang, C-H, Mai, D-T, Nguyen, T., Nguyen, D-T et al (2020) Novel biogenic silver nanoparticles used for antibacterial effect and catalytic degradation of contaminants. *Res Chem Intermed*, 46, 1975–1990.
- 99. Zhao, X., Lv, L., Pan, B., Zhang, W., Zhang, S. and Zhang, Q. (2011) Polymer-supported nanocomposites for environmental application: a review. *Chem Eng J*, 170, 381–394.
- 100. Roldán, M. V, de Oña, P., Castro, Y., Durán, A., Faccendini, P., Lagier, C. et al (2014) Photocatalytic and biocidal activities of novel coating systems of mesoporous and dense TiO₂-anatase containing silver nanoparticles. *Mater Sci Eng C Mater Biol Appl*, 43, 630–640.
- 101. Dachs, J., Lohmann, R., Ockenden, W.A., Méjanelle, L., Eisenreich, S.J. and Jones, K.C. (2002) Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environ Sci Technol* 36, 4229–4237.
- 102. Torres, M.A., Barros, M.P., Campos, S.C.G., Pinto, E., Rajamani, S., Sayre et al (2008) Biochemical biomarkers in algae and marine pollution: a review. *Ecotoxicol Environ Saf*, 71, 1–15.
- 103. Vernouillet, G., Eullaffroy, P., Lajeunesse, A., Blaise, C., Gagné, F. and Juneau, P. (2010) Toxic effects and bioaccumulation of carbamazepine evaluated by biomarkers measured in organisms of different

trophic levels. Chemosphere, 80, 1062-1068.

- 104.Correa-Reyes, G., Viana, M.T., Marquez-Rocha, F.J., Licea, A.F., Ponce, E. and Vazquez-Duhalt, R. (2007) Nonylphenol algal bioaccumulation and its effect through the trophic chain. *Chemosphere*, 68, 662–670.
- 105. Eichhorn, P., Rodrigues, S. V, Baumann, W. and Knepper, T.P. (2002) Incomplete degradation of linear alkylbenzene sulfonate surfactants in Brazilian surface waters and pursuit of their polar metabolites in drinking waters. *Sci Total Environ*, 284, 123–134.
- 106. Watkinson, A.J., Murby, E.J., Kolpin, D.W. and Costanzo, S.D. (2009) The occurrence of antibiotics in an urban watershed: from wastewater to drinking water. *Sci Total Environ*, 407, 2711–2723.
- 107.Gibs, J., Stackelberg, P.E., Furlong, E.T., Meyer, M., Zaugg, S.D. and Lippincott, R.L. (2007) Persistence of pharmaceuticals and other organic compounds in chlorinated drinking water as a function of time. *Sci Total Environ*, 373, 240–249.
- 108. Huerta-Fontela, M., Galceran, M.T. and Ventura, F. (2011) Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. *Water Res*, 45, 1432–1442.
- 109.Gee, R.H., Rockett, L.S. and Rumsby, P.C. (2015) Considerations of endocrine disrupters in drinking water. In. Endocrine disruption and human health, Eds Philippa D. Darbre, Elsevier, London pp: 319-341
- 110. Weber, R., Gaus, C., Tysklind, M., Johnston, P., Forter, M., Hollert, H. et al (2008) Dioxin- and POPcontaminated sites—contemporary and future relevance and challenges. *Environ Sci Pollut Res*, 15, 363–393.
- 111. Zhao, L., Hou, H., Zhu, T., Li, F., Terada, A. and Hosomi, M. (2015) Successive self-propagating sintering process using carbonaceous materials: a novel low-cost remediation approach for dioxincontaminated solids. *J Hazard Mater*, 299, 231-240.
- 112. Schröder, H.F. (1996) Chapter 6. Separation, identification and quantification of surfactants and their metabolites in waste water, surface water and drinking water by LC-TSP-MS, FIA-TSP-MS and MS-MS. J Chromatogr Libr, 59, 263–324.
- 113. Abd El-Gawad, H.S. (2014) Aquatic environmental monitoring and removal efficiency of detergents. Water Sci 28, 51–64.
- 114. Malaguerra, F., Albrechtsen, H.-J. and Binning, P.J. (2013) Assessment of the contamination of drinking water supply wells by pesticides from surface water resources using a finite element reactive transport model and global sensitivity analysis techniques. J Hydrol 476, 321–331.
- 115. Pradeep, T. and Anshup, (2009) Nanotechnology applications for clean water, Nanotechnology Applications for Clean Water. Elsevier. doi:10.1016/B978-0-8155-1578-4.50024-X
- 116. Szabo, J. and Minamyer, S. (2014) Decontamination of chemical agents from drinking water infrastructure: a literature review and summary. *Environ Int*, 72, 119–123.
- 117. Broséus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B.et al (2009) Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. *Water Res*, 43, 4707–4717.
- 118. Caus, A., Vanderhaegen, S., Braeken, L. and Van der Bruggen, B. (2009) Integrated nanofiltration cascades with low salt rejection for complete removal of pesticides in drinking water production. *Desalination*, 241, 111–117.
- 119. López-Roldán, R., Rubalcaba, A., Martin-Alonso, J., González, S., Martí, V. and Cortina, J.L. (2015) Assessment of the water chemical quality improvement based on human health risk indexes: Application to a drinking water treatment plant incorporating membrane technologies. *Sci Total Environ*, 540,334-343.
- 120.Richardson, S. and Postigo, C. (2012) Drinking water disinfection by-products, in: Barceló, D. (Ed.), Emerging organic contaminants and human health SE - 125, The handbook of environmental chemistry. Springer Berlin Heidelberg, pp. 93–137.
- 121. Hamidin, N., Yu, Q.J. and Connell, D.W. (2008) Human health risk assessment of chlorinated disinfection by-products in drinking water using a probabilistic approach. *Water Res*, 42, 3263–3274.
- 122. Richardson, S.D., Fasano, F., Ellington, J.J., Crumley, F.G., Buettner, K.M., Evans, J.J. et al (2008) Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ Sci Technol*, 42, 8330–8338.
- 123.Gao, Y., Li, Y., Zhang, L., Huang, H., Hu, J., Shah, S.M. et al (2012) Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide. *J Colloid Interface Sci*, 368, 540–546.

- 124. Mohammad, A.W., Teow, Y.H., Ang, W.L., Chung, Y.T., Oatley-Radcliffe, D.L. and Hilal, N. (2014) Nanofiltration membranes review: recent advances and future prospects. *Desalination*, 356, 226–254.
- 125.Janegitz, B.C., dos Santos, F.A., Faria, R.C. and Zucolotto, V. (2014) Electrochemical determination of estradiol using a thin film containing reduced graphene oxide and dihexadecylphosphate. *Mater Sci Eng C Mater Biol Appl* 37, 14–19.
- 126. Wen, Y., Niu, Z., Ma, Y., Ma, J. and Chen, L. (2014) Graphene oxide-based microspheres for the dispersive solid-phase extraction of non-steroidal estrogens from water samples. *J Chromatogr A*, 1368, 18–25.
- 127.Padhye, L.P., Yao, H., Kung'u, F.T. and Huang, C.-H. (2014) Year-long evaluation on the occurrence and fate of pharmaceuticals, personal care products, and endocrine disrupting chemicals in an urban drinking water treatment plant. *Water Res*, 51, 266–276.
- 128. Jiang, X., Jiang, Y., Shi, G. and Zhou, T. (2014). Graphene oxide coated capillary for the analysis of endocrine-disrupting chemicals by open-tubular capillary electrochromatography with amperometric detection. *J Sep Sci*, 37, 1671–1678.
- 129. Xue, F., Gao, Z.-Y., Sun, X.-M., Yang, Z.-S., Yi, L.-F. and Chen, W. (2015) Electrochemical determination of environmental hormone nonylphenol based on composite film modified gold electrode. J Electrochem Soc, 162, H338–H344.
- 130.Zeumer, R., Hermsen, L., Kaegi, R., Kühr, S., Knop, B. and Schlechtriem, C.(2020) Bioavailability of silver from wastewater and planktonic food borne silver nanoparticles in the rainbow trout Oncorhynchus mykiss. *Sci Tot Env*, 706, 135695.
- 131.Nowack, B. and Bucheli, T.D. (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut*, 150(1),5-22.
- 132. Marimuthu,S., Antonisamy, A., Malayandi, S., Rajendran, K., Tsai, P-C, Pugazhendhi, A. et al (2020) Silver nanoparticles in dye effluent treatment: a review on synthesis, treatment methods, mechanisms, photocatalytic degradation, toxic effects and mitigation of toxicity. *J Photochem Photobio B: Bio*, 205, 111823.
- 133.Loosli,F., Wang, J., Rothenberg, S., Bizimis,M., Winkler,C., Borovinskaya, O., Flamignie, L. and Baalousha, M. (2019) Sewage spills are a major source of titanium dioxide engineered (nano)-particle release into the environment. *Env Sci: Nano*, 6, 763-777
- 134.Benn, T.M. and Westerhoff, P. (2008) Nanoparticle silver released into water from commercially available sock fabrics. *Environ Sci Technol*, 42, 4133–4139.
- 135.Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S. et al (2008) Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ Pollut* 156: 233–239.
- 136.Mueller, N.C. and Nowack, B. (2008) Exposure modeling of engineered nanoparticles in the environment. *Environ Sci Technol*, 42, 4447–4453.
- 137.Kiser, M.A., Ryu, H., Jang, H., Hristovski, K. and Westerhoff, P. (2010) Biosorption of nanoparticles to heterotrophic wastewater biomass. *Water Res*, 44, 4105–4114.
- 138. Holsapple, M.P., Farland, W.H., Landry, T.D., Monteiro-Riviere, N.A., Carter, J.M., Walker, N.J. et al (2005) Research strategies for safety evaluation of nanomaterials, part II: toxicological and safety evaluation of nanomaterials, current challenges and data needs. *Toxicol Sci*, 88, 12–17.
- 139.Powers, K.W., Brown, S.C., Krishna, V.B., Wasdo, S.C., Moudgil, B.M. and Roberts, S.M. (2006) Research strategies for safety evaluation of nanomaterials. part VI. Characterization of nanoscale particles for toxicological evaluation. *Toxicol Sci*, 90, 296–303.
- 140. Lowry, G. V, Hotze, E.M., Bernhardt, E.S., Dionysiou, D.D., Pedersen, J.A., Wiesner, M.R. et al (2010) Environmental occurrences, behavior, fate, and ecological effects of nanomaterials: an introduction to the special series. *J Environ Qual*, 39, 1867–1874.
- 141. Mackevica, A., Skjolding, L.M., Gergs, A., Palmqvist, A. and Baun, A. (2015) Chronic toxicity of silver nanoparticles to Daphnia magna under different feeding conditions. *Aquat Toxicol*, 161, 10–16.
- 142. Starnes, D.L., Unrine, J.M., Starnes, C.P., Collin, B.E., Oostveen, E.K., Ma, R. et al (2015) Impact of sulfidation on the bioavailability and toxicity of silver nanoparticles to Caenorhabditis elegans. *Environ Pollut*, 196:239-246.
- 143.Książyk, M., Asztemborska, M., Stęborowski, R. and Bystrzejewska-Piotrowska, G. (2015) Toxic effect of silver and platinum nanoparticles toward the freshwater microalga Pseudokirchneriella subcapitata. *Bull Environ Contam Toxicol*, 94, 554–558.
- 144. Dominguez, G.A., Lohse, S.E., Torelli, M.D., Murphy, C.J., Hamers, R.J., Orr, G. et al (2015) Effects

of charge and surface ligand properties of nanoparticles on oxidative stress and gene expression within the gut of *Daphnia magna*. *Aquat Toxicol*, 162, 1–9.

- 145. Antonietti, M. (2001) Surfactants for novel templating applications. *Curr Opin Colloid Interface Sci*, 6(3), 244-248.
- 146.Franklin, N.M., Rogers, N.J., Apte, S.C., Batley, G.E., Gadd, G.E., Casey, P.S., 2007. Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl₂ to a freshwater microalga (Pseudokirchneriella subcapitata): the importance of particle solubility. *Environ Sci Technol*, 41, 8484–8490.
- 147. John, V.T., Simmons, B., McPherson, G.L. and Bose, A. (2002) Recent developments in materials synthesis in surfactant systems. *Curr Opin Col Interf Sci*, 7(5–6), 288-295.
- 148. Santra, S., Tapec, R., Theodoropoulou, N., Dobson, J., Hebard, A., Tan, W. (2001) Synthesis and characterization of silica-coated iron oxide nanoparticles in microemulsion: the effect of nonionic surfactants. *Langmuir*, 17, 2900–2906.
- 149. Mauter, M.S. and Elimelech, M. (2008) Environmental applications of carbon-based nanomaterials. *Environ Sci Technol*, 42, 5843–5859.
- 150. Yang, K. and Xing, B. (2010) Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chem Rev*, 110, 5989–6008.
- 151.Karn, B., Kuiken, T. and Otto, M. (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. *Environ Health Perspect*, 117,1823-1831
- 152. Handy, R.D., Von Der Kammer, F., Lead, J.R., Hassellöv, M., Owen, R. and Crane, M. (2008) The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology*, 17(4), 287-314
- 153.Glassman, H.N. (1948) Surface active agents and their application in bacteriology. *Bacteriol Rev*, 12, 105–148.
- 154. Jiang, J., Oberdörster, G. and Biswas, P. (2009) Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanoparticle Res* 11, 77–89.
- 155. Wang, D., Lin, Z., Yao, Z. and Yu, H. (2014) Surfactants present complex joint effects on the toxicities of metal oxide nanoparticles. *Chemosphere*, 108, 70–75.
- 156.Sayes, C.M., Liang, F., Hudson, J.L., Mendez, J., Guo, W., Beach, J.M. et al (2006) Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro. *Toxicol Lett*, 161, 135–142.
- 157. Wallace, W., Keane, M., Murray, D., Chisholm, W., Maynard, A. and Ong, T. (2007) Phospholipid lung surfactant and nanoparticle surface toxicity: Lessons from diesel soots and silicate dusts, in: Maynard, A., Pui, D.H. (Eds.), Nanotechnology and Occupational Health SE - 4. Springer Netherlands, pp. 23–38.
- 158.158.Zhang, L.W., Zeng, L., Barron, A.R. and Monteiro-Riviere, N.A. (2007) Biological interactions of functionalized single-wall carbon nanotubes in human epidermal keratinocytes. *Int J Toxicol*, 26, 103–113.
- 159.Lovern, S.B. and Klaper, R. (2006) Daphnia magna mortality when exposed to titanium dioxide and fullerene (C60) nanoparticles. *Environ Toxicol Chem*, 25, 1132–1137.
- 160.Baalousha, M. (2009) Aggregation and disaggregation of iron oxide nanoparticles: influence of particle concentration, pH and natural organic matter. *Sci Total Environ*, 407, 2093–2101.
- 161. Ouyang, K., Walker, S., Yu, X-Y, Gao, C-H, Huang, Q and Cai, P. (2018) Metabolism, survival, and gene expression of pseudomonas putida to hematite nanoparticles mediated by surface-bound humic acid. *Env Sci Nano*, 5, 682-695.
- 162.Gao, J., Powers, K., Wang, Y., Zhou, H., Roberts, S.M., Moudgil, B.M. et al (2012) Influence of Suwannee River humic acid on particle properties and toxicity of silver nanoparticles. *Chemosphere* 89, 96–101.
- 163.Li, M., Pokhrel, S., Jin, X., M\u00e4dler, L., Damoiseaux, R. and Hoek, E.M.V. (2011) Stability, bioavailability, and bacterial toxicity of Zno and iron-doped Zno nanoparticles in aquatic media. *Environ Sci Technol*, 45, 755–761.
- 164. Yang, S.P., Bar-Ilan, O., Peterson, R.E., Heideman, W., Hamers, R.J. and Pedersen, J.A. (2013) Influence of humic acid on titanium dioxide nanoparticle toxicity to developing Zebrafish. *Environ Sci Technol*, 47, 4718–4725.
- 165. Wang, Z., Quik, J.T.K., Song, L., Van Den Brandhof, E.-J., Wouterse, M. and Peijnenburg, W.J.G.M.

(2015). Humic substances alleviate the aquatic toxicity of polyvinylpyrrolidone-coated silver nanoparticles to organisms of different trophic levels. *Environ Toxicol Chem*, 34, 1239–1245.

- 166.Huang, Y.Q., Wong, C.K.C., Zheng, J.S., Bouwman, H., Barra, R., Wahlström, B. et al (2012) Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts. *Environ Int* 42, 91–99.
- 167. Alexander, H.C., Dill, D.C., Smith, L.W., Guiney, P.D. and Dorn, P. (1988) Bisphenol a: Acute aquatic toxicity. *Environ Toxicol Chem* 7, 19–26.
- 168. Shi, Y., Zhang, J.H., Jiang, M., Zhu, L.H., Tan, H.Q. and Lu, B. (2010) Synergistic genotoxicity caused by low concentration of titanium dioxide nanoparticles and p,p,-DDT in human hepatocytes. *Environ Mol Mutagen*, 51, 192–204.
- 169. Cohn, B.A., Wolff, M.S., Cirillo, P.M. and Sholtz, R.I. (2007) DDT and breast cancer in young women: new data on the significance of age at exposure. *Environ Health Perspect* 115, 1406–1414.
- 170.Rogan, W.J. and Chen, A. (2005) Health risks and benefits of bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT). *Lancet*, 366(9487),763-773.
- 171.Rogan, W.J. and Ragan, N.B. (2003) Evidence of effects of environmental chemicals on the endocrine system in children. *Pediatrics*, 112, 247–252.
- 172.Zhao, J. and Castranova, V. (2011) Toxicology of nanomaterials used in nanomedicine. *J Toxicol Environ Heal Part B*, 14(8),593-632.
- 173.O'Mullane, D.M., Kavanagh, D., Ellwood, R.P., Chesters, R.K., Schafer, F., Huntington, E. et al (1997) A three-year clinical trial of a combination of trimetaphosphate and sodium fluoride in silica toothpastes. *J Dental Res*, 76(11),1776-1778.
- 174.Xie, C., Liang, G., PuYue, P. and Bing, Y. (2009) Combined effects of sodium fluoride and nano-TiO₂ on human bronchial epithelial cells. *J Environ Occup Med*, 26, 242–244.
- 175.Hartmann, N.B., Legros, S., Von der Kammer, F., Hofmann, T. and Baun, A. (2012) The potential of TiO₂ nanoparticles as carriers for cadmium uptake in Lumbriculus variegatus and Daphnia magna. *Aquat Toxicol*, 118-119, 1–8.
- 176. Mitra, S., Keswani, T., Dey, M., Bhattacharya, S., Sarkar, S., Goswami, S. et al (2012). Copper-induced immunotoxicity involves cell cycle arrest and cell death in the spleen and thymus. *Toxicology*, 293, 78–88.
- 177.Fan, W., Cui, M., Liu, H., Wang, C., Shi, Z., Tan, C. et al (2011) Nano-TiO₂ enhances the toxicity of copper in natural water to Daphnia magna. *Environ Pollut*, 159, 729–734.
- 178.Du, H., Zhu, X., Fan, C., Xu, S., Wang, Y. and Zhou, Y. (2011) Oxidative damage and OGG1 expression induced by a combined effect of titanium dioxide nanoparticles and lead acetate in human hepatocytes. *Environ Toxicol*, 1–8.
- 179. States, J.C., Barchowsky, A., Cartwright, I.L., Reichard, J.F., Futscher, B.W. and Lantz, R.C. (2011) Arsenic toxicology: translating between experimental models and human pathology. *Environ Health Perspect*, 119(10),1356-1363.
- 180.Guan, X., Du, J., Meng, X., Sun, Y., Sun, B. and Hu, Q. (2012) Corrigendum to "application of titanium dioxide in arsenic removal from water: a review" [J. Hazard. Mater. 215-216 (2012) 1-16]. J Hazard Mat, 221–222:303
- 181. Wang, D., Hu, J., Irons, D.R. and Wang, J. (2011) Synergistic toxic effect of nano-TiO₂ and As(V) on Ceriodaphnia dubia. *Sci Total Environ*, 409, 1351–1356.
- 182.Hu, X., Chen, Q., Jiang, L., Yu, Z., Jiang, D. and Yin, D. (2011) Combined effects of titanium dioxide and humic acid on the bioaccumulation of cadmium in Zebrafish. *Environ Pollut*, 159, 1151–1158.
- 183. Yang, W.-W., Miao, A.-J. and Yang, L.-Y. (2012) Cd²⁺ toxicity to a green alga *Chlamydomonas reinhardtii* as influenced by its adsorption on TiO₂ engineered nanoparticles. *PLoS One*, 7(3):e32300.
- 184.Gardea-Torresdey, J.L., Parsons, J.G., Gomez, E., Peralta-Videa, J., Troiani, H.E., Santiago, P. et al (2002) Formation and growth of Au nanoparticles inside live Alfalfa plants. *Nano Lett*, 2, 397–401.