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# A REVIEW OF STUDY ON REMOVAL OF SOME BIOLOGICAL AND CHEMICAL POLLUTANTS FROM WATER / WASTEWATER USING DIFFERENT TYPES OF NANOMATERIALS IN TURKMENISTAN

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**ABSTRACT:** The results reached by the research confirm and point out that the expansion of industry's economic capacity and the transition to market mechanisms for the development of the economy cause a reduction in reserves of clean water, shallowing of mountain and trans-boundary rivers, the decline of fish stocks, and the emergence of a real threat of a water ecological crisis in the republic. The increasing water demand with stringent health standard and emerging contaminants caused that the traditional water/wastewater treatment technologies remain ineffective for providing adequate safe water. Now, nanotechnology-based multi-functional and highly efficient processes are providing affordable solutions to water/wastewater treatments that do not rely on large infrastructures or centralized systems. The present study is briefly discussed the availability and practice of different nano-materials (particles or fibers) for removal of bacteria, inorganic solutes, heavy metals, metal ions, complex organic compounds, natural organic matter, nitrate, and other pollutants found in surface water, ground water, and/or industrial water. Recently, nano-technology and nano-science are greatly developed and produced environmentally-safe, economical, and efficient materials for environmental engineering, these engineered nano-materials are promising for water treatment due to their unique physicochemical properties that enable the heavy metals scavenging with high adsorption capacity and selectivity even at very low concentrations. Efficient heavy metals removal from water was reached via the simple adsorption technique. The current review discussed the heavy metals were removed by using various Nano-materials like zeolite, polymers, chitosan, metal oxides, and metals under different conditions. The new studies focused on nano-materials functionalization in order to improve properties of separation, stability, and adsorption capacity. Different molecules such as bio-molecules, polymers, inorganic materials were used in functionalization process. By providing the magnetic properties to the adsorbent, its separation becomes easier via magnetic separation techniques. This review provided precious information regarding the use of engineered nano-materials for the removal of toxic heavy metals that will guide the researchers intending to fabricate new nano-materials for water/wastewater remediation. It should be noted, that all experiments are conducted at lab-scale for toxic metals in aqueous solutions and studies are needed to evaluate the process efficiency at pilot and large scale using real wastewater

**Key words:** Water, wastewater, pollutants, Nanomaterials, surface water, ground water and industrial water.

## INTRODUCTION

Central Asia (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan) -have

similar natural conditions. Joint use of trans-boundary rivers is one of important characteristics of that region, where developing the nations is directly depends on efficient water

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resources management. The Republic of Turkmenistan and other countries that emerged from the former Soviet Union are among those facing such challenges (Roberts *et al.*, 2012) as water pollutants.

Turkmenistan is one of central Asian republics locating in its Southwestern lies between latitudes and 43° 48'N, and longitudes 52° 27' and 67° 41'. Its area (without the Caspian offshore area) is 491.2 thousand square kilometers. The territory extends for 1,100 Km from west to east and for 650 Km from north to south. To the east and north, Turkmenistan borders Uzbekistan, to the northwest Kazakhstan, to the west over the Caspian Sea, Azerbaijan, to the southern Iran, and to the southeast Afghanistan (Stanchin and Lerman, 2007).

Rapid industrialization and population growth play a vital role in environmental contamination (Nurtazin *et al.*, 2020). Clean water, fresh air, and a pristine environment are becoming rare amenities across Asia. Over the past 50 years all of these factors have profoundly changed natural ecosystems and water quality, challenges which might be exacerbated by climate change in the region, although the overall impact of climate change on water quantity and quality will be marginal compared to socioeconomic changes, even by 2100 (Evans *et al.*, 2012). Asia is no exception; as a result, 40% of the global death toll due to unsafe or inadequate supply of water, sanitation, and hygiene occurs in Asia (WHO, 2015).

Many rivers still in good condition so there are opportunities to avoid pollution and begin restoration. However, severe organic pollution is already affecting around one in seven rivers across Latin America, Africa and Asia. This poses a growing risk to public health, food security and the economy (United Nation Environment Programme, 2016, (UNEP).

Due to climate change, two-thirds of mankind will face water scarcity by 2025, while by 2050, global food production must increase by at least 50% to feed 9 billion people. To overcome water scarcity, 15 million m<sup>3</sup>/day of untreated wastewater is used globally for crop irrigation, polluting the soil with pathogens, heavy metals and excess salts. Since 10% of the global population consumes food from crops

irrigated with wastewater, pathogens transmitted through the food chain cause diseases especially in young children and women (Ungureanu *et al.*, 2020).

The earth is covered by 70% of water, but the percentage of fresh water is only 2.5%. More than half is trapped in polar ice, glaciers and permafrost, which means that humankind survives on less than 1% of the planet's total reserves (Orlovsky and Orlovsky, 2014). According to WHO the water quality of about 70% river water was contaminated due to pollutants in India and some of the river water was too poor for human consumption (Gupta *et al.*, 2017).

Water is used in all aspects of our lives, but we can divide that usage into three major sectors. Globally, agriculture is responsible for around 70% of our total consumption, with industry next at 20%, and domestic use at 10%. There are major regional variations in these proportions. In Asia and Africa, for example, 80% of water use is accounted for by the agricultural sector. In Europe and North America, the largest share is consumed by industry.

Huge volumes of wastewater are generated daily in households, industries and agriculture. The volume of wastewater accounts for 50–80% of the domestic household water uses and the global wastewater discharge was estimated at 400 billion m<sup>3</sup>/year, polluting approximately 5500 billion m<sup>3</sup> of water/year (Ungureanu *et al.*, 2020). Wastewater usually consists of 99% water and 1% suspended, colloidal and dissolved solids. It is well known that wastewater, depending on its source, is loaded with pollutants such as organic matter, suspended solids, nutrients (mainly nitrogen and phosphorus), heavy metals, emerging contaminants (antibiotics, hormones, personal care products, pesticides, polycyclic aromatic hydrocarbons, phenolic compounds, volatile organic compounds, antibiotic resistant bacteria and genes) and pathogenic microorganisms (bacteria, viruses, protozoans and parasitic worms) (Ungureanu *et al.*, 2020).

In many developing countries (like Turkmenistan) the bulk of domestic and industrial wastewater is discharged without any treatment or after primary treatment only. In Latin America about 15% of collected wastewater

passes through treatment plants (with varying levels of actual treatment). In Venezuela, 97% of the country's sewage is discharged raw into the environment. Even a highly industrialized country such as China discharges about 55 % of all sewage without treatment. In a relatively developed Middle Eastern country such as Iran, the majority of Tehran's population has totally untreated sewage injected into the city's groundwater (**Dhote et al., 2012**).

Water is contaminated by biological pollutants (bacteria, viruses, and parasites) and chemical pollutants might be either organic (pesticides, fertilizers, oil, detergents, and plastic discharged from domestic, industrial / agricultural waste) or inorganic (metals, acids, salts of domestic and industrial effluents). The health problems caused by potable contaminated water may range from simple toxicity and stomach ache to deadly diseases or sudden death (**Mallikarjunaiah et al., 2020**).

Growing number of industrial activities create undesirable ecological and global health impact due to the use of huge amount of chemical and harmful heavy metals (**Kabir et al., 2017**). Arsenic (As), Cadmium (Cd), Copper (Cu), Chromium (Cr), Zinc (Zn), Nickel (Ni), Lead (Pb) and Mercury (Hg) are carcinogenic and show toxicity even at tiny amount (**Kabir et al., 2020**). Moreover, the presence of different dyes in water reduces light penetration, prevents the photosynthesis of aqueous flora (**Tkaczyk et al., 2020**).

Membrane processes like microfiltration (MF), ultra filtration (UF), nano filtration (NF), and reverse osmosis (RO), which are pressure-driven filtration processes, are considered as some new highly effective processes. Alternative methods of removing large amounts of organic micro pollutants are being considered. Water/wastewater treatment by membrane techniques is cost-effective and technically feasible and can be better alternatives for the traditional treatment systems because of their high efficiency in removal of pollutants meets the high environmental standards (**Amin et al., 2014**). NF and RO have proved to be high effective filtration technologies for removal of micro pollutants. RO is relatively more effective than NF but higher energy consumption in RO

makes it less attractive than NF where removal of pollutants is caused by different mechanisms including convection, diffusion (sieving), and charge effects. Although NF based membrane processes are quite effective in removing huge loads of micro pollutants, advanced materials and treatment methods are required to treat newly emerging micro pollutants (**Abdel-Raouf et al., 2019**).

Nanotechnology and nano-materials have been considered effective in solving water problems related to quality and quantity. The attentions were directed toward cost-effective and new fabricated nano-materials for the application in water/wastewater remediation, such as carbon nanotubes (CNTs), dendrimers, zeolite, carbonaceous, polymer based, chitosan, ferrite, magnetic, metal oxide, bimetallic and metallic, etc (**Kumar et al., 2014**).

### Surface Water

According to United States Geological Survey surface water is water on surface of the planet such as in a river, lakes, wetland or ocean. It can be contrasted with groundwater and atmospheric water. Non –saline surface water uses in replenished by precipitation and by recruitment from groundwater .It lost through evaporation, seepage into the ground where it become groundwater used by mankind for agriculture, living industry or discharged to the sea where it becomes saline

### Ground Water

Water below the land surface, both from unsaturated and saturated zones, is referred to as groundwater. This source is estimated to contain more than 100 times that available from streams and freshwater lakes. Since groundwater is difficult to observe and track directly, monitoring, modeling, and mapping are crucial to its shared and sustainable use (**Brands et al., 2016**).

### Industrial Water

Manufacturing and other industries use water during the production process for either creating their products or cooling equipment used in creating their products. According to the United States Geological Survey (USGS).

## Aim of Study

The paper has three main sections following the introduction:

Section (1) discusses the traditional and current practices in water/wastewater treatment.

Section (2) describes mainly the properties and types of nanomaterials and their importance in water/wastewater treatment.

Section (3) discusses different types of nanomaterials focusing on membranes for treating a variety of pollutants in water/wastewater. The application of nanomaterials is reviewed based on their functions in unit operation processes.

The study is based on general historical, objective and description and analytical research principles. Applying these methods in the research can consider scientific information as an integral system in which each previous approach indirectly or directly influenced the next one (**Goundar, 2012**). All this together made it possible to compile a systematic series of scientific and theoretical calculations on the given issue. The views of authors are discussed regardless of ethnocultural preferences and political inclinations, which necessitates a thorough comparison of facts and phenomena in aggregate, that is, a comprehensive study of the problem. In addition, a systematic approach, which takes into account both the features of the research objects themselves and the factors that determine these features, is used in the paper. Such approaches allow to identify not only gaps in the studied subject, but also some particular aspects of the problem that might not have come to the scholars' attention for one reason or another. In general, this gives the opportunity to objectively compare these aspects and, on their basis, determine the prospects for further research (**Alimbaev et al., 2020**).

## Nanotechnology for Water/Wastewater Purification

Without treatment of wastewater, water pollution is occurring. Discharging of wastewater with different kinds of pollutants contaminates the water bodies posing a serious risk to the environment and living organisms. The major wastewater contaminants include inorganic

compounds, organic pollutants, and many other complex compounds (**Mallikarjunaiah et al., 2020**). Heavy metals are the most dangerous of the different forms of aquatic pollutants ones, because they are harmful even at very low concentrations and cause threatening in the environment (**Ali and Llahi, 2019**).

Freshwater sources/resources are depleting due to prolonged droughts, growth of population, climate changes threats, and strict water quality standards (**Amin et al., 2014; Dinesh et al., 2020; Mallikarjunaiah et al., 2020**). The existing water treatment systems, distribution systems, and disposable habits coupled with huge centralized schemes are no longer sustainable. The current studies don't probably discuss the practices that ensure the availability of water for all users in accordance with the stringent water quality standards (**Dinesh et al., 2020**).

Many commercial and noncommercial technological developments are employed on daily basis but nanotechnology has proved to be one of the advanced ways for water/waste water treatment (**Amin et al., 2014**). Developments in nanoscale research have enable to invent economically feasible and environmentally stable treatment technologies for efficiently treating water/wastewater while ever increasing water quality standards. Nanotechnology advancement has created the opportunities to meet the fresh water demands of the future generations (**Kumar et al., 2014**). It is proposed that nanotechnology can adequately address many of the water quality issues by using different types of nanoparticles and/or nanofibers. Nanotechnology uses materials of sizes smaller than 100nm in at least one dimension meaning at the level of atoms and molecules as compared with other disciplines such as chemistry, engineering, and materials science (**Mallikarjunaiah et al., 2020**).

## Nano-Bioremediation

The removal of environmental contaminants (such as heavy metals, organic and inorganic pollutants) from contaminated sites using nanoparticles/nanomaterial formed by plant, fungi and bacteria with the help of nanotechnology is called nano-bioremediation. NBR is the emerging technique for the removal of pollutants for environmental cleanup. Current

technologies for remediation of contaminated sites include chemical and physical remediation, incineration and bioremediation. With recent advances, bioremediation offers an environmentally friendly and economically feasible option to remove contaminants from the environment. Three main approaches of bioremediation include use of microbes, plants and enzymatic remediation (Yadav *et al.*, 2017).

In the context of treatment and remediation, nanotechnology has the potential to provide both water quality and quantity in the long run through the use of, for example, membranes enabling water reuse, desalination. In addition, it yields low-cost and real-time measurements through the development of continuous monitoring devices. Nanoparticles, having high absorption, interaction, and reaction capabilities, can behave as colloid by mixing mixed with aqueous suspensions and they can also display quantum size effects. Energy conservation leading to cost savings is possible due to their small sizes; however, overall usage cost of the technology should be compared with other techniques in the market (Amin *et al.*, 2014).

Recent research attempts have focused on developing polymer-based nanocomposite membranes for sustainable water purification, aimed at enhancing fouling resistance and surmounting the trade-off relationship between permeability and solute rejection. Among different nanocomposites, polymer-based nanocomposite membranes have driven considerable attention in recent years. Polymeric nanocomposite membranes (PNC) are fabricated by dispersing nanoparticles (NPs), nanotubes, nanofibers, or nanosheets into the polymer matrix via several techniques. The incorporation of engineered nanoparticles including metal oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, MgO, Fe<sub>2</sub>O<sub>3</sub>, and zeolite) metals (Cu, Ag) carbon-based materials (graphene, carbon nanotube (CNT), carbon nanofibers (CNFs)) and nanofiber polymers (polyurethane, polylactic acid, polyethylene oxide, in polymer matrices imparts tunable physicochemical properties and unique functionalities to the membranes. Nanocomposite membranes have emerged as promising water purification technologies to overcome the limitations associated with conventional polymeric membranes by offering

enhanced hydrophilicity, thermal and mechanical stability, permeability, targeted degradation, solute rejection, and magnetic, antimicrobial, and antifouling properties (Esfahani *et al.*, 2018)

### Applications of Nano-Particles

Wastewater treatment has been investigated with available techniques including precipitation, sedimentation, reverse osmosis, ion exchange, membrane process, electrochemical treatment, and adsorption. Among all the mentioned techniques, the adsorption process has been widely explored because adsorption-based systems are simple to design, easy to operate, and economical and show more efficient at removing of different toxic pollutants including metals. For high efficient removal of heavy metal ions from wastewater, nano-particles as adsorbents must satisfy the following criteria:

1. The nano-sorbents shouldn't be toxic.
2. The sorbents should demonstrate high sorption efficiency and selectivity at very low concentration of pollutants.
3. The adsorbed pollutant could be easily removed from the surface of the nano-adsorbent.
4. Infinite recycling of the sorbents.
5. The reversible process should be capable of getting back the adsorbent.

Adsorption of metal ions on iron nano-particles has been investigated as a promising agent for the exclusion of organic pollutants and heavy metal ions from water and wastewater. Nano-particles deposited on the surface of functioning materials have risk potential since nano-particles might release and emit to the environment where they can accumulate for long periods of time. Till now, no online monitoring systems exist to provide reliable real time measurement data on the quality and quantity of nano-particles present only in trace amounts in water (Lu *et al.*, 2017).

### Removal of Pollutants Using Different Nanomaterials

#### Disinfection

Biological contaminants can be classified into three categories, namely, microorganisms, natural organic matter (NOM), and biological

toxins. Human pathogens and free living microbes are examples for microbial pollutants. The removal of cyanobacterial toxins is an issue in conventional water treatment systems (Amin *et al.*, 2014). In both ground and surface water pathogens (such as: bacteria, protozoans, and viruses) may cause contamination (Pandy *et al.*, 2014). The toxicity of the standard chlorine chemical disinfection as well as the formation of carcinogenic and harmful by-products has already been mentioned. Chlorine dioxide is costly and results in the production of dangerous substances as chlorite and chlorate in manufacturing process (Saqib *et al.*, 2018). Ozone, on the other hand, has no residual effects but produces unknown organic reaction products. For UV disinfection, longer exposure time is required for effectiveness and also there is no residual effect. Despite advances in disinfection technology, outbreaks from waterborne infections are still occurring. So, advanced disinfection technologies must, at least, eliminate the emerging pathogens, in addition to their suitability for large-scale adoption. There are many types of nanomaterials for example: Ag, titanium, and zinc capable of disinfecting waterborne disease-causing microbes. Due to their charge capacity, they possess antibacterial properties. Photocatalysts made of  $TiO_2$  and metallic and metal-oxide nanoparticles are among the most promising nanomaterials with antimicrobial properties. The efficacy of metal ions in water disinfection has been highlighted by many researchers (Abba *et al.*, 2018)

#### Silver Nanoparticles (SNPs)

Due to its low toxicity and microbial inactivation in water, silver is the most widely used material with well-reported antibacterial mechanism. Silver nanoparticles are made from its salts as silver nitrate and silver chloride, and their effectiveness as biocides has been reported. Though the antibacterial effect is size dependent, smaller Ag nanoparticles (8nm) were found to be the most efficient while larger particle size (11–23nm) had lower bactericidal activity. Also, truncated triangular silver nanoplates exhibited better antibacterial effects than the spherical and rod-shaped nanoparticles indicating their shape dependency. The mechanisms involved during the bactericidal

effects of Ag nanoparticles as the formation of free radicals damaging the bacterial membranes, interactions with DNA, adhesion to cell surface altering the membrane properties, and enzyme damage (Deshmukh *et al.*, 2019). Because of its high antimicrobial activity Immobilized nanoparticles are important. Embedded Ag nanoparticles have been reported as very effective against both Gram-positive and Gram-negative bacteria. Poly ( $\epsilon$ -caprolactone-) based polyurethane nanofiber mats containing Ag nanoparticles were prepared as antimicrobial nanofilters. Water filters prepared by polyurethane's foam coated with Ag nanofibers have shown good antibacterial properties against *Escherichia coli* (*E. coli*) (Deshmukhet *al.*, 2019).

Finally, the efficiency of Ag nanocatalyst alone and in combination with carbon covered in alumina for the degradation of microbial pollutants in water has been demonstrated. Although Ag nanoparticles have been used efficiently to inactivate bacteria and viruses as well as reducing membrane biofouling, their long-term efficacy against membrane biofouling has not been reported mainly due to loss of silver ions with time. So, further work to reduce this loss of silver ions is required for long-term control of membrane biofouling. Alternatively, doping of Ag nanoparticles with other metallic nanoparticles or its composites with metal-oxide nanoparticles can solve the issue and this could also lead to the parallel removal of inorganic/organic compounds from water/wastewater (Abdel-Raouf *et al.*, 2019).

#### $TiO_2$ Nanoparticles

$TiO_2$  nanoparticles are one of the most promising photocatalysts for water purification (Li *et al.*, 2008). The basic mechanism of a semiconductor-based photocatalysts like low-cost  $TiO_2$  having good photoactivity and nontoxicity involves the production of highly reactive oxidants, such as OH radicals, for disinfection of microorganisms, bacteria, fungi, algae, viruses, and other.  $TiO_2$ , after 8 hours of simulated solar exposure, has been reported to reduce the viability of several waterborne pathogens such as protozoa, fungi, *E. coli*, and *Pseudomonas aeruginosa*. A complete inactivation of fecal coliforms under sunlight is

reported in a study expressing the photocatalytic disinfection efficiency of TiO<sub>2</sub> (Lu *et al.*, 2017). The synthesis of visible-light-activated TiO<sub>2</sub> nanoparticles has attracted considerable interest, and TiO<sub>2</sub> nanoparticles and nanocrystallines exposed to UV-visible light exhibited strong bactericidal activity against *E. coli*. Metal-doped TiO<sub>2</sub> nanoparticles, sulfur, and iron, several studies have shown great antibacterial effects against *E. coli* (Liao *et al.*, 2020). Nanoparticles of transition metal oxides were used to modify TiO<sub>2</sub> photocatalysts and showed great promise for water disinfection.

### Carbon Nanotubes (CNTs)

The backbone of these nanomaterials comprises of carbon and found in variety of shapes such as hollow tubes (carbon nanotube, *i.e.*, CNT), sheets (graphene, graphene oxide, *i.e.*, GO), and spheres (such as fullerenes) (Ojha, 2020). They serve as an excellent material for water treatment over other macromolecules because of their higher ratio of surface area by volume (Kang *et al.*, 2007). CNTs are synthesized as single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs), the unique physical, cytotoxic, and surface functionalizing properties of CNTs, their fibrous shape, the size and length of the tubes, are the reasons to the effect of antimicrobial of CNTs. The mechanisms of killing bacteria by CNTs are also due to the production of oxidative stress, disturbances to cell membrane. Although single-walled CNTs are more detrimental against microorganisms than multiwalled CNTs, dispersivity of CNTs is a more important parameter than length (Mauter and Elimelech, 2008). The large surface area-by-volume ratio of graphene sheets and other carbon-based nanomaterials serves as an excellent sorbent for bacteria and viruses. SWNT-based filters have been developed to adsorb these microbes into the micropores of the materials (Yang *et al.*, 2010).

The whole cytotoxicological mechanism for bacterial and virus inactivation by carbon-based nanomaterials can be summarized under three basic points, *i.e.*, cell membrane damage, oxidative stress, and sorption phenomenon (Ojha, 2020). CNTs (one of nanosorbents) have been shown to be extremely successful in

removal of bacterial pathogens and biological impurities have received special attention for their excellent capabilities of removing biological contaminants from water. CNTs have antimicrobial characteristics against different microorganisms including bacteria such as *E. coli* and *Salmonella ssp* and viruses.

### Desalination

Desalination is regarded as an important alternative for obtaining fresh water source. Despite its high cost, membrane based desalination processes cover most of the desalination capability out of with reverse osmosis RO accounting for just 41% Parameters that control the desalination cost increase the flux of water through membrane to reduce the fouling. Recent developments in membrane technology have resulted in energy efficiency in RO plants (Greenlee *et al.*, 2009). NF has also been evaluated for desalinating seawater. Nanomaterials are very useful in developing more efficient and less expansive nanostructured and reactive membranes for water/wastewater treatment and desalination such as CNT filters. Nanomaterials give opportunities to control the cost of desalination and maximize its energy efficiency and among these are CNTs, zeolites, and graphene. The controlled synthesis of both the length and diameters of CNTs has enabled them to be used in RO membranes to achieve high water fluxes (Abdel-Raouf *et al.*, 2019).

### Toxicity of Heavy Metals to Living Organisms and Ways of Removing Pollution

Toxic heavy metals such as lead, cadmium, mercury, chromium, and arsenic have the maximum potential to cause harm as a result of their widespread use, toxicity in elemental or combined forms, and widespread distribution in the environment. These five elements have a strong affinity for sulfur in the human body, and usually they bind via thiol groups (–SH) to enzymes responsible for controlling the speed of metabolic reactions (Mallikarjunaiah *et al.*, 2020). The resulting sulfur-metal bonds prevent the enzymes from working, which deteriorates human health and leads to death in some cases. Mercury and lead damage the central nervous system, while cadmium causes degenerative bone disease, while chromium (hexa-valent

form) and arsenic are carcinogens that may induce cancer. Exposure to lead and mercury can cause the development of autoimmunity, which can result in joint diseases (rheumatoid arthritis), kidney diseases, circulatory and nervous system disorders, and fatal brain damage in humans. In children, exposure to lead and mercury causes reduced intelligence, impaired development, and an increased risk of cardiovascular disease. Cadmium can disrupt the endocrine system, damage fragile bones, and affect the regulation of calcium in biological systems and is known to be a mutagen and carcinogen. Chromium causes Hair loss, headaches, diarrhea, nausea, and vomiting in humans (**Abdel-Raouf *et al.*, 2019**).

The presence of lead in water may be due to the application of lead and Polyvinyl Chloride (PVC) pipes in addition to a spill of sewage from industries such as battery making, metal plating, electrical equipment, chemicals, steel, iron, and copper. Lead compounds are generally toxic pollutants with the ability to bioaccumulate in tissues of the human body. Human intestine absorbs lead, which may cause colics, skin pigmentation, and paralysis due to overexposure. Exposure to high levels of Pb (II) could damage the central nervous system and even cause a death. Chromium (VI), another toxic heavy metal pollutant, might lead to gastrointestinal disorders; liver, kidney, and lung cancer; cardiovascular shocks; and other health issue (**Orlovsky and Orlovsky, 2014**).

At acidic pH levels, heavy metals tend to form free ionic species, with more protons required to saturate metal binding sites. This means that at higher hydrogen ion concentrations, the adsorbent surface become more positively charged, thus reducing the attraction between an adsorbent and metal cation. As a result, heavy metals become more available, thereby increasing their toxicity to microorganisms and plants. At basic conditions, metal ions replace protons to form other species, such as hydroxo-metal complexes that are soluble as in the case of Cd, Ni, and Zn, but insoluble in the case of Cr and Fe. Heavy metal solubility and bioavailability can be influenced by a small change in the pH level (**Ayangbenro *et al.*, 2017**). Owing to large changes on the Earth's resources, environmental sustainability finds ways to reduce the harvesting of nonrenewable

resources, as well as the impact of the activities associated with them on the Earth's biosphere.

Different types of nanomaterials have been introduced for removal of heavy metals from water / wastewater such as nanosorbents including CNTs, zeolites, and dendrimers and they have exceptional adsorption properties. The ability of CNTs to adsorb heavy metals such as  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  and metalloids such as arsenic (As) compounds is reviewed by many researchers. Composites of CNTs with Fe and cerium oxide ( $\text{CeO}_2$ ) have also been reported to remove heavy metal ions in few studies. Cerium oxide nanoparticles supported on CNTs are used effectively to adsorb arsenic. Fast adsorption kinetics of CNTs is mainly due to the highly accessible adsorption sites and the short intraparticle diffusion distance (**Tahoon *et al.*, 2020**).

Metal based nanomaterials proved to be better in removing heavy metals than activated carbon, for example, adsorption of arsenic by using  $\text{TiO}_2$  nanoparticles and nanosized magnetite. The utilization of photocatalysts such as  $\text{TiO}_2$  nanoparticles has been investigated in detail to reduce toxic metal ions in water. In a study, the effectiveness of nanocrystalline  $\text{TiO}_2$  in removing different forms of arsenic is elaborated and it has shown to be more effective photocatalyst than commercially available  $\text{TiO}_2$  nanoparticles with a maximum removal efficiency of arsenic at about neutral pH value. A nanocomposite of  $\text{TiO}_2$  nanoparticles anchored on graphene sheet was also used to reduce Cr (VI) to Cr (III) in sunlight (**Yang *et al.*, 2020**).

The capability of removing heavy metals like As is also investigated by using iron oxide nanomaterials ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) as cost-effective adsorbents by many researchers. Arsenic removal was also investigated by using high specific surface area of  $\text{Fe}_3\text{O}_4$  nanocrystals. Polymer-grafted  $\text{Fe}_2\text{O}_3$  nanocomposite was effectively used to remove divalent heavy metal ions for copper, nickel, and cobalt over a pH range of 3 to 7 (**Al-Saad *et al.*, 2012**).

## Removal of Organic Contaminants

### Carbon Nanotubes (CNTs)

Different types of nanomaterial like nanosorbents such as CNTs, polymeric materials



(e.g., dendrimers), and zeolites have exceptional adsorption properties and are used for removing organics from water/wastewater. Due to their exceptional water treatment capabilities and adsorption of organics CNTs have received special attention on CNTs. The removal of NOM by CNTs is higher when compared with carbon-based adsorbents mainly due to large surface areas and other factors. CNTs are also effective to remove polycyclic aromatic organic compounds and atrazine (Amin *et al.*, 2014).

### Zero-Valent Iron

Nanocatalysts including semiconductor materials, zero-valence metal, and bimetallic nanoparticles have been used to degrade environmental pollutants such as PCBs, pesticides, and azo dyes due to their higher surface area and shape dependent properties. Magnetic nanosorbents also have proved effective in removing organic pollutants (Amin *et al.*, 2014). Iron oxide nanomaterials have shown better removal capabilities of organic pollutants than bulk materials. Fe<sub>2</sub>O<sub>3</sub> nanoparticles have also been used for the removal of colored humic acids from wastewater. Chlorinated organic compounds and a polychlorinated biphenyls PCBs have been converted successfully using nZVI as well as inorganic ions such as nitrate and perchlorate (Lu *et al.*, 2017).

### Other Nanomaterials

#### Hydrogel Nanoparticles

Utilization of polymer nanocomposites- especially in the form of hydrogel- for the removal of heavy metals ions from the contaminated water has been established, recently. These nanocomposite hydrogels may swell in water allowing for a high adsorption capacity (Amin *et al.*, 2014). Hydrogels consist of acrylic, vinylic, and other functional monomers, such as acrylic acid (AA), acrylamide (AM), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), hydroxyl ethyl methacrylamide (HEMA), N-isopropyl acrylamide (NIPAM), N-vinyl imidazole (NI), and 4-vinyl pyridine (NVP), have already proven to be excellent adsorbents for heavy metals and some other soluble species (Tran *et al.*, 2010).

From the adsorption studies, the maximum removal efficiency of metal ions toward the nanohydrogel was discovered to be in the following order: Pb(II) > Hg(II). Furthermore, the adsorption of Cu(II) ions from aqueous solutions onto poly(acrylic acid-co-acrylamide) hydrogels was investigated. The hydrogels were prepared via free radical solution polymerization and the maximum metal uptake was verified by varying the ratio of acrylamide/acrylic acid moieties on the surfaces of hydrogels and the amount of cross-linking agent. Swelling results showed that hydrogels would swell up to 70,000% with appropriate selection of cross-linking agent amount and monomer ratio (Orozco-Guareño, *et al.*, 2010).

### Membrane Filtration

Hybrid membrane processes have been developed with the purpose to improve performance in terms of product quality, plant compactness, environmental impact, and energy use. Examples of membrane integrated processes include multi-stages pressure-driven membrane processes (ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED)), or applications concern seawater desalination, wastewater treatment, separation in biotechnology and food industries, and chemical production (Charcosset, 2016). For the last few years, a great attention has been paid attention on development of unconventional and methods for wastewater treatment, such as pressure driven membrane operations, namely ultrafiltration which helps eliminate colloids, suspended and macromolecular matter, and reverse osmosis (Feng *et al.*, 2012), which helps remove mineral substances and low-molecular organic compounds

#### Ultrafiltration

Ultrafiltration (UF) is a membrane technique working at low trans membrane pressures for the removal of dissolved and colloidal material. The application of ultrafiltration technology to wastewater is a relatively recent concept. Although in the beginning, it is already commonly used in many industrial applications such as food or pharmaceutical industries. Since the membrane pore sizes are larger than dissolved metal ions in the form of hydrated

ions or as low molecular weight complexes, these ions can pass through without any difficulty. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was suggested (Abdel-Raouf *et al.*, 2019).

Micellar enhanced ultrafiltration (MEUF) process has been used for the removal of Copper, Chromate, Zinc, Nickel, Cadmium, Selenium, Arsenate, and Organics like Phenol, O-cresol. Metals removal was enhanced by combining the MEUF treatment with electrolysis or with powdered activated carbon (PAC). Cetyl-peridinium Chloride (CPC) and Sodium dodecyl sulphate (SDS) surfactants removal from the MEUF was also enhanced by the MEUFACF (activated carbon fiber) combined treatment. Surfactant has been recovered from the MEUF retentive solution by treating the retentive with HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, NaOH solution but retentive solution needs further treatment. Electrolysis was found better in the separation of metal and surfactant from the MEUF retentive solution. The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution (Mungray *et al.*, 2011).

### Reverse osmosis

Reverse Osmosis (RO) is the finest of all membrane filtration systems, it is a membrane based technology to purify water by separating the dissolved solids from feed stream resulting

in permeate and reject stream for a wide range of applications in domestic as well as industrial applications (Ahuchaogu *et al.*, 2018). It accounts for more than 20% of the world's desalination capacity (Fig. 1).

The application of methodology of membrane separation in water/wastewater treatment is increased because of the stringent standards of water quality. Nanofiltration (NF) is one of the commonly used membrane processes for water/wastewater additionally other applications as desalination. Due to lower energy consumption and higher flux rates, NF has replaced reverse osmosis (RO) membranes in many applications. Nano-filtration (NF) is the intermediate process between UF and RO. NF is an attractive technology for the removal of heavy metal ions such as nickel, chromium, copper and arsenic from wastewater. There are many studies on the removal of heavy metal by NF and RO membranes (Shon *et al.*, 2013).

By the way, improving the UF processes for water treatment containing organic and inorganic solutes, dendritic polymers are used as water-soluble ligands for radionuclides and inorganic anions. Nearly complete reduction of 4-nitrophenol was seen when using a composite membrane composed of alumina and polymers through layer-by-layer adsorption of polyelectrolytes and citrate-stabilized Au nanoparticles. Finally, the addition of metal oxide nanoparticles including silica, TiO<sub>2</sub>, alumina, and zeolites to polymeric ultrafiltration membranes has helped reduce fouling in Fig. 2 (Amin *et al.*, 2014).

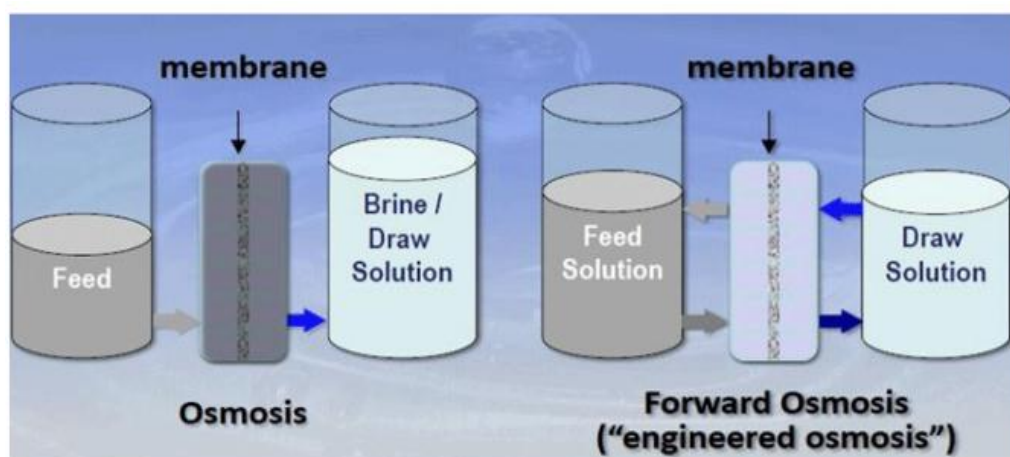
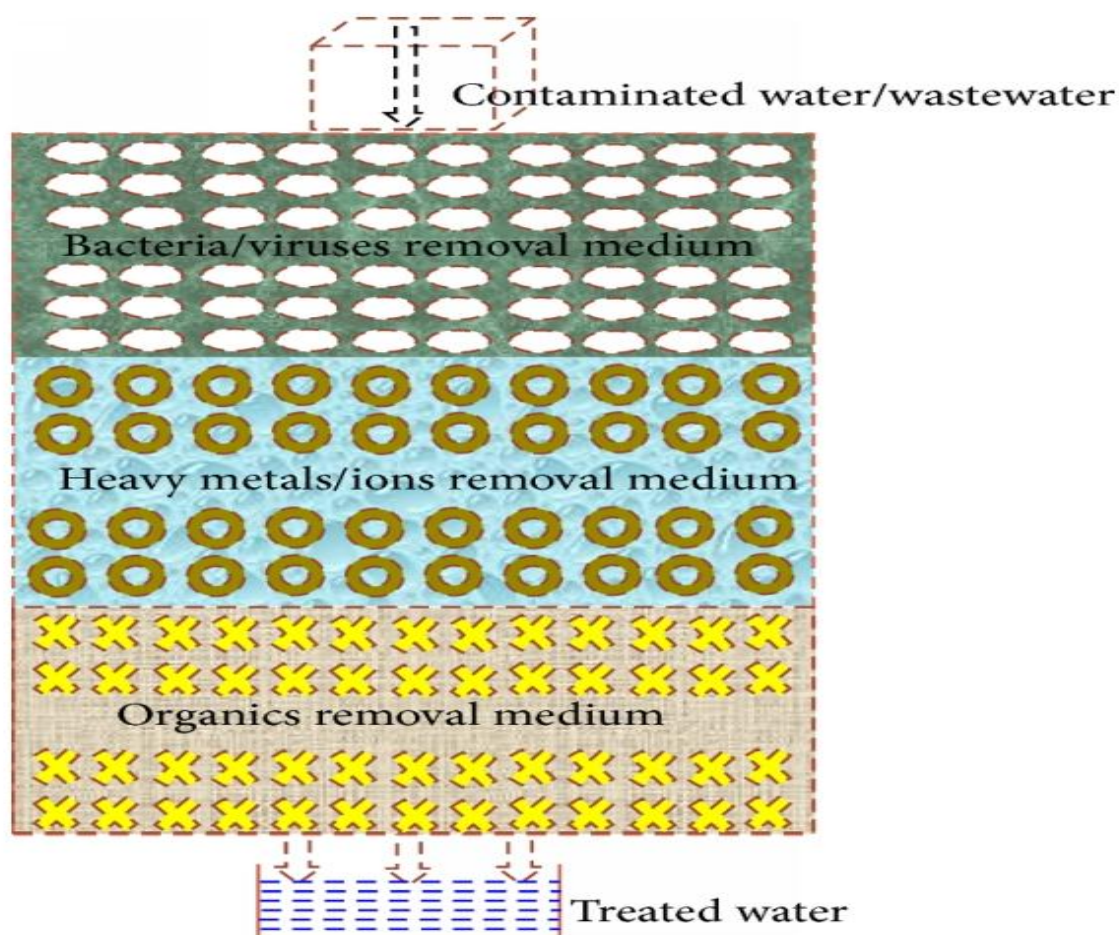


Fig. 1. Osmotically driven membrane process



**Fig. 2. Schematic of a proposed composite nanofibrous media/membrane filters for complete removal of contaminants from water/wastewater**

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## استعراض لدراسة إزالة بعض الملوثات البيولوجية والكيميائية من المياه / مياه الصرف الصحي باستخدام أنواع مختلفة من المواد النانوية في تركمانستان

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تستند الدراسة إلى مبادئ بحثية تاريخية وموضوعية و وصفية تحليلية. يتيح تطبيق هذه الأساليب في البحث اعتبار المعرفة العلمية كنظام متكامل يؤثر فيه كل نهج سابق بشكل غير مباشر أو مباشر على النهج التالي. كل هذا معًا جعل من الممكن تجميع سلسلة منهجية من الحسابات العلمية والنظرية حول هذه القضية. تتم مناقشة آراء المؤلفين بغض النظر عن الميول العرقية والثقافية والأيديولوجية، الأمر الذي يتطلب مقارنة شاملة للحقائق والظواهر في مجموعها، أي دراسة شاملة للمشكلة. بالإضافة إلى ذلك، يتم استخدام نهج منظم، يأخذ في الاعتبار ميزات كائنات البحث نفسها والعوامل التي تحدد هذه الميزات، في البحث. تسمح هذه الأساليب بتحديد ليس فقط الثغرات في الموضوع تحت الدراسة، ولكن أيضًا بعض الجوانب المعينة للمشكلة التي ربما لم تلفت انتباه العلماء لسبب أو لآخر. بشكل عام، يتيح هذا الفرصة لمقارنة هذه الجوانب بموضوعية، وعلى أساسها، تحديد احتمالات إجراء مزيد من البحث. تؤكد نتائج البحث وتشير إلى أن نمو الإمكانات الاقتصادية في الصناعة والانتقال إلى آليات السوق لتنمية الاقتصاد أدى إلى انخفاض احتياطات المياه النظيفة، وضحلة الجبال والأنهار العابرة للحدود، انخفاض أعداد الأسماك، وظهور تهديد حقيقي لأزمة بيئية مائية في تركمانستان. تظل تقنيات معالجة المياه/ مياه الصرف الصحي التقليدية غير فعالة لتوفير مياه آمنة مناسبة بسبب زيادة الطلب على المياه إلى جانب الإرشادات الصحية الصارمة والملوثات الناشئة. توفر العمليات متعددة الوظائف وذات الكفاءة العالية القائمة على تقنية النانو حلولًا ميسورة التكلفة لمعالجة المياه/ مياه الصرف الصحي التي لا تعتمد على بنية تحتية كبيرة أو أنظمة مركزية. الهدف من هذه الدراسة هو مراجعة التطبيقات الممكنة للجسيمات النانوية/الألياف لإزالة الملوثات من المياه/ مياه الصرف الصحي. ستعرض بليجاز مدى توافر وممارسة المواد النانوية المختلفة (الجسيمات أو الألياف) لإزالة الفيروسات، والمذيبات غير العضوية، والمعادن الثقيلة، وأيونات المعادن، والمركبات العضوية المعقدة، والمواد العضوية الطبيعية، والنترات، والملوثات الأخرى الموجودة في المياه السطحية، والأرض. الماء أو المياه الصناعية. في الأونة الأخيرة، لوحظت تطورات كبيرة في مجال تكنولوجيا النانو وعلوم النانو التي تنتج مواد آمنة بيئيًا واقتصادية وفعالة للهندسة البيئية. تعد هذه المواد النانوية المصممة هندسيًا واعدة لمعالجة المياه نظرًا لخصائصها الفيزيائية والكيميائية الفريدة التي تمكن المعادن الثقيلة من الكسح بقدرة امتصاص عالية وانتقائية حتى عند التركيزات المنخفضة جدًا. تم الوصول إلى إزالة فعالة للمعادن الثقيلة من الماء عن طريق تقنية الامتزاز البسيطة. ناقشت المراجعة الحالية إزالة المعادن الثقيلة باستخدام مواد نانوية مختلفة مثل الزيوليت والبوليمرات والكيوتوزان وأكاسيد المعادن والمعادن في ظل ظروف مختلفة. ركزت الدراسات الجديدة على وظائف المواد النانوية من أجل تعزيز خصائص الفصل والاستقرار والقدرة على الامتزاز. تم الوصول إلى عملية التفعيل باستخدام جزيئات مختلفة مثل الجزيئات الحيوية والبوليمرات والمواد غير العضوية وما إلى ذلك من خلال توفير الخصائص المغناطيسية لمادة الامتصاص، يصبح فصلها أسهل عن طريق تقنيات الفصل المغناطيسي. قدمت هذه المراجعة معلومات ثمينة فيما يتعلق باستخدام مواد النانو المصممة هندسيًا لإزالة المعادن الثقيلة السامة التي ستوجه الباحثين الذين يعتزمون تصنيع مواد نانوية جديدة لمعالجة المياه / مياه الصرف الصحي. وتجدر الإشارة إلى أنه يتم إجراء جميع التجارب على نطاق معمل للمعادن السامة في المحاليل المائية وهناك حاجة إلى دراسات لتقييم كفاءة العملية على نطاق تجريبي وعلى نطاق واسع باستخدام مياه الصرف الصحي الحقيقية. أخيرًا، يتم تقديم التوصيات بناءً على الممارسات الحالية لتطبيقات تكنولوجيا النانو في صناعة المياه لوحدة تنقية مياه قائمة بذاتها لإزالة جميع أنواع الملوثات من مياه الصرف الصحي.

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