



Heavy Metal Removal Using Nanoparticles: A Review

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Authors' contributions

This work was carried out in collaboration among all authors. Author Abhishek has collected and studied all the information provided in this paper under supervision of authors MS and VD. The Layout of the paper has been designed by author VD. All authors read and approved the final manuscript.

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ABSTRACT

Increased industrial activities and their improper handling of the by-products leads to contamination of the environment and the injudicious usage have led to air, soil and water/aquatic pollution. The main causative agent now-a-days are the heavy metal ions and thus there is a greater need to treat environmental toxicity. There are several methods for treating are developed such as chemical precipitation, filtration, and adsorption but they have some drawbacks such as too expensive with low efficiency in removing the heavy metals and along with toxicity. So, for to deal with such aspect the emerging nanotechnology have gained popularity. Several nanoparticles are being synthesized to remove the heavy metals metal ion inside the water. Heavy metal toxicity is being dealt by the help of nanoparticles and nanomaterials. In this review, some nanomaterials are produced such as silver nanoparticles, gold nanoparticles and metal oxide nanomaterials have been described that efficiently remove the heavy metals present in the water. This review aims at remediation of heavy metal toxicity in the water with help of nanomaterials in the most efficient and effective manner.

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1. INTRODUCTION

Earth being created life started by Big Bang theory and life started to being evolved billions of years ago from inorganic matter to organic and further leading to the world we are living today. The biotic and abiotic components compose the whole environment. In today's world, environmental pollution such as pollution of soil, air and aquatic habitat has originated from waste generated by several industries. And among these water plays a vital role in human existence as well as ecology. Water resources being necessary for life, human consumption, economic advancement, environment protection as well as sustainability of farming. Water resources are gradually becoming more toxic as result of increased industrialization and huge population boom. The environment pollution issues are speeding by the time due to development in several countries, which leads to serious and the damage to the environment that cannot be replaced by the ecosystem continuously [1]. Wastewater, Untreated medical waste, Industrial Waste water, dyes and pharma industries waste leads to gradual increase in the environment pollution thus affecting quality of life. According, to several studies, heavy metal accumulation is a serious concern nowadays because heavy metal toxicity has been occurring due to exaggerated exposure of heavy metals. Several reasons for the pollution of water such as agricultural waste i.e., chemical used in fertilizers, pesticides, medical untreated waste dumped into water stream, paper industry waste mainly containing Lead (Pb), industrial waste dumped without proper treatment into the water body being the main causative agent of Water pollution [2].

The density of heavy metals, including metalloids, is five times more than that of water, which is similar to how dangerous it is for human health despite only being present in extremely little amounts, or at ppb levels. [2]. Metals such as Mercury (Hg), Cadmium. (Cd), Lead (Pb), Chromium (Cr), Arsenic (As), Iron (Fe) and other semi metals possess high bio toxicity. The toxicity due to heavy metal is being observed when heavy metals contaminate the environment i.e., by incorporating in air, groundwater soil and biosphere [3]. As result of many studies conducted; several findings indicate that mining of metals, agriculture agrochemicals & metal processing [4,5] & paper printing industries are

the maximal suppliers of Heavy Metal (HM) ions [6].

Heavy metals ion can be taken up by plants and animal through ground water or water stream and thus accumulate in body. Heavy metal accumulation in animal bodies due to a complicated feeding chain. Small concentration /Minimal concentration of metals like Zinc (Zn), Iron (Fe), Copper (Cu), Cobalt (Co) and Molybdenum (Mo) are beneficial to human health and relatively less toxic.

Heavy metals pose a serious hazard to both human and animal existence. Higher concentrations may result in organ failure, nausea, vomiting, stomach pain, and finally malignancy. Separation of heavy metals and pollutants presence in wastewater is very much necessary. There are several methods incorporated. Such as chemical precipitation method, exchange of ions, membrane separation and adsorption for removal. Adsorption being the simplest, economical and advantageous method and thus most widely in use for the sewage treatment. Adsorbents such as Silver (Ag), Gold (Au), Nanoparticles and metal oxides nanomaterials can be effectively utilized for removing of heavy metal in most effective and efficient manner. Nanoparticles being absorptive with a large surface area as along with being shapeless, easy to use and manufacture. Silver Nanoparticles is most effective as it is least reactive if left as residue even after treating wastewater & also possessing antimicrobial activities. It has strong adsorption ability for heavy metal toxicity elimination. This review aims at removal heavy metal contamination present in water at large scale operations.

2. WATER POLLUTION

Various organic compounds and inorganic contaminants such as contaminants with high density, metal sand, dyes are endocrine-disrupting compounds, pharmaceutical chemicals, and personal health care products have often been observed in numerous ways in the drinking water sources along with wastewaters worldwide which plays major role in causing several impacts on living organisms [6,7]. Water pollution is the addition of the substance which are not appropriate and the addition of substance or energy forms that directly or indirectly can harm the nature of the aquatic body which negatively affects. Water is

being polluted by several methods and one is being impaired by anthropogenic contaminants and as result of these contaminants it may not be suitable for human use i.e., drinking water or may hamper the biotic community such as fish living there. There are several ways in which water body is being polluted such as untreated sewage waste, waste from industries i.e., chemical dumped or water used for cooling the machines, fertilizers and pesticides, dyes etc. Among them a major constituent are the heavy metals being used in various fields [2].

2.1 Why Removal of Heavy Metals

Heavy Metals are naturally occurring substances which have specific density larger than 5g/cm^3 [8], [9] and these are also higher in atomic weight, possesses high stability but their biodegradability is of very low level, which eventually lead to bioaccumulation i.e., accumulation inside the body and biomagnification [9] i.e., multiplication of the amount in living organisms and the environment [10]. Some elements are essential for body for the living beings possessing an important usage in the body's metabolism [11].

Few of the Heavy metals like Iron, Zinc, Cobalt, Copper, Manganese, Magnesium, are the essentially required essential elements for the organisms which is having a very significant role in metabolism in the organism body. Certain heavy metals (HM) are ingested on a daily basis at far lower doses than 100 mg, which can result in a number of major health issues [12]. Some other metals listed as Lead ions, Cadmium metal, Mercury, Arsenic, Chromium metals ions etc are highly poisonous even present in very trace amount. The intake of such metals can be traced from the food chain or water stream which are carrying these metals. The discharge of these heavy metals into lakes, oceans and ground water is due to long evolutionary processes observed as breaking of rocks due to rain or change in climate; which contain metals, eruption due to bursting of volcano leading to ash formation, burning fossils, extraction of metals from mines and several industries whose activities have significantly raised the level of pollutants in water source causing the dreadful threat to the Human life and biodiversity. Main route for the transfer of these contaminants is through water being used for drinking obtained via ground or water stream. Concentration of Heavy metal with symptoms and disease due to excess and deficiency in Table 1.

A huge increase in World's population of Human, Natural disaster and depleting water sources due to climate change have resulted to scarcity of hygienic drinking potable water for consumption. Heavy metals ions such as Lead, Chromium, Manganese, Nickel, Cadmium, Mercury [13] are severely toxic water polluting agents which imposes serious health related issues in living organisms [3]. Disposing of untreated waste from the industrial processes which contain these contaminants creates a lot of harm into water system biota by degrading the purity of surface water & water obtained from ground which results irreversible damage and degrading life's quality of the existing fauna as well as flora.

Various types of pollutants dumped into nearby flowing stream and effluents runoff from industries namely fertilizers, paints leather, metal fabrication, battery production, electroplating, mining & Newspaper printing press etc. Leading to Heavy metals deposition due to its nature of presence for a very long time period ions into the food chain as they are not easily decomposed and via; bio magnification resulting in Heavy metal poisoning of living organism.

2.1.1 Lead (Pb)

Lead released into biosphere by various processes incorporated in industries such as production of Pb-acid containing batteries, ceramics coating, metal polishing or finishing industries, wall paints, and cloth dyes used for coloring [10]. Its permissible or allowable value of lead ions in drinkable water is 10 microgram/Liter as per the guidelines provided by World Health Organization [10]. The excessive quantity of Pb ions available in potable water can leads to various serious health hazards such as anemia, tumor, kidney malfunction, uncontrolled muscle shaking, stomach distress, etc. [17]. Lead metal ions which are present in human body fluid can pass over the blood-brain barrier thus causing neurological as well as causing hemorrhage [18]. Lead introduced into the body cells via channel for calcium ions transfer and thus joins with proteins namely; Firstly, Calmodulin proteins and Secondly Ubiquitous proteins, which are responsible for death of cells as well as body muscle contraction. Most toxic element on global scale. Low level of Pb in adults, new born and children can cause low intelligence. Pb II has also been observed to cause damage in brain along with mental retardation and disturbance of mind as well as serious drop in hemoglobin production in blood [7].

Table 1. Heavy metals concentration and its effect when deficient or present in excess [14-16]

HM	Avg. amount (g)	Avg. Daily requirement	Disorder due to deficiency	Disorder due to excess
Fe ion	3-5	1-2	Anemia, tiredness, irritability and low memory.	Liver failure, arthritis, sugar, hemochromatosis, weakness due to damage in neurons, testicular atrophy,
Zn ion	2-3	15-20	Slow growth, upset stomach, skin allergy, alopecia, improper growth of genitals and failure to thrive.	Reduction in Cu absorption, gastritis, high fever, sideroblastic anemia, heavy metal fume fever, nausea.
Co	1.1	0.001	Heart failure, hyperthyroidism, pericardial effusion, tiredness, polycythemia neuron and muscular problems and improper digestions.	Increased thyroid hormone, cardiomyopathy, swelling of neck, allergic skin reaction, cough, pulmonary fibrosis, breath shortness, and decreased iodine uptake.
Cu ion	0.1	2-5	Anemia, mental retardation, growth retardation, drop in body temperature, changes in the aortic muscle of heart, ortho brittleness & horn like syndrome in the occipital region	Nausea, improper bowel movement, diarrhea, hyper sweating, kidney malfunction, Wilson's disease and idiopathic fibrous formation in lungs.
Mn ion	0.015	2-5	Child Improper growth, weak bones, intolerance to glucose, and altered forms of fat and carbohydrate metabolic activities.	Anorexia nervosa, tiredness, headache, leg cramps, disturbed speech, encephalitis and Parkinson diseases likewise syndrome.
Cr	0.006	0.005	Slower response to simple sugar metabolism which is available in blood stream which result increased risk of sugar.	Irritation in trachea, oral squamous cell carcinoma, melanoma, tumor in Gastro Intestinal Tract, CNS and lung malfunction ⁸ .

Middle age group people 30-50 years old can be affected by Anaemia & Hypertension i.e. High blood pressure as a result of prolonged exposure. High level of Lead can cause a very significant damage to brain and kidneys. Miscarriage in pregnant women and male infertility on chronic exposure.

2.1.2 Mercury (Hg)

Mercury is one among the most persistent environment contaminant, generally released into the atmosphere and aquatic biosystem via. industrial byproducts in river, heavily mining of metals, bursting of volcanos, fossil fuel, and burning of coal [14,19]. Mercury is available in 3 states in water namely, i.e., firstly metallic, Mercury oxide or mercuric oxide; secondly mercurous ion, and lastly mercuric ion [15]. From all forms, mercuric form (Hg^{2+}) is highly toxic, and it gets converted to methylmercury. Mercury exposure to humankind can cause mercury poisoning which leads to toxic effect on neurologic, allergic reaction, brain, and mercury poisoning in children, improper function of pulmonary muscles, gingivitis, etc., central nervous system [16]., gastrointestinal and Renal system. Inhaling mercury vapours, injecting or absorbing mercury can cause skin cancer. Mercury has been recognized as a worldwide pollutant due to widespread presence all over biosphere, refractory properties, heavy bioaccumulation in environment, and toxicity into ecosystems and even human health [20].

2.1.3 Cadmium metal

Cadmium is a transition type metal which is obtained largely in mineral form by combination with zinc metal but in metallic ores form only in combination with copper and lead. The most common way which attributed to the pollution in environment is by release of cadmium metal ion into the surrounding which leads to widespread misuse along with improper heavy metal disposal results in the pollution of the earth. Most toxic cancer-causing element. Cd enters body by various polluted sources such as water, air, soil and food articles. Its poisoning cause effects such as cancer and toxicity of skeletal, renal, genital, neurological and circulatory systems [20].

2.1.4 Nickel metal

Nickel metal is a widely used metal in industries because of its resistance to corrosion properties

which leads its way into water resources [20]. Untreated discharges of byproduct into environment along with various industrial processes such as industries includes steel products manufacturing plant, metal obtaining operations from mines, operating plating techniques by the help of electricity, ceramic coating, power plant, landfills, battery production, etc., [21]. Long term of significant exposure to heavily Nickel-polluted environments have capability to produce several health implications whose effects in human population varies from slightly signs of dermatitis to severe lung problems, along with heart as well as renal failure, at more lethally lead to tumor, GIT problems (e.g., improper digestion, upset stomach) also even chest pain. Since Nickel is easily available in surrounding and its minute exposure is unavoidable its presence even in minute amounts is unavoidable. Although high amount is too much harmful for human population to survive. Severe health issues are related with Nickel-poisoning arises only due exposure of high amount doses for a significant long-time interval of Nickel present in nearby or nearby Nickel processing areas.

2.1.5 Copper (Cu)

Naturally occurring element from wildfire, dust storms and other sources such as mining, manufacture of metals. Copper metal is a very essential element required for the proper production of enzymes, tissue growth in living organisms and formation of bones. And in plants it can be utilized for the production of seeds and also the chlorophyll generation. Copper occurs in 3 forms of ion which are cuprous ion having one positive charge (Cu^{+}), cupric ion having two positive charge and copper oxide form (Cu_2O). Cupric ion is designated to be the most toxic and harmful of the 3 forms resulting to various health related. Its toxicity may cause health issues like stomach pain, nausea, headache, kidney failure, CNS discomfort, short term mucosal inflammation, and also depression in humans.

2.1.6 Cobalt (Co)

By "George Brandt, a Swedish chemist and mineralogist" It is a frequent by-product of the mining of copper and nickel and is an extremely dense but brittle metal. Its toxicity manifest decreased pulmonary functions, increased frequency of cough leading to the irritation of respiratory cilia, resistant system sensitization, pneumonitis, and idiopathic fibrosis.

2.1.7 Arsenic (As)

Arsenic gets ingested inside body through drinking water and food. Arsenic being emitted by coal fired power generating plants and volcanism. A long interaction exposure (6–10 or more years) direct or indirect ingestion [22] of the poisonous inorganic into the human body. Biomagnification of arsenic from eating material obtained and drinkable water that may lead to the condition known as arenicolids. Some serious health conditions such as melanoma, bladder carcinoma, renal and respiratory disorders, skin disorders, increased Blood Pressure (BP) and reproductive disorders.

2.1.8 Manganese (Mn)

Mn appears silvery-grey, easily breakable, and lustrous type transition metal. Manganese is an element which occurs naturally in rocks, present in soil, and drinking water. Mn is abundantly present within natural form in surrounding and made up of about 0.10 % of the outermost layer of the mother earth crust. Increased human activities such as steel production and mining have increased its level in the environment. Manganese is a demanding regulatory recommendation substance, and when present at above the recommended amount in drinking water leads to pollution which causes symptoms like sleeplessness and anorexia. Its exposure may lead to neurological condition called manganese whose symptoms are as similarity with Parkinson's disease like symptoms such as shakiness, stiffness, slow muscle movement along with severe depression condition, restlessness and hostility.

To deal with such harmful and lethal side effects of heavy metals toxicity it is the most alarming situation to control heavy metal pollution by incorporating reliable and developed forms of processes to protect the huge population which is at risk of being infected by such problems.

So, for this to tackle most appropriate technology is the Nanotechnology which is in its growing phase and also being most significant and effective to deal with such condition.

3. NANOTECHNOLOGY

Nanotech is the “art and science of manipulating the matter at the nanoscale (down to 1/100,000

the width of a human hair) to create new and unique materials and products useful in the upcoming future”. “Nanotechnology” refers to the procedure of developing useful materials, tools, and systems by modifying matter on a size of 1 to 100 nanometres. Nanotechnology covers a vast range of disciplines, includes materials science along with mastery of physics, chemistry, biology field, mathematics accuracy, and engineering precision [26,27]. Nanotechnology is a developing field that is becoming crucial in permitting advancements of new and useful instruments in medical science, such as nanomedicine help for diagnostic and screening purposes like early cancer detection and help in making synthetic cellular proteins like receptors along with effective drug delivery. Nanotechnology provides us the nanomaterials application in the process such as decontamination of water with help of various mechanisms including eliminating out the contaminants or causative agents with help of processes such as adsorption, eradication of HMs and inactivation of diseases causing agents and degradation of severely poisonous substances to less poisonous substances. A few usages technology in healthcare include fabrication of medication by drug delivery systems, gene therapy, tissue engineering, and genetic codon and amino acid sequencing for both nonporous and nano spray materials. Nanotechnology mainly deals at nanoscale level particles known as nanoparticles and nanomaterial. As such for removal of these heavy metal ions there are silver & gold nanoparticles are being used and metal oxide nanomaterials are being utilized in various processes.

A nanoparticle is a superfine particle is usually known as a particle of matter which ranges from 1nanometer to 100 nanometers in diameter. The naming can even be used for some bigger particles ranging up to 500 nm. Nanofibers and nanotubes are nanomaterials that are size lesser than 100 nm in only 2 dimensions. Nanoparticles not clearly visible by using ordinary optical microscopes which were used earlier for visualizing the cells and microorganisms, it requires advance type electron microscopes or microscopes with laser for observing the particles of nanoscale range. They are being of nanoscale in measurement can easily pass through membranes.

Table 2. Corresponding references for their amount by WHO [23], [24], [25]

HM	Permissible limit depicted by WHO (in microgram/liter)	Symptoms and resulting disease by consuming heavy metal contaminated water
Cd	3	Hypertension, chronic kidney dysfunction, bone defects, multiple myeloma, gastrointestinal disorder, renal failure, chance of still birth, and severe damages to DNA and membranes, and sometimes leads to death.
Hg	6	Dermatitis, vomit, minor psychological changes, dizziness, shakiness, hypertension, loose motion, gum inflammations, mercury poisoning, destruction to CNS and DNA, unwanted deposition in muscle tissues, hepatic system and even result to death.
As	10	Cut on skin tissue and liver, peripheral neuritis, bladder carcinoma, adenocarcinoma, gangrene formation, sugar, high blood pressure, cardiac problem, degeneration of DNA, altered gene expression, which eventually leads to death.
Pb	10	Brain and nervous system malfunction, lower intelligence, tiredness, loss of hunger, sleeplessness, kidney malfunction, stomachache, under development, congenital insensitive, high BP, arthritis, birth related defects, high damage to hepatic organ, renal, GIT malfunction, mentally not responding and eventually leads to death.
Cr	50	Cardiovascular diseases, neurons-based disorder, damage to blood cells, liver, kidney, lungs and GIT tract system disorders, adenocarcinoma results finally death
Ni	70	Allergic contact skin infection, squamous cell carcinoma, abdomen and inflammation in the respiratory tract muscle, failure of hepatic system and sometime lead to death.
Mn	10	Parkinson like syndromes, cognitive dysfunction, hepatic diseases, and poor muscle control, neurotoxicity and severe destruction to CNS.

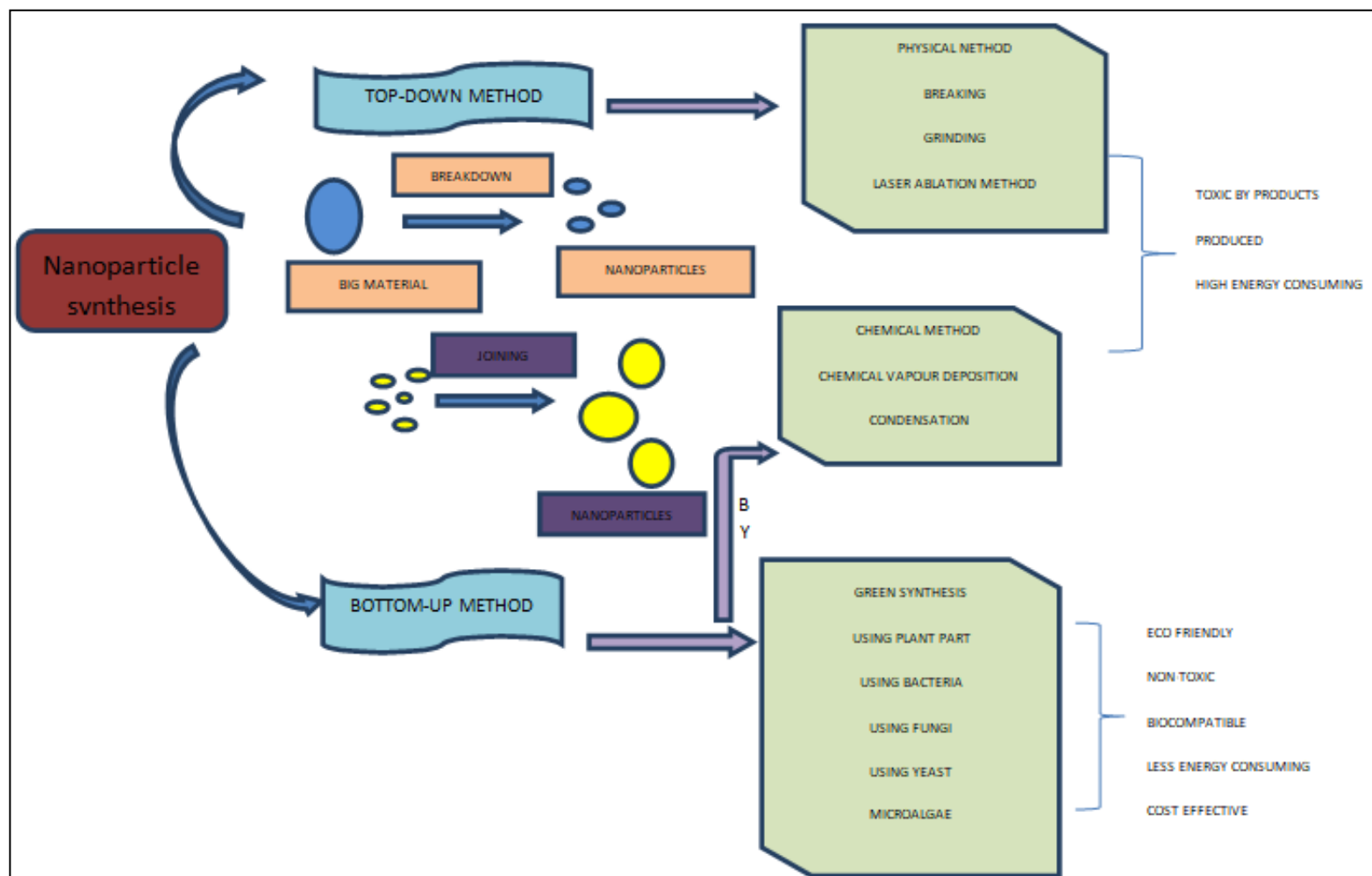


Fig. 1. Methods used in the synthesis of Nanoparticles

Nanomaterials are fascinating because of the sheer photo-magnetic, electrical, and other features that emerge at this scale only. Researchers formulated a developed type classification system for Nano structure materials, where zero-dimension, One-dimension, Two-dimension and Three-dimension Nano structure materials are included. Obvious representation of Zero-dimensional nanomaterials is having every dimension of element within the range of nanoscale (no dimensions, or below 100 nm). A 1D nanomaterial are in range of nanoscale. Nanotubes are tube like structure, nanorods are like rods of nanometer scale, and nanowires are like wire of nanoscale level. In 2D nanomaterials, 2 of the dimensions need not to be nanoscale which includes nanofilms, nanolayers, and nano coatings. 3D nanomaterials are also known as bulk nanomaterials because the measurement is not bound to the nanoscale in any single dimensions. Nanocrystal structure or bulk nanomaterials can be composed with various positions of nanosized crystals, generally in diverse universal orientations. These emerging features could have a significant impact on the electronics, healthcare, drug delivery, pollution eradication and other industries. The two types of nanomaterials are nanostructured. The former refers to condensed bulk materials or dispersed nanomaterials made of grains which are of nanometre size range, two different approaches are being used to synthesize nanomaterial, such as Top-Down and Bottom-Up method. Firstly Top-down method involves bulk material, which is broken down into nanomaterials. These methods are an extension of those that have been utilized to create particles with a diameter of less than a micron or equal to nanoscale.

4. NANOADSORBENT

Nano adsorbent are the nanomaterial which can adsorb the harmful element over it and remove it. The small size and large surface area facilitates its high chemical reactivity as well as adsorption process capacity of these nanomaterials. Nanosized adsorbing materials possessing enlarged surface area along with modifications over the surface which helps in increasing the adsorption capability. There are number of nano adsorbing materials present such as organic compounds which are activated carbon (AC), along with carbon-based nanotubes (CNTs), graphene, carbon-based nanofibers (CNFs), inorganic compounds which includes metal ores

and metal in oxides form, and hybridized substances also known as Next-Gen hybrids which are of great importance regarding the purification of waste water. Nano-adsorbents possesses some specialized capacity used in developing an adsorbing material which shows various adsorption location having super activity during the process as a result of their large surface area, short particle-particle diffusion distance, huge energy over the surface, and size of adsorbent depending on surface structures. Nano adsorbents can be of different forms, such 0D, 1D, 2D, and 3D. Zero-Dimensional nanomaterials such as quantum dot structure, carbon dot structure, fullerenes, magnetic nanoparticles, polymer dot and up conversion nanoparticles. Due to their unique properties like optical stability, wavelength-dependent photoluminescence, chemical inertness, cellular permeability, and biocompatibility, these nanoparticles are utilized in different fields such as used as biosensing device, biomedical instruments, cosmetics, biochips, bioelectronics etc. One-Dimensional nanomaterials such as nanostructures and nanowires has been used in various fields, such as photocells, used as biosensors, Lithium-ion batteries, biomedicine, catalysis, and ultracapacitors due to their size, shape, and configuration. It has exceptional characteristics, which include a significant aspect ratio configuration, high stability, large surface area, good mechanical or electrochemical-charge carrier, and a specific connectivity effect, have sparked great deal of interest in improving current performance and discovering new uses that can be utilized in very future. Two-Dimension materials such as silicate clay, GO (Graphene Oxide), and RGO (Reduced Graphene Oxide) are used. Such nanoparticles have their own unique properties which are uniform geometries, high surface area ratios, and zeta-potential as well as exceptional physical, chemical, optical, and biological properties. Because of its high anisotropy and chemical functionalities, it has been used in a variety of sectors, which include nanomedicine in the biomedical industry, particularly in the areas of multimodal imaging biosensing, antibacterial agents, and tissue engineering, well-designed gadgets catalysis, series, and energy resources. Bundles of nanowires and nanotube included in three dimensions (3D). A few applications for materials are solar energy harvesting, energy storage, chemical separation, sensors, drug delivery, non-toxic and enhanced optical devices and even in internet working.

4.1 Why Nanomaterials

Nanomaterials have emerging features that can have a significant impact on the medical field, electronics, health sector and many more. Nanomaterials can be produced on the basis of their physical interaction, chemical interaction or biological interaction depending on the methods used in the synthesis. Two different approaches can be used for the synthesis of these nanomaterials i.e., Top-Down method and Bottom-Up method. In Top-Down method widely used it has usage of various mechanical and chemical ways to decrease the bulky sized get converted to nanoscale range [28,29]. It is an extension of method which being utilized for creating the particles with a diameter of less than a micron scale. It is being relied on either remediation or downsizing of the bulky material by specialized processes e.g., sputtering, decomposition by the help of heating, mechanical milling, ablation by laser, etching, and also lithography. In Bottom-Up method it involves the alternate strategies that have potential to produce less waste and are more profitable. Its approach is most commonly considered for synthesis of nanoparticles, because it requires a homogeneous system where catalysts, substance which increase the speed of reaction without actually being consumed in the reaction and is obtained at the end of the reaction, generate nanostructures which are regulated only by catalytic activities, nature of the media in which reaction takes place, and conditions. It is process of building a substance from the ground level by either "atom-by-atom, molecule-by-molecule, or cluster-by-cluster". It is being employed for producing nanocrystals for commercial purpose by sol-gel, electrodeposition, etc [30]. "Nanostructured materials" correlates to measuring unit known as nanometer. Nanostructures possess significant characteristics which are significantly variable as compared with naturally present materials, such as electric plus magnetic property, optical properties, and dielectric properties along with some advanced therapeutic usage. Nanoparticles can be used for versatile action for sensing pollutants from surrounding, health related products and drugs from pharma company, telecommunications devices and optronics machines, clothing industry products, pollution control also skincare products [31].

Several nanoparticles of metals and metal oxides are also being utilized for the treatment of the waste. Some are being enlisted: -

4.1.1 Nanosized metal oxides (NMOs)

Removal of pollutants from water bodies, the most commonly used NMOs. It includes nanomaterials being composed metal oxides which are easily available. These NMOs are presently used in varied forms, listed as nanoparticles, nanotubes, nanostructures etc. Varied shape and particles size of Nanosized metal oxides is both significant factors which alters their adsorption performance of NMOs.

4.1.2 Nanosized Iron oxides (NFeOs)

Iron metal (Fe) is among the most distributed elements on the earth crust. It's easy availability as natural resource and less effort in production helped nanosized ferric oxides particles (NFeOs) are cost effective adsorbents substances used in hazardous metal adsorption. Since known from ages iron metal being environment friendly, Iron oxides nanoparticles can be dumped directly to the polluted location as it has minimal risk of producing less harmful changes in aquatic source. The most deeply studied NFeOs for removal of the toxic metals from water containing goethite (-FeOOH), hematite (-Fe₂O₃) [32,33], hydrated amorphous Iron oxides [34], maghemite (-Fe₂O₃) [35,36], along with magnetite (Fe₃O₄) [37,38] and iron/iron oxide [39,40].

4.1.3 Nanosized Aluminium oxides compound also known as Alumina (Al₂O₃)

It is extensively studied adsorbing materials used for removing HMs since long time period, Al₂O₃ is known for being highly active in adsorption as compared to Aluminum ion. The -Al₂O₃ nanomaterials can be produced by using solvent-gel mechanism which works efficiently as solid phase extraction materials which are used for detecting the concentration and presence of the ion. Modification of -Al₂O₃ nanoparticles with usage several functional groups result in chemical modifications which contain some donating type atoms are thought to increase their adsorption activity with respect to heavy metal ions, [41-44]. Modifier element is made to stick on the surface of alumina, the process of removal is modified according to the situation. Targeted metals are removed with lots of precision by adsorption of material to be adsorbed on the surface of the alumina nanomaterials but it can result to surface binding/chemical-bonds among particles of recently introduced chemicals.

4.1.4 Nanosized zinc oxides (NZnO)

Zinc being an environmentally friendly material, Zinc oxides nanoparticles effectively utilized in catalyst industries [45,46], gas sensing devices [47] production, solar energy to electricity converting devices [48] production units and other industries. Zinc oxide NPs are substance which are competent for water remediation processes. Due to its special features namely high-capability of oxidation, a broad linear gap in the band which are present in Ultraviolet spectral zone, also a significant photocatalytic activity [49]. Acting as an adsorbent, Zinc Oxide was mostly commonly applied for removal of hydrogen sulfide (H₂S). Zinc Oxide compound is a whitish color with crystalline texture and present in 3 specified crystalline forms, i.e., hexagon wurtzite form, cubical zinc blende form and lastly rock salt type. It has been observed that nanostructured Zinc Oxide could efficiently use in removal the heavy metals ions with nanoscale zinc oxide nanoparticles by "solution-combustion method (SCM)". It is all in comparison with two titanium dioxide powder forms, such as P25 and another type being prepared by a homogeneous mixture precipitation method taking place at less than normal temperature of preparation, the nano powder of zinc shows the high speed of copper ions removal from the required solution [50]. Nanostructured zinc oxide formation such as plate having large surface area being obtained by several methods, such as using an aqueous solution in a closed vessel [51], chemical vapor deposition method (CVD) [52,53], electrochemical deposition method (EDM) [54], and microwave method [47]. The Zinc oxides nanosheets are being prepared via hydrothermal approach that were used for adsorbing lead (Pb) ions eventually treated hydrothermally in the aqueous solution which contains source of sulfur. Due hydroxy functional groups present at surface, the resulting Zinc oxide nanosheets delivers a good capability to lead ion with 2 positive charges as 6.7 mg/g. The lead ions are loaded over Zinc Oxide nanostructured sheets were then placed into a Teflon-lined stainless-steel autoclave machine which contains a source of sulfur which is stored at approx. 120 °C for nearly half day., produced Zinc Oxide/lead Sulfide nanocomposite which exhibits the potential usage in catalytic converted with help of light having conversion fields, energy-transforming devices and LED or devices used for detection. This new strategy can be considered suitable for producing new products

based on loading of metals which are Nano metal oxides.

4.1.5 Carbon Nanomaterials (CNMs)

Carbon abbreviated as "C" is a diversified element possessing characteristics such as catenation and formation of allotropes. Graphite having planar structure or layer form, being an allotrope, it shows properties such as high adsorption capability and conduction of charge, thus it is largely used in field of nanotech. Carbon nanomaterials (CNMs) are the materials which possess particle having grain size that is order of billionth of a meter i.e., nanometers, due to relatively increased surface area it shows significantly more chemical reactive mechanism and shows electric properties usually not seen in the carbon family along with mechanical property [55]. Thus, it can also be utilized as remarkable and effective manner in treating waste.

4.1.6 Silver Nanoparticles (AgNPs)

The silver nanoparticles used for such process are less than 100 nm. Showing various physical along with intramolecular properties of silver nanoparticles, huge interest developed in utilizing such particles in commercial way by making high value product. As a result of this it has become the most widely used nanomaterial commercially (more than 400 products). Generation at world level of AgNPs oscillated in range of 300 and 1000 tons in 2015-2016. The AgNPs may be introduced into sewage: incorporation with antimicrobial agents [56] and metal coatings, personal healthcare products, paints and also daily usage appliances production. Water treatment is one such process that can be attained by the usage of silver nanomaterials working as catalysts due to its large surface area [57,58] less toxic and non-reactive nature all along [59].

4.1.7 Gold Nanoparticles (AuNPs)

Water contaminants due to heavy usage of non-degradable elements, chemicals, soaps, and chemicals used in killing pests used in fields have significantly decreased the availability of potable water and soil pollution. AuNPs has been showing high potential in dealing with the harmful impacts of water pollution. Researches also shows that generation of AuNPs is cost effective technology for protecting the water from spoilage. Nanosized gold particles has several specialized properties, depicted as high catalytic

activities, visible top surface plasmon [60]. resonance and color changes [61-64], chemically stable as gold particles is with least reactive nature against any other component which make it more effective and useful than any other materials. Gold Nanoparticles are very effective catalyzers for varied chemical reactions, which are included such as hydrocarbon oxidation, Carbon-Carbon (C-C) coupling, hydrogenation-dehydrogenation, reduction and oxidation reactions (redox reaction) [65]. Gold nanoparticles have shown a huge interest because of high selectivity of several organic or inorganic elements along with pollutants including chemically used for killing pest and insects [66] and diseases causing agents [67].

5. APPROACH FOR HEAVY METAL REMOVAL

The need for developing effective and efficient processes utilized for removing Heavy metals widening in understanding of various types of ways and processes namely chemical oxidation of HMs, reduction, chemical precipitation in the reaction [68], ultrafiltration by using filter papers, method used for exchange of ions [69], membrane filtration process, reversal of osmosis process [70], and adsorption. Considering all the benefits and downsides of all such techniques are observed, process of adsorption being considered as one of the best and efficient plus affordable option in separating heavy metals ions from the desired solution, because of its high specificity, flexibility in design and fast operations, high performance and cost-effectiveness [71].

5.1 Adsorption

This process is a simple phenomenon related to surface which is particularly determined by the increased number of the specified component (known as adsorbate) which may be available in a gas form or liquid flowing stream on the surface or interface of a pores containing solid component (adsorbent). Various types of interactions take place, includes physical adsorption, chemical adsorption, electrostatic, ion exchange method, complexation of surface method, along with precipitate formation.

Physical adsorption is very weak type of adsorption but eventually much common process which involves the flowing movement from high concentration to low concentration of Heavy Metal ions into the hollow space over the carbon-

based adsorbent which subsequently occurs on the top spot of layer. The major aspect of physical forces involved which are controlling this adsorption process are weak force type of interaction, hydrophobicity water repelling, hydrogen-hydrogen bonding, polarity (possessing charge) and steric hinderance, dipole- induced dipole interactions, and pie-pie interactions [72].

Chemical adsorption is a process being affected by the Chemical groups that are involved in the adsorption process have an impact on it because their presence on the uppermost surface of the desired adsorbent material makes it possible for chemisorption in addition with physical adsorption to take place. Main step in chemisorption is the sharing of electrons between the pollutant particles and the surface of the adsorbent, which produces chemical bonds that are comparably stronger than physical ones.

Electrostatic attraction or adsorption is considered as secondary type of interaction occurring between positively charged Heavy metal ions and negatively charged carbon adsorbents, especially in the presence of desired functional groups. Yet, one of the primary mechanisms for adsorption of heavy metal by graphene-based adsorbents is by ion exchange between heavy metal ions and functional groups containing oxygen [73].

5.2 Nanofiltration Membrane Technology

It is a filtration technology has been considered as substitute technique for treatment of water especially surface one. Huge popularity and fervor for investigation with kin interest demonstrating its untapped potential for resolving various environmental issues, including the removal of contaminants or pollutants, the reuse of water, and the production of other products using the exact same material that is of much greater value than previously [74]. Works as an effective filtration process which allows specified molecules and elements to cross through this membrane while stopping others molecules. Membranes refer here as selectively permeable membrane acting as blockage to non-specified ions and compounds. The pore size over the membrane shows overall the average size of pores present on the membrane's surface which can allow on material which is of size equal or less than pore size of membrane, thus it also shows that the particles which are not allowed to pass are of larger size than the pore size.

The process included in adsorption and removing the pollutants from the polluted water is drastically affected by various process and defined parameters. More interestingly starting concentration along with temperature, useable dosage of adsorbing substance, and required time of reaction are among the most important conditions which affects the ongoing process. Relationship in such process at a given specified temperature, occur intermediately in the balanced amounts of pollutant being adsorbed on the component and the amount of water used is called an adsorption isotherm. Again, using the used adsorbents in other process is very much necessary for the affordable and cost effectiveness of the process, desorption process requires to be analyzed and accessed. Better desorption properties will certainly be helpful in reducing the overall pricing of the process thus making it more feasible, making it the major objective for industries established.

5.3 Removal of Lead by Adsorption

Lead ions are released in the environment by various industrial procedures that are being utilized in industries lead-acid based batteries, ceramic coating, electro plating industries and final metal production, paints production, and dyes used in the textile industries. The products containing lead ions as main constituent, and plumbing fixtures products are denoted as general source for the availability of polluting particles in aquatic habitat. Allowable amount of Pb ions in drinkable water is marked at value 10 microgram/Liter as per the guidelines provided by WHO. The superparamagnetic properties of γ -Fe₂O₃ nanoparticles showcase the excellent capability Iron oxide nanoparticles to separate contaminants from polluted water via the adsorption process. The adsorption capacity of the substance can be largely hampered by the power of Hydrogen ion, by the help of functional hydroxyl groups present all over the surface of maghemite nanoparticles are being delivered with positive charge or removed i.e., proton added or proton removed, based on the pH of water being utilized. The adsorbing activity of lead ions involved in the electrostatic interaction, and ion exchange method during the process.

6. APPLICATION

- Nanotechnology is utilized for sustainable development, growth and competition in several fields for application associated to industries. The properties of nanoparticles

based on the physical and chemical properties provide us with various useful functions that are being enlisted such as research and development in fields of science and technology. Nanotech is also being employed in the agriculture sector [75] by increasing the production by using fertilizers such as Nano urea and providing food security by protecting food grains from spoilage due to changing climate. Nanotechnology can be potentially used for detecting or sensing the diseases and enhancing the absorption of nutrients in the plants [76-78].

- Researchers and scientists are trying to produce various products by using the metallic nanoparticles as a result of increase of resistance against microbes [79] and resistance against heavy metal ions, usage of antibiotics for developing strains which are resistant [80]. In nanotechnology field silver nanoparticles gained enormous focus due to its unique characteristics such as being much chemically stable and catalytic effects of these nanoparticles have a huge advantage against various nanomaterials. Due to its inhibitory process towards microbes, Antiviral [81,82], antibacterial and anti-inflammatory properties [83,84] of silver nanoparticles are being employed in the food packaging of fruit juices or keeping the fruits and vegetables fresh for a long duration as compared with the earlier times [85-87].
- Silver Nanoparticles can also be used for production of medicines, lotions and ointments for treating wounds as it possesses antimicrobial activities leading to conditions unfavorable for the microbes to grow thus avoiding the infection over the wound or cut [88,89]. AgNPs synthesized are considered to be severely toxic against several pathogens which are resistant to multiple drugs. A significant increment of these silver nanoparticles can severely affect the bacterial by eventually rupturing the bacterial cell wall [56,90].
- Various diseases can be detected and treated by the usage of the nanotechnology. Bird flu, commonly known as avian influenza, is a new disease-causing bacterium and the virus that spreads the Ebola virus around the world [91,92]. Viruses are being exposed to living organism on everyday basis, some the new disease are very much difficult to be

treated. So, Silver nanoparticles are being as a tool for the treatment on research basis due to its physio-chemical and biological properties [92]. Lots of focus delivered for effective and efficient treatment of diseases [2].

- In food packaging industries nanotechnology have played very significant role by employing the nanoparticles which are having properties of either controlling the growth of microbes so that the food can be preserved for longer time [93]. To extend the shelf life of food along with maintaining the quality at maximum level so the material to be used should be possessing antimicrobial and antifungal properties so that spoilage of food can be minimized. It can be obtained by addition of materials that may be organic or inorganic. In food packaging the material used is known as protectants. AgNPs used as a perfect example for the food packaging for food, fruits and even fruit juice to keep them preserved for longer duration. Silver nanoparticles are being excellently showing anti cancerous properties by inhibiting the growth of tumor cells with no toxic effect inside the human body [94].
- Among several nanoparticles Gold also being used for the cleaning of the air in the room and in removing the odor being created and also removal of highly harmful gases like carbon monoxide produced by the incomplete burning of coal and it is like a slow poison whose mechanism by attaching with the hemoglobin and form a complex which is very much stable than compound formed by the adjoining of hemoglobin and oxygen, emission management and water purification by removing the heavy metal ions. These nanoparticles are of nanoscale so can easily enter tissues and capable to attack pathogens and increasing the efficiency of lymphoid cells thus enhancing the working of immune cells showing a potential to be highly useful in immunotherapy for tumor [95]. Gold nanoparticles can also be used as biosensors as it delivers high precision of detecting heavy metal even at very low concentration and can also be used colorimetric reporter as it possesses high coefficient and size dependent optical properties [96].
- With the usage of nanotechnology in the current scenario it can be used as sensing devices for the air pollutants which will be effective in control of air pollution [97] as it is being very important to keep regular check over the quality of air being essential for the survival of the living organisms on the planet [98].
- Nanoparticles are heavily utilized in medical field also specifically to even in studies of teeth. It can be used for the detection and treatment of cancer [99]. The nanoparticles can be used as markers which are easily being able to detect the presence of diseases by detecting the antigens or detecting the antibodies being generated in response of antigen [100]. Even so, a great deal of nanomaterials is utilized in the medical area for early disease identification and pre-clinical testing in order to prevent serious conditions. Gold nanoparticles are being providing a very effective method in detecting the tumor cells as well as in the treatment by integrating with the chemotherapy as loading the drugs over the nanoparticles. These particles been showing various forms of gold nanoparticles been utilized namely gold nanotubes, nanospheres of gold, gold nano stars, gold nanorods and along with gold nanocages being extensively used in the various fields and even in the medical field. In the advancement of chemical synthesis as they possess diverse shapes and different range of particle size.
- Gold nanocomposites are being generated linked with silica which is much more sensitive in detecting the presence of ions of toxic metals as the presence of contaminant over the complex formed of gold and silica as it changes during the reaction marking its presence in surrounding [101].
- The discharge of dyes used in textiles, pharma industries, pesticides in agriculture, and personal daily care products into the surrounding will cause a menace nearby, no proper treatment may lead several health hazards to human life (e.g., digestive disorder, weak immunity, or reproductive health related issues) once it enters into the body via food chain. The useful properties of silver nanoparticles are widely used in providing vast range of fields other than removing hazardous elements from water. AgNPs are induced in biomedicine by producing medicine, beauty products, drug delivery [102] for

treatment of disease and chemotherapy for cancer, packaging of food for keeping fresh for longer duration and preservation, clothing industry, producing bio related sensors, biology field, Plasmonic, DNA sequencing by studying and detecting sequences accurately, and energy generation by using nanoparticles [96].

- The catalytic breakdown of substance related to contamination is one of the most demanding technological processes for the treating the contaminated waterbody [103]. Silver Nanoparticles or Silver Nanoparticles composites with large specific surface area, crystalline structure showed enormous capability for the elimination of various types of pollutants from the surrounding. Silver nanoparticles are decorated catalyst which have a very vital role in addressing some issues related to water pollution by decomposing the various kinds of pollution causing substances including dyes, such as Methylene Orange dye, Congo red dye, acid orange dye, and Remazol red dye [103].
- Used as environmental sensors: - As to tackle with the issues of environment pollution i.e., silver nanoparticles firstly it requires the detection of the pollutants or sensing their presence with help of biosensors capable to detect their presence even present in minimal amount. Sensor is a type of converter device which can detect various physical and chemical phenomena along with mechanical properties from surrounding environment as input and then display the output signal in form of electric or optical signal. Pollutant detection technique should be cheaper and easily available along with high effectiveness and efficient working. Nano sensors are the type of sensors dealing with the particles of nanoscale range which are highly sensitive and accurately measures the quantitative and qualitatively in most efficient manner.

7. CHALLENGES

Being a new technology for the treatment of the wastewater as to cop. In particular, nanotechnology is crucial in resolving these issues. Following studies, the immense capability of nanotechnology was demonstrated and it was used to treat water in the twenty-first century. Nanotechnology was proposed as an alternate

approach to clean up the current environmental pollutions, which is thought to be a cheap and efficient one. Due to the finance related crisis, technology related challenges, expensive implementation budget, and potential risks related to environment along with human health, nanotechnology being employed in treating the polluted water source and its only availability in laboratory and small-scale investigations. Another significant issue is the absence of mechanistic investigation of nanomaterials employed in water treatment. The long time depending on nanotechnology for treating wastewater and its toxic harmful effects of nanomaterials used [104], [105].

8. CONCLUSION

The Nanotechnology is being the growing technology with lots of possibility in various streams from medical and health care, food packaging to dealing with the environmental pollution. Nanoparticles are being applied in this field as to obtain maximum amount of result which was not possible with the previous technology which were dealing on macroscopic level whereas nanotechnology deals on the nanoscale level. So, it is of great importance in tackling the problem that is generated by the improper usage of heavy metals leading to pollution of the biosphere. The Heavy metals are the key source of worry at the current situation for the environment as well as human health protection. These ions are being incorporated in the environment at an extreme level via water and food chain lead to several complication in the life of living beings by accumulating inside body at such a large level causing heavy metal toxicity and even diseases such as multiorgan failure, congestion, cancer etc. Nanomaterials are being extensively researched for the elimination of such pollutants as a measure to reduce toxicity from the water. According to intermetallic competitive adsorption, the order of the adsorption capacity is $Hg^{2+} > Ni^{2+} > Cr^{3+} > Co^{2+} > Pb^{2+}$, which closely corresponds to the order of the hydration energies of the metals. In order to examine the effectiveness of ZnNP and AgNPs adsorbent at 500mg and 1000mg dosages for eliminating of metallic ions from aqueous solution, batch tests were conducted. Compared to ZnNP, AgNPs (500mg) has been shown to be a more effective adsorbent. Although the quantity of adsorbed metal ions increased with increased contact time, ZnNP and AgNPs respectively, were able to adsorb 50% and 80% of all metal ions within about half an

hour. Because of nanoparticles possess huge surface area and compact size, they have great capability to absorb a large number of impurities. Most in demand technique is the adsorption technique which is very simple and highly effective and it can be used to eliminate heavy metal ions from water. Different nanoparticles are used among them silver nanoparticles emerge as the better among as it is very less reactive when left in open environment and vast application from food, cosmetics to healthcare and waste water treatment by removing heavy metal ion by adsorption process.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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