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Role of nanotechnology in removing metal ions from waste water: A brief review

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Abstract

Clean and affordable water to meet basic human needs has become a majestic challenge to the current century. All around the world, water supply thrash about to keep up with the rapid demand growth, which is aggravated by climate change at global level, population growth and deterioration of water reservoirs. The need for technological innovation to enable water management integration could not be overstated. In past the remedial technologies used for the waste water treatment were chemical precipitation, chemical coagulation, ion exchange etc. But with the advent of technology they are now being replaced by nanotechnology, as it is lucrative method. Nanotechnology carries immense potential in advanced treatment of water and wastewater to increase treatment efficiency as well as to augment water supply during safe use of irregular water sources. These technological progresses have been traced to the physicochemical properties of nanomaterials, the current review article outlines the limitations and opportunities to discuss further benefits on these unique technological advancements for sustainable water and waste water management.

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Introduction

Water has always been connected with the existence of life globally. From early civilizations till modern world, water has been a central premise linked to economic development. Water is one of the purest signs of prosperity, health, peacefulness, beauty, and originality. Shortage of water has become most concerning issue of this century. Ninety seven percent of the water present on the earth planet is salt water and remaining 3 percent is free, two third of which is frozen and the remaining 1 percent is not distributed evenly. In the near future, world's population will rise from 6.5 billion to 9 billion by the year 2050 so the demand of fresh water will increase greatly. In developing countries including Pakistan the shortage of clean water is a serious problem. In addition to this, various agricultural and industrial activities pollutes the natural water resource including rivers and lakes. According to World Health Organization (WHO), 80 percent of diseases in developing countries are waterborne. All the living things need water to survive so it is the foremost requirement for life. Water problem is much serious in comparison to oil problem, alternative sources of energy for oil can be made but the substitution of water is not possible as this is essential for the survival. More practical and cost effective approach is needed for the efficient cleaning of water such as cleaning it where it is needed instead of centralized location and distributing it later (Savage and Diallo, 2005; Pendergast and Hoek, 2011). Hence, advanced and cost effective water treatment is required.

Recent advancement in nanotechnology offers leapfrogging concerns to develop water supply systems for next generations. Past water treatment, discharge practices, and distribution which greatly rely on centralized systems and conveyance, were not sustainable. Efficient plus multifunctional processes enabled by nanotechnology are visualized to provide high level of performance, reasonable water and wastewater treatment solutions that doesn't rely on large infrastructures (Qu *et al.*, 2012).

Nanotechnologies facilitated water and wastewater treatment assured not only to get through main challenges faced by accessible treatment technologies but provide new treatment capabilities as well that can permit economic deployment of irregular water sources to increase the water supply (Patra *et al.*, 2012).

Application of nanotechnology for the treatment of wastewater would surely help our environment, industry, as well as human being as it has shown excellent results in every field (Pandey *et al.*, 2011). Extraction, chemical oxidation and adsorption are the traditional and effective techniques for the removal of contaminants from wastewater but they are very expensive. However, nanotechnology is very cost effective and efficient (Fact Sheet, 2009). Wide range of applications such as nanosorbents, catalytic membranes, bioactive nanoparticles such as silver, iron, titanium oxides and many other are offered by nanomaterials due to their unique active surface area (Chorawalaa and Mehta, 2015). Materials have the particle size ranges from 1nm to 100nm are called nanomaterials. Nanomaterials have high reactivity, novel size and shape dependent properties.

They also have large surface area than bulk particles, their reactivity towards a particular compound can also be increased by the attachment of other functional groups (El Rahman and Gepreel, 2013; Imtiaz, 2011). Moreover the mobility of nanomaterials in solution is so high and because of their small size they have small adsorption ability and high reactivity (Gao *et al.*, 2008).

Among all the contaminants present in the wastewater, ions of heavy metal like Hg^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} are present in the large quantity and with the advancement in nanotechnology, nanomaterials are efficiently used to remove heavy metal ions (Qu *et al.*, 2012). Presently nanomaterials that are used extensively include Carbon nano tubes (CNTs), nano composites, zero-valent metal nanoparticles and metal oxides nanoparticles (Gadupudi *et al.*, 2010).

Current and potential applications of nanotechnology for treatment of water and wastewater

Nanomaterials have been normally defined as particles < 100 nm in one dimension at least. A few of these applications develop smoothly scalable size

dependent properties of nanoparticles. They usually narrate to the high specific surface area for example high reactivity, fast dissolution and strong sorption (Patra *et al.*, 2012). Such applications in unit operation processes are discussed in this review paper based on nanomaterial functions (Table 1).

Table 1. Potential application of nanotechnology.

Applications	Nanomaterials	Advantageous nanomaterial properties	Facilitated technologies	References
Adsorption	Carbon nano tubes	Highly assessable, High specific surface area & adsorption sites, tunable surface chemistry, interactions, & easy reuse	Adsorption of recalcitrant contaminants & Contaminant pre-concentration	Yang and Xing, 2010
	Nano scale metal Oxide	Short intra-particle diffusion distance, High specific surface area, more adsorption sites, easy reuse & some are super paramagnetic	Slurry reactors & Adsorptive media filters	Pan <i>et al.</i> , 2008
Membranes and membrane processes	Nano zeolites	Hydro philicity & Molecular sieve	Thin film with High permeability nano-composite membranes	Qu <i>et al.</i> , 2013
	Carbon nano tubes	Anti microbial activity	Anti biofouling membranes	Yang and Xing, 2010
	Nano TiO	Photo-catalytic activity, hydro philicity & chemical stability at high level	Reactive membranes, high performance thin film nanocomposite membranes	Li <i>et al.</i> , 2003
Disinfection & microbial control	Nano Ag	wide-spectrum and strong antimicrobial activity, low toxic effect to humans & ease of use	Anti biofouling Surface with POU water disinfection	Sharma <i>et al.</i> , 2009
	Carbon nano tubes	Antimicrobial activities with fiber shape & conductivity	Anti biofouling Surface with POU water disinfection	Yang and Xing, 2010
	Nano TiO ₂	Photo catalytic ROS generation, high level of Stability chemically & low human toxic effects & cost	POU to decontamination & full scale disinfection	Li <i>et al.</i> , 2003

Nano process for removal of heavy metal ions from waste water

Heavy metal ions are removed by different techniques used traditionally (Jing *et al.*, 2006), such as Photo catalysis, Adsorption, Nano filtration and Electrochemical oxidation which involves the utilization of Titanium Oxide, polymer membrane,

Zinc Oxide, ceramic membrane, carbon nanotubes, submicron nanopowder, nanowire membrane, Oxides of metal, nanoparticles with magnetic field and nanostructure boron doped diamond (The Millennium Development Goal Report, 2007), but due to its high efficiency, cost effectiveness and simple in operation for removal of traces of heavy

metal ions, adsorption (Neeta and Gupta, 2016) is considered as most promising one for the removal of heavy metal ions. According to Lenoble *et al.*, 2002, Arsenic is one of the most toxic heavy metal ion found

in contaminated water. At low value of pH, arsenate adsorption is preferential, on the other hand for arsenite, maximum rate of adsorption could be gained between 4 and 9 pH (Meagan and Menachem, 2008).

Table 2. Removal percentage of heavy metals using activated carbon.

Elements	Initial concentration	Residual concentration	Removal percentage (%)
Cadmium	30	4	86
	50	8.1	84
Lead	30	5	83
	50	13	74
Chromium	30	14.8	50.6
	50	25	48
Nickel	30	3	90
	50	6.1	87
Zinc	30	4.9	83.6
	50	9.4	81.2

Nanomaterials for adsorption

Contaminants mostly found in the wastewater of several industries are Dyes and heavy metals. In particular, agrochemical, petrochemical and fertilizers industries discharge heavy metals in their waste water whereas dyes are usually found in waste water discharged by dye manufacturing industries, distilleries, electroplating factories and many food companies (Deliyanni and Bandosz, 2011).

It is also reported that an anionic dye favored electrostatic interactions with heavy metals or might generate new specific sites in favor of adsorption process (Wang *et al.*, 2012).

Nanoparticles when are used as adsorbents, nano sized zero valent ions or nano filtration membrane grounds pollutant removal or separation from waste water while nanoparticles that are used for chemical or photochemical oxidation as catalysts effects the destruction of contaminants there.

Scientists has classified nanomaterials in four basic classes specifically, dendrimers, metalcontaining nanoparticles, carbonaceous and zeolites nanomaterials.

They are usually evaluated as functional materials for purification of water (Dimitrios *et al.*, 2011). With the most recent developments in nanotechnology, a variety of nanoparticles have been synthesized very successfully and have received significant attention to resolve environmental issues (Wu *et al.*, 2008). Particles of Iron have been known as novel adsorbent, which offers an inexpensive and attractive method for removing heavy metal ions. They usually have simple synthesizing method with high surface area and good magnetic properties (Pollard *et al.*, 1992).

When using nanomaterials as sorbents for removal of different ions of heavy metal in industrial effluents, nanomaterials should persuade the following criterions: i) The nanosorbents should be nontoxic in nature (Deliyanni and Bandosz, 2011). ii) The sorbents should have relatively high capacity of sorption and selectivity to the concentration of pollutants at low level. iii) The adsorbed pollutant can be easily removed from the surface of the nano adsorbent. iv) The sorbents can be recycled substantially (Lee *et al.*, 2010). Uptil now, a range of nanomaterials like carbon nanotubes, material composites based on carbon, nanometal or oxides of metals and polymeric sorbents are studied in

removing ions of heavy metal from aqueous solutions, and the derived results point out that these nanomaterials had shown high level of adsorption.

that are used commonly in modern years in removing heavy metals and the reason for their usage is due to their high sorption capacities and non toxic property.

Carbon based nanomaterials

Carbon Based nanomaterials are one of those inorganic materials (Trevino *et al.*, 2013)

Activated carbon is being widely used adsorbents for adsorption of metal ions (Dimitrios *et al.*, 2011).

Table 3. Review of major water contaminants and their health impacts on different areas.

Pollutants	Origin	Permissible limit	Affected countries	Population at risk	Health effects
Pesticides	Farming, effluents	DDT: 1 ppb; Carbofuran: 40 ppb; Simazine: 4 ppb	US, Kenya, Egypt, India, European Union, Africa, China, Australia	Poisoning: 28 million agricultural workers in the developing countries. ~18,000 deaths	Cancer, cardiovascular/reproductive/neurological disorders, liver/kidney problems
Halogenated organics	Chlorination, effluents, home insecticide	CCl : 5 ppb; TCE: 5 ppb; TTHMs: 80 ppb 4	Japan, Central Asia, Arabian Peninsula, Sweden, Poland, Germany, USA, Egypt, China	180 million people in US consume chloraminated water	High toxicity to liver and kidney, carcinogenic. TCE: Lung/liver tumor
Fluoride	Geological origin, mineral weathering, coal mining	-2 ppm	Asia, Mexico, Australia, Argentina, Africa, New Zealand	62 million (India)	Dental and skeletal fluorosis, Muscle fibre regeneration, nervous system malfunction
Arsenic	Geological origin	10 ppb	Bangladesh, India, China, Pakistan, Nepal, Myanmar, Vietnam	65 million (Asia)	High blood pressure, glucosuria, hyperpigmentation, keratoses, cancer
Mercury	Industrial pollution, dental filling, Food (fish)	- 2 ppb	Indonesia, China, Africa, Philippines, Japan, Kazakhstan, USA, Brazil, Australia, Taiwan, EU	~630,000 infants are born with high Hg content in the blood every year (USEPA)	Neurotoxicant, tremors, respiratory failure, gastrointestinal failures, and kidney damage

Activated carbon was the first and the most widely used adsorbent. It possesses a large surface area with different surface functional groups which includes carboxyl, phenol, carbonyl, lactone, quinine and other groups that are bounded at the edges of the graphite like layers (Wang *et al.*, 2012). So Activated Carbon is considered as a good adsorbent for removing ions of heavy metal and other inorganic substances, many organic compounds in liquid and gas phases. They are very much porous and amorphous solid material. It consists of micro crystallites with graphite lattice that are usually made in small pills or in powder form. It can eliminate a extensive range of toxic metals

(Dubey and Xavier, 2015), but at ppb levels, it is mostly difficult to remove heavy metals. By time, with the advancement of nanotechnology, carbon nanotubes, grapheme and fullerene are created and widely used as nanosorbents.

Some Batch experiments were conducted to investigate the capability of activated carbon for the subtraction of Cadmium, Lead, Chromium, Nickel and Zinc from industrial effluents (Erdem *et al.*, 2004; Wu *et al.*, 2008; Global Water Supply and Sanitation Assessment Report, 2008; Liu and Zhang, 2007).

Data in Table 2 showed the effects of different concentrations of metals like Cadmium, Lead, Chromium, Nickel and Zinc on the removal percentage of these heavy metals. It resulted as, at low level of heavy metal concentration, the removal percentage was comparatively high and progressively decreased with the increase of heavy metal concentration.

CNTs are now a day is used as nanosorbents separately initially which show selected sorption efficiency of divalent metal ions (Pradeep and Anshup, 2009). Krystyna and Michał, 2010 provided the benefits and disadvantages of heavy metals sorption onto activated carbon, carbon nanotubes and magnetic nanoparticles encapsulated by carbon mainly during sorption studies specifically based on Co^{2+} and Copper ion. But the results revealed the fact that carbon nanomaterials have considerably higher sorption effectiveness comparing with activated carbons (Jjemba, 2004). Afterwards, to improve the sorption capacities, CNTs are customized by combing with other metal ions or metal oxides, oxidation and coupling with specific organic compounds (Deliyanni *et al.*, 2007). Carbon nanotubes with hydroxyquinoline were customized for the removal of Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn (Taras, 1991). Currently, three main methods for CNT synthesis are considered: a) Arc Discharge Method b) Laser Ablation Method & c) Chemical Vapor Deposition. Carbon nanotubes are of majorly two types a) SWCNTs (Single Walled Carbon Nanotubes) b) MWCNTs (Multi Walled Carbon Nano Tubes) (Deliyanni *et al.*, 2007; Long and Yang, 2001). As because of CNTs highly porous structure, large specific surface area and strong interaction between CNTs and pollutant molecules, their aqueous streams as well as applicability for removing hazardous pollutants from gas have been studied comprehensively (Balkanski *et al.*, 1998).

Nanoparticles of metal oxides

Heavy metal ions in wastewater are removed by the inorganic nanomaterials, which are made by the metal or metal oxide.

There is a long list of nano sized metals or metal oxides some of them includes cerium oxides, magnesium oxides, manganese oxides titanium oxides, ferric oxides, copper oxides, silver nanoparticles and many others. Specific affinity and high surface area are offered by these particles (Gupta, 2016). Metal oxides have been extensively used as sorbents for removing heavy metals from wastewater, as they provide negligible secondary pollution and environmental impact. (Agnihotri *et al.*, 2005) Because of their high surface area nano sized particles have greater efficiency towards removal of heavy metals in wastewater.

This is because they have high surface area and greater number of active sites. But their high surface energy and nano size makes them resistant and thus they cannot easily separated from wastewater. For the removal lead, in most water cleaning processes nanoparticles suspensions of TiO_2 , CeO_2 , and Fe_3O_4 were made and tested in laboratory (Fabrega *et al.*, 2012). The results obtained clearly depicts that these nanoparticles can be used in the removal of lead through the process of adsorption.

Aluminum oxides Nanoparticles: For heavy metals Alumina (Al_2O_3) is a conventional adsorbent. The nanoparticles are considered to be more adoptively active than Alumina in huge quantity. It can be synthesized by solution gel method and can be used in the separation or pre concentration of trace metal ions in which it is used as solid phase extraction material (Goswami and Purkait, 2005).

Zinc oxides nanoparticles: Due to its vast usage ZnO is considered as environmental friendly material, some of its uses are as in catalyst industry, gas sensors and solar cells. Recently, for the removal of heavy metals nano sized ZnO can be used very effectively. The Cu ions present in the solution can be removed by ZnO nano powder more efficiently than with TiO_2 powder. The nano structured ZnO has many advantages because of their high surface area, they are simple and can be prepared in less cost and can be morphologically altered easily (Erdem *et al.*, 2004).

Titanium oxides nanoparticles: Due to their different surface planes, it has been tested that bulk and nanoparticle TiO shows different catalytic reactivity, chemical behavior and surface acidity. Comparatively TiO nanoparticles were found to be more efficient to remove many ion such as Zn, Pb, Cd, Cu and Ni in parallel with bulk particles from a solution which has pH 8 and a tap water.

Waste-water treatment-challenges

Prominent changes have been made regarding the concept of water quality, the methods to treat wastewater, and its effects on the human health during the period of past 150 years. Two basic aspects must be considered while looking to the importance of water i.e the quality and quantity of available water (Table 3). The United Nation has set a goal as a part of "Millennium Development Goals 2015", to reduce the number of people by half who do not have access to safe drinking water which is the necessity of life (Zhang *et al.*, 2008). Chemistry of nanomaterial is highly acknowledgeable in comparison to traditional and old techniques. Mostly the surface sites of the adsorbent particles are used in the process of adsorption. The reduction in the adsorbent particle from bulk to nano dimensions greatly increases the surface to volume ratio of the adsorbent particles. This increase will result in the availability of large number of atoms or molecules for the adsorption of contaminants on the surface. Therefore the surface energy of the adsorbent particles increases greatly accordingly. This offers many benefits to Waste water treatment:

Even at low concentration, effective contaminant removal can occur efficiently.

After treatment, less waste will be generated because of less requirement of nanomaterial.

Important reactions can be done due to nanotechnology because nanoscale causes increases in surface atom and consequently surface energy which cannot happen with corresponding bulk material.

Potential effects of nanotechnology

Nanotechnology can be beneficial as well as has many adverse effects. Some of the positive points are as under:

It is very economical on materials. By the discovery of alternative energy method which is hybrid automobiles has played a major role in decreasing the price by new developments in nanotechnology (Pradeep and Anshup, 2009).

Waste production is minimized on raw materials. Large sample testing will be done on a smaller scale and which has made the use of raw materials more efficient. The reaction rates are increased by the use of nanoscale reagents and the efficiency of reactions is also increased (Pradeep and Anshup, 2009).

They have many Biological applications too. By the development of small probes on surfaces for agricultural applications and thus, helps in control of soil, air and water contamination.

They are also used in Biomedical applications as well that includes the medical diagnostics and different treatments.

It provided Cleaner and more efficient industrial processes.

It plays a crucial role in improving the air, water and soil quality as it has ability to detect the pollutants and then removing them.

It reduces the amount of waste generated because of its high accuracy.

As more effective solar cells are used thus it has abundant power.

Plays a major role in eliminating Green House Gases (GHGs) and other pollutants from the air.

There is fewer requirements of huge industrial plants for the treatment of waste water.

It also plays crucial role in the remediation of the environment.

There are few risks also which are associated with the nanoparticles. These risks are as under:

One of the major problems of nanomaterials is the nanoparticle analysis method with the improvements in nanotechnology. New and better nanoparticles are being developed.

The major problem of nanomaterials is the nanoparticle analysis method. As nanotechnology improves, new and novel nanomaterials are gradually developed. Though, the materials vary by shape and size which are important factors in determining the toxicity. Lack of information and methods of characterizing nanomaterials make these technologies extremely difficult to detect the nanoparticles in air for environmental protection (Krystyna and Michał, 2010).

We should have the complete information of the chemical structure while determining the toxicity of material and how changes in functional group will change its properties.

Full risk assessment of the safety on human health and environmental impact should be conducted at all stages of nanotechnology. The risk assessment would include the exposure risk and its chances of exposure, toxicological analysis, transport risk, persistence risk, transformation risk and their potential to be recycled (Liu and Zhang, 2007).

In order to determine its negative impacts on the environment, life cycle risk assessment can be used.

For the synthesis of nanoparticles there is a demand for very high energy.

Nanoparticles which persist in the environment do not degrade easily.

Their risks are very high as they do not recover very fast and have low recycling rates.

Lack of trained engineers and workers that causes occupational and technical risk.

Conclusion

Nanotechnology for water and wastewater treatment is acquiring momentum globally. The unique properties of nanomaterials and their junction with current treatment technologies provide great opportunities to revolutionize water and wastewater treatment techniques.

The nanoparticles involved in the removal of ions use traditional techniques like photocatalysis, nanofiltration etc. Nanomaterial for adsorption causes separation of pollutants from water by using nanofiltration membranes. Carbon based nanotechnology is used for its high sorption capacity. And nanoparticle of metal oxide provides high surface area specificity. Many nanotechnologies highlighted in this review are still in the laboratory research stage and some have made their way to pilot testing and commercialization.

The challenges faced by water and wastewater treatment nanotechnologies are important, but many of these challenges are possibly only temporary, including technical hurdles, high cost, and potential environmental and human risk.

To overcome these hurdles, collaboration between research institutions, industry, government, and other stakeholders is vital.

It is our belief that advancing nanotechnology by carefully navigating its direction while avoiding unintended consequences can surely provide robust solutions to our water and wastewater treatment challenges, both incremental and revolutionary.

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