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New trends in removing toxic metals from drinking and wastewater by biomass materials and advanced membrane technologies

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Abstract

The pollutants are the harmful substances that are most dangerous and found in water. Some of them are non-biodegradable and cannot convert into harmless substances show high level of toxicity at low concentrations in the bodies of living organisms. Water contamination also adding pollutants and heavy toxic metals such as lead, mercury and chromium to natural water resources and overall lethal effects to the living organism living in ecosystem. There are many methods used for removal of toxic metal from drinking and wastewater such as adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, and oxidation and biosorption processes. Adsorption is most reliable among all methods because economically positive testing and technically simplest to separate chemicals found in water. Many adsorbents and advancements in membrane filtration systems have been designed for the treatment of contaminated metal found in drinking and wastewater. This article focuses on modification in sorbents for improving their efficiency and new developments in conventional methods of extraction of heavy metals from water. This article also focuses on the recent developments and modern applications in methods for of treatments and removal of heavy metals from drinking and industrial wastewater.

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Introduction

Heavy metals are highly toxic because these affected the organisms on the biosphere .These heavy metals mostly found in drinking and wastewater and therefore contaminated water bodies such as drinking water, pool water, water found in seas and oceans. These metals should be separated by advanced methods and membrane filtration methods such as micellar enhancer membrane system.

We also dependent of water to live and survive on earth. All the biochemical reactions takes place in the presence of water (Srivastava *et al.*, 2008). Various toxic metals that show high level of toxicity such as Copper, zinc, manganese, iron, and cobalt play a vital role in biochemical process of living organism.

Excessive levels of highly toxic metals resulted in harmful effects on living parts of body such effects have been seen on kidney, liver, bone and brain. Various toxic metals that showed damaging effects such as arsenic, cadmium, lead, mercury, chromium are the toxic, even at small that amoun measurement have been taken in chemical units such as parts per billion. These are not converted into less toxic substance and accumulate in the main system of the living organism (Zak *et al.*, 2012). In common conditions, living systems of the organisms can tolerate the small amount of the heavy metals without facing any serious health problems. So, we needed advanced technologies and membrane systems for extraction of the heavy metals.

But long term contact with the heavy metal cause the accumulation of the heavy metal in the body which result in the failure of the organ system and even cause death (Kamran *et al.*, 2013). Extreme level of the toxic metal allowed to presence in the water is settled by the World Health Organiztion (WHO) is zero and very small amount is allowed. In water source, extreme level of the heavy metal is set at Pb (10ppb), Cd (3ppb), As (10ppb) and Cr (100ppb). Excessive release of the heavy metal is not saving for living organism and that leads to destruction of habitat. (Wang *et al.*, 2012).

This article focused on advanced and membrane based innovative methods have been used for the removal of the heavy metals from the water. There is still now no detail information about the efficient work removal of the metals. Various commonly used methods for treatment of heavy metals are precipitation, adsorption, ion-exchange (Hua *et al.*, 2012). Membrane treatment is basically one step method and give good results. Adsorption is a method used for the treatment of the water in that low cost adsorbant is used that have capacity to bind with metals. Adsorbant may have the origin minerals, organic and agricultural. Different techniques have been used for the treatment of the inorganic effluents. There is more need to understand heavy metals toxicity and so that more and more advanced systems could be taken into consideration for extraction of heavy metals.

Heavy metals Toxicity

Heavy metals are usually measured to be those whose density more than 5 g/cm^2. Arsenic is typically considered as a hazardous heavy metal still it is in fact a semi-metal. Heavy metals can cause severe health effects, as well as reduction in growth and development of cancer, organ damage, nervous system damage, and in extreme cases, death. Experience to some metals such as mercury and lead that might also cause development of autoimmunity in which immune system of person damage and attacks its own cells.

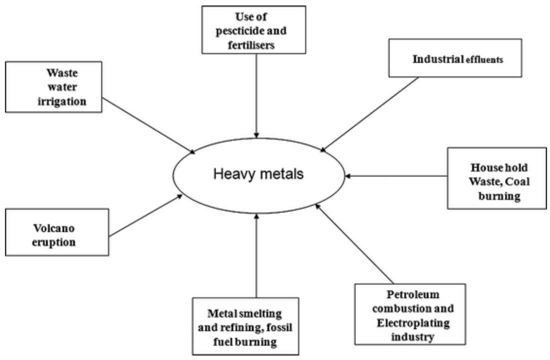

Fig. 1. Sources of Heavy Metals.

Sources of inorganic pollutants

Heavy metals such as mercury, lead, tin, cadmium, selenium, and arsenic are discharged to environment through different human activities and deposited in ground water and soil also leads to water and soil pollution (Babel *et al.*, 2003). In developing counties, more consideration is required to solve environmental issues so that drainage of water and waste water into lakes and rivers is extremely common. The human activities can cause poisoning of fresh water resources which affects the entire ecosystem (Gupta *et al.*, 2015).

Table. 1. Six Toxic Pollutants are given.

The Top Six Toxic Threats:	Estimated Population at risk at Identified Sites*(million people)	Estimated Global Impact** (million people)	Harmful Effects on Health	Major Targeted Organ	Industrial Role in Spreading of Pollutants	Precautionary Measures
Lead	10	18-22	Kidney Failure	Kidney	Major	Chemical
Mercury	8.6	15-19	Brain Damage	Brain	Major	Chemical
Chromium	7.3	13-17	Cancer	Liver, Skin	Major	Chemical
Arsenic	3.7	5-9	Comma	Skin	Major	Chemical
Pesticides	3.4	5-8	Headache, Nausea, Vomiting	Multiple Organs	Major/Minor	Biological
Radionuclides	3.3	5-8	Cancer	Skin	Minor	Biological

Hazardous effect of heavy metals

As chemical pollutants more heavy metals were testing from point of analysis of determination and high level of toxicity. The increase level of heavy metals has adverse effects on aquatic plants and animals and might comprise a public health issue where organisms are used for food. These can cause food poisoning, initiate cancer, and consequence in brain damage when found high level the normal levels (Sekhar *et al.*, 2003). The environmental protection agencies for the environmental monitoring have set acceptable limits for heavy metals levels in drinking water because of their harmful effects on living system (Wang *et al.*, 2004).

Table2. The hazardous effects of some metals are on biological systems

Metal	Source	Route of Entry	Toxicity Effect	Level (mg/L)
Arsenic	Pesticides, fungicides, metal smelters	Inhalation and ingestion	Irritation of respiratory system, Liver and Kidney damage, Loss of appetite, nausea and vomiting etc.	0.020
Cadmium	Welding, electroplating, pesticide fertilizer, Cd-Ni batteries	Inhalation and ingestion	Lung, liver and kidney damage; Irritation of respiratory system	0.06
Chromium	Paints, electro plating and metallurgy	Inhalation, ingestion, and absorption through skin	Lung damage and Irritation or respiratory system	0.05
Mercury	Pesticides, batteries, paper industry	Inhalation, ingestion and absorption through skin	Irritation of respiratory system; lung, liver kidney damage, and loss of hearing and muscle coordination	0.01
Lead	Paint, pesticide, smoking, automobile emission,mining,	Inhalation and ingestion	Lung and liver damage; loss of appetite, nausea	0.15
Nickel	Electrochemical industries	Inhalation	Lung, liver and kidney damage	0.1

Conventional Methods for Heavy Metal Removal

Various processes have been used for heavy metals from water comprised such as chemical precipitation, flotation, adsorption, ion exchange and electrochemical deposition. Chemical precipitation is most extensively used for heavy metal elimination from inorganic effluent. Alteration of pH to the basic conditions such as pH 9-11 is the most important parameter that considerably enhanced heavy metal exclusion by chemical precipitation. Lime and limestone are most frequently working precipitant agents due to their accessibility and low-cost in most of countries (Aziz *et al.*, 2008).

Removal of heavy metals by adsorption

Adsorption is known to be one of the best of the technologies for the decontamination of water because it is an effective, economical and ecofriendly treatment technique. It is a process strong enough to realize water reuse obligation and high runoff standards in the industries. Adsorption is basically a mass transfer process by which the metal ion is transferred from the solution to the surface of sorbent, and becomes bound by physical and/or chemical interactions. All adsorption bonding. Physical adsorption can only be occurred in the environment of low temperature and under appropriate pH conditions. This kind of adsorption involves a strong interaction results from chemical reaction between the adsorbent and the adsorbate. This interaction creates new types of electronic bonds such as Covalent, Ionic.

Adsorption on modified agriculture and biological wastes (Biosorption)

Recently, a large deal of interest in research for removal of heavy metals from industrial effluent has been paying attention on the use of agricultural by-products as adsorbents (Soto *et al.*, 2016). The use of agricultural by-products in bioremediation of heavy metal ions, is known as bio-sorption. This utilizes inactive microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways mainly chelation and adsorption of uptake. The mechanism of up-taking heavy metal ions can take place by metabolism-independent metal-binding to the cell walls and external surfaces (Deliyanni *et al.*, 2007). This involves adsorption processes such as ionic, chemical and physical adsorption.

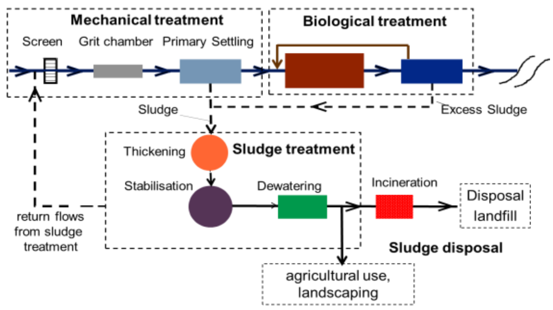

Fig. 2. Processes of a conventional metals precipitation treatment plant.

Adsorption on modified natural materials

Natural zeolites used widely due to their important properties as ability to ion exchange. Most commonly considered natural zeolites, clinoptilolite revealed to have high selectivity for specific heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II). It was confirmed that ability to ion exchange of clinoptilolite depends on pre-treatment process and that breaking in improves its ion exchange ability and removal efficiency (Burakov *et al.*, 2018). The ability of different types of synthetic zeolite for heavy metals removal was recently investigated. The role of pH is a key factor for the selective adsorption of different heavy metal ions (Barakat *et al.*, 2008).

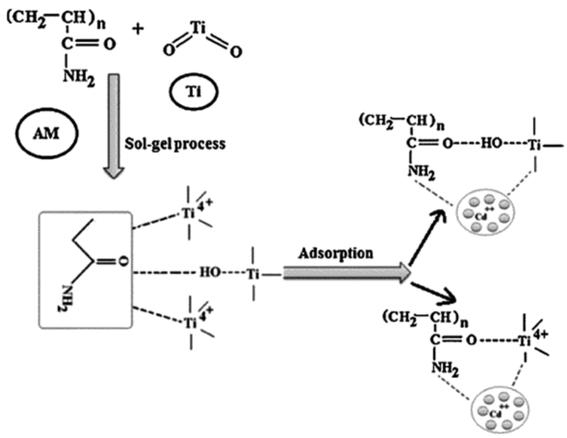

Fig. 3. The adsorption mechanism of Cu(II) on hydrous TiO_2.

Adsorption on modified biopolymers and hydrogels

Biopolymers are technologically important because they are proficient of concentration lowering of transition metal ion unit to billion concentrations, extensively accessible, and environmental safe. Advance attractive feature of biopolymers is to possess a number of different rotational functional groups, such as hydroxyl and amine that will increase efficiency of uptake of metal ion and maximum chemical loading possibility. New polysaccharide based materials describing as adapted biopolymer adsorbents resulting from chitin, chitosan, and starch for removal of heavy metals from the wastewater.

There are two major ways for the preparation of sorbents that contain special polysaccharides such as cross linking reactions, reaction between hydroxyl or amino groups of the chains with a coupling agent to form watery insoluble cross linked networks and the immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials (Crini *et al*., 2005). These two important features of modified polymers makes special and modified polymers which are synthetically resistant to environmental changes and environmental friendly. Chitin is a type of mucopolys accharide extract from crustacean especially in shells, that are waste materials of industries working on seafood processing. Chitosan can be shaped by deacetylation of chitin and it is the most important derivative of chitin. Chitosan in partly converted crab shell waste is a powerful chelating agent and interacts very efficiently with transition metal ions (Pradhan *et al*., 2005).

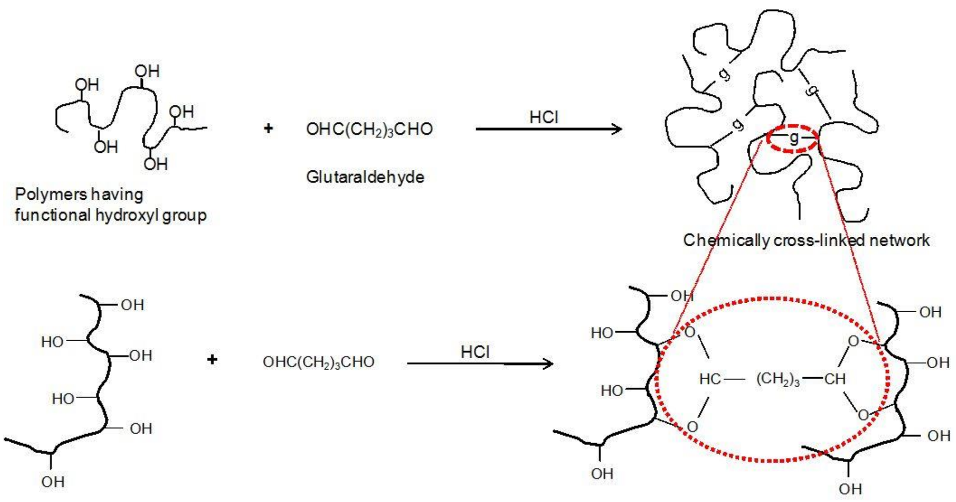

Fig. 4. Three-dimensional network formation of cationic hydrogel.

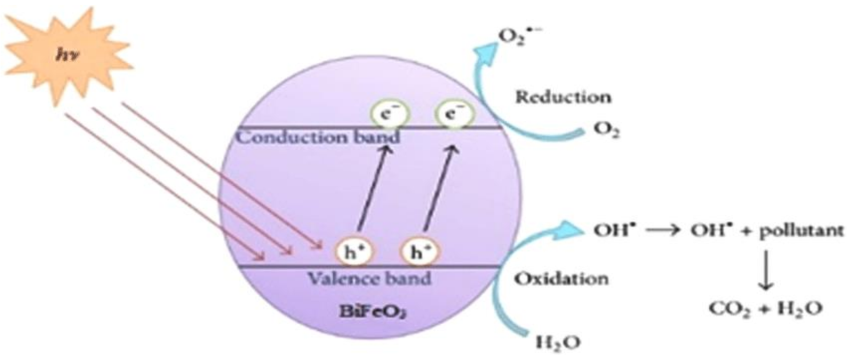

Fig. 5. The conceptual reaction path of photocatalysis over TiO_2.

Electrodialysis

In compared to RO membrane method, ED used a lower hydraulic operation at room temperature and does not usually generate any pollutant causing agents. In electrodialysis, ion exchange membranes consist of cationic and anionic membranes are arranged in parallel stacks. Within stacks, a diluted feed stream, a concentrate stream and an electrode stream are flowed across the IEMs (Babilas *et al*., 2018) . An electrical current is then supplied to electrodes to initiate the charge in the feed solution by which positively charged metal ions will migrate to the cathode. These ions pass through the negatively charged membrane but are retained by the positively charged membranes.

In the same way, ions that negatively charged have resolved migrate towards anode by passing through positively charged membrane but retain by the anionic membrane. Due to measures of the stacks, feed stream contain ions determination depleted into dilute streams and concentrate streams.

Heavy metals removal by different membrane processes

Membrane filtration has traditional significant interest for treatment of inorganic effluent because of capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater (Chatterjee *et al.*, 2017).

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Complexation-Enhanced UF (CEUF)

CEUF is well known as polymer supported with UF, polymer enhanced UF, simply polymer UF, or polymer assisted UF, but principle is same and mode of action of each polymer is different fron each other. CEUF be at the started by using the biological material such as Saccharomyces cerevisiae, sodium alginate, and polymers of monosaccharides extract from seaweed to for complexation with metal ions. (Crini *et al.*, 2014). The method of CEUF is based on chelation or complexation process that uses polymers with property of chelating is additional to the feed solution (Petrov *et al.*, 2004). The active functional groups of polymer ligands allow attachments of various metal ions to two or three donor atoms of polymer ligands through the electrostatic force of interaction. The interaction is simply designed by using two-phase zone model in which metal ions are effectively attached to polyelectrolyte macromolecules by specific functional groups of ligands such as carboxylic, amide and sulfones via electrostatic interaction (Chen *et al.*, 2014).

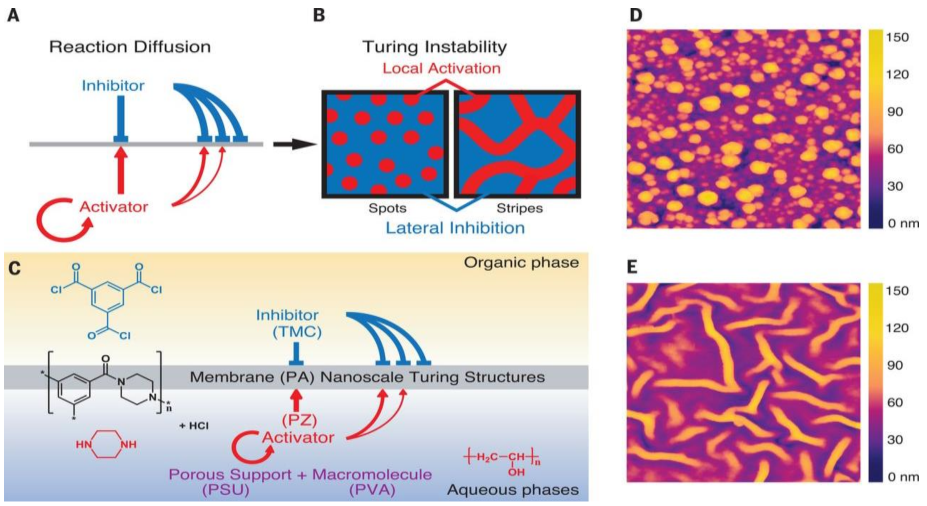

Fig. 7 . Meachamism of action of Interfacial polymerization.

Micellar-enhanced UF (MEUF)

Micellar-enhanced UF (MEUF) is mainly showed functionality for prevention of heavy metal ions from passing through membrane with many small pores through arrangement of larger molecular weight of micelles in contact between metal ions and the surfactants (Tortora *et al.*, 2016). Micellar enhanced UF especially uses charged surfactants as the micelle agents to form micellar compounds with metal ions. This method was at first introduced by (Landaburu *et al.*, 2012) in 1980s for removing of organic compounds such as 4-tert-butyl-phenol mand metal ions such as Zn from from aqueous solution. Micellar-enhanced UF fundamentally requires the addition of cationic or anionic surfactants to the aqueous stream containing heavy metals (Bade *et al.*, 2011).

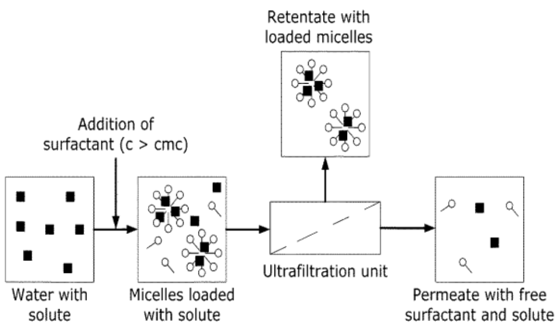

Fig. 6. Formation of Micellar-enhanced UF.

Membranes with thin film layer

Membranes with thin film layer basically comppосed of thin selective layer supported by a porous substrate to efficiently remove small ionic ions. The common methods for producing an ultrathin film on the porous membrane are interfacial polymerization (IP) and the layer-by layer approach (Chun *et al.*, 2017).

Interfacial polymerization (IP)

The IP technique is used to form a polyamide layer through the reaction of nucleophile reactants as reaction of amines and alcohol and electrophile reactants with reaction between isocyanates and acid chloride. The polycondensation of two reactants yields PA with a linear polymeric chain. The PA layer formed on the substrates of the NF membranes normally has looser structure than the PA layer on the RO membranes. For nitrocellulose filter and RO membranes, most modifications are carried out on the PA layer, as the porous substrate does not really play a key role in selective separation.

Conclusion

These are the most commonly methods that have been used for treatment and extraction of heavy metals. So, when is low levels of toxic metals in drinking and wastewater by using the above mentioned water extraction systems, all living organisms can be free from all fatal diseases. Chemical precipitation, adsorption, membrane filtration. Electrodialysis, and photocatalysis treatment technologies have been developed for removal of heavy metal contaminated water resources. Newly developed adsorbents and advancements in membrane filtration systems are are the most scientific methods for treatment of the heavy metals that contaminated the wastewater. The newly developed technique such as photocatalysis is a way for cleaning of water and reliable treatment for heavy metals extraction with many advantages. The treatment systems should have has no toxic effects on all organisms found earth and environment friendly.

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