

# Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review

Abdel-Raouf MS\* and Abdul-Raheim ARM

Egyptian Petroleum Research Institute, 1-Ahmed El-Zomor St, Nasr City, Cairo, Egypt

## Abstract

The recent researches are moving to removal of the agricultural and industrial pollutants from sewage treatment and discuss the possibility of the re-use of this water for agricultural purposes. The chemical contaminants represent the most dangerous types of contaminants found in the water for a many reasons, they are non- biodegradable environmentally and their high toxicity at very low concentrations in addition to the cumulative impact in the bodies of living organisms. The most toxic heavy metals are lead, mercury and chromium. It was estimated that the estimated that global impact of lead is 18-22 million people and of mercury 15 to 19 million people at 2010 according to Blacksmith Institute's World worst pollution problems. Contamination of the water resources with these elements, leads to polluting of the entire food chain and represents a real threat to the ecosystem. Thus, pure water shortage becomes a crucial problem worldwide. Among the most important research that can contribute to solving the problem of those related to water purification and improving the quality and re-use even in agriculture, for example, instead of wasted and discarded. There are many scientific methods applied in this regard. They include adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, and oxidation and biosorption processes. Some of these techniques however, have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products. Among all these techniques, the adsorption is economically favorable and technically easy to separate. Instead of using commercial materials researchers have worked on inexpensive materials such as natural and agricultural products. Several works concerned the removal of heavy metals but the present work focuses on the sorbents based on biomass and their efficiency in removal of heavy metals from waste water.

**Keywords:** Heavy metals; Removal; Ion selective; Membrane filtration; Adsorbent; Bio-sorbents

## Introduction

### Problem statement

As a result of different human activities, the world is facing serious threats of air, land, and water pollutions. Water pollution in particular, has raised severe environmental impacts. In addition to the shortage of resources of water due to drought and misuse, production of large volumes of wastewater has put a lot of pressure on the humankind. There are different types of water contaminants. They are summarized in Figure 1. Among these pollutants, the inorganic pollutants are extremely harmful due to their high toxicity and non-biodegradability.

### Sources of inorganic pollutants

Heavy metals, like mercury, lead, tin, cadmium, selenium, and arsenic are introduced to the environment by different human activities and deposit slowly in the surrounding water and soil [1-4]. In many developing countries, little attention is paid to the environmental issues that the drainage of waste water into lakes and rivers is very common. The uncontrolled activities cause poisoning of fresh water resources which affects the entire eco-system. The top six toxic pollutants are given in Table 1 whereas the major sources of heavy metals are presented in Figure 2.

### Hazardous effect of heavy metals

As potent pollutants, heavy metals were intensively investigated from the point of view of persistence and toxicity. The accumulation of heavy metals certainly has adverse effect on aquatic flora and fauna and may constitute a public health problem where contaminated organisms are used for food. They can cause poisoning, initiate cancer, and result in brain damage when found above the tolerance levels [5-8]. The agencies

for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The hazardous effects of some metals are listed in Table 2 [9].

### Conventional Methods for Heavy Metal Removal

The conventional technologies include physical, chemical or biological (Figure 3) [10-16]. Some of these methods are illustrated in Figure 4. Each of these methods has its advantages and disadvantages so that they are inadequate to deal with the wastewater treatment problem; the advantages and disadvantages of the conventional methods for metal removal are listed in Table 3.

### 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 [17-20]. All adsorption

\*Corresponding author: Abdel-Raouf MS, Egyptian Petroleum Research Institute, 1-Ahmed El-Zomor St, Nasr City, Cairo, Egypt, Tel: +20222747847; E-mail: [drmanar770@yahoo.com](mailto:drmanar770@yahoo.com)

Received December 18, 2016; Accepted January 16, 2017; Published January 23, 2017

Citation: Abdel-Raouf MS, Abdul-Raheim ARM (2017) Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review. J Pollut Eff Cont 5: 180. doi: [10.4172/2375-4397.1000180](https://doi.org/10.4172/2375-4397.1000180)

Copyright: © 2017 Abdel-Raouf MS, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

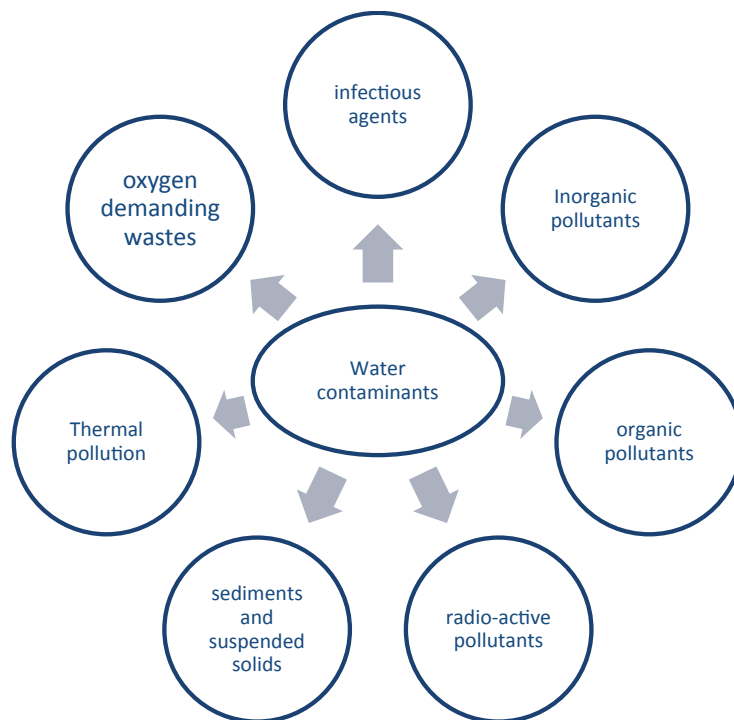


Figure 1: Different water contaminants.

The Top Six Toxic Threats:	Estimated Population at risk at Identified Sites*(million people)	Estimated Global Impact** (million people)
1. Lead	10	18-22
2. Mercury	8.6	15-19
3. Chromium	7.3	13-17
4. Arsenic	3.7	5-9
5. Pesticides	3.4	5-8
6. Radionuclides	3.3	5-8

\*Population estimates are preliminary and based on an ongoing global assessment of polluted sites.

\*\*Estimated global impact is extrapolated from current site research and assessment coverage.

Table 1: The top six toxic threats.

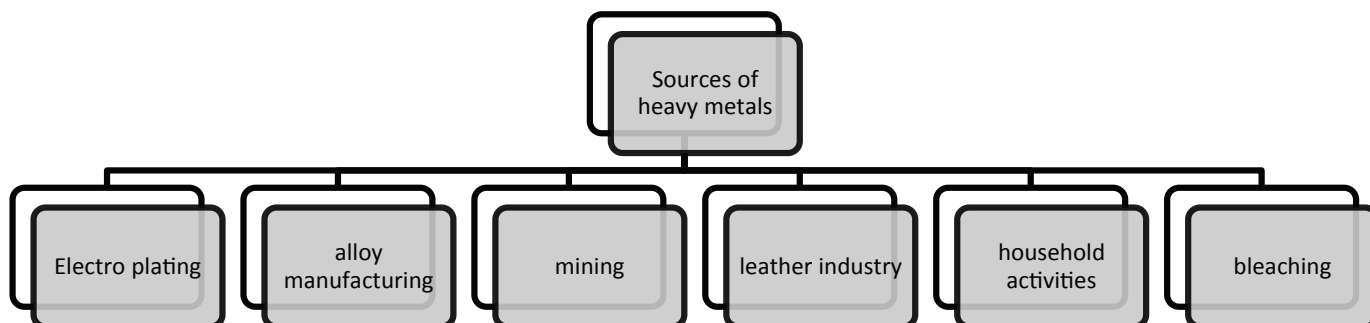


Figure 2: Main sources of heavy metals.

mechanisms are dependent on solid-liquid equilibrium and on mass transfer rates. Based on the types of intermolecular attractive forces adsorption could be divided into the following types [21,22].

#### Physical adsorption

It is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction or hydrogen

Metal	Source	Route of Entry	Toxicity Effect	Permission 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(vapor)
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

Table 2: The sources, route of entry and hazardous effect of some heavy metals.

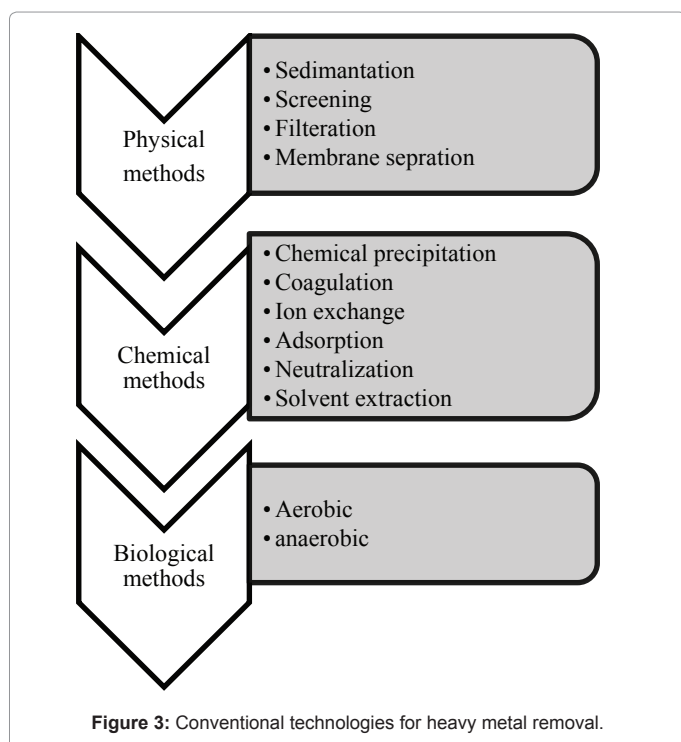


Figure 3: Conventional technologies for heavy metal removal.

bonding. Physical adsorption can only be occurred in the environment of low temperature and under appropriate pH conditions.

### Chemical adsorption

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 (Covalent, Ionic).

### General mechanism of adsorption

In general, the main steps involved in adsorption of pollutants on solid adsorbent are:

1. Transfer of the metal ion from bulk solution to the outer surface of the adsorbent.
2. Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure.
3. Adsorption of adsorbate onto the active sites of the pores of adsorbent.

4. The overall rate of adsorption is governed by either film formation or intra particle diffusion or both as the last step of adsorption are very fast as compared to the other two steps.

### Low cost adsorbents

There are several locally existing materials that can be used for the removal of heavy metals. Low cost adsorbents such as natural materials, agricultural wastes, modified biopolymers, or industrial by-products are found to be more encouraging in heavy metal removal due to the following considerations [6,17]. (I) They are economical, (II) they are metal selective, (III) they are regenerative, (IV) absence of toxic sludge generation (V) metal recovery and (VI) they are highly effective.

Recently, research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents through biosorption process. Moreover, biopolymers are posse a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake. The origin of the biomass must be taken into account while choosing the biomass for metal removal.

Classic biosorbents can be derived from three sources as follows:

1. Non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.
2. Algal biomass.
3. Microbial biomass, e.g. bacteria, fungi, and yeast [9,23,24].
4. Agricultural products.

In the next sections of this review, the removal of heavy metals by different agricultural wastes, modified biopolymers and bio-based nanocomposites will be discussed.

### Removal of Heavy Metals by Agricultural Wastes

Numerous agricultural wastes such as wool, rice, straw, coconut husks, peat moss, exhausted coffee [25-27], waste tea [28], rice hulls [29-31], cork biomass [32], seeds of *Ocimum basilicum* [33], coconut shells [34], soybean hulls and cotton seed hulls [35], saw dust of walnut [36] untreated coffee dust [37], papaya wood [38], peanut hulls [39], citrus peel [40] were used as sorbents for metal removal. However, sea weeds, molds, yeasts, bacteria have been tested for metal biosorption

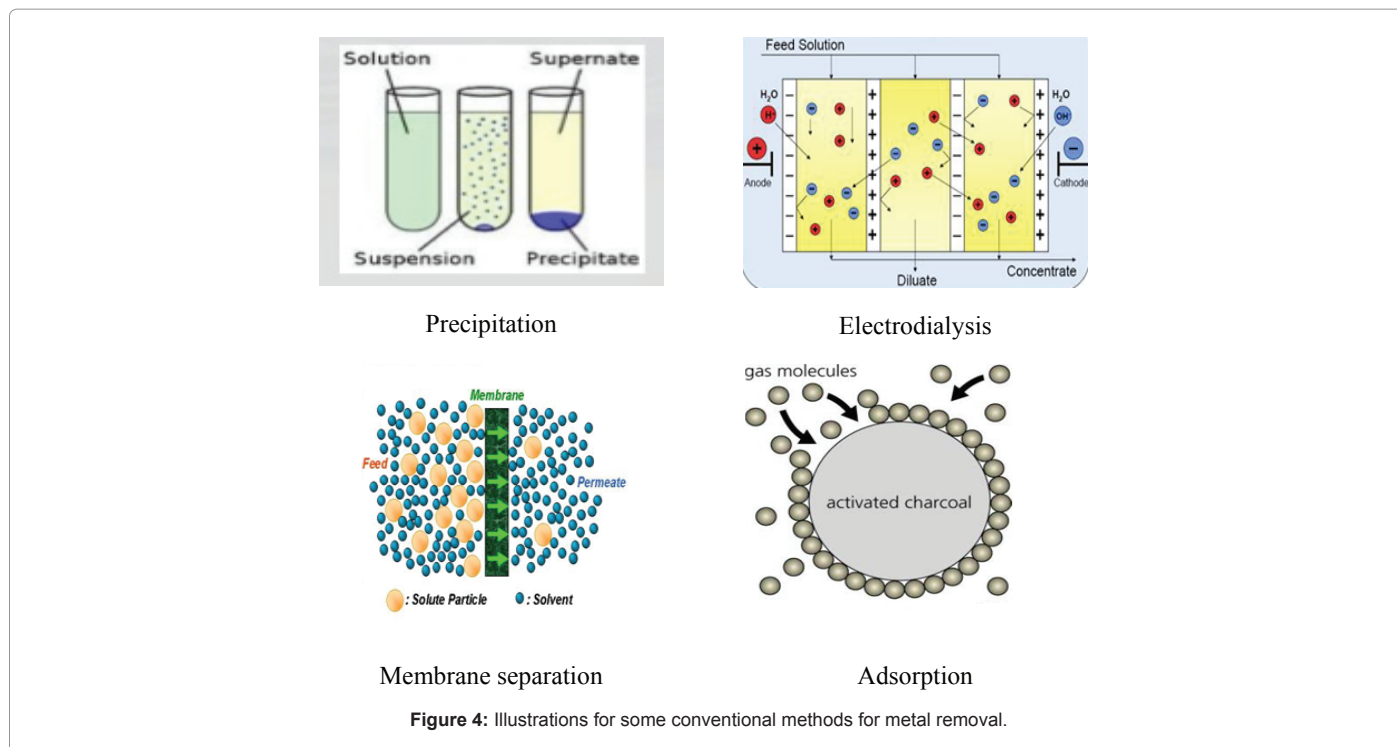


Figure 4: Illustrations for some conventional methods for metal removal.

Conventional treatment	Advantages	Disadvantages	Ref.
Chemical precipitation	It is relatively simple, inexpensive cost and non-metal selective	Large production of sludge, slow metal precipitation and poor settling	[85-87]
Ion exchange	Metal selective	Elevated	[88-89]
	High treatment capacity	maintenance cost	
Membrane filtration	Fast kinetics	Low flow rate	[13,90-92]
	Removing suspended solid, organic compounds and heavy metals. Various types of membranes are found according to the size of the particle such as ultrafiltration, nanofiltration and reverse osmosis	High cost	
Electrochemical treatment	Meal selective,	pH sensitive	[90,92]
	Reduced sludge production	Relatively high cost	
Coagulation and flocculation	Simple and non-metal selective	Production of sludge, transfer of toxic compounds into solid phase	[91,93,94]

Table 3: Advantages and disadvantages of some heavy metals removal conventional methods.

with encouraging results [41-44]. Table 4 shows various agricultural sorbents and the metal they removed [45-50].

The parameters which have been investigated for optimizing the use of adsorbent in wastewater treatment include:

1. Nature of adsorbent and adsorbate,
2. Metal concentration,
3. Temperature and pH of the aqueous solution,
4. Kinetics of adsorption,
5. Adsorption isotherm and
6. The contact time

Most of these wastes were used without chemical modification [34-51]. Thus they showed poor metal removal in addition to their non-metal selectivity.

## Removal of Heavy Metals by Chemically-Modified Agricultural Wastes

The need for strong adsorbents has been emerged due to the intensification of industrial activity and environmental stress. To overcome this problem, several works have been done in order to extract effective materials by chemical treatment or chemical modification of these wastes.

An abundant source of potentially metal-sorbing biomass is lingo-cellulosic agricultural waste materials. These materials could be reasonably priced alternate for the treatment of heavy metals in wastewater [52].

Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons,

ash and many more compounds that contain a variety of functional reactive groups. Cellulose and starch are the most potential candidates accepting chemical modification by various reactions, i.e. ethoxylation, carboxy methylation, amidation...etc.

There are two main ways for preparation of sorbents containing polysaccharides:

1. Crosslinking reactions, a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble cross-linked networks (gels);
2. Immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials.

Cellulose is the first abundant biopolymer on earth. It can be

obtained from different sources Figure 5. It is a crystalline homopolymer of glucose with  $\beta$ 1 4 glycosidic linkage and intramolecular and intermolecular hydrogen bonds, Figure 6 [53]. Chemical modification of cellulose has resulted in tremendous number of cellulose derivatives. In this respect, Polysaccharides (PS) of cellulose, soluble, corn- and maize-derived starches with variable amylose/amylopectin content were cross-linked with epichlorohydrin (EPI) to form polymeric adsorbents. The properties of the cross-linked PS-EPI materials were prepared by varying the synthesis conditions (nature of polysaccharide, temperature, and reagent ratios) to afford network polymer materials with tunable properties [54].

Mahajan and Sud [55] used Dalbergia sissoo pods, a lignocellulosic nitrogenous waste biomass, was evaluated for sequestering of Cr (VI) from synthetic wastewater. In terms of their structure, Dalbergia sissoo

The agricultural waste	The metal they removed	Reference
Tea industry waste	Cd (II), Cu (II),	[45]
	Ni (II)	Maloc and Nuhoglu [47]
	Cr(VI)	Maloc and Nuhoglu [48]
Pretreated rice husk	Cd (II)	Kumar and Bandyopadhyay [46]
Grape stalk wastes	Cu (II), Ni (II)	Villaescusa et al. [50]
Dehydrated wheat stalk	Cu (II)	Ozer and Ozer [49]
Potato peels	Cu (II)	Amana et al. [95]
Maize cob and husk	Zn (II), Cd (II) and Pb (II)	Igwe et al. [96]
	Pb (II)	Abdel-Ghani et al. [97]
Water melon shell	Cu (II)	Banerjee et al. [98]
Cork powder	Zn (II)	Kanawade and Gaikwad [99]
Tobacco stem	Cr(VI)	Sheth et al. [100]

Table 4: Some agriculture waste-based sorbents.

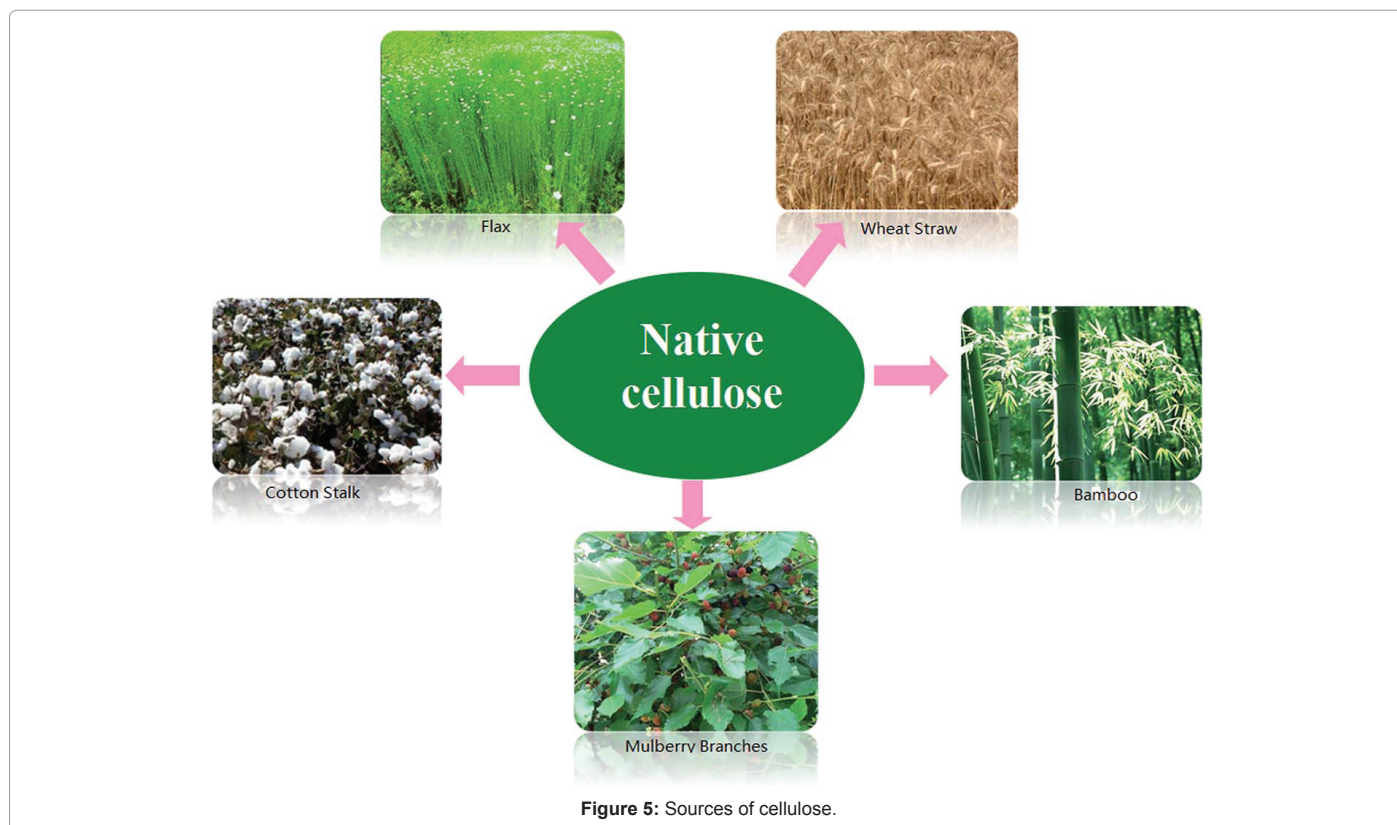


Figure 5: Sources of cellulose.



Pods (DSP) can be regarded as a ligno-cellulosic agricultural waste material containing reasonable amount of proteins and fibers. The metal removal capacity was examined versus many factors, such as effects of pH adsorbent dose, initial metal-ion concentration, stirring speed, and contact time.

In our previous work [56], hydrogels nanoparticles were synthesized by graft copolymerization of acrylic acid and N-isopropylacrylamide (NIPA) onto carboxymethyl cellulose (CMC). The prepared nanogels were used to remove copper and lead ions from aqueous solutions. The effects of pH, time, crosslinker concentrations, temperature, and initial metal ion concentration on the metal ion removal capacity were investigated.

Furthermore, Tripathy et al. [57] have investigated the +ve metal ion (i.e.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ ) sorption behavior of cellulose-based superabsorbent hydrogels. Sorption results showed that the values of the +ve percent ion uptake were 13.8, 11.5, 9.8, 9.0 and 8.7 at the maximum values, separately. In addition, cyanoethyl cellulose-based

superabsorbent hydrogels were prepared and used for the adsorption of copper (II) ions from aqueous solutions. It was found that metal-ion removal depends on the protonation and deprotonation properties of acidic and basic groups, i.e. pH value of the medium [58].

Moreover, cellulose was grafted into acrylamide to prepare hydrogels for use in water and metal ions sorption [59]. The conditions of grafting were investigated and the sorption of different metal ions by grafted cellulose was investigated.

Cellulose derivatives were also applied for preparation of hydrogels used in water treatment and heavy metal removal. Hydroxyethyl cellulose (HEC) was grafted by acrylic acid (AA), and a mixture of acrylic acid (AA) and Acrylamide (Am) with two different AA/Am composition ratios (70/30 and 30/70) to produce HEC-g-AA (copolymer I) and of HEC-g-AA-Am copolymers (copolymer II & copolymer III) respectively, using potassium persulphate/ sodium bisulphate as redox initiation system [60]. The optimal conditions for removal of Ni from aqueous solutions using the prepared copolymers were studied through variation of pH, agitation time, and metal ion concentrations.

Starch or amyllum is a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. This polysaccharide is produced by most green plants as an energy store. It is the second abundant carbohydrate after cellulose and it exists in large amounts in staple foods such as potatoes, wheat, maize (corn), rice, and cassava, Figure 7.

It has unique structure since it consists of two types of molecules: the linear and helical amylose and the branched amylopectin, Figure 8. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight.

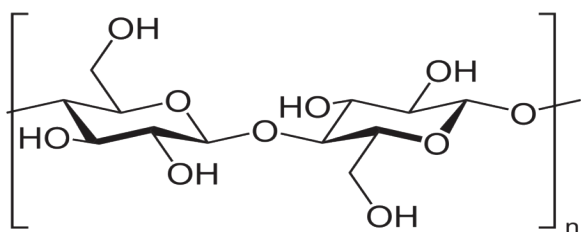


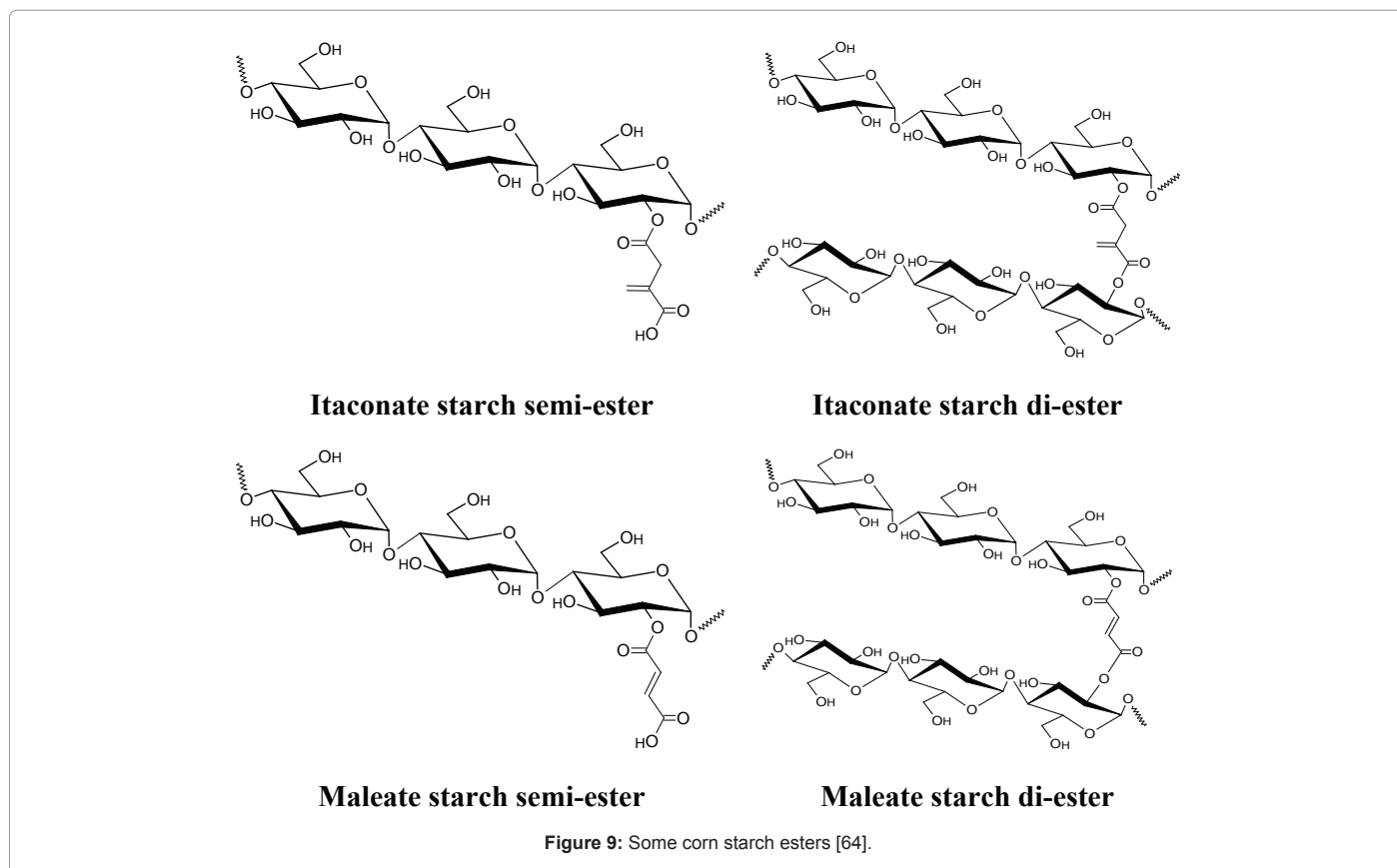
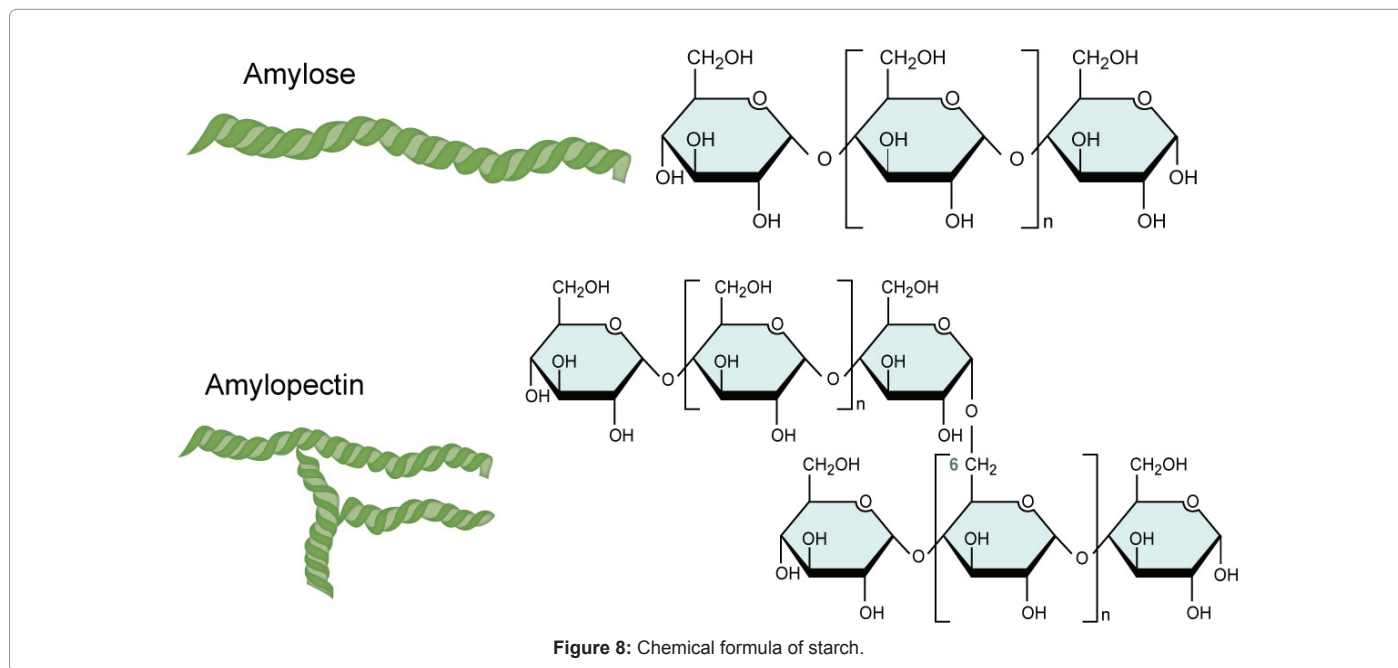
Figure 6: Chemical structure of cellulose.



Figure 7: Some sources of starch.

Intensive researches have been made to use starch and its modified products in removing heavy metals from wastewater. In this respect, Graft copolymers of cassava starch and acrylonitrile were synthesized in aqueous solution using ceric ammonium ion as the initiator. The grafted copolymer and the hydrolyzed graft copolymer (hydrogel)

were used as sorbent for the uptake of heavy metals from the aqueous media. The sorption capacity was evaluated by measuring the extent of sorption of nickel, copper, and lead metal ions, under equilibrium conditions [61].



Hydrogels based on saponified products of poly (acrylonitrile, AN)-starch composites were prepared, characterized and their water absorbency properties examined. The water absorbency properties of these hydrogels were found to rely on variables affecting the magnitudes of both polymerization and saponification. The prepared hydrogels were used to abstract some heavy metals from aqueous solution [62].

The removal efficiency of metal ions from their aqueous solution by crosslinked carboxy methyl corn starch was investigated [63]. Lead, cadmium, and mercury ions in water were almost completely removed when 1% starch (DS 0.081, pH 6.0) was used. Starch could be recovered by washing the metal ions from the complex with weak acid (pH 2.0) although the metal-binding activity of the starch was slightly reduced by this process.

Corn starch has been modified with naturally occurring compounds, maleic acid (MA) and itaconic acid (IA), by esterification in an aqueous medium catalyzed by NaOH to produce adsorbents for heavy metals removal in water. The effect of the mono and di-substitution with both acids, on the solubility and the swelling capacity of the modified starch has been investigated.

Additionally, the capability of the modified starches with itaconic acid to adsorb aqueous metal cations such as Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> was monitored and the data were compared with the native corn starch. The modified and native starches showed reasonable adsorption capacity for all the investigated cations. It was shown that the native

starch did not exhibit selectivity for any of the cations, whereas the itaconate starches removed higher content of Pb<sup>2+</sup> with the lowest hydration radius in comparison with other ions [64]. The structural formulae of the prepared esters are given below in Figure 9.

Starch was functionalized by acid hydrolysis and/or oxidized by nitrogen oxides to create carboxylic groups at C-6. Sorption of Cu<sup>2+</sup> ions was investigated as a function of hydrogel structure and environmental factors. Hydrogels exhibit structure-property relationship in the sorption of Cu<sup>2+</sup> ions. The hydrogel that showed the maximum ion uptake was used to study the effect of contact time, temperature, pH, and Cu<sup>2+</sup> ions concentration on the sorption capacity. Figure 10 shows the suggested interaction between the Cu<sup>2+</sup> ions and the carboxylated starch [65].

Furthermore, Khalil and Abdel-Halim [66] prepared anionic starch containing carboxyl groups and studied its utilization as chelating agent. Sorption efficiency of the alkali treated samples increased with increasing the acrylic content. The sorption values for different heavy metals depended on the metal ion and follow the order Hg<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Pb<sup>2+</sup>. The proposed structure of starch-metal chelates is given in Figure 11.

Recently, [67] prepared a novel cross-linked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) by grafting copolymerization reaction of corn starch, acrylamide (AM), and sodium xanthate using epichlorohydrin (EPI) as cross-linking reagent

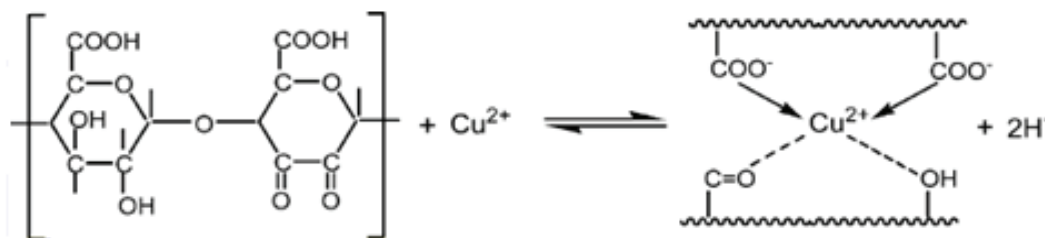
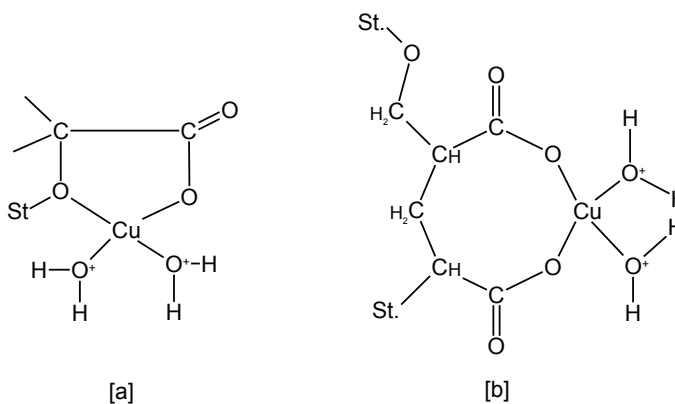


Figure 10: Possible interaction between the carboxylated starch and Cu<sup>2+</sup> ions [65].



[a] Proposed structure of the metal chelate with CMS carboxymethylate starch.

[b] Proposed structure of the metal chelate with alkali treated starch graft copolymer.

Figure 11: Proposed structure of starch-metal chelates.



and ceric ammonium nitrate (CAN) as initiator. The performance of the prepared hydrogel was investigated in wastewater treatment.

Lately, the adsorption processes of metal anions by amphoteric starch with quaternary ammonium and carboxymethyl groups have been investigated. Xu et al. [68] studied the removal of Pb (II) from aqueous solution by adsorption on a series of cross-linked amphoteric starches with different DS. It was found that the adsorption capacity was dependent on the pH of the solution, the dose of the cross-linked amphoteric starch, and the initial concentration of Pb (II) ion. The suggested reactions involved in the preparation process are shown in the following scheme (Figure 12).

Cross-linked amphoteric starches (CASS) were also used for removal of Cr (VI) from aqueous solution [69]. The adsorption process was found to be dependent on initial pH, concentration of Cr (VI), dose of CAS, and temperature. Furthermore, cross-linked starch phosphate carbamates were prepared and used to adsorb Cu (II) ions from an aqueous solution. Batch adsorption experiments were carried out as a function of adsorption time, adsorbents dose, pH, substitute groups' content, initial Cu(II) ions concentrations, and temperature [69,70].

### Removal of Heavy Metals by Nanocomposites based on Biopolymers

In spite of their ultimate importance, biopolymers when used in neat form they have a few hindrances that limit their utilization, for instance, their low surface area and difficulty of separation from solution. On the other hand, magnetic sorbents have a high surface area and are easy to be isolated from the medium and control in complex multiphase systems with an outer magnetic field. Hybrid composites (organic and inorganic) of high stability can be obtained by forming a polymer shield over an inorganic Nano material along these lines joining the upsides of both materials. Composites made from various polysaccharides comprise another class of naturally safe materials for diverse biological and industrial applications. It was stated that magnetic Nano-materials functionalized with biopolymers, for example, chitosan [71,72], gum Arabic [73],  $\beta$ -cyclodextrine [74] and cellulose [75], have been utilized for the exclusion of toxic metals from aqueous solution.

Very little work has been done for preparation of starch composite. In this respect, the starch extracted from potato peels was adapted with acrylic acid. Nanoparticles composed of modified starch polymer and  $\text{Fe}_3\text{O}_4$  (modified potato starch-magnetic nanoparticles, MPS-MNPs) were synthesized. The prepared Nanoadsorbents were used for selective abstraction of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  ions from water [76]. The grafting reaction of acrylic acid onto starch is provided in.

Starch-graft copolymers are strongly required in industry due to their low cost and biodegradability and thus environmental friendly. Starch-graft copolymers have become the focal point for the preparation inorganic-organic superabsorbent Nanocomposite because of due to environmental concerns.

It has been shown that starch can effectively stabilize Nanoscale magnetite particles, and starch-stabilized magnetite nanoparticles (SMNP) are potent sorbents for in situ remediation of arsenic-contaminated soils [77].

An et al. [78] developed a new engineered strategy to minimize the production and arsenic leachability of the process waste left behind. They prepared and tested a new class of starch-bridged magnetite nanoparticles for removal of arsenate.

A low-cost, "green" starch at 0.049% (w/w) was used as an additive to depress the agglomerating of the nanoparticles.

Very recently, synthetic nanoscale zerovalent iron (NZVI) stabilized with two polymers, Starch and Carboxymethyl cellulose (CMC) were investigated and compared for their capability in removing As (III) and As (V) from aqueous solutions as the most promising iron nanoparticles form for arsenic removal [79]. Furthermore, [80] studied the removal of copper (II) and lead(II) ions from aqueous solutions by Starch-graft-acrylic acid/montmorillonite (S-g-AA/MMT) Nanocomposite. Several factors affecting removal efficiency were investigated. They include treatment time with the solution, initial pH of the solution, initial metal ion concentration, and MMT content.

### Future Trends

Guar gum as a natural environmentally friendly biopolymer

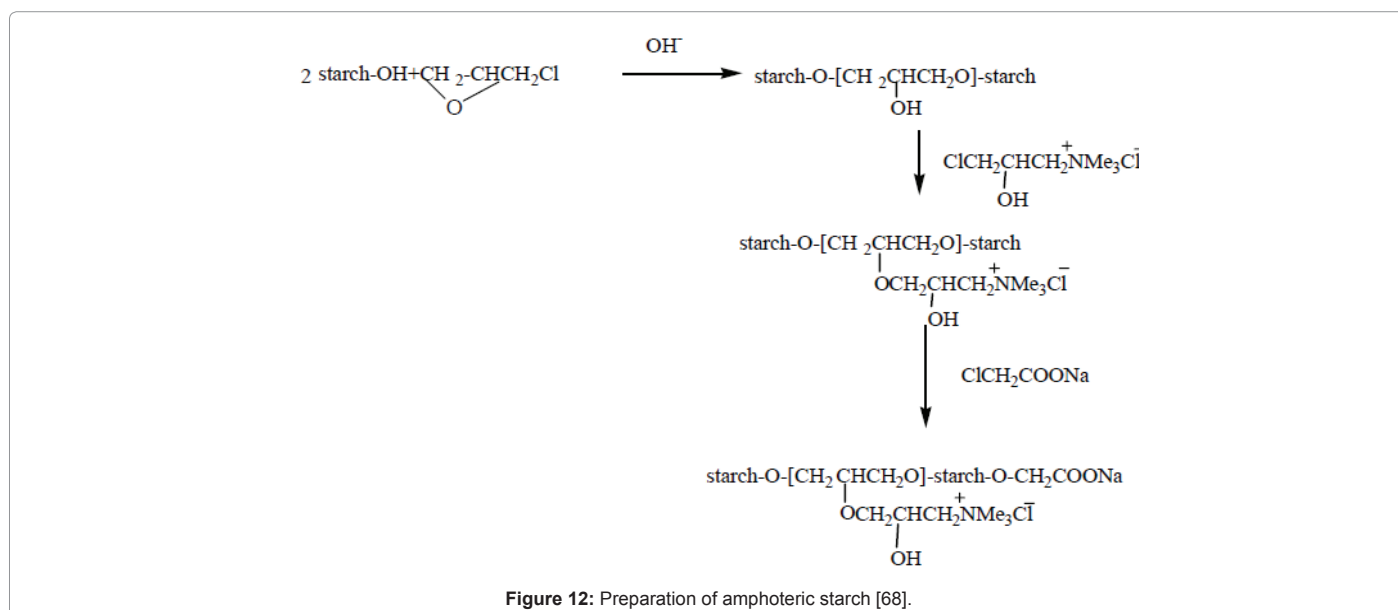


Figure 12: Preparation of amphoteric starch [68].

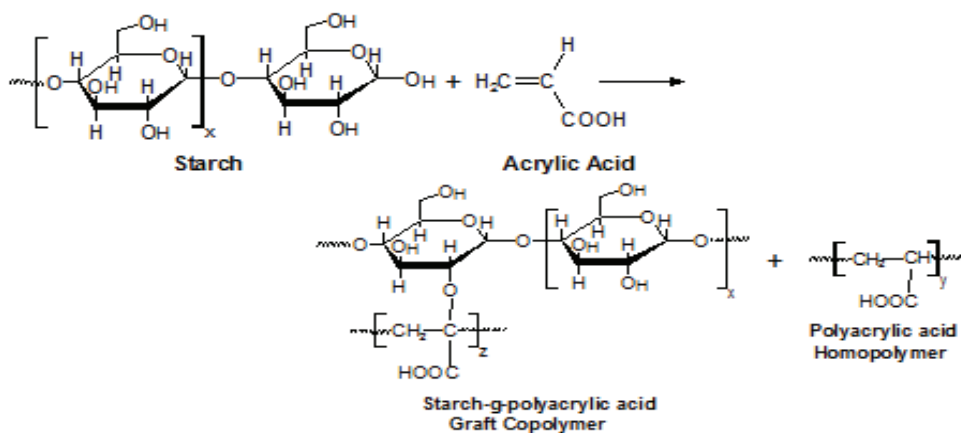


Figure 13: Modification of starch by acrylic acid [76].

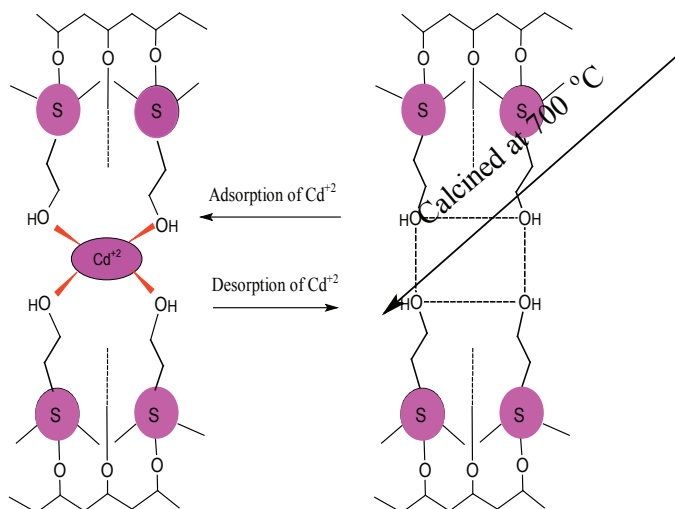
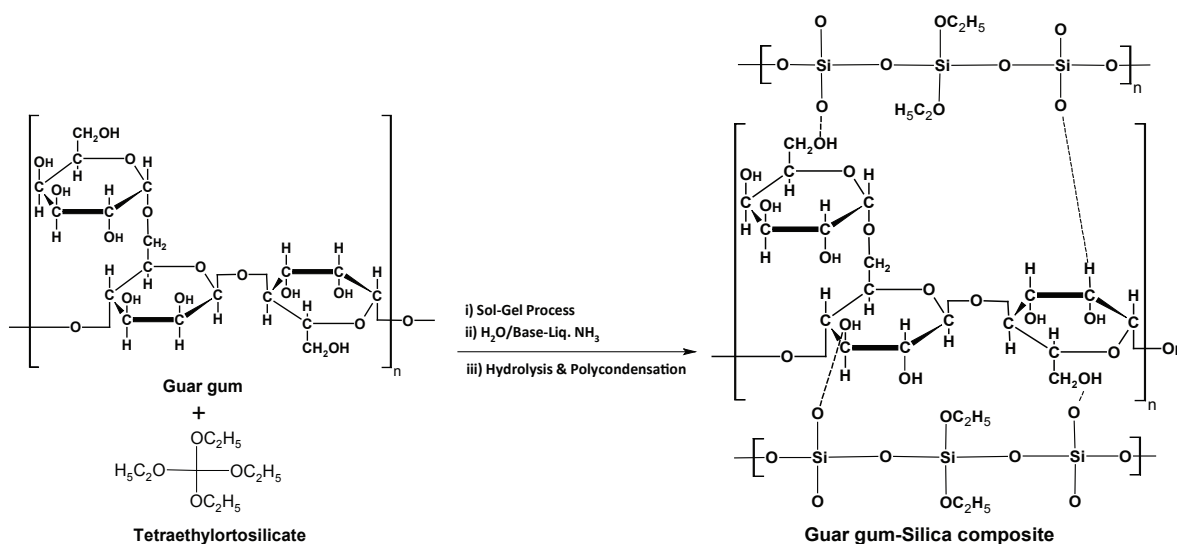


Figure 14: The suggested mechanisms of removal of  $Cd^{2+}$  by guar gum silica nanocomposites.

broke ranks and quickly found its place among the most important carbohydrates. It is now used effectively in water treatment. In this respect, guar gum silica nanocomposites were effectively used in removal of Cd (II) from aqueous solution. Maximum removal was attained at pH 8, contact time 2 hours, Cd (II) concentration 100 mg/L, temperature 30°C and adsorbent dose 10 mg [81]. The suggested mechanisms are illustrated in Figure 14.

As a natural biopolymer, guar gum (GG) was covalently grafted [82] on the surfaces of multiwall carbon nanotube (MWCNT) to gain GG-MWCNT composite. Then iron oxide nanoparticles were covered by the

GG-MWCNT to prepare the magnetic GG-MWCNT-Fe<sub>3</sub>O<sub>4</sub>.

Furthermore, Polyacrylamide chains were grafted onto CMG backbone to obtain a novel polymeric flocculant based on polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM). The flocculation characteristics of grafted and ungrafted polysaccharides had been evaluated in kaolin suspension and municipal sewage wastewater.

A novel hydrogel [83] based on guar gum (GG) was prepared by the polymerization grafting of acrylamide onto guar gum, using potassium bromate/thiourea dioxide redox system for promoting the polymerization reaction. The so prepared polyacrylamide/guar gum graft copolymer was then cross-linked with glutaraldehyde (GA) to gain the sorbent material in the form of hydrogel. The obtained hydrogel was used for removal of hexavalent chromium ion (Cr (VI)) from aqueous solution.

Khan et al. [84] prepared Guar gum-nano zinc oxide (GG/nZnO) as economic and ecofriendly biocomposite. These composites were used adsorbents for enhanced removal of Cr (VI) from aqueous solution. The data revealed that the maximum adsorption was achieved at 50 min contact time, 25 mg/L Cr (VI) conc., 1.0 g/L adsorbent dose and 7.0 pH.

Our current research targets are to prepare multi-purpose interpenetrating polymer networks based on biopolymers for environmental and economical considerations.

## Conclusion

Green chemistry approach focuses on replacing the synthetic polymers by naturally occurring materials by maximizing the utilization of biopolymers in different industrial, biological, and medical applications for economical and environmental concerns. In this respect, the application of biopolymers in water treatment was thoroughly studied.

Sources and hazardous effects of heavy metals were mentioned and conventional technologies for waste water treatment were reviewed. It was established that alleviating the environmental pollution of heavy metals by adsorption is more beneficial than other methods. Removal of heavy metals by different agricultural wastes was mentioned. Furthermore, the application of chemically modified agricultural wastes in water treatment was reviewed. Finally, utilization of nanocomposites based on biopolymers was discussed.

## References

1. Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J Hazard Mat* 97: 219-243.
2. Sergeev VI, Shimko TG, Kuleshova ML, Maximovich NG (1996) Groundwater protection against pollution by heavy metals at waste disposal sites. *Wat Sci Tech* 34: 383-387.
3. Some L, Lagerkvist R (2002) Sources of heavy metals in urban wastewater in Stockholm. *Sci Tot Environ* 298: 131-145.
4. Gupta VK, Nayak A, Agarwal S (2015) Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environ Eng Res* 20: 1-18.
5. Horsfall Jr M, Horsfall MN, Spiff AI (1999) Speciation of heavy metals in intertidal sediments of the Okrika river system, Rivers State Nigeria. *Bullet Chem Soc Eth* 13: 1-10.
6. Sekhar KC, Kamala CT, Chary NS, Anjaneyulu Y (2003) Removal of heavy metals using a plant biomass with reference to environmental control. *Inter J Min Pro* 68: 37-45.
7. Trueby P (2003) Impact of heavy metals on forest trees from mining areas. In: *International Conference on Mining and The Environment III*, Sudbury, Ontario, Canada.
8. Wang D, Sun W, Xu Y, Tang H, Gregory J (2004) Speciation stability of inorganic polymer flocculant PACI Colloids and Surfaces. *Physicochem Eng Asp* 243: 1-10.
9. Abas SNA, Ismail MHS, Kamal ML, Izhar S (2013) Adsorption process of heavy metals by low cost adsorbent: A review. *World App Sci J* 28: 1518-1530.
10. Aroua MK, Zuki FM, Sulaiman NM (2007) Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration. *J Hazard Mat* 147: 752-758.
11. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. *J Environ Manag* 92: 407-418.
12. Ho Y-S, McKay G (1999) Pseudo-second order model for sorption processes. *Pro Biochem* 34: 451-465.
13. Petrov S, Nenov V (2004) Removal and recovery of copper from wastewater by a complexation-ultrafiltration process. *Desal* 162: 201-209.
14. Williford C, Bricka RM (2000) Physical separation of metal-contaminated soils *Environmental Restoration of Metals-Contaminated Soils*. 1st edn., CRC Press LLC, Boca Raton, FL 121-165.
15. Gupta VK, Ali I, Saleh TA, Nayak A, Agarwal S (2012) Chemical treatment technologies for waste-water recycling: An overview. *RSC Adv* 2: 6380-6388.
16. Saleh TA, Gupta VK (2012) Column with CNT/magnesium oxide composite for lead (II) removal from water. *Environ Sci Pollut Res* 19: 1224-1228.
17. Babel S, Kurniawan TA (2005) Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. In: *Southeast Asian Water Environment 1: Selected Papers from the First International Symposium on Southeast Asian Water Environment (biodiversity and Water Environment)*, Bangkok, Thailand.
18. Gupta V, Nayak A (2012) Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe<sub>2</sub>O<sub>3</sub> nanoparticles. *Chem Eng J* 180: 81-90.
19. Gupta V, Srivastava S, Mohan D, Sharma S (1998) Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions. *Waste Management* 17: 517-522.
20. Gupta VK, Agarwal S, Saleh TA (2011) Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J Hazard Mat* 185: 17-23.
21. Shah BA, Shah AV, Singh RR (2009) Sorption isotherms and kinetics of chromium uptake from wastewater using natural sorbent material. *Inter J Environ Sci Tech* 6: 77-90.
22. Tripathi A, Ranjan MR (2015) Heavy Metal Removal from Wastewater Using Low Cost Adsorbents. *J Biore Biodeg* 6: 315.
23. Bose P, Bose MA, Kumar S (2002) Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. *Advances Environ Res* 7: 179-195.
24. Reddad Z, Gerente C, Andres Y, Le Cloirec P (2002) Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ Sci Technol* 36: 2067-2073.
25. Bhattacharya Ak, Mandal SN, Das SK (2006) Adsorption of Zn (II) from aqueous solution by using different adsorbents. *Chem Eng j* 123: 43-51.
26. Eccles H (1999) Treatment of metal-contaminated wastes: why select a biological process? *Trends Biotechnol.* 17: 462-465.

27. Orhan Y, Büyükgüngör H (1993) The removal of heavy metals by using agricultural wastes. *Water Sci Tech* 28: 247-255.
28. Ahluwalia SS, Goyal D (2005) Removal of heavy metals by waste tea leaves from aqueous solution. *Eng Life Sci* 5: 158-162.
29. Ajmal M, Rao RA, Anwar S, Ahmad J, Ahmad R (2003) Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. *Bioresour Technol* 86: 147-149.
30. Marshall WE, Champagne ET, Evans WJ (1993) Use of rice milling byproducts (hulls & bran) to remove metal ions from aqueous solution. *J Environ Sci Health Part A* 28: 1977-1992.
31. Tarley CRT, Arruda Zezzi MAZ (2004) Biosorption of heavy metals using ricemilling by-products. Characterisation and application for removal of metals from aqueous solutions *Chemosph* 54: 987-995.
32. Chubar N, Carvalho JR, Correia MJN (2003) Cork biomass as biosorbent for Cu (II), Zn (II) and Ni (II) Colloids and Surfaces. *Physicochem Eng Asp* 230: 57-65.
33. Melo JS, D'souza SF (2004) Removal of chromium by mucilaginous seeds of *Ocimum basilicum*. *Bioresour tech* 92: 151-155.
34. Babel S, Kurniawan TA (2004) Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan *Chemosph* 54: 951-967.
35. Bailey SE, Olin TJ, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals *Water Research*. 33: 2469-2479.
36. Bulut Y, Tez Z (2003) Removal of heavy metal ions by modified sawdust of walnut. *Freseni Environ Bullet* 12: 1499-1504.
37. Oliveira WE, Franca AS, Oliveira LS, Rocha SD (2008) Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *J Hazard Mat* 152: 1073-1081.
38. Saeed A, Akhter MW, Iqbal M (2005) Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separat purif Tech* 45: 25-31.
39. Johnson PD, Watson MA, Brown J, Jefcoat IA (2002) Peanut hull pellets as a single use sorbent for the capture of Cu (II) from wastewater. *Waste Manage* 22: 471-480.
40. Ajmal M, Rao RA, Ahmad R, Ahmad J (2000) Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. *J Hazard Mat* 79: 117-131.
41. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour technol* 98: 2243-2257.
42. Mane P, Bhosle AB, Jangam CM, Vishwakarma CV (2011) Bioadsorption of selenium by pretreated algal biomass. *Advances in applied science research* 2: 202.
43. Moustafa M, Idris G (2003) Biological removal of heavy metals from wastewater. *Alexand Eng J* 42: 767-771.
44. Wu J, Zhang H, He PJ, Yao Q, Shao LM (2010) Cr (VI) removal from aqueous solution by dried activated sludge biomass. *Journal of hazardous materials* 176: 697-703.
45. Cay S, Uyanik A, Ozasik A (2004) Single and binary component adsorption of copper (II) and cadmium (II) from aqueous solutions using tea-industry waste. *Separat Purif Tech* 38: 273-280.
46. Kumar U, Bandyopadhyay M (2006) Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour Tech* 97: 104-109.
47. Malkoc E, Nuhoglu Y (2005) Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *J Hazard Mater* 127: 120-128.
48. Malkoc E, Nuhoglu Y (2007) Potential of tea factory waste for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies. *Separat Purif Tech* 54: 291-298.
49. Ozer A, Ozer D, Ozer A (2004) The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters. *Proce biochem* 39: 2183-2191.
50. Villaescusa I, Fiol N, Martinez M, Miralles N, Poch J, et al. (2004) Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Res* 38: 992-1002.
51. Jafar A, Kurniawan T (2010) In: RR Lovely (Ed.) Low-cost process for heavy metal removal. Adsorbents for heavy metals uptake sorbent from environmental microbe-metal interaction aqueous solutions, *Desalination* 235: 330-339.
52. Sud D, Mahajan G, Kaur MP, (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review. *Bioresour Tech* 99: 6017-6027.
53. Demirbas A (2005) Estimating of structural composition of wood and non-wood biomass samples. *Ener Sour* 27: 761-767.
54. Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog Poly Sci*. 30: 38-70.
55. Mahajan G, Sud D (2012) Modified agricultural waste biomass with enhanced responsive properties for metal-ion remediation: a green approach. *Appl Water Sci* 2: 299-308.
56. Farag RK, EL-Saeed SM, Abdel-Raouf ME (2015) Synthesis and investigation of hydrogel nanoparticles based on natural polymer for removal of lead and copper (II) ions *Desalination Water Treatm* 57: 16150-16160.
57. Tripathy J, Mishra DK, Behari K (2009) Graft copolymerization of N-vinylformamide onto sodium carboxymethylcellulose and study of its swelling, metal ion sorption and flocculation behavior. *Carbohydr Polym* 75: 604-611.
58. Kamel S, Hassan E, El-Sakhawy MS (2006) Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions. *J Appl Polym Sci* 100: 329-334.
59. Nada AM, Alkady MY, Fekry HM (2008) Synthesis and characterization of grafted cellulose for use in water and metal ions sorption. *Bio Resour* 3: 46-59.
60. Samaha SH, Essa DM, Osman EM, Ibrahim SF (2015) Synthesis and characterization of Hydroxyethyl cellulose grafted copolymers and its application for removal of nickel ions from aqueous solutions. *Int J Eng Inn Res* 4: 645-653.
61. Ekebafé LO, Ogbeifun DE, Okieimen FE (2012) Removal of heavy metals from aqueous media using native cassava starch hydrogel African. *J Environ Sci Tech* 6: 275-282.
62. Hashem A, Affif M, El-Alfy E, Hebeish A (2005) Synthesis, characterization and saponification of poly (AN)-starch composites and properties of their hydrogels. *Am J Appl Sci* 2: 614-621.
63. Kim BS, Lim ST (1999) Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch. *Carbohydr Polym* 39: 217-223.
64. Soto D, Urdaneta J, Pernia K, Leon O, Munoz-Bonilla A, et al. (2016) Removal of heavy metal ions in water by starch esters. *Starch* 68: 37-46.
65. Chauhan K, Chauhan GS, Ahn JH (2010) Novel polycarboxylated starch-based sorbents for Cu<sup>2+</sup> ions. *Indust Eng Chem Res* 49: 2548-2556.
66. Khalil MI, Abdel-Halim MG (2001) Preparation of anionic starch containing carboxyl groups and its utilization as chelating agent. *Starch* 53: 35-41.
67. Chang Q, Hao X, Duan L (2008) Synthesis of crosslinked starch-graft-polyacrylamide-co-sodium xanthate and its performances in wastewater treatment. *J Hazard Mater* 159: 548-553.
68. Xu S-M, Feng S, Peng G, Wang JD, Yushan A (2005) Removal of Pb (II) by crosslinked amphoteric starch containing the carboxymethyl group. *Carbohydr Polym* 60: 301-305.
69. Xu SM, Zhang SF, Lu RW, Yang JZ, Cui CX (2003) Study on adsorption behavior between Cr (VI) and crosslinked amphoteric starch. *J Appl Poly Sci* 89: 263-267.
70. Guo L, Zhang SF, Ju BZ, Yang JZ (2006) Study on adsorption of Cu (II) by water-insoluble starch phosphate carbamate. *Carbohydr Polym* 63: 487-492.
71. Pineda MG, Torres S, López LV, Fernández S, Saade H, et al. (2014) Chitosan-coated magnetic nanoparticles prepared in one-step by precipitation in a high-aqueous phase content reverse microemulsion. *Molecules* 19: 9273-9287.
72. Tran HV, Tran LD, Nguyen TN (2010) Preparation of chitosan/magnetite composite beads and their application for removal of Pb (II) and Ni (II) from aqueous solution. *Mat Sci Eng* 30: 304-310.
73. Banerjee SS, Chen DH (2007) Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. *J Hazard Mater* 147: 792-799.
74. El-Kafrawy AF, El-Saeed SM, Farag RK, El-Saied HAA, et al. (2016) Adsorbents



- based on natural polymers for removal of some heavy metals from aqueous solution. *Egypt J Petrol*.
75. Carpenter AW, de Lannoy CF, Wiesner MR (2015) Cellulose nanomaterials in water treatment technologies. *Environ Sci Tech* 49: 5277-5287.
76. Abdul-Raheim ARM, El-Saeed Shimaa M, Farag Reem K, Abdel-Raouf Manar E (2016) Low cost biosorbents based on modified starch iron oxide nanocomposites for selective removal of some heavy metals from aqueous solutions. *J VBRI Pres* 7: 402-409.
77. Zhang M, Pan G, Zhao D, He G (2011) XAFS study of starch-stabilized magnetite nanoparticles and surface speciation of arsenate. *Environ pollut* 159: 3509-3514.
78. An B, Liang Q, Zhao D (2011) Removal of arsenic (V) from spent ion exchange brine using a new class of starch-bridged magnetite nanoparticles. *Water Res* 45: 1961-1972.
79. Mosaferi M, Nemati S, Khataee A, Nasseri S, Hashemi AA (2014) Removal of Arsenic (III, V) from aqueous solution by nanoscale zero-valent iron stabilized with starch and carboxymethyl cellulose. *J Environ Health Sci Eng* 12: 74.
80. Guclu G, Emik S, Lyim TB, Ozgumus S, Ozyurek M, et al. (2010) Removal of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions from aqueous solutions by starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite hydrogels. *Polymer bulletin* 65: 333-346.
81. Singh V, Singh SK (2015) Cadmium (II) removal from aqueous solution using guar gum-silica nanocomposite. *Adv Mater Lett* 6: 607-615.
82. Yan L, Chang PR, Zheng P, Ma X (2012) Characterization of magnetic guar gum-grafted carbon nanotubes and the adsorption of the dyes. *Carbohydr Polym* 87: 1919-1924.
83. Abdel-Halim ES, Al-Deyab SS (2011) Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion. *Carbohydr Polym* 86: 1306-1312.
84. Khan TA, Nazir M, Ali I, Kumar A (2013) Removal of Chromium (VI) from aqueous solution using guar gum-nano zinc oxide biocomposite adsorbent. *Arab J Chem*.
85. Chen Q, Luo Z, Hills C, Xue G, Tyrer M (2009) Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide. *Water Res* 43: 2605-614.
86. Kousi P, Remoudaki E, Hatzikioseyan A, Tsezos M (2007) A study of the operating parameters of a sulphate-reducing fixed-bed reactor for the treatment of metal-bearing wastewater. *Adv Mat Res* 20-21: 230-234.
87. Ku Y, Jung I-L (2001) Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. *Water Res* 35: 135-142.
88. Dizge N, Keskinler B, Barlas H (2009) Sorption of Ni (II) ions from aqueous solution by Lewatit cation-exchange resin. *J Hazard Mat* 167: 915-926.
89. Hamdaoui O (2009) Removal of copper (II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling. *J Hazard mat* 161: 737-746.
90. Chen L, Chen Q (2003) Industrial application of UF membrane in the pretreatment for RO system. *J Memb Sci Technol* 4: 009.
91. Gunatilake SK (2015) Methods of Removing Heavy Metals from Industrial Wastewater. *J Multidis Eng Sci Studi* 1.
92. Kurniawan TA, Chan GYS, Lo W-H, Babel S (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chem Eng J* 118: 83-98.
93. Benefield LD, Judkins JF, Weand BL (1982) Process chemistry for water and wastewater treatment. Prentice Hall Inc.
94. Lopez-Maldonado EA, Oropeza-Guzman MT, Jurado-Baizaval JL, Ochoa-Teran A (2014) Coagulation-flocculation mechanisms in wastewater treatment plants through zeta potential measurements. *J Hazard Mate* 279: 1-10.
95. Aman T, Kazi AA, Sabri MU, Bano Q (2008) Potato peels as solid waste for the removal of heavy metal copper (II) from waste water/industrial effluent. *Colloid Surf B Bio* 63: 116-121.
96. Igwe JC, Ogunewe DN, Abia AA (2005) Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non-aqueous solution by maize cob and husk. *Afri J Biotech* 4: 1113-1116.
97. Abdel-Ghani NT, Hefny M, El-Chaghaby GAF (2007) Removal of lead from aqueous solution using low cost abundantly available adsorbents. *Intern J Environ Sci Tech* 4: 67-73.
98. Banerjee K, Ramesh ST, Gandhimathi R, Nidheesh PV, Bharathi KS (2012) A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. *Iran J Energy Environ* 3: 143-156.
99. Kanawade SM, Gaikwad RW (2011) Removal of zinc ions from industrial effluent by using cork powder as adsorbent. *Intern J Chem Eng Appl* 2: 199.
100. Sheth KN, Soni VM (2004) Comparative study of removal of Cr (VI) with PAC, GAC and adsorbent prepared from tobacco stems. *J Indust Pollu Cont* 20: 45-52.