

Comparative Analysis of Various Adsorbents used for Bioremediation of Copper from the Aqueous Environment

Akshaya Priyah¹, Vignesh Kumar C^{2*}
akshayapriyah2000@gmail.com, cvk.bio@psgtech.ac.in

Department of Biotechnology, PSG College of Technology, Peelamedu, Coimbatore 641004, India¹

Abstract. Aqueous environments are facing many challenges. The most important challenge among them is the pollution due to heavy metals. These heavy metals which is left untreated in aqueous environments can cause profound impacts in all living creatures which is in contact with untreated water. Of many heavy metals, copper is found in large amount in aqueous environments. Therefore, a need arises to tackle this issue of copper contamination. There are various ways to remove heavy metals. Of these, bioadsorption is gaining more importance in removing heavy metals from aqueous environments due to its various advantages and its increased capacity of adsorbing copper ions. Bioadsorption is a surface phenomenon where the heavy metals are adsorbed to the adsorbent (biological material), thereby facilitating removal of heavy metal from aqueous environments. Biological material can include agricultural waste residues, microbial cells like fungi, yeast, bacteria, etc. The main focus of this study is to compare and review on various adsorbents used for removing copper based on its efficiency, cost of production and availability.

Keywords: Heavy metals, aqueous environments, copper, bioadsorption, adsorbents.

1 Introduction

Environmental pollution is one of the increasing problems that is found everywhere today. Both organic and inorganic pollutants are called as environmental pollutants. Organic pollutants can be degradable but inorganic pollutants like heavy metals cannot be degraded and so it continues to stay in environment for a long time and poses a serious threat not only to marine life but also to humans and other living creatures. Heavy metals include copper, lead, zinc, cadmium, chromium, arsenic, mercury etc. Of these, copper is the most widely used heavy metal. It can be released accidentally or due to human induced activities like mining or from a large number of electrical industries. It can also be from battery making industries, while performing copper electroplating, from copper smelting plants and other activities. This metal when released into aqueous bodies can become a part of food chain which can lead to bio magnification and can cause detrimental to living creature. The toxic nature of copper can causes various irritations in skin, affects the respiratory organ of fishes (gills), interferes in their smelling capacity which helps them to find food for them, etc. On an overall, it has the most tremendous and lethal effect on all life forms.

TABLE 1 : MPC Standards of copper

Element	MPC in water(mg/l)	MPC ^a in waste waters(mg/l)	MPC ^b in waste waters(mg/l)
Copper	0.1	1.0	0.1

Copper consumption (Table 1) in high amounts can cause various disorders by forming various deposits in kidney,liver, brain and other vital organs in humans (Jaishankar *et.al.*, 2014). Various techniques used in removing copper from aqueous environments includes precipitation, membrane separation, floatation, biosorption, adsorption, ion exchange (Fig. 1).

Fig. 1:Various mechanism of Biosorption:Biosorption can be done in many ways like ion exchange,chelation,surface adsorption,electrostatic interaction.

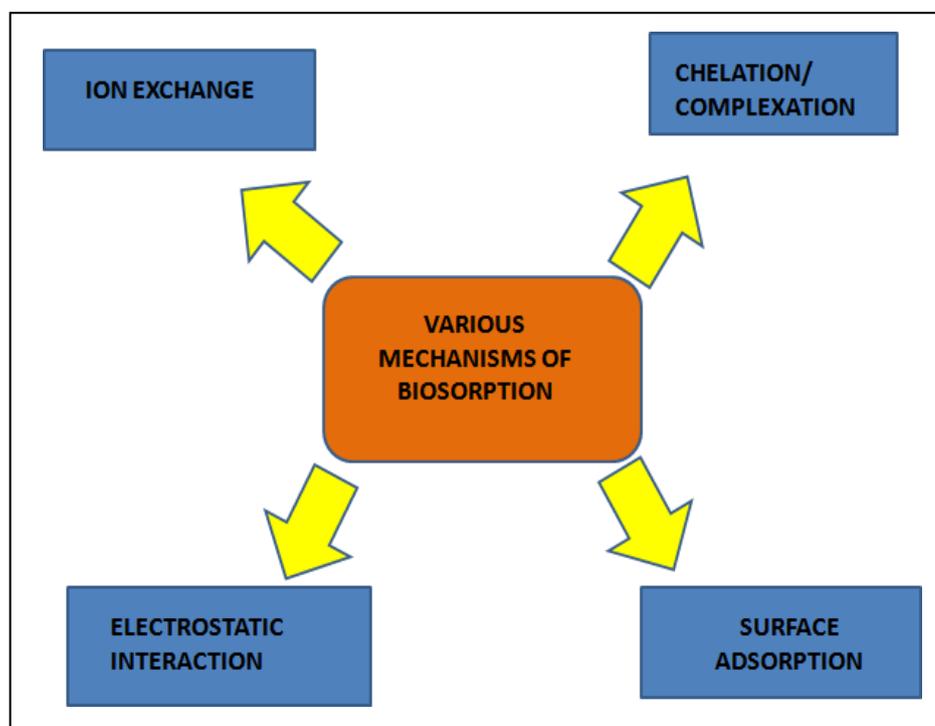
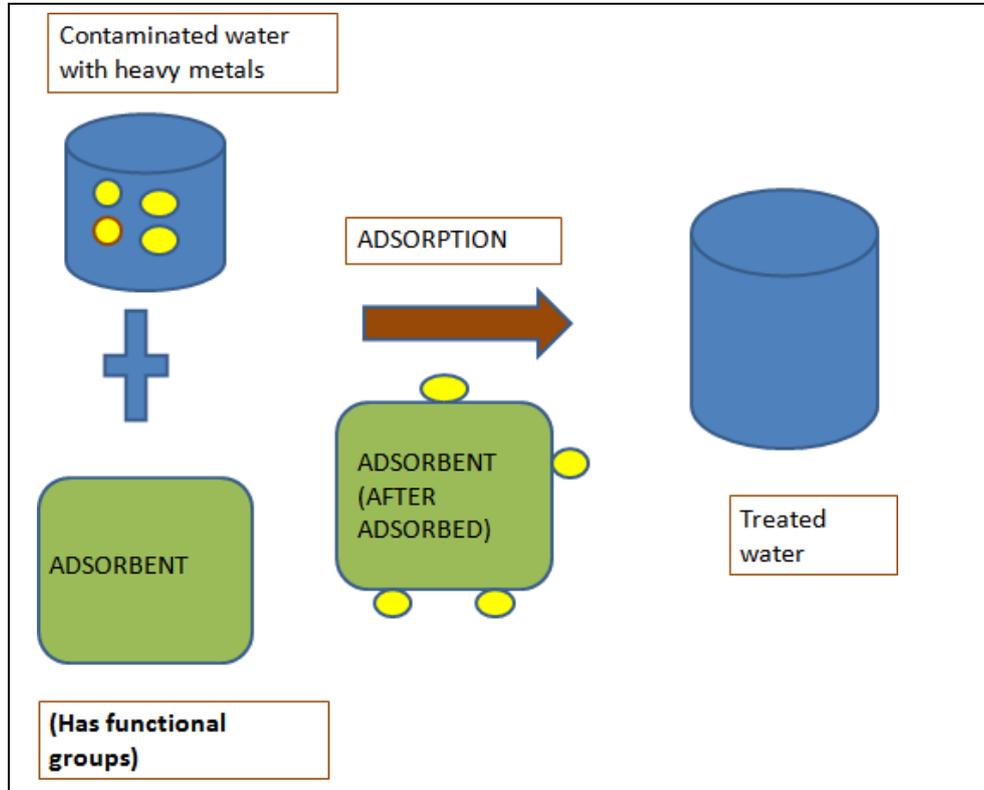


Fig. 2: Overview of Adsorption.



When heavy metals contaminated water is in contact with bioadsorbent, heavy metals gets adsorbed on these adsorbent as they contain suitable functional groups and aids in removing heavy metals from water.

Of these adsorption is most trusted method due to its various advantages. Adsorption is a process of removing pollutant from liquid environments using solid through either physical or chemical interactions (fig. 2). Adsorbents are substances to which the pollutant is being adhered to as a result of adsorption process. Different types of adsorbents are used in removing heavymetals. Adsorbents from various sources can be classified into natural based and microbial based adsorbents. Natural based adsorbents are adsorbents that are obtained from nature which is either treated or untreated and subjected for adsorption process (Ojedokun *et.al.*, 2015 and Soumi *et.al.*, 2021). Microbial based adsorbents are microbial cells like algae, mushroom, bacteria, etc. that are grown and used for adsorbing copper.

2 Natural based adsorbents

Natural adsorbents are used in two ways. They are unmodified and modified adsorbents. Unmodified adsorbents are used as such in adsorption process where as modified adsorbents were converted to certain form and then subjected to treatments of activation and adsorption process like activated carbon (O.Yavuz *et.al.*, 2002 and Babel *et.al.*, 2013).

3 Unmodified Natural adsorbents

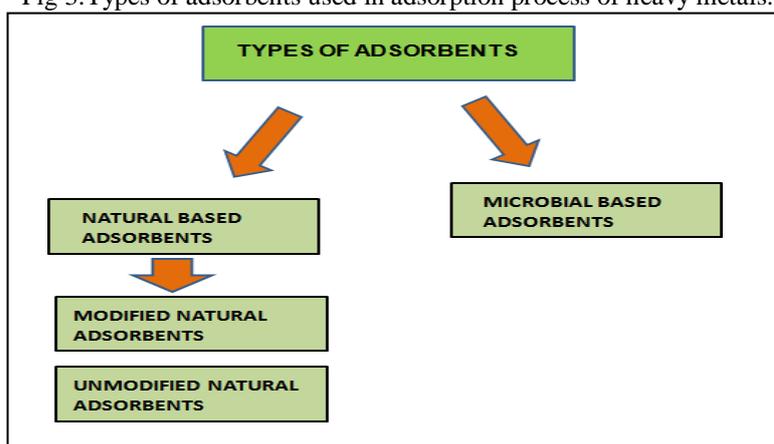
Some of the unmodified natural adsorbents include zeolite, flyash, sawdust, dolomite, clays. These adsorbents since as they were not subjected to any treatment process showed very less efficiency in copper adsorption (Fig. 3). Even though certain minerals like dolomite, haematite, zeolites are porous in nature but they seem to exhibit poor adsorption and this seems that there is a need for a treatment to increase their adsorption capability (D.B.Singh, *et.al.*, 1998). Natural dolomite was more efficient in adsorption than haematite which showed adsorption capacity of 0.244mg/g only. Natural dolomite had a adsorption capacity of 1.02 mg/g. Among zeolites, haematites, flyash and natural dolomite, the zeolites showed more efficiency of adsorption of copper of 1.64 mg/g. But, the adsorption efficiency of these adsorbents are very low when compared to other natural unmodified adsorbents like clay and saw dust. Saw dust showed a good adsorption efficiency of 13.8mg/g. Saw dust was more efficient in copper adsorption than clay which showed only 9.58mg/g of adsorption of copper ions. Clay showed increased adsorption of copper ions than flyash. So, researchers wanted to increase these adsorbents efficiency of adsorption of copper ions, thus they subjected them to various modifications. The data of various adsorbents used without any modifications and their adsorption efficiencies are listed in table 2.

Table 2: Natural adsorbents and their modification

Name Of the adsorbent	Nature of the Modification	Adsorption efficiency(mg/g)	Reference
Zeolite	Natural	1.64	Babelet.al., (2013)
Clays	Natural	9.58	Abolinio <i>et.al.</i> , (2003)
fly ash	Natural	1.39	Panday <i>et.al.</i> , (1985)
Sawdust	Natural	13.8	Ajmalet.al., (1998)
Haematite	Natural	0.2444	D.B.Singh <i>et.al.</i> , (1998)
natural dolomite	Natural	1.02	O.Yavuz <i>et.al.</i> , (2002)
Orange peel	Interaction of methyl acrylate	289	Feng <i>et.al.</i> , (2009)
Rubber wood sawdust	activated with phosphoric acid	15.72	Helenet.al., (2005)
Alginate	functionalized with nano particles	52.67	Alina <i>et.al.</i> , (2020)
Flyash	treated with NaOH	64	Wanget.al., (2006)
<i>Saccharomyces cerevisease</i>	Heat killed	9.01	Machado <i>et.al.</i> , (2009)

soyhulls	Base extracted followed by citric acidmodification	154.90	Wartelle <i>et.al.</i> , (2000)
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Fig 3:Types of adsorbents used in adsorption process of heavy metals.



4 Modified natural adsorbents

Since naturally available unmodified adsorbents showed very poor adsorption capacity of copper of less than 20mg/g, to increase their capacity of adsorption towards copper, they were subjected to various modifications. Mostly the adsorbents were converted into activated carbon and they were subjected to acidic or alkaline treatments for its enhancement. This type of modified adsorbents showed little more efficiency in adsorbing copper. Since by chemical treatment, we are imparting functional groups that interact and binds to copper ions. The flyash when used without any treatments gave only an adsorption efficiency of 1.39 mg/g but when they were treated with sodium hydroxide, the adsorption of copper increased from 1.39 to 64 mg/g (Wang *et.al.*, 2007). This is due to that sodium hydroxide imparted negatively charged hydroxyl groups making the molecule to bind it to positively charged copper ions. When the saw wood of rubber is used, only 13.8mg/g of copper adsorption was accounted but when they were subjected to phosphoric acid treatment, it showed increase in adsorption of copper from 13.8 to 15.72mg/g (Helen Kalavathy *et.al.*, 2006). Clay showed adsorption efficiency of 9.58 but when it is activated via hydrochloric acid treatment, it showed 83.3 mg/g in adsorbing copper.

Modification of the adsorbents are done by imparting negatively charged groups like carboxyl's (citric acid) or hydroxyl's or phosphate (phosphoric acid) etc. Citric acid modified adsorbents showed increased adsorption towards copper when compared to other treatments (BoZhu *et.al.*, 2008 and L.H. Wartelle *et.al.*, 2000.) since a molecule of citric acid gives three carboxyl groups thus facilitating increased adsorption. One such example of citric acid modified adsorbent is soyhulls. Soyhulls are cheap source of raw material for adsorption. Despite this, India is the fourth largest producer of soybeans, this gives an idea of large availability of soyhulls. And these soyhulls when base extracted and subjected to citric acid, it showed an enormous increased adsorption of copper that is 154 mg/g. This citric acid modified

soyhulls also has an adsorption towards other heavy metal like lead,zinc.Thus due to its vast availability in the country, low cost of raw material,capacity of adsorbing various heavy metals on its surface makes soyhull a good candidate to remove aqueous environments that are contaminated with heavy metals via adsorption.Orange peel showed a good increased adsorption of copper when they were cross linked with methyl acrylate.It showed adsorption capacity of 289mg/g.The adsorption capacity of chemically modified orange peel was more efficient then citric acid modified soyhulls. When iron nanoparticles are functionalized with alginate particles,it showed copper adsorption capacity of 52.67mg/g.But this capacity of adsorption of copper ions was much lower than the adsorption capacity of citric acid modified soyhulls and chemically modified orange peel.Iron nanoparticles functionalized with alginate was more efficient than soyhull based alginate bioadsorbent.The information of various modified adsorbents, their adsorption capacity of copper and the strategy used for adsorption of copper are mentioned in table 2.

5 Microbial adsorbents

After natural modified and unmodified types of adsorbents, the most popular adsorbent that was appreciated are the microbial adsorbents.Generally microorganisms play an important role in removing various contaminants present in polluted environments.Various people also identified the effective potential of different microbial cells in adsorbing the copper ion which is found in contaminated environments. The adsorption of copper by microbial cells was possible since the surface of microbes have some charged groups on it ,for example,bacteria cell wall contains various anionic functional groups (carbonyl groups, amine group, sulfhydryl group, phosphoryl group) enabling adsorption or if the microbes had poor surface charge groups, it is enhanced by subjecting it to treatments (Wayne E. Marshall *et.al.*, 1995).

Bacteria are one of the unicellular organisms and prokaryotes that had been exploited for studying the adsorption capacity of copper.Bacteria are very small in size and had the capacity to grow in different environmental conditions.Based on the cell wall of bacteria,bacteria was categorized into gram positive and gram negative bacteria.The cell wall of bacteria had various negatively charged functional groups like carboxyl,amino, phosphoryl and various sulfhydryl groups.These negatively charged group interacts with positively charge copper ion and thus facilitation the adsorption of copper ions to the surface of bacteria.

Gram positive bacteria showed increased adsorption of copper compared to gram negative bacteria since gram positive bacteria had a very thick peptidoglycan layer and other glycoproteins facilitating more adsorption of copper towards its surface.On the other hand,Gram negative bacteria exhibited less adsorption of copper on its surface due to presence of thin layered peptidoglycan and presence of less glycoproteins (Navarre *et.al.*, 1999).*Bacillus.sp* showed more efficiency in adsorbing copper ions than gram negative *E.coli* species and *Pseudomonas putida*. The *Bacillus sp* had an adsorption capacity of 16.3 mg/g (Salman *et.al.*, 2015 and Bilal *et.al.*, 2013).But this adsorption capacity of bacteria was very much lower than certain modified natural adsorbents.Some of the adsorption capacities of bacterial bioadsorbent are mentioned in table 3.

TABLE 3: Microorganism Based adsorbents

Types of microbial cell	Adsorbent	Adsorbent efficiency	Reference
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Bacterial	<i>Bacillus sp</i>	16.3	Salman <i>et.al.</i> , (2015)
	<i>Escherichia coli</i>	5.86	Bilal <i>et.al.</i> , (2013)
	<i>Pseudomonas putida</i>	8	Salman <i>et.al.</i> , (2015)
Algae	<i>Spirogyra(green algae)</i>	133	Gupta <i>et.al.</i> , (2006)
	<i>Eckloniasp</i>	90	Feng and Aldrich(2004)
	<i>Ulva Lactuca</i>	52.1	Cochrane <i>et.al.</i> , (2006)
	<i>Turbinariaormate</i>	104.2	Cochrane <i>et.al.</i> , (2006)
	<i>Fucusvesiculosus</i>	114	Cochrane <i>et.al.</i> , (2006)
	<i>Callithamnion corymbosum</i>	47.62	Alina <i>et.al.</i> , (2020)
	<i>Chlorella</i>	33.4	Maznahet. <i>al.</i> , (2012)
	<i>Codiumvermilara</i>	16.52	Romera <i>et.al.</i> , (2007)
	<i>Gelidium</i>	31.37	Vilaret. <i>al.</i> , (2007)
	<i>Cystoseiracrinitophylla</i>	160	Christofordiset. <i>al.</i> , (2015)
	<i>Sargassum sp.</i>	71.4	Jacinto <i>et.al.</i> , (2009)
	<i>Chlorococcum</i>	19.3	Jacinto <i>et.al.</i> , (2009)
	<i>Padina sp.</i>	50.87	Kaewsarn P. (2012)
<i>gracillaria sp.</i>	72.44	Sheng <i>et.al.</i> , (2008)	
Fungi	<i>Flammulina velupties</i>	8.13	Lia <i>et.al.</i> , (2018)
	<i>Auricularia polytricha</i>	6.04	Lia <i>et.al.</i> , (2018)
	<i>Pleurotuseryngii</i>	4.29	Lia <i>et.al.</i> , (2018)
	<i>Pleurotus ostreatus</i>	5	Lia <i>et.al.</i> , (2018)
	<i>Schizophyllum commune</i>	1.52	Veit <i>et.al.</i> , (2005)
	<i>Aspergillus niger</i>	26	Gautam <i>et.al.</i> , (2014)
	<i>Rhizopusoryzae</i>	19.4	Bilale <i>et.al.</i> , (2013)
	<i>Mucorruoxii</i>	52.2	Bilale <i>et.al.</i> , (2013)
	<i>Trametes versicolor</i>	60.98	Sahanet. <i>al.</i> , (2010)

Algae are very large in terms of their size in comparison to bacteria, thus providing a large surface for high adsorption capacity of copper. The capacity of binding to metal ions in algae is similar to bacteria, as algae cell wall also contains negatively charged functional groups. Algae are found in multiple environments. Different types of algae do exist. They are green algae which is also sometimes called as micro algae. There are brown algae which is most called as marine algae or popularly known as brown algae and there is also red algae that can be found in environments. Among various microbial cells exploited for adsorption of copper, the algae showed the more efficient copper adsorption. From various data collected, it was seen that brown algae type of algal species showed more adsorption towards copper (Alina Roxana

Lucaciet.al., 2020).Some of the examples of green algae include *chlorella* and *spirogyra*.*Spirogyra* species of algae showed more efficient copper adsorption than *chlorella*. Among various macro algae, *Turbunariaormate* macro algae showed more efficient copper adsorption than other species of macro algae like *Ulva*, *Lactuca* and *Fucusvesiculosus sp* (E.L. Cochrane et.al.,2006). The *Cystoseira* species showed increased adsorption towards copper than *Spirogyra* and *Cystoseira* species showed adsorption capacity in the range of 160mg/g (Christofordis,et.al.,2015)

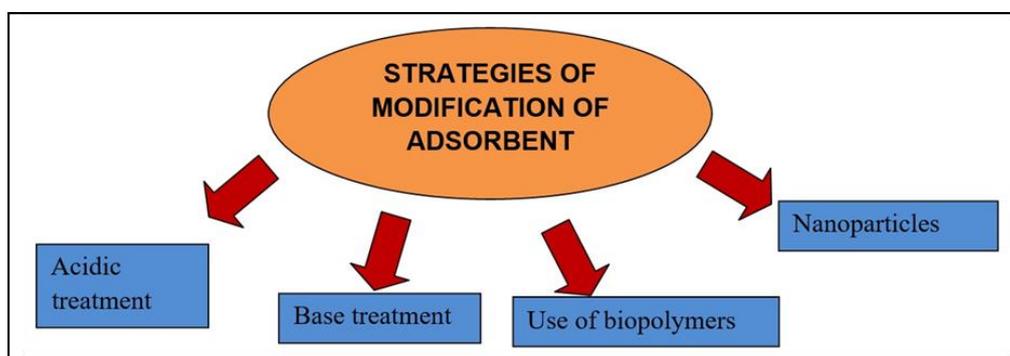
Fungi are also one of the microbial cells that showed adsorption towards copper. Fungi include mushroom,yeasts,molds.Cell wall of fungi contains chitin,mannans, glucans and various other lipids.They also have various anionic functional groups like sulphydryl groups,carboxyl groups, amino groups, etc. Various species of fungi showed different adsorption capacity based on their presence of functional groups in it.Fungi also showed good amount of copper binding capacity (Sahanet.al.2010,).

Even both live and dead fungi was able to bind to copper but the active fungal cells showed more copper uptake since it was actively involved in metabolizing copper. Dead fungal cells were rarely preferred since it lacks metabolizing capacity and only the functional groups present in its surface renders it adsorption capacity. Overall,the adsorption capacity of fungi was much less than algae.But few fungal species showed good adsorption capacity of copper than few bacterial species.

6 Modification Strategies of natural adsorbents and alternate adsorbents

There are various strategies through which adsorbent can be modified to increase its adsorption efficiency (fig. 4).Some of the most widely used are mentioned here. They include acidic and basic treatments of adsorbents, using various biopolymers, nanoparticles functionalized with various functional groups.When adsorbent is subjected to mineral acids like hydrochloric acids, phosphoric acids showed a good result on adsorption of copper in few adsorbents.Organic acids can also be used to enhance the adsorption of copper. An example to it is citric acid. (M. Helen Kalavathy et.al,2005). Sodium carbonate, sodium hydroxide treatment has also proven to increase the adsorption capacity of copper being adsorbed to the surface of the adsorbent. (Wanget.al,2007). Notable examples of base treated adsorbents are wheat straw,flyash.

Fig 4:Strategies of modifying adsorbents.



The use of Biopolymers by grafting suitable biopolymers on the surface of adsorbent will facilitate efficient adsorption of copper since biopolymers contain negatively charged functional groups thereby enhancing the binding of positively charged copper ions (Feng *et al.*, 2009). Nanoparticles also showed increased adsorption towards copper due to their high surface area to volume ratio. Iron nanoparticles functionalized with alginate particles act as the effective adsorbent of copper from an aqueous environment (Alina Roxana Lucaci *et al.*, 2020).

7 Conclusion

Despite the existence of different methods like precipitation, ion exchange, precipitation, Flocculation in removing copper from aqueous environments. Each adsorbent had its own limitations. Some of the methods generate a large amount of sludge. Some processes involve huge costs for its production process. But adsorption can be one of the best techniques through which adsorption of copper and other heavy metals can be removed from an aqueous environment. It can be exploited for making use of different adsorbents that are very low in cost like agricultural waste materials and possess some advantages like they are largely available, easy to recover metals once they are adsorbed and these metals once recovered can be used for other purposes.

A large number of agricultural waste materials are available across the country especially in North India wherein regions like Punjab, Haryana and other areas where they practice stubble burning which involves the burning of agricultural waste materials and this leads to air pollution. So, these leftover agricultural wastes in fields can be made as a useful source by making these as an adsorbent of copper with the help of suitable modifications. Because, using agricultural products, its modified form showed more adsorption towards copper. This implies that pre-treatment can enhance the adsorption capacity of adsorbent, thus helping the efficient removal of copper from polluted environments. Using adsorbents directly without any modification showed poor efficiency of adsorption of copper as seen in table 1. Modification enhances the adsorption of copper towards the adsorbent. Modification is done by using various mineral acids (like hydrochloric acid) or organic acid (like citric acid) or treating with base (like NaOH). Among these, citric acid is used for the modification for surface features of adsorbent showed more adsorption because they contained more negatively charged groups thus interacting with positively charged copper ion and facilitating removal of copper ion from contaminated aqueous environments. Agricultural based adsorbents has also certain limitations, it requires more cost for its production as it involves modification and they can't uptake various heavy metals at a time. On comparing various adsorbents for copper, microbial based adsorbents showed increased levels of adsorption. Microbial based adsorbents has more advantages and they are used for a wide range of conditions. The cost of production involved will be much less. Microbial based adsorbents can be used for various heavy metal uptake at a time. There is no need for chemical additions. A large quantity of contaminated water can also be easily treated by using microbes as adsorbents. On the other hand, the chemicals used for desorption of copper from microbial adsorbents should be cautiously selected or else it would affect the surface features of microbes. Algae cells exhibited increased high copper adsorption when compared to other microbial cells like bacteria, fungi and yeasts. By analyzing various adsorbents, it can be found that the interaction occurring between the surface of an adsorbent and the metal ion forms complexes and removes the contaminant. Of the various microbial

cells used for adsorption, algal species exhibited more adsorption due to their large surface and presence of more anionic ligands. Of various species of algae, marine algae (macroalgae) showed good adsorption of copper. There is always a need for a novel adsorbent. Continuous improvement is needed from the existing adsorbents because resources available are not enough to adsorb copper efficiently from aqueous environments, new adsorbents can be discovered through studying and analysing its surface properties and then by making modifications/pre-treatments would enhance copper removal from the environment and reduce heavy metal toxicity.

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