Biosorption of Heavy Metals from Wastewater by Using Microalgae

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Abstract

Most heavy metals are well-known toxic and carcinogenic agents and when discharged into the wastewater represent a serious threat to the human population and the fauna and flora the receiving water bodies. Microalgae culture offers an interesting step for wastewater treatments, because they provide a tertiary biological treatment coupled with the production of potentially valuable biomass, which can be used for several purposes. Microalgae cultures offer an elegant solution to tertiary and quandary treatments due to the ability of microalgae to use of cell wall biosorption mechanism. Their capacity to remove heavy metals is also affected by pre-treatment of biomass, surrounding condition such as pH, light intensity, temperature and biotic factors. In the current review we will highlight on the role of micro-algae in the treatment of wastewater.

Keywords: heavy metals; microalgae; biological treatment; biomass; cultures; biosorption.

Introduction

Modern industry is, to a large degree, responsible for contamination of the environment. Lakes, rivers and oceans are being overwhelmed with bacteria and waste matter. Among toxic substances reaching hazardous levels are heavy metals.

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc. Thus, metal as a kind of resource is becoming shortage and also brings about serious environmental pollution, threatening human health and ecosystem. Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) (Jianlong Wang; Can Chen, 2009).

There is a wide range of treatment methods such as membrane filtration, adsorption, ion exchange, reverse osmosis, chemical precipitation, or solvent extraction, which have classically been employed for stripping toxic metals from wastewaters. However, these methods have disadvantages, like incomplete metal removal, high reagent or energy requirements, and generation of toxic sludge or other heavy metal-containing waste products that may sometimes be more toxic than their parent ones (Gakwisiri et al, 2012). The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams despite its extensive use in the water and wastewater treatment industries. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon (Rerge et al, 2012).

Number of advantages for these methods can be enumerated such as reduced requirement for chemicals, low operating costs, eco-friendliness (as no toxic sludge results), and high efficiency at low levels of contamination. They also offer possibilities for metal recovery and biosorbent regeneration afterward.

A huge interest has recently arisen toward using various kinds of readily available and inexpensive biomass of several microorganisms and microalgae, in particular for removal of heavy metals. Microorganisms are in fact considered intrinsically more efficient in the bioaccumulation of heavy metals when exposed to low concentrations in their surrounding aqueous environment.

Microalgae are used in bioremediation of metal-contaminated sites due to:

- Their ability to tolerate those metals,
- Their high yields of recovery per unit mass,
- Their high specific outer area coupled with a cell wall loaded with ionisable groups (Gakwisiri et al, 2012).

Among them, microalgae have proved to possess high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals. Of the many types of biosorbents recently investigated for their ability to sequester heavy metals, microalgal biomass has proven to be highly effective as well as reliable and predictable in the removal of heavy metals from aqueous solutions (Priyadarshani et al, 2011).

Biosorption of Heavy Metals by Microalgae

Microalgae uptake metal, either actively (bioaccumulation) and/or passively (biosorption) (Fourest and Roux, 1992). This is due to affinity of algal surfaces for heavy metals leading to their adsorption and precipitation. The biosorption is passive non-metabolic process of binding various chemicals on biomass (Volesky, 1990a). Most studies of biosorption for metal removal deal with the use of either laboratory-grown microorganisms or biomass generated by the pharmacology and food processing industries or wastewater treatment units (Tsezos and Volesky, 1981; Hussein et al, 2004).

Biosorption utilizes the ability of certain materials to accumulate heavy metal ions from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake . It is an economical and effective method to remove heavy metals from wastewater. Marine algae with large available quantities in many regions are a kind of promising biological resources. The cell wall matrix of algae contains complex hetero polysaccharides that can provide amino, carboxyl and sulphate groups.

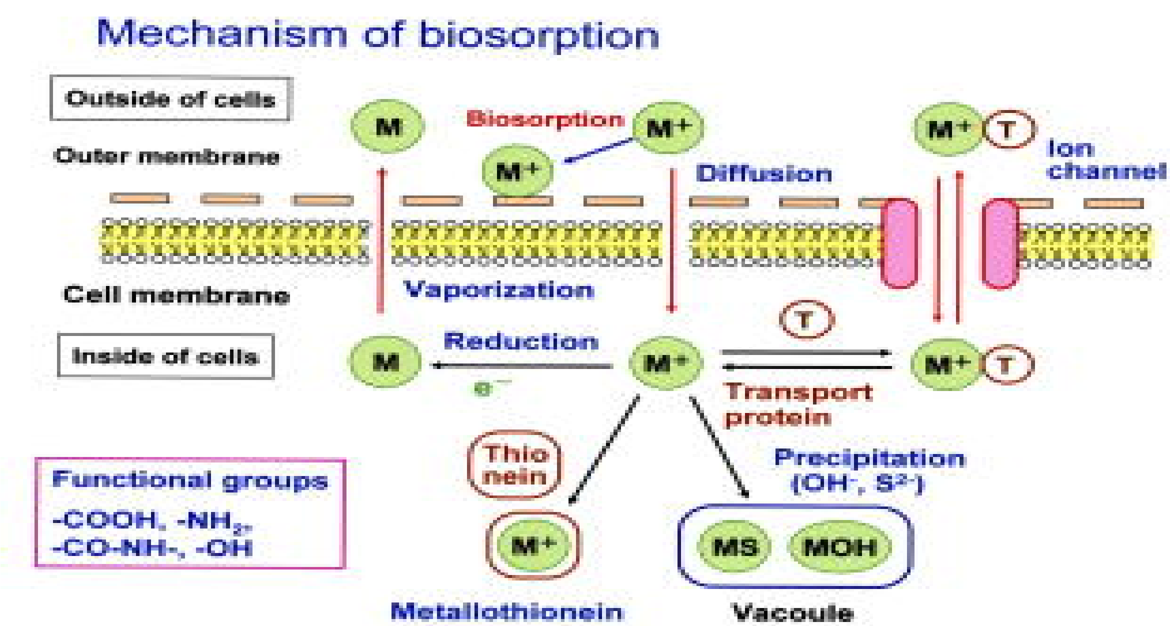


Figure 1:- Mechanism of biosorption

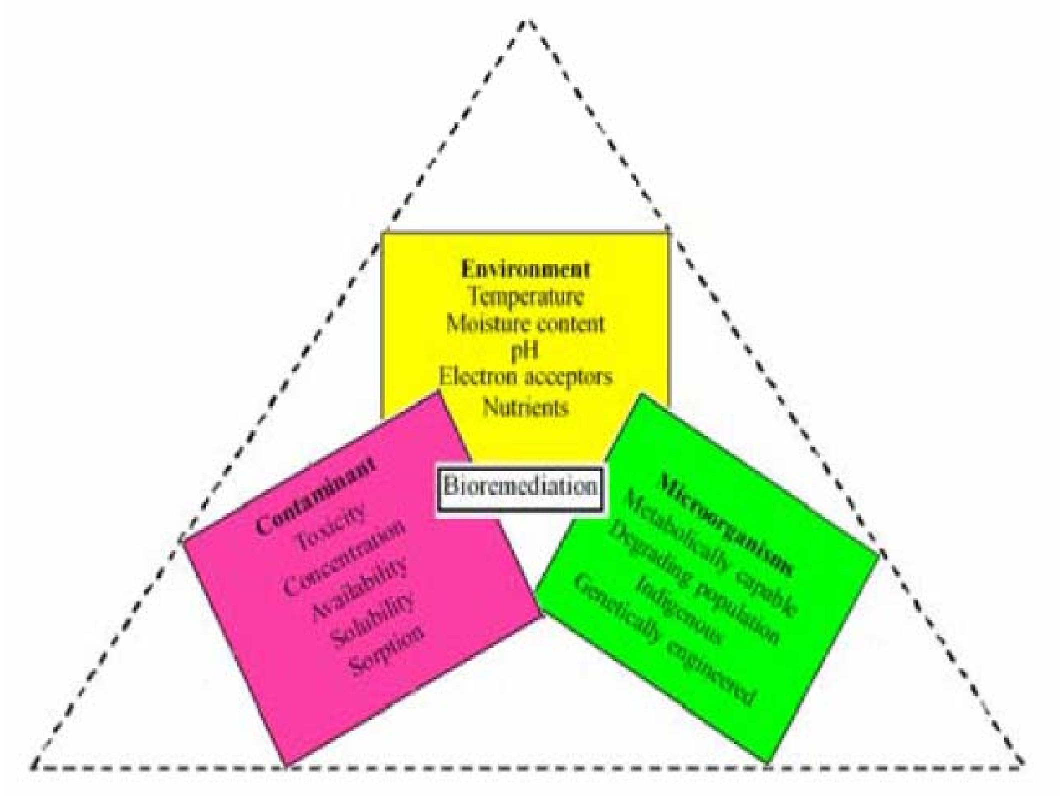


Figure 2:- The environment factor influencing such remediation or biorsption as mentioned (Priyadarshani et al,2011)

Table 1:- Biosorption of heavy metals with Green algal species.

S No.	Algal Species	Heavy Metal	PH	Temp. (^{0}C)	Eq. Time	Q_{max} (mg/g)	Reference
1	*Caulerpa lentillifera*	Pb/Cd/Cu	5	21	30 min.	28.98/4.70/8.26	Apiratikul And Pavasant, 2008
		Cu	5/4/3		20 min.	5.56/4.23/2.64	Pavasant et al, 2006
		Cd				4.68/4.32/2.93	
		Pb				28.72/23.95/15.79	
		Zn				2.66/1.65/1.37	
2	Chaetomorha linum	Cd	5	25	24 min	53.75	Hashim and Chu, 2004
3	*Chlamydomonas reinhardtii*	Hg/Cd/Pb	5/5/6	25	1 h	72.18/42.71/97.38	Tüzün et al,2005
4	*Chlorella miniata*	Cr	4	25	150 h	34.60	Han al et al, 2007
5	*Chlorella vulgaris*	Cu	5	25	15 min	58.80	Al-rub et al, 2006
		Cd/Ni	4	25	24 h	86.60/58.40	Aksu and Donmiz, 2006
		Ni/Pb/Zn	5	20	----	29.29/131.36/43.43	Ferrlira et al, 2008
6	*Cladophora glomerata*	Pb	4.5	30	3 h	73.50	Jalali et al, 2002
7	*Gracilaria salicornia*	Cd	5	25	24 h	17.92	Hashim and Chu, 2004
8	*Lyngbya putealis*	Cr	2	25	2 h	36.13	Kiran et al, 2007
9	*Microcystis novacekii*	Pb	5	21	4 h	80.00	Ribeiroa et al, 2010
10	*Oedogonium hatei*	Cr	2	45	15 min	31.00	Gupta and Rostogi, 2008
11	*Ulva spp*	Cr	2	----	2 h	30.20	Murphy et al, 2008
12	*Ulva lactuca*	Pb	4.5	30	30 min	126.50	Jalali et al, 2002
		Pb/Cd	5	20	1 h	34.70/29.20	Sari and Tuzun, 2008

Table 2:- Biosorption of heavy metals with Red algal species.

S No.	Algal Species	Heavy Metal	PH	Temp. (^{0}C)	Eq. Time	Q_{max} (mg/g)	Reference
1	*Gracilaria*	Pb	4.5	30	3 h	41.80	Jalali et al, 2002

	canaliculata						
2	*Gracilaria changii*	Cd	5	25	24 h	25.76	Hashim and Chu, 2004
3	*Gracilaria corticata*	Pb	4.5	30	3 h	54.00	Jalali et al, 2002
4	*Gracilaria edulis*	Cd	5	25	24 h	26.88	Hashim and Chu, 2004
5	*Hypnea valentiae*	Cd	6	30/40/ 50/60	5 h	16.66/18.42/ 21.52/23.14	Rathinan et al, 2010
6	*Mastocarpus stellatus*	Cd	2.4/ 4/6	25	3 h	23.52/26.88/ 28.32	Herrero et al, 2008
7	*Palmaria palmate*	Cr	2	----	2 h	33.80	Murphy et al, 2008
8	*Polysiphonia lanosa*	Cr	2	----	2 h	45.80	
9	*Polysiphonia pavonia*	Pb	4.5	30	3 h	217.40	Jalali et al, 2002
10	*Polysiphonia violacea*	Pb	4.5	30	3 h	102.00	

Table 3:- Biosorption of heavy metals with Brown algal species.

S No.	**Algal Species**	**Heavy Metal**	**PH**	**Temp. (^{0}C)**	**Eq. Time**	**Q_{max} (mg/g)**	**Reference**
1	*Cystoseira baccata*	Pb	4.5	15/25/ 35/45	4 h	147.11/136.75 /134.68/142.97	Lodeiro et al, 2006
		Cd				50.58/55.08/56.20/46.08	
2	*Fucus spiralis*	Pb/Cd/ Zn	5	25	1 h	43.50/42.10/32.30	Freitas et al, 2011
3	*Fucus vesiculosus*	Cr	2	----	2 h	42.70	Murphy et al, 2008
4	*Laminaria hyperborean*	Cd/Pb/ Zn	5	25	1 h	31.30/50.30/19.20	Freitas et al, 2011
5	*Nitzschia closterium*	Pb/Zn/ Cd/Ni/ Fe	5	25	100/40/40/ 60/50 min	130.08/86.40/ 116.72/87.94/ 81.45	Duygu and Bikem, 2013
6	*Padina tetrastomatica*	Cd	5	25	24 h	59.36	Hashim and Chu, 2004
7	*Sargassum baccularia*	Cd	5	25	24 H	82.88	
8	*Sargassum*	Cd/Zn	5	30	5	83.41/41.86	Fagundes et al, 2007

	filipendula				days		
9	*Sargasum hystrix*	Pb	4.5	30	3 h	285.00	Jalali et al, 2002
10	*Sargassum muticum*	Cd/Pb/Zn	5	25	1 h	38.40/38.20/34.10	Freitas et al, 2008
11	*Sargassum siliquosum*	Cd	5	25	24 h	81.76	Hashim and Chu, 2004
12	*Sargassum sp.*	Pb	5	25/40/55	2 h	258.00/266.00/251.00	Martins et al, 2006
13	*Sargassum wightii*	Cu	4.5	30	6 h	115.00	Vijavaraghavan and prabu, 2006
14	*Turbinaria conoides*	Pb	4.5	30	2 h	439.40	Senthikumar et al, 2004

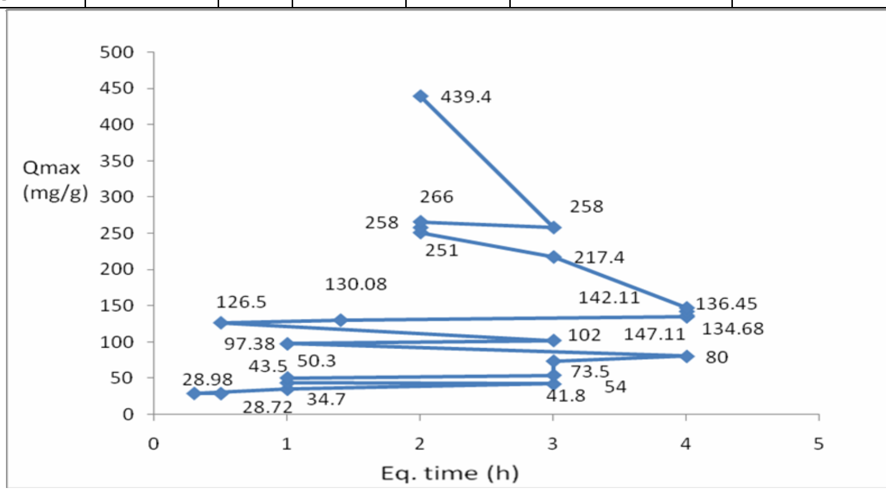
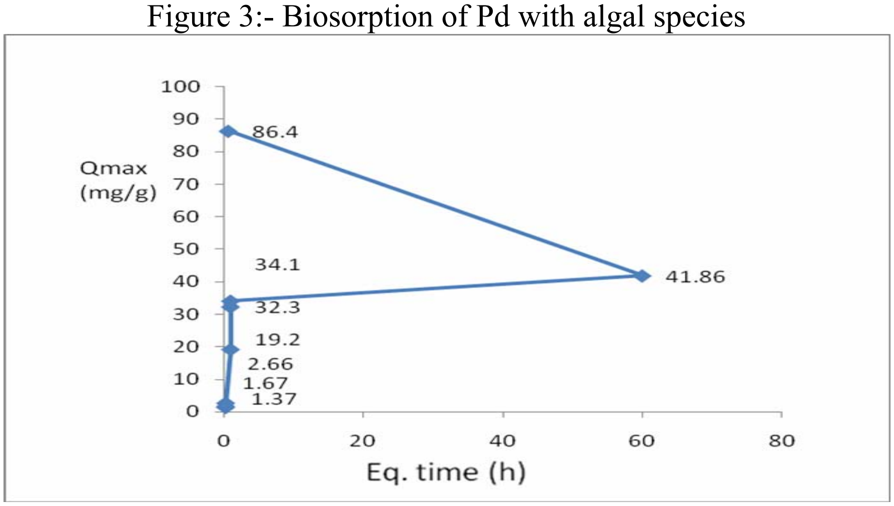


Figure 3:- Biosorption of Pd with algal species



.Figure 4:- Biosorption of Zn with algal species.

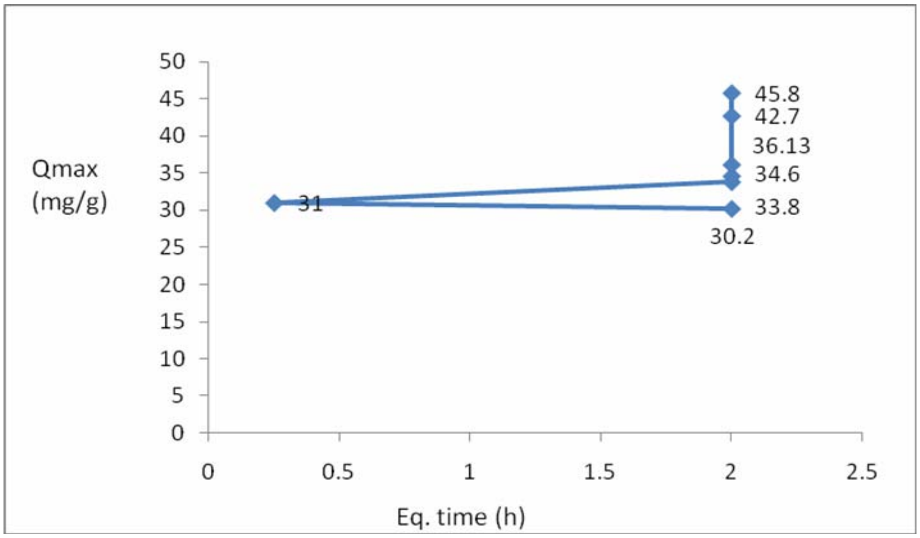


Figure 5:- Biorsption of Cr with algal species.

Effect of Pre-Treatment on Biosorption

As the biosorption process involves in mainly cell surface sequestration, the modification of cell wall can greatly alter the binding of metal ions. A number of methods have been employed for cell wall modification of microbial cells in order to enhance the metal binding capacity of biomass and to elucidate the mechanism of biosorption. The physical treatments include heating/boiling, freezing/thawing, drying and lyophilization. The various chemical treatments used for biomass modification include washing the biomass with detergents, cross-linking with organic solvents, and alkali or acid treatment. The pre- treatments could modify the surface characteristics/groups either by removing or masking the groups or by exposing more metal binding sites (Vieira and Volesky, 2000). Algal cells killed by extreme chemical and physical conditions may also show very different properties for metal accumulating, compared with the original . Now various pre-treatment methods were reported to deal with the cells of S. cerevisiae. Physical methods include vacuum and freeze-drying, boiling or heating, autoclaving, mechanical disruption. Chemical methods include treatment with various organic and inorganic compounds, such as acid and caustic, methanol, formaldehyde, etc. Some methods are found to improve metal biosorption to some extent. Acid treatment of biomass almost has no influence on metal biosorption (Kapoor and Viraraghavan, 1995; Wang, 2002a). S. cerevisiae were modified by methanol, formaldehyde and glutaraldehyde respectively, and then used for Cu^{2+} removal. The results showed that esterification of carboxyl and methylation of amino groups present in the cell wall significantly decreased the biosorption capacity of copper, which suggests that both carboxylic and amine groups play an important role in biosorption of copper. However, glutaraldehyde-treated biomass almost retained the original biosorption capacity (Wang, 2002a).

Due to the important role of cell wall for metal biosorption by nonviable cells, metal biosorption may be enhanced by heat or chemical sterilization or by crushing. Thus degraded cells would offer a larger available surface area and expose the intracellular components and more surface binding sites because of the destruction of the cell membranes (Errasquin and Vazquez, 2003). The equilibrium uptake capacity of lead Pb^{2+} (in mg/g) decreased in the order: original cell (260)N 5 times autoclaved cell for 15 min (150)N grinded cell after drying (100)N autoclaved cell for 5 min (30)N. Brown alga F. vesiculosus for the removal of copper, cadmium, lead and nickel was investigated. Metal sorption yields were modified using different kinds of pre treatment reagents: HCl, $CaCl_2$, formaldehyde, Na_2CO_3 and NaOH. The Langmuir Isotherm was applied to both the non treated and all treated biomass tests. Calcium chloride was the only chemical that improved the maximum sorption capacity of the biomass (Rincon et al, 2005). Pre treatment of Mucor rouxii biomass with detergent and alkali chemicals such as NaOH, Na_2CO_3, and $NaHCO_3$ were investigated for the biosorption of $Pb^{2+,}$ Cd^{2+}, Ni^{2+} and Zn^{2+} (Yan and Viraraghavan, 2000). Different alkaline treatments were also studied (1 M NaOH/20 °C/24 h and 10 M NaOH/107 °C/6 h) (Spanelova et al, 2003). The effect of pre- treatment of A. niger biomass on biosorption of lead, cadmium, copper and nickel was studied. Pre-treatment of live A. niger biomass using sodium hydroxide, formaldehyde, dimethyl sulphoxide and detergent resulted in significant improvement in biosorption of lead, cadmium and copper in comparison with live A. niger cells. Pre -treatment of A. niger reduced biosorption of nickel, compared with live cells (Kapoor and Viraraghavan, 1998). Some modifications can be introduced either during the growth of a microorganism or in the pre-grown biomass because the condition in which microorganisms grow affects its cell components or surface phenol type, which in turn affects its biosorption potential (Vianna et al, 2000). Variation in growth conditions possibly brings about changes in composition of the cell surface, thereby affecting metal biosorption characteristics of the biomass (Mehta and Gaur, 2005).

Some work has been done on the effect of cultural conditions of cells on their biosorptive capacity, such as the effect of glucose, cysteine, glucose, ammonium sulphate, phosphate, ammonium chloride, C, N, P, S, Mg and K-limited conditions, which could refer to the review (Wang and Chen, 2006). For example, Mapolelo and Torto, 2004 reported that the pre -treatment of the S. cerevisiae by using 10–20 mmol/l glucose increased the removal efficiency by 30–40 % for Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, but by using 60 mmol/l glucose decreased almost 50 % removal for $Cr^{6+.}$ The mechanism for Cr^{6+} uptake may differ from other metal ions (Stoll and Duncan, 1996) investigated the uptake of Cu^{2+}, Cr^{6+} Cd^{2+}, Ni^{2+} and Zn^{2+} from electroplating effluent by living cells of S. cerevisiae. The results showed that pre-treatment of the yeast cells with glucose increased the amount of metal removed, while direct addition of glucose to the yeast-effluent solution had no effect on the amount of metal accumulated.

Dostalek et al. 2004 investigated biosorption of Cd2+, Cu2+ and Ag + ions by C, N, P, S, Mg and K-limited cells of S. cerevisiae. The binding capacity of yeast cells for cadmium decreases in the order: K-limited ≥ Mg-limited ≅ C-limited NN-limited ≅ S-limited N P-limited. For Ag+ ions: P-limited NK-limited NC-limited ≥ N-limited ≅ Mg-limited NS-limited. For copper ion: K-limited NMg-limited ≥ Climited NN- limited ≅ P-limited NS-limited. Addition of L-cysteine into the growth medium increased the biosorption capacity for silver, protein and sulphydryl group content of the freeze-dried and viable yeast cells, although the increase of concentration of L-cysteine (from 1 to 5 mmol/l) decreased the cell numbers in comparison with the control test without L-cysteine (Simmons and Singleton, 1996).

Factors Affecting Nutrient Removal

Nutrient uptake are not only affected by the availability of nutrients, they also depend on complex interactions among physical factors such as pH (Azov and Shelef, 1987), light intensity, temperature (Talbot and De la Noie, 1993), and biotic factors. The first biotic factor significantly influencing algal growth is the initial density, it is expected that the higher the algal density, the better the growth and the higher the nutrient removal efficiency (Lau et al, 1995). However, the high algal density would lead to self-shading, an accumulation of auto inhibitors, and a reduction in photosynthetic efficiency (Fogg, 1975; Darley, 1982; Raouf et al, 2012).

Discussion

Biosorption of Pb with different algal species corresponding to contact time shows maximum 439.4 mg/g (2 h) and minimum 28.72 mg/g (1 h). Significant biosorption is shown by brown algae i.e. minimum 134.68 mg/g (4h) and maximum 439.40 mg/g (2h) and red algae biosorption minimum 41.80 mg/g (3 h) and maximum 217.40 mg/g (3 h). The green algae biosorption is minimum 28.72 mg/g (3 h) and maximum 131.6 mg/g (3 h).

Biosorption of Zn with different algal species corresponding to contact time shows more biosorption is 86.40 mg/g (0.66 h) and minimum 1.37 mg/g (0.3 h). Significant biosorption is shown by brown algae i.e. minimum 32.30 mg/g (1 h) and maximum 96.40 mg/g (0.66 h) and green algae biosorption is minimum 1.37 mg/g (0.3 h) and maximum 43.43 mg/g (1 h).

Biosorption of Cr with different algal species corresponding to contact time shows more biosorption is 45.80 mg/g (2 h) and 30.20 mg/g (2 h). Significant biosorption is shown by red algae biosorption minimum 33.80 mg/g (2 h) and maximum 45.80 mg/g (2 h). The green algae biosorption is minimum 30.20 mg/g (2 h) and maximum 36.13 mg/g (2 h).

Conclusions

Biosorption offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solutions. The process of biosorption has many attractive features including the selective removal of metal(s) over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operational costs. The biosorbents can easily be produced using inexpensive growth media or obtained as a byproduct from some industry. The judicious choice of biosorbent can also compete the commercial ion exchange resins which have conventionally been used in the removal of metal(s).

There is a need to have more knowledge of the basic mechanisms involved in order to develop better and effective biosorbents. The major question that still remains to be answered is that although the sorbents are effective, the underlying technology is sound and environmental awareness is growing very fast, still biosorption is not a popular wastewater treatment technology. Critical analysis reveals that not all metal-polluted wastewater generating industries have the interest or capability to treat effluents. Thus, most of the industries opt for just basic treatment to comply with the legalities. To attract more usage of biosorbent technology, certain strategies have to be formulated to centralize the facilities for accepting the used biosorbent where further processing of the biosorbent can be done to either regenerate the biomass or then convert the recovered metal into usable form. This will further require an interdisciplinary approach with integration of metallurgical skills along with sorption and wastewater treatment to develop biosorption technology for combating heavy metal pollution in aqueous solutions.

The biosorption for Pb and Zn is effective only by brown algae and green algae don't seems useful. The biosorption of Cr is effective only by red algae and green algae don't seems useful.

Authors have studied biosorption of Pd, Zn, Cr on different algal species done by various researchers[3, 8, 10, 15, 18, 20, 22, 23, 27, 28, 32]. We are of the opinion that significant Pd removal is by Turbinaria conoides species of Brown algae (fig. 3 & table 3), Zn maximum removed by Nitzschia closterium species which is also belongs to Brown algae (fig. 4 & table 3) and Cr is highly removed by Polysiphonia lanosa species of Red algae (fig. 5 & table 2).

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