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Biosorption of Cadmium by Green Algae – A Review

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ABSTRACT

Cadmium as a chief pollutant in aqueous environment poses a potential threat to human health. It causes serious metal toxic effects and accumulation throughout the food chain. As a result, the systemic body is subjected to the corporate risk of genetical malfunction. The culprits are no doubt the effluents from industries like smelting, dyeing, mining etc. In an attempt to get rid of the cadmium contamination problems, many researchers have tried their best to prove that the biosorption is a feasible and potential technique for cadmium heavy metal decontamination making use of panacea, the green algae, which is the centre point of this study. The purpose of this article is to review how best the green algae be put into use as biosorbent for the complete obliteration of cadmium metal ion from aqueous phase. The various constraints and operational conditions of biosorption processes have been elaborately dealt with.

1. Introduction

The term heavy metal refers to any metallic chemical element that has a relatively high density (greater than 5 g/cm^3) and is toxic or poisonous at low concentrations [1,2]. Heavy metals such as Cadmium, mercury, chromium, zinc, copper, nickel, lead, cobalt and arsenic are known to be significantly toxic. Heavy metals are introduced into natural waters from industrial effluents including paint and pigment manufacturing, textile dyeing, leather tanning, electro-plating, metal finishing, photography, porcelain enameling, battery manufacturing, fertilizer industries and steam electric power plants [3-5]. Heavy metals are natural components of the Earth's crust. Heavy metals are persistent environmental contaminants since they neither be degraded nor destroyed. Discharge of these heavy metals from industrial effluents into natural water is a serious cause of water degradation or water pollution. The human tissues imbibe the heavy metals through the food chain. When the body does not metabolize the heavy metals, they become toxic. If these heavy metals are consumed beyond the permitted concentration, they accumulate in the human body and cause serious health disorders [6, 7]. Hence, it is a must to treat the metal contaminated waste waters before its discharge, to protect the human life and environment.

Removal and recovery of heavy metals are very important with respect to environmental and economic aspects [8]. Many methods that are being employed to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, solvent extraction, electrochemical treatment technologies, etc., [9, 10]. These conventional physicochemical methods are expensive, not eco-friendly and inefficient for the metal removal from dilute solutions containing from 1 to 100 mg/L of dissolved metal. As a result researchers threw a focus on new and alternative technologies to get rid of trace metals from contaminated waters [11] and industrial effluents.

Biosorption of heavy metals from aqueous solutions is relatively a modern process that has been assured as a very sanguine process in the removal of heavy metal contaminants proved to be an efficient, competitive, clean and inexpensive technology for the treatment of low-concentration effluents [12, 13].

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2. Experimental Methods

2.1 Cadmium

Cadmium with atomic weight 112.4 and density 8.69 g/cm^3 is one of the high priority toxic heavy metal responsible for polluting the ecosystems and with the maximum potential threat to humans and the environment. Cadmium has been incorporated in the red list of priority pollutants by Department of Environment, UK [14] and in List I (the "black list") of Directive 76/464/EEC [15]. USEPA has also classified cadmium as group B1 carcinogen [16].

The major sources of cadmium discharge into the environment through wastewater streams are drained out of electroplating, smelting, paint pigments, batteries, fertilizers, alloy and mining industries [17]. Cadmium occurs in 0 and +2 oxidation states. Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) dominate at high pH whereas Cd^{2+} and aqueous sulphate species dominate at lower pH (<8). It precipitates in the presence of phosphate, arsenate, chromate, sulphide , etc., shows mobility at pH range 4.5-5.5 [18,19], interacts with essential nutrients ,competes with gastrointestinal absorption of zinc, inhibits zinc, enzymes, decreases copper in liver & plasma, binds to ferritin, decreases hemoglobin – anemia, deposits in bones and does not generate free oxygen [20].

Cadmium is non-biodegradable [21], toxic even at low concentration and enters the food chain [22] and causes serious human diseases and disorders. The outbreak of the Itai-Itai bone disease in Japan in the year 1960 is caused by cadmium contamination in combination with a diet low in calcium and vitamin D drew the attention of the general public and regulatory bodies to Cadmium that had been discharged to the environment at an unchecked rate for more than one century [23]. The cadmium exposure leads to adverse health effects to human viz. renal dysfunction, liver damage, bone degradation, hypertension and can disrupt protein metabolism [24, 25]. Tobacco smoke is an important source of cadmium exposure. Smoking one pack a day, can imbibe 5-10 times the amount of cadmium obtainable through a regular diet due to which Urinary excretion is slow and biological half-life can be up to 30 years.

Maximum permissible limit of Cd^{2+} 0.1 $mgmL^{-1}$ in drinking water was set by U.S. authorities [26]. The recommendations of WHO are much more stringent in this context as the maximum permissible limit of Cd^{2+} is fixed as 0.005 mgL^{-1} [13] in drinking water. Soil natural concentration: >1 ppm, Plant concentration: 0.005-0.02 ppm, Plant toxicity level: 5-30 ppm and USEPA MCL in water: 0.005 ppm [27, 19]. Permissible limits for industrial effluent discharge (in mg/L) into inland surface waters Indian Standards: 2490(1974) is 2 mg/L and into public sewers Indian Standards: 3306(1974) is 1 mg/L [28].

2.2 Biosorption

Biosorption is a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed as a very promising process in the removal of heavy metal contaminants. The biosorption process gives rise to certain potential advantages over conventional treatment methods include: low operating cost, minimization of chemical or biological sludge, highly effective efficiency of heavy metal removal from diluted solutions, regeneration of biosorbents, possibility of metal recovery and being eco-friendly [29].

Lot of research has been undertaken for developing and employing cost effective biosorbents for the treatment of wastewaters carrying heavy metal cadmium [30]. The mechanisms of biosorption are generally based on physico-chemical interactions between metallic ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelation or complexation [31]. Functional groups most commonly involved in such interactions include carboxylate, hydroxyl, amine, sulphonate and phosphoryl groups present in cell wall components such as polysaccharides, lipids and proteins [32]. The band assignments of the FTIR for typical functional groups present in biomass are illustrated in Table 1 [33, 34].

Table 1 Characteristic FT-IR adsorption peaks for different functional groups

Name of the functional groups	Functional group	Wave numbers (cm^{-1})
Hydroxyl	–OH	3200–3600
Amine	$–NH_2$, $–R_2NH$	3200–3500(–NH); 1500–1650(C–N and N–H)
Carboxylate ions	–COOM	1400–1650
Carboxyl	–COOH	1670–1760(C=O); 1000–1300(C–O);
Methyl, methylene groups	$–CH_3$, $–CH_2–$	2800–3000
Sulfur group	–SO–	1000–1400; 1000–1300(–SO_3)
Carbonyl	–HC=O, $R_2C=O$	1680–1750(C=O)
Phosphorous group	–PO–	1000–1400

Table 2 Summary of work done by various researchers using green algae for the removal of cadmium

Biosorbent	pH range	Optimum pH	Initi. conc range mg/L	Initial conc $C_o$mg/L	Temp C°	Time minutes	Dosage g/L	Max uptake of metal (mg/g)	Ref.
Chlorella vulgaris	2-6	4	25 - 200	200	20	60-120	0.75	111.1	35
Chaetomorphalinum	2-5	5	50 - 400	100	25	-	14.79	53.95	36
Ulvasp.	2-6	5.5	25 - 225	112.4	22	60	1	65.19	37
Chlamydomonasreinhardtii	2-7	6	20 - 400	200	25	120	0.8	77.56	38
Ulvaonoi	2-11.5	8	10 - 500	100	20	120	1	61.9	39
C.vulgaris	2-6	4	25 - 150	150	25	-	1	86.6	40
Caulerpalentillifera	2-8.5	5	10 - 350	10	21	20	16.7	4.7	41
Codiumvermilara	2-6	6	10 - 150	50	-	120	0.5	21.8	42
Spirogyra insignis	2-6	6	10 - 150	50	-	120	1	22.9	42
Oedogoniumsp.	2.99 – 6.05	5	20 – 200	200	25	55	1	88.2	43
Ulvalactuca	2- 8	5	10 - 400	-	20	60	20	29.2	44
Ulvalactuca	2-6	5	20 – 400	67.5	20	60	0.8	34.61	45
Ulvalactuca	2-5.5	5.5	10 – 800	50	-	-	1	46	46
Caulerpafastigiata	2-8	5.5	30 – 100	30	25	60	10	16.13	47
Ulvalactuca	2-8	5.5	3 – 100	10	30	120	10	99.2%	48

2.3 Green Algae

Green algae chiefly contain cellulose in the cell wall, and a high content of proteins is bonded to the polysaccharides. These compounds possess functional groups such as amino, carboxyl, sulfate, and hydroxyl which play important roles in the biosorption. Few green algae species are *Chlorella vulgaris Scenedesmus abundans, Cladophora fascicularis, Chlamydomonas reinhartii, Spirulina sp., Chlamydomonas reinhardtii, Caulerpa lentillifela, Gedogonium, Ulvalactuca, Caulerpa fastigiata, Cladophora crispate.*

3. Results and Discussion

3.1 Effect of pH

Earlier studies on heavy metal biosorption have indicated that pH is an important parameter affecting the biosorption of heavy metals [49-52]. The effect of pH on the biosorption of cadmium onto different species of green algae were studied in a pH range, 2-8.5 and the results were tabulated in Table 2. From the table it is evident that optimum pH is in the range of 4 – 6 for maximum cadmium biosorption by most of all green algae. The extent of cadmium biosorpton varies for different green algae species because of the variation in the cellular constituents. The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the bio-mass and the metal chemistry in solution [53-55]. At lower pH, the absorption of cadmium by green algal biomass was less due to the higher concentration of the positively charged hydrogen ions in the solution compete with metal ions for binding on the active sites (the functional groups) on the surface of the algal cell wall [56].

As the pH increased (>2-6), functional groups such as carboxyl, phosphate, imidazole and amino groups would be exposed due to deprotonation and carried negative charges thus facilitating the biosorption of more metal ions with positive charge [57,58]. The lowest biosorption values were observed at pH 2.0 for cadmium metal ions (Table 2). Researcher Christ [59] deduced that the algal cells could augment a net negative charge at pH above 3. The decrease in biosorption at higher pH values (pH > 6) may be attributed to that the amount of OH^- ions is increased in the solution, so metal ions react with OH^- ions and are precipitated as a metal hydroxide in basic conditions [60,61]. At higher pH, the separation was also low compared with the optimum condition. This can be explained as the binding site may not activate in basic conditions [62]. The influence of pH on the biosorption of Cd(II)ions was studied by the researcher Arica [38] using green algae *Chlamydomonas reinhardtii* are presented in Fig. 1.

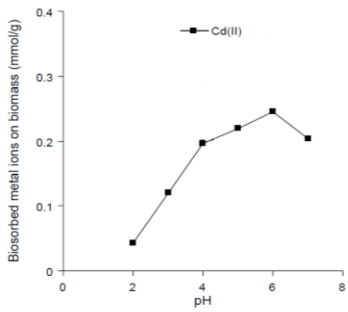

Fig. 1 Effect of pH on cadmium removal [38]

3.2 Effect of Initial Concentration

The effect of initial cadmium ion concentration on the biosorption of cadmium by the different types of green algae biomass was explored by several researchers. They noticed the influence of initial metal concentration by varying the initial metal concentration and keeping the other experimental conditions such as biomass, pH and temperature constant. The data gathered were shown in Fig. 2 and Table 2.

From the table, it was observed that more the metal adsorption capacity, lesser would be the removal efficiency of cadmium with an increase in initial cadmium ion concentration. Evidently presumed an increase in the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and the metal solution [63]. Further, the number of collisions between metal ions and biosorbent increases with increasing initial metal concentration, and thus the biosorption process enhances [64, 65]. The reduction in the removal efficiency of cadmium ions might be due to insufficient binding sites for adsorption. Researcher Kumar [66] also thought that a lower removal efficiency at higher concentrations was due to the saturation of binding sites [67, 68].

Relatively greater ionic radii of Cd might have increased its affinity towards biomass. Authors Tobin and Al-Qunaibit [69, 70] suggested that larger metal ions are attracted more strongly than smaller ones, primarily due to strong electrostatic interaction with binding sites of biomass.

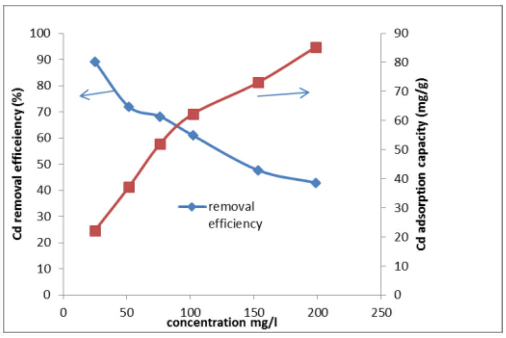

Fig. 2 The effect of initial cadmium concentration on the biosorption of Cd(II) ions using green algae *Chlorella vulgaris* [35]

3.3 Effect of Sorbent Dosage

The dosage of a biosorbent strongly influences the extent of biosorption. The influence of biosorbent dose on biosorption capacity and removal efficiency of cadmium from aqueous solution was examined by various research scholars using different green algae. The observed data are represented in Table 2. The dependence of biosorbent loading on the biosorption of cadmium was studied by varying the amount of adsorbent while keeping all other variables (pH, adsorbate concentration, contact time, and temperature) constant. The effect of biosorbent dosage on the biosorption of Cd(II)ions was studied by the researcher Gupta and Rastogi [43] using green algae *Oedogonium sp* are presented in Fig. 3.

The increase in biosorption percentage of cadmium with the increase in biomass concentration was likely due to the increased surface area of the biosorbent, which in turn increases the number of binding sites [63, 66, 71]. A further increase in biomass concentration did not culminate to a significant improvement in biosorption yield. It could be explained as a consequence of a partial accumulation of biomass, which results in a decrease in effective surface area for the biosorption [72]. However, the quantity of biosorbed solute per unit weight of biosorbent decreases with increasing biosorbent dosage which may be due to the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent or the biosorbent surface sites remain unsaturated during the biosorption process, resulting in low metal uptake [73-75]. Similar observation has been noted in a number of research studies [76-78].

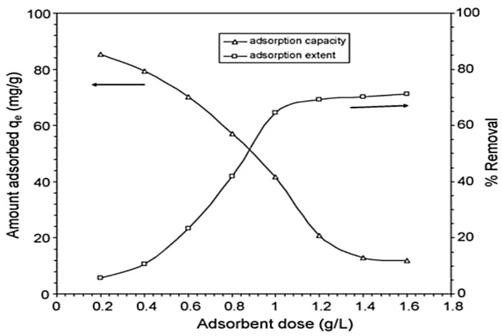

Fig. 3 The effect of biosorbent dosage on the biosorption of Cd(II) ions using green algae *Oedogoniumsp* [43]

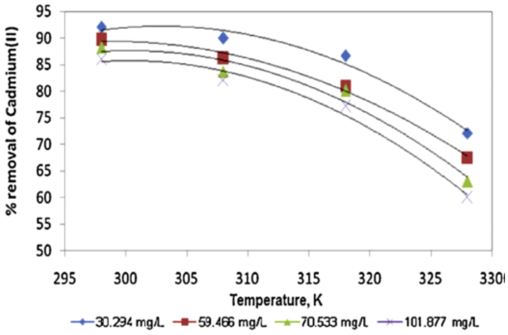

Fig. 4 Effect of temperature on percent adsorption of Cd^{2+} on *C. fastigiata* [47]

3.4 Effect of Temperature

The effect of temperature on cadmium ion uptake capacity of different green algae studied by various researchers were shown in Fig. 4 and Table 2.The reports found in the literature give different opinion on the effect of temperature. The first is that increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles because liquid viscosity decreases as the temperature constant increases. This shows that the adsorption process was endothermic [79-81]. Few have reported temperature independent effect of Cd(II) uptake on biosorption capacity [38,82]. A decrease in the biosorption of Cd(II) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution. These results indicate the exothermic nature of biosorption process [35, 43, 47, 83, 84].

3.5 Effect of Contact Time

The effect of contact time is one of the important parameters for biosorption of cadmium. The experimental data indicate that the amount of each heavy metal adsorbed increase rapidly with the contact time up to 30-60 min (Fig. 5). This phenomenon could be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. After this equilibrium period, the amount of biosorbed Cd(II) on the algal biomass becomes slower and no further significant change with time was noted. The slowing down of metal uptake may be due to difficulty in occupying the remaining vacant sites and repulsive forces between the solute molecules on the adsorbent [85-87].

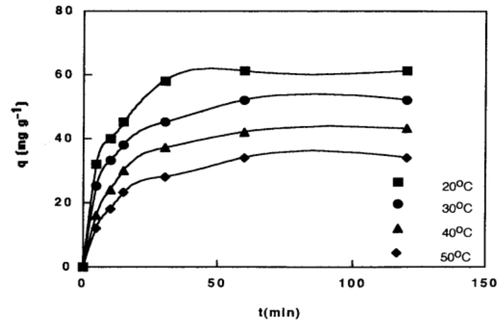

Fig. 5 Change of cadmium(II) biosorption kinetics according to temperature [35]

4. Conclusion

This paper sums up various research oriented studies that have been performed by many other researchers on the adsorption of cadmium heavy metal by different green algae. It was determined that green algal biomass possesses significant affinity to cadmium. The observed facts can be summarized as follows:

- Uptake capacity of the green algae biomass was strongly affected by the experimental parameters such as pH, temperature, biomass dosage and initial metal ion concentration.
- Functional groups play important roles in the metal uptake by the biosorbents.
- Biomass is relatively economic and easily available in abundance.
- Biosorption tenders a number of advantages including low operating costs, minimization of the volume of chemical and/also biological sludge to be handled.

In a nutshell, it can be concluded that the *green algae* is an effective and economic biomass for the removal of Cadmium from aqueous phase.

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