



Characteristics, performances, equilibrium and kinetic modeling aspects of heavy metal removal using algae

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ARTICLE INFO

Keywords:

Biosorption
Algae
Heavy metals
Modification
Biosorption mechanism

ABSTRACT

Heavy metals from industrial effluent are major threat to environment because of their major toxicity effect. The treatment of metal contaminated wastewater is of special concern. This comprehensive review emphasis on the use of algae as the potential source of biosorbent, in this context variety of algae used by various researchers for the heavy metal biosorption is reviewed. The procedures for the biosorbent preparation, modification and their application towards the heavy metals were discussed. The effect of significant parameters in the metal biosorption process was presented. This review reports the biosorption isotherm and kinetic models, thermodynamic aspects of the metal biosorption by algae. The complex mechanisms of metal biosorption by algal presented along with the various instrumental techniques. It was evident from the literature survey that the algae demonstrated with excellent biosorption capabilities towards the removal of various toxic heavy metals.

1. Introduction

The pollution due to hazardous chemicals entails severe damage to the living system and environment (Ansari and Malik, 2007). Over the past years, there is an increased utilization of heavy metals in various industrial sectors (Dursun, 2006). The toxic heavy metals from industrial effluent cause higher toxicity effect to the biotic system. Heavy metals are non-degradable in nature and their removal from the effluent prevents the cycling of contaminants, further possible to recover the metal and reuse (Volesky, 2007). The atomic weights of the heavy metals usually lies between 63.5 and 200.6, and the heavy metal specific gravity are $> 5.0 \text{ g/cm}^3$. Heavy metals classified into three types such as toxic, precious and radionuclides. The specific property and the concentration range of the heavy metal determines the beneficial or toxicity effects to the living systems (Fu and Wang, 2011; Wang and Chen, 2009).

The presence of heavy metal beyond a certain concentration limit causes serious health hazards to human beings apart from damage to the environment. Minor exposure to zinc leads to the loss of appetite, muscular stiffness, irritability and nausea (Bhattacharya et al., 2006). Cadmium gets readily accumulated in human's, results in lung insufficiency, renal and liver disturbances, bone damage, cancer, hypertension and nephrotoxic effects (Nordberg et al., 1993). Manganese triggers low hemoglobin levels, neurotoxicity and gastrointestinal

accumulation (Parvathi et al., 2007). Iron develops infection, cardiomyopathy, neoplasia, arthropathy, various neurodegenerative and endocrine disorders (Shreemoyee et al., 2011). Copper causes hypoglycemia, kidney damage, lethargy and anorexia, increased heart rate, nausea, severe headaches, hair loss, anemia, stomach intestinal distress and risk for lung cancer (Pellera et al., 2012). Chromium in aqueous solution exists in trivalent and hexavalent oxidation states. Compared to trivalent chromium, hexavalent chromium is more toxic. Hexavalent chromium consequence to ulcerations, dermatitis, vomiting, severe diarrhea, liver damage, allergic skin reactions, nausea, hemorrhage, pulmonary congestion, genetic disorders, carcinogenic, birth defects and reduce reproductive healthiness (Rangabhashiyam and Selvaraju, 2015a). The toxic effects of mercury include Rheumatoid arthritis, brain damage, chest pain, dysfunction of liver, kidney, gastrointestinal tract and nervous system deterioration (El-Shafey, 2010). Lead has the toxicity effects of anemia, brain damage, mental deficiency, anorexia, encephalopathy, cognitive impairment, renal and circulatory system damage, vomiting, insomnia, headache, dizziness, weakness of muscles, irritability, hallucination (David et al., 2008; Naseem and Tahir, 2001). Arsenic is associated with the diseases of cancer, hyper- and hypopigmentation, hyperkeratosis, gangrene, liver fibrosis, peripheral neuropathy, gastric complications and diabetes (Iriel et al., 2015).

In view of the various hazardous effects of toxic heavy metals, the employment of suitable treatment method is highly indispensable. The

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<https://doi.org/10.1016/j.biteb.2018.07.009>

Received 23 June 2018; Received in revised form 27 July 2018; Accepted 28 July 2018

Available online 16 August 2018

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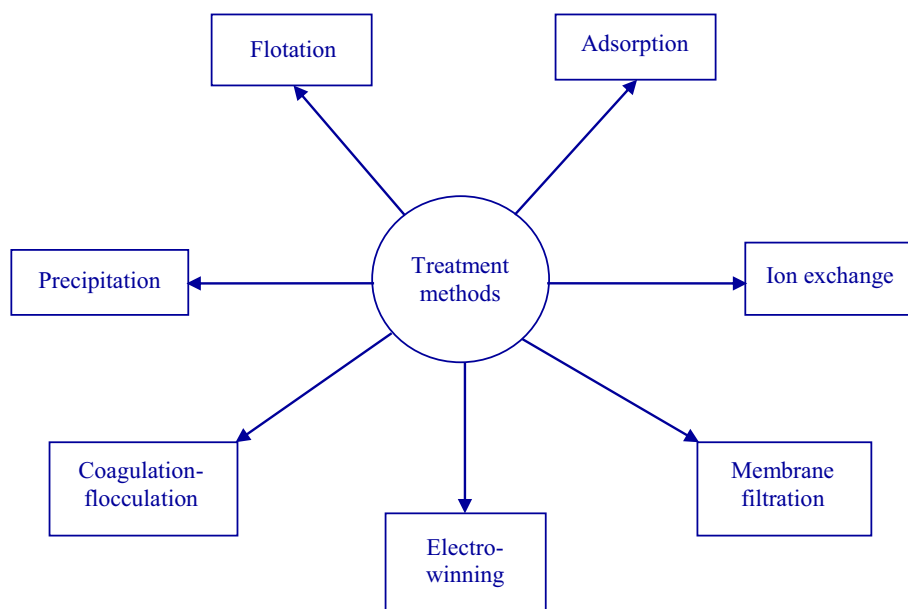


Fig. 1. Treatment technologies available for the removal of toxic heavy metals.

merits and demerits of conventional methods (Fig. 1) like adsorption, precipitation, ion-exchange, electro-winning, coagulation–flocculation, flotation and membrane filtration towards heavy metal removal were discussed. Adsorption is an effective method for the removal of heavy metal from industrial wastewater. The adsorption process offers the advantages of design flexibility and efficient adsorbents regeneration by desorption. The adsorption performance was based on the type of adsorbent used in the process. Activated carbon adsorbents with the larger micropore, mesopore volumes and higher surface area are suitable for the better heavy metal removal process. Activated carbon is an expensive material and the cost factor was based on the category of activated carbon quality. Higher quality of the activated carbon will cost more price of activated carbon (Crini, 2005). Precipitation employs anions in order to precipitate the insoluble metal salts in water. Even though the precipitation is an economical process, factors like low solution pH and presence of other ions affects the process efficiency. The process involves the usage of additional chemical precipitant; the drawbacks are the lack of necessary binding sites, higher water content sludge generation and environmental risks (Gray, 1999). Ion exchange process holds the advantages of fast kinetics, large volume treatment capacity and efficient process. The ion exchange process makes use of solid form ion exchanger, which exchanges either the anions or cations with the working solution. The disadvantages of this method are expensive, non-selective process, highly sensitive to solution pH and ineffective in concentrated metal solution. Electro-winning process involves the passage of electric current through a metal bearing aqueous solution, consisting of cathode plate and an insoluble anode. The positively charged metal ions adhere to the surface of negatively charged cathodes, the process progression leads to metal deposition and metal recovery. Corrosion is the demerit of this process, and requires frequent replacement of electrodes (Kurniawan et al., 2006). Coagulation removes soluble heavy metal from the aqueous solution. Flocculation involves the polymers, which form the bridge between the flocs and binding particles outcome into large agglomerates. The advantage of using coagulation–flocculation process is the good sludge settling and dewatering characteristics, whereas the disadvantages are higher chemical consumption and increased volume of sludge generation (Aderhold et al., 1996). Flotation employs bubble attachment to separate heavy metal from the aqueous solution. The merits of this process include metal selectivity, low retention time and the removal of small particles. The drawback of this method is the requirement of high cost

for initial investment and maintenance (Rubio et al., 2002). Membrane filtration process with different membranes types were used for heavy metal removal. The merits of this process are less generation of solid waste, minimum chemical consumption, small requirement of work space, selective metal removal and the demerits are high cost is needed for initial investment, maintenance and operation. The process over a period causes the fouling of membrane, which affects the flow rate (David et al., 2008). The industrial scale practice of conventional process are expensive, show evidence of major technical constrain of chemical sludge generation and incomplete metal removal. Further, there is an increasing stringent rule, restrictions over the discharge of industrial effluent into the environment. Therefore, an alternative process to combat the problems associated with the toxic heavy metal separation is obligatory.

The current review presents the state of art of biosorption technology, characteristics features of algae as biosorbent and its assessment of the biosorption capacity towards toxic heavy metals removal. The preparations of biosorbent using various algal biomasses and the role of significant parameters influences over the heavy metal biosorption were discussed. The biosorption isotherm models, kinetic models, thermodynamics aspects with the recent important findings using algal biosorbents were presented. Further, the present review elaborates the mechanisms associated with the biosorption of metal using algae.

2. Biosorption technology

The biosorption of heavy metals indicate one type of application of the sorption process. Biosorption process is defined as the property of the biomass having certain specific type of biomolecules in it, able to bind and concentrate selective ions present in the aqueous solutions. The biosorption process occurs mainly because of the affinity between the adsorbate and biosorbent (Volesky, 2007). The practice of biosorption technology has the advantages of low operating cost, eco-friendliness, better performance, biosorbent reusability, short operation time, high specificity and free from the formation of secondary pollutants (Rangabhashiyam et al., 2014a; Ahmet et al., 2011).

Biosorption process carried out utilizing the dead biomass of various biological sources. The dead biomass was preferred over the live biomass since the dead biomass does not require the culture growth media. Such growth medium will increases the chemical and biological oxygen

Table 1
Biological materials for the removal of toxic heavy metals.

Biological materials type	Biomass	Metal	References
Lignocellulose	Banana peels, sugarcane bagasse and watermelon rind	Cu(II)	Liu et al., 2012
	Palm Tree Leaves	Zn(II)	Al-Rub, 2006
	Tree fern	Cu(II)	Ho, 2003
	Banana stem	Pb(II)	Noeline et al., 2005
	Coir pith	Co(II), Cr(III), Ni(II)	Parab et al., 2006
	Rice husk	Cu(II), Pb(II)	Wong et al., 2003
	Sugarcane bagasse	Zn(II);Fe(III); Ni(II)	Pereira et al., 2010; Ezzat et al., 2011; Aloma et al., 2012
	<i>Caryota urens</i> inflorescence	Cr(VI)	Rangabhashiyam and Selvaraju, 2015b
	<i>Mangifera indica</i> sawdust	Cr(VI)	Meghna and Monoj, 2013
	<i>Sterculia guttata</i> shell	Cr(VI)	Rangabhashiyam and Selvaraju, 2015c
	<i>Hevea brasiliensis</i> saw dust	Cu(II)	Kalavathy and Miranda, 2010
	Orange peel	Cd(II), Cu(II), Pb(II)	Lasheen et al., 2012
	Grapefruit peel	Ni(II)	Torab-Mostaedi et al., 2013
	Sunflower hull	Cu(II)	Witek-Krowiak, 2012
	<i>Eichhornia crassipes</i> root	Cr(VI)	Anil et al., 2012
	Corn stalk	Cu(II)	Vafakhah et al., 2014
	<i>Kosteletzkya pentacarpos</i> root	Cd(II), Zn(II)	Stanley et al., 2016
	<i>Dicerocaryum eriocarpum</i> mucilage	Zn(II), Ni(II), Fe(II), Cr(III), Cd(II)	Bassey et al., 2016
	<i>Pterospermum acerifolium</i> shells	Cr(VI)	Rangabhashiyam and Balasubramanian, 2018a
Fungi	<i>Trametes versicolor</i>	Cu(II)	Subbaiah et al., 2011
	<i>Aspergillus niger</i>	Pb(II)	Malihe et al., 2008
	<i>Mucor rouxii</i>	Pb(II), Ni(II), Cd(II), Zn(II)	Yan and Viraraghavan, 2003
	<i>Botrytis cinerea</i>	Cd(II), Cu(II)	Tamer and Sibel, 2005
	<i>Termitomyces clypeatus</i>	Cr(VI)	Lata et al., 2011
	<i>Aspergillus terreus</i>	Cu(II)	Cerino-Cordova et al., 2012
	<i>Yarrowia lipolytica</i>	Ni(II)	Shinde et al., 2012
	<i>Amanita rubescens</i>	Pb(II), Cd(II)	Ahmet and Mustafa, 2009
	<i>Microsphaeropsis</i> sp.	Cd(II)	Xiao et al., 2010
	<i>Pleurotus ostreatus</i>	Cu(II), Ni(II), Zn(II), Cr(VI)	Javaid et al., 2011
	<i>Lactarius scrobiculatus</i>	Pb(II), Cd(II)	Anayurt et al., 2009
	<i>Mucor hiemalis</i>	Ni(II)	Shroff and Vaidya, 2011
	<i>Aspergillus terreus</i>	Pb(II)	
	<i>Clitopilus scyphoides</i>	Cd(II)	Moussous et al., 2012
	<i>Mucor plumbeus</i>	Pb(II)	Akar et al., 2013
	<i>Aspergillus flavus</i> , <i>Aspergillus gracilis</i> , <i>Aspergillus penicillioideus</i> , <i>Aspergillus restrictus</i> and <i>Sterigmatomyces halophilus</i>	Cd(II), Cu(II), Fe(II), Mn(II), Pb(II) and Zn(II)	Amna et al., 2018
	<i>Ustilago maydis</i>	Cu(II),Cd(II), Cr(III), Ni(II), Zn(II)	Sargina et al., 2016
Bacteria	<i>Acinetobacter</i> sp.	Zn(II)	Tabaraki et al., 2013
	<i>Acinetobacter junii</i>	Cr(VI)	Paul et al., 2012
	<i>Bacillus brevis</i>	Cr(VI), Ni(II), Zn(II)	Kumar et al., 2009
	<i>Micrococcus luteus</i>	Pb(II), Cu(II)	Puyen et al., 2012
	<i>Streptomyces rimosus</i>	Cd(II)	Selatnia et al., 2004
	<i>Ochrobactrum</i> sp.	Cd(II)	Khadivinia et al., 2014
	<i>Curtobacterium</i> sp.	Ni(II), Pb(II)	Masoumi et al., 2016
	<i>Pseudomonas</i> sp.	Cd(II), Pb(II)	Huang and Liu, 2013
	<i>Streptococcus equisimilis</i>	Ni(II), Cd(II)	Costa and Tavares, 2016
	<i>Bacillus</i> sp.	Pb(II)	Ren et al., 2015
	<i>Pseudoalteromonas</i> sp.	Cd(II), Pb(II), Zn(II)	Li et al., 2017
	<i>Bacillus arsenicus</i>	As(III), As(V)	Podder and Majumder, 2016

demand in the industrial wastewater. The dead biomass can be modified through activation methods in order to improve their performance. Further, the dead biomass subjected as biosorbent are usually not affected by the heavy metal toxicity. The use of biological materials offers the benefits of uniform biosorbent size, simple regeneration, effective removal at low metal concentration and uncomplicated mathematical modeling (Gupta et al., 2010; Malik, 2004; Mustafa and Ahmet, 2010; Rangabhashiyam et al., 2018; Dhankhar and Hooda, 2011; Rangabhashiyam and Balasubramanian, 2018b; Baysal et al., 2009). Many researchers for the toxic heavy metals removal have explored wide varieties of biosorbents from the sources of lignocellulose, fungi, bacteria and algae. A few examples were mentioned for each type of biosorbent source (Table 1) except algae, which will be discussed in detail in the later section of this article.

3. Algae as a source of biological material for heavy metal removal

Algae extensively explored as biosorbents for the sequestration of toxic heavy metals because of their ubiquitous in nature. Algae are renewable type natural biomass shows different affinities for the removal of various heavy metals. The algal type of micro and macro algae exhibits constitutive mechanisms for the biosorption of toxic heavy metals from wastewater. The biosorption capacities of certain algal biomass towards the certain metals are comparatively higher than the commercially available adsorbents like activated carbon, synthetic ion-exchange resin and natural zeolite (Doshi et al., 2006). The worldwide production of seaweeds was > 3 million tons per annum. The potential harvest estimated of about 2.6 million tons of red algae and 16 million tons of brown algae, supplied as food and algal products such as agar, alginate, and carrageenan respectively (Chen, 2012). The

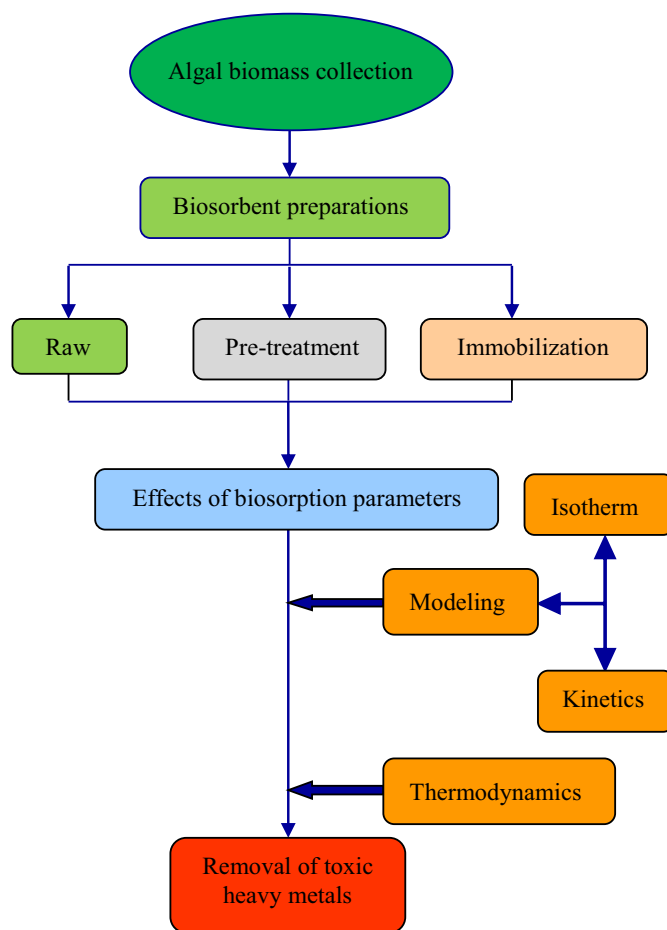


Fig. 2. A generalized presentation of distinct stages of biosorption process using algal biomass towards the removal of toxic heavy metal.

advantages of employing algal biomass for metal removal includes higher efficiency, simple handling, free from nutrient requirements, economical, easy biomass collection, wide availability of biomass both in fresh and saltwater, comparatively higher surface area and higher binding affinity towards the heavy metals (Maria et al., 2012; Sari and Tuzen, 2008a, 2008b). A schematic diagram of biosorption process for the sequestration of heavy metal using algal biomass was represented in Fig. 2.

3.1. Habitat and classification of algae

Algae are widely distributed in the ecosystems of both water as well as in land. Algae found in freshwater, aquatic, marine and terrestrial environments. Algae also occurs on the rocks surface in symbiosis along with fungi like lichen, deserts and sometimes even in snow where the plants cannot grow. Most of the algae are photosynthetic and perform similar ecological, biological functions to that of plants, but they don't have any common evolutionary background and their aspects of biochemistry varies considerably (Lesmana et al., 2009; Christaki et al., 2013).

Algae falls under the category of eukaryotes, contains chlorophyll and performs photosynthesis process. Most of the algae are microscopic in size, whereas a number of forms of algae are macroscopic in nature and grows even above 100 ft. in length (Madigan et al., 1997). Algae are large, diverse group and classified into two types of unicellular (microalgae) and multicellular (macroalgae). It was estimated of about 55,000 species and > 100,000 strains of terrestrial, fresh water brackish and marine algae. Macroalgae are relatively large belongs to the type of multicellular organization and photoautotrophic organisms.

Macroalgae are similar to the lower plants composed of thallus structure, whereas the root and shoot systems are completely absent. Microalgae are the most primal forms of the plants, unicellular organization otherwise simple-multicellular photosynthetic organisms. The normal size of the microalgae was about 400 μm and diameter in the range of 1–30 μm (Carlsson et al., 2007; Ullah et al., 2015; Raslavicius et al., 2014; Stanislav and Christina, 2016). Fig. 3 presents the outline classification (Madigan et al., 2000; Stanislav and Christina, 2016) of macroalgae (according to the thallus color derived from photosynthetic pigmentation) and microalgae (based on their abundance distribution).

Other characteristics features like the chlorophyll nature, cell wall structure, motility type and carbon reserve polymers produced were

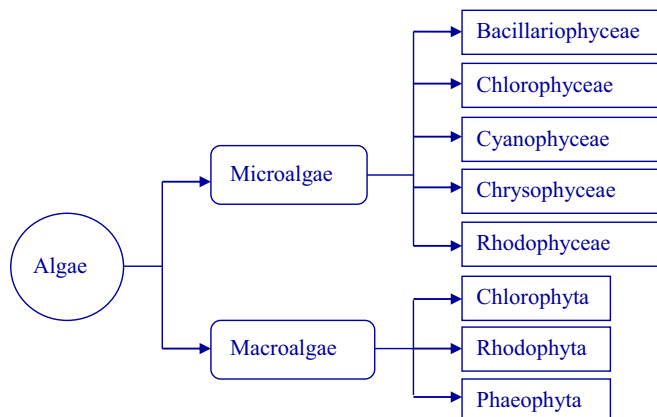


Fig. 3. The outline classification of algae.

also the criteria's used to classify the algae. All the algal types contain chlorophyll a and the presences of some other types of chlorophyll are responsible for the distinguishing feature of particular algal type. The reserve polymers are produced in algae through the photosynthesis activity, the vital characteristics used in the algal classification. Microalgae was also categorized into different classes on the basis of their life cycle, pigmentation and cellular membrane structures, additionally grouped under the criteria of autotrophic, heterotrophic, mixotrophic, photosynthetic, non-photosynthetic, eukaryotic and prokaryotic cellular organization (Madigan et al., 1997; Wang and Chen, 2009; Stanislav and Christina, 2016).

4. Role of algal functional groups in binding of metal ions

Biomolecules such as the carbohydrates, proteins, and lipids are distributed on the cell wall surface of algal biomass, which could react with the heavy metal ions. The surface of the algal biomass are referred as the mosaic form because of the different functional groups like amide, carboxylate, thiols, phosphate and hydroxide offered by the biomolecules are responsible for metal ions binding. The monomer of protein is amino acids, which provides amino functional group and the polysaccharides supplies the functional groups like amino, carboxyl groups and sulfate. The functional groups of carbohydrates, proteins and lipids includes amino, carboxyl, thio ether, sulfhydryl, imidazole group of histidine, the oxygen, phosphate, phenolic, nitrogen of the peptide bond and amide moieties are responsible for the coordinating bond with the metallic ions (Monteiro et al., 2012; Wang and Chen, 2009; Gupta et al., 2010; Gardea-Torresdey et al., 1990; Kaplan, 2013).

The cell wall components of algae like teichuronic acid, peptidoglycan, teichoic acid and the other biomolecules are polyelectrolytes in nature that have specific charged groups with it. The amphoteric property of algal cell wall was due to the existence of anionic and cationic sites. Further the functional groups are either protonated or deprotonated, which was controlled by the solution pH. The functional groups of the algal biomass play significant contributions in the removal of heavy metals from the aqueous solutions. (Chojnacka et al., 2005). Cellulose is the main constituent of green algae (Chlorophyta). The high percentage of the algal cell wall is composed of the protein molecules, which was bound with polysaccharides and forms glycoproteins. Such compounds have the functional groups of amino, carboxyl, hydroxyl and sulfate. Red algae also called as Rhodophyta, contains cellulose and the specific presence of sulphated polysaccharides composed of galactans make its main contribution in the biosorption process. The brown algae otherwise called as Phaeophyta, the cell wall of brown algae commonly consists of three components. Cellulose acts as the component of the structural support. Alginic acid was the polymer of guluronic, mannuronic acids and complexed with light metals such as sodium, potassium, calcium and magnesium are the corresponding salts and sulphated polysaccharides such as fucoidan. Alginates and sulfate are the major active groups in case of the brown algae (Romera et al., 2006; Chen et al., 2002; Sheng et al., 2004).

The protonated *Laminaria digitata* biomass has the free carbonyl double bond of the carboxyl functional group; such acid functional groups of alginic acid are vital component in the divalent metals biosorption. The chromium solution contact with the biomass results in complexation of the carbonyl group through coordination bonds. The carboxylic groups was verified as the main functional group for the removal of heavy metals and other functional groups like hydroxyl, amino and sulfonic groups was also demonstrated (Dittert et al., 2012). Marine macroalgae *Pelvetia canaliculata* consists of the functional groups like hydroxyl, carboxyl, methyl, sulfate esters, ether, sulfonate and alcohol. The carbonyl double bond from the carboxylic functional group exhibits interactions with the lead and cadmium ions. The biosorption capacity of the algal biomass depends on the presence of such sites on the alginate polymer (Hackbarth et al., 2014). Functional groups of carboxylic and sulfonic distributed on the surface of the

macro-algae *Pelvetia canaliculata* (Linnaeus), plays an important role in the removal of copper and zinc ions from the aqueous solutions (Girardi et al., 2014). The surface function group of fresh water algae *Anabaena sphaerica* biomass such as hydroxyl, carboxyl, amino and carbonyl groups possessed significant contribution in the biosorption of cadmium and lead (Azza et al., 2013). In the removal of lead using the algal biomass of *Microcystis novacekii*, specific interactions of lead with the functional groups like hydroxyl, phosphate, and sulfonate groups was observed (Ribeiro et al., 2010). Methylated biomass of *Spirulina platensis* was used for the biosorption of hexavalent chromium. The process of methylation had reduced the amount of carboxylate species in the biomass resulted in the formation of methyl esters. The consequence of the decreased amount of the negatively charged group carboxylate functional group might favor the biosorption of chromate ions (Finocchio et al., 2010). The interactions of heavy metal ions and protons with the algal biomass of *Vaucheria* sp., *Spirogyra* sp., *Oedogonium* sp., represented that metal ions biosorbed on the surface of algae through electrostatic attraction to negative sites (Crist et al., 1988). Calcium treated *Undaria pinnatifida* biosorbent was checked for the removal of zinc and cadmium. The contribution of carboxylic groups from the biosorbent was considered as the significant functional group in the metals binding. Other chemical groups like sulphydrils and sulfonates containing S and N also involved in the removal of heavy metals by the biosorbent (Cazon et al., 2013). The biomass of *Gracilaria verrucosa* investigated towards hexavalent chromium removal. The biomass composed of polysaccharides, polyunsaturated, saturated fatty acids, lipids, steroids, hemagglutinin and prostaglandins. The functional groups like hydroxyl, carbonyl, and amino groups were the important surface active groups of biomass for hexavalent chromium biosorption (Ata et al., 2012). Functional groups such as carboxyl, hydroxyl, sulfate and amino groups having O, N, S, P, involved in the direct participation of metal ions binding. The functional groups are distributed in algal cell wall polysaccharides (Gonzalez et al., 2011).

5. Preparation methods of algal biosorbents

Algae as a source of biosorbent used in various forms like raw, pre-treated and in the immobilized for the removal of heavy metal from aqueous solutions. The unmodified form of biosorbent preparation from algae denotes a simple approach because of the easy process of washing, drying and sieving of raw algal biomass. The raw algal biomasses for biosorbent preparation are naturally distributed in plenty and the procedures do not involve any chemical pre-treatments. The potential evaluation of the algal biosorbent for the heavy metals removal checked by the pre-treatment of the biomass and the process includes physical or chemical methods. Algae immobilization can be performed by entrapment of the biomass in chitin, chitosan, alginate or cellulose derivatives. The process of biomass immobilization offers the advantages of solid structures with suitable size, biomass reuse after regeneration, easy separation process, good mechanical strength, high rigidity and porous nature provides better removal efficiency (Rangabhashiyam et al., 2014a; Arica et al., 2005; Bayramoglu et al., 2006; Rajeshwari et al., 2012). Table 2 represents the biosorption performance of raw, pre-treated and immobilized algal biosorbents towards the removal of heavy metal ions.

5.1. Raw algae

The blue green alga *Anabaena sphaerica* was used for the removal of cadmium and lead from aqueous solution without any modifications. The cultivated algal biomass was separated through centrifugation, washed thoroughly with distilled water and dried in hot air oven. The dried biomass was ground and further sieved to 0.2 mm size biosorbent. The distinct functional groups of algal biomass mainly contribute in the biosorption of cadmium and lead. At the optimum operating biosorption condition, the maximum biosorption capacities towards cadmium

Table 2
Heavy metals biosorption capacity of various algal biomass.

Species of algae	Metal ions	Biosorption capacity (mg/g)	References
Raw form of algal biomass			
<i>Enteromorpha</i> sp.	Cr(VI)	5.3475	Rangabhashiyam et al., 2016b
<i>Caulerpa fastigiata</i>	Pb(II)	16.11	Sarada et al., 2014a
<i>Spirulina platensis</i>	Ni(II)	69.04	Celekli and Bozkurt, 2011
<i>Spirulina platensis</i>	Cd(II)	73.64	Celekli and Bozkurt, 2011
<i>Cladophora fascicularis</i>	Cu(II)	102.309	Deng et al., 2006
<i>Cladophora fascicularis</i>	Pb(II)	198.912	Deng et al., 2006
<i>Sargassum sinicola</i>	Cd(II)	62.42	Monica et al., 2011
<i>Sargassum lapazeanum</i>	Cd(II)	71.20	Monica et al., 2011
<i>Corallina mediterranea</i>	Co(II)	76.2	Ibrahim, 2011
<i>Sargassum wightii</i>	Pb(II)	170.74	Tamilselvan et al., 2012
<i>Caulerpa racemosa</i>	Cr(III)	59.0	Tamilselvan et al., 2012
<i>Lobophora variegata</i>	Cd(II)	192.22	Jha et al., 2009
<i>Lobophora variegata</i>	Pb(II)	370.88	Jha et al., 2009
<i>Cystoseira indicia</i>	Cu(II)	103.093	Akbari et al., 2015
<i>Cystoseira indicia</i>	Co(II)	59.524	Akbari et al., 2015
<i>Cladophora</i> sp.	Cu(II)	13.7	Lee and Chang, 2011
<i>Laminaria digitata</i>	Cr(VI)	125.99	Dittert et al., 2014
<i>Anabaena sphaerica</i>	Cd(II)	111.1	Azza et al., 2013
<i>Anabaena sphaerica</i>	Pb(II)	121.95	Azza et al., 2013
<i>Macrocystis pyrifera</i>	Zn(II)	59.49	Cazon et al., 2012
<i>Macrocystis pyrifera</i>	Cd(II)	100.04	Cazon et al., 2012
<i>Sphaerococcus coronopifolius</i>	Hg(II)	111.11	Lyamlouli et al., 2014
<i>Ulva lactuca</i>	Cd(II)	29.2	Sari and Tuzen, 2008a, 2008b
<i>Durvillaea antarctica</i>	Cu(II)	91.49	Cid et al., 2015
<i>Scenedesmus incrassatulus</i>	Cr(VI)	4.4	Jacome et al., 2009
<i>Ascophyllum nodosum</i>	Zn(II)	42.0	Romera et al., 2007
<i>Chondrus crispus</i>	Cd(II)	75.2	Romera et al., 2007
<i>Asparagopsis armata</i>	Cu(II)	21.3	Romera et al., 2007
<i>Ascophyllum nodosum</i>	Ni(II)	43.3	Romera et al., 2007
<i>Asparagopsis armata</i>	Pb(II)	63.7	Romera et al., 2007
<i>Chlamydomonas angulosa</i>	Cr(VI)	5.32	Dwivedi et al., 2010
<i>Aulosira fertilissima</i>	Cd(II)	14.57	Singh et al., 2007
<i>Spirogyra hyalina</i>	Hg (II)	35.71	Kumar and Oommen, 2012
<i>Chlorella vulgaris</i>	Zn(II)	43.41	Ferreira et al., 2011
<i>Mastocarpus stellatus</i>	Cd(II)	66.32	Herrero et al., 2011
<i>Oedogonium hatei</i>	Ni(II)	40.9	Gupta et al., 2010
<i>Sargassum filipendula</i>	Cd(II)	103.5	Ayushi et al., 2017
<i>Scenedesmus quadricauda</i>	Cd(II)	135.1	Mirghaffari et al., 2015
<i>Maugeotia genulflexa</i>	As(III)	57.48	Ahmet et al., 2011
<i>Chlorella vulgari</i>	Cd(II)	35.31	Cheng et al., 2016
Pre-treated form of algal biomass			
<i>Oedogonium hatei</i>	Ni(II)	44.2	Gupta et al., 2010
<i>Oedogonium hatei</i>	Cr(VI)	35.2	Gupta and Rastogi, 2009
<i>Cystoseira indicia</i>	Cd(II)	19.56	Mohammad et al., 2011
<i>Cystoseira indicia</i>	Ni(II)	16.17	Mohammad et al., 2011
<i>Nizimuddiniana zanardini</i>	Pb(II)	110.35	Mohammad et al., 2011
<i>Pelvetia canaliculata</i>	Cr(III)	31.19	Vilar et al., 2012
<i>Laminaria japonica</i>	Pb(II)	346.02	Luo et al., 2006
<i>Sargassum</i> sp.	Cu(II)	87.05	Chen and Yang, 2005
<i>Spirulina maxima</i>	Pb(II)	42.0	Gong et al., 2005
<i>Sargassum filipendula</i>	Cu(II)	152.51	Klen et al., 2010
<i>Sargassum glaucescens</i>	Co(II)	38.0	Ebrahimi et al., 2009
<i>Cystosera indica</i>	Mo(VI)	18.32	Kafshgari et al., 2013
<i>Laminaria japonica</i>	Zn(II)	56.88	Lee et al., 2004
<i>Chaetomorpha linum</i>	Cu(II)	92.77	Ajjabi and Choub, 2009
<i>Chaetomorpha linum</i>	Zn(II)	128.97	Ajjabi and Choub, 2009
<i>Sargassum filipendula</i>	Cd(II)	115.78	Luna et al., 2010

Table 2 (continued)

Species of algae	Metal ions	Biosorption capacity (mg/g)	References
<i>Sargassum filipendula</i>	Zn(II)	44.91	Luna et al., 2010
<i>Hizikia fusiformis</i>	Ni(II)	13.898	Shin and Kim, 2014
<i>Hizikia fusiformis</i>	Zn(II)	10.555	Shin and Kim, 2014
<i>Hydrodictyon reticulatum</i>	Cd(II)	12.74	Ammari et al., 2017
<i>Undaria pinnatifida</i>	Cu(II)	125.9	Cho et al., 2013
<i>Laminaria digitata</i>	Cr(III)	41.0	
<i>Caulerpa serrulata</i>	Cd(II)	2.12	Mwangi and Ngila, 2012
<i>Caulerpa serrulata</i>	Pb(II)	2.16	Mwangi and Ngila, 2012
<i>Caulerpa serrulata</i>	Cu(II)	5.27	Mwangi and Ngila, 2012
<i>Laminaria japonica</i>	Cd(II)	104.54	Liu et al., 2009
<i>Laminaria japonica</i>	Ni(II)	66.34	Liu et al., 2009
<i>Spirulina platensis</i>	Cr(VI)	16.7	Finocchio et al., 2010
<i>Cystoseira indica</i>	Pb(II)	282.41	Moghaddam et al., 2013
<i>Ulva lactuca</i>	Cd(II)	41.8	Harja et al., 2015
<i>Sargassum glaucescens</i>	Zn(II)	29.13	Dabbagh et al., 2016
<i>Mastocarpus stellatus</i>	Cd(II)	66.32	Herrero et al., 2008
<i>Chaetomorpha</i> sp.	Zn(II)	115.198	Fatih and Abdulkarim, 2017
<i>Polysiphonia</i> sp. <i>Ulva</i> sp. <i>Cystoseira</i> sp.			
Immobilized form of algal biomass			
<i>Sargassum duplicatum</i>	Cu(II)	17.93	Suharso et al., 2010
<i>Chlorella sorokiniana</i>	Cr(III)	69.26	Akhtar et al., 2008
<i>Scenedesmus quadricauda</i>	Zn(II)	55.2	Bayramoglu and Arica, 2009
<i>Scenedesmus quadricauda</i>	Ni(II)	30.4	Bayramoglu and Arica, 2009
<i>Scenedesmus quadricauda</i>	Cu(II)	75.6	Bayramoglu and Arica, 2009
<i>Chlorella sorokiniana</i>	Ni(II)	60.38	Akhtar et al., 2004
<i>Chlorella sorokiniana</i>	Cu(II)	179.90	Petrovic and Simonic, 2016
<i>Chlorella sorokiniana</i>	Ni(II)	86.49	Petrovic and Simonic, 2016
<i>Chlorella sorokiniana</i>	Cd(II)	164.50	Petrovic and Simonic, 2016
<i>Chlorella</i> sp.	Cu(II)	33.4	Maznah et al., 2012
<i>Chlorella</i> sp.	Zn(II)	28.5	Maznah et al., 2012
<i>Sargassum</i> sp.	Ni(II)	28.17	Yang et al., 2011
<i>Synechococcus</i> sp.	Cd(II)	57.76	Saeed and Iqbal, 2006
<i>Chlorella minutissima</i>	Cr(VI)	57.33	Singh et al., 2012
<i>Chlamydomonas reinhardtii</i>	Hg(II)	116.8	Bayramoglu et al., 2006
<i>Chlamydomonas reinhardtii</i>	Cd(II)	88.6	Bayramoglu et al., 2006
<i>Chlamydomonas reinhardtii</i>	Pb(II)	384.4	Bayramoglu et al., 2006
<i>Spirulina platensis-maxima</i>	Cu(II)	196.99	Peter et al., 2016
<i>Spirulina platensis-maxima</i>	Cd(II)	213.58	Peter et al., 2016
<i>Micractinium reisseri</i>	Cu(II)	1.710	Lee et al., 2016
<i>Isochrysis galbana</i>	Cr(III)	335.27	Kadimpati et al., 2013

and lead were 111.1 mg/g and 121.9 mg/g respectively (Azza et al., 2013). The brown alga *Sargassum muticum* collected from the location of Cuba north coast was cleaned with deionized water, by that the interference of ions effect on the biosorption process can be prevented. The cleaned algal biomass was dried at 60 °C, ground and sieved to the size of < 0.1 mm. The maximum biosorption capacity of *Sargassum muticum* for hexavalent chromium was 196.1 mg/g (Bermudez et al., 2012). The green algae *Ulva lactuca* evaluated for the removal of mercury from contaminated waters with high salinity without any particular type of pre-treatment. The *Ulva lactuca* biomass was collected in the region of Mondego estuary in Portugal. The biomass was washed using the distilled water, air-dried for several days and a finally dried at 40 °C for 24 h. The dried biomass was milled through domestic coffee

grinder (Henriques et al., 2015). The collected samples of green alga *Maugetia genuflexa* were washed with deionized water for several times in order to remove the sand particles and debris. The washed biomass was sun dried for two days and further in hot air oven at 60 °C for 60 min. Then the dried biomass was cutted and sieved to obtain the biosorbent in the mesh sizes range between 0.150 and 0.250 mm. The maximum monolayer biosorption capacity of *Maugetia genuflexa* biomass was found as 57.48 mg/g. The functional groups of carboxyl, hydroxyl, and amide groups were involved in the biosorption of As(III) onto algal biomass (Ahmet et al., 2011).

The pellet form of blue green algae *Spirulina platensis* after harvesting was washed with distilled water, centrifuged and oven dried at 80 °C for 24 h. Then the dried biomass was grinded and sieved to obtain the particles sizes between 75 and 100 µm mesh sizes. The maximum biosorption capacity of metal ions on the surface of *Spirulina platensis* was found as 73.64 mg/g and 69.04 mg/g for cadmium and nickel ions respectively (Celekli and Bozkurt, 2011). The brown algae *Durvillaea antarctica* was studied for the removal of lead from acidic aqueous solutions. The biomass of *Durvillaea antarctica* was collected in the region of bay of Valparaíso, Chile. The sampled algal biomass was first washed in tap water and then with distilled water to remove salts. The algal biomass then dried in the hot air oven at 50 °C for 48 h. The dried biomass of *Durvillaea antarctica* was then cutted into pieces of approximately 0.5–1 cm size (Hansen et al., 2013). The green algae *Cladophora fascicularis* was sampled along the Qingdao seashore, China. The sampled biomass was washed several times using distilled water to get rid of dirt, oven dried at 60 °C for 24 h and segmented in the size range of 4–5 mm. The maximum uptake of *Cladophora fascicularis* towards lead was 198.5 mg/g and the functional groups like amido, hydroxy and carboxyl could combine intensively with the lead ions (Deng et al., 2007). Three species of brown algae such as *Hizikia fusiformis*, *Laminaria japonica* and *Undaria pinnatifida* were collected in the region of southern coast of South Korea. The collected biomasses were oven dried at 50 °C for 24 h and grinded using homogenizer. Finally the biomass size in the range of 0.21–0.31 mm were selected for the biosorption studies towards lead, cadmium, manganese, copper and chromium ions removal (Lee and Park, 2012). The green alga *Ulva lactuca* collected from the Suez Bay, Red Sea was used for the biosorption of cadmium ions from the aqueous solutions. The collected biomass was cleaned by tap water and washed finally using the distilled water to remove the particulate material bound on the biomass surface. The cleaned biomass dried at the room temperature, grinded in electrical mill and sieved to obtain the uniform particle sizes of 0.210 mm (Ghoneim et al., 2014). The biomass of brown algae such as *Lessonia nigrescens* and *Durvillaea antarctica* was employed for the removal of cadmium. The two algal biomasses were sampled in the bay of Valparaíso, Chile. Then the samples were washed in tap water, finally with distilled water and dried at 50 °C. The dried biomass of *Durvillaea antarctica* and *Lessonia nigrescens* were cut into the size range of 0.5–1 cm length and 1–1.5 cm length, 0.5–1 cm diameter. Such sizes are useful in easy handling and possibility in real treatment process (Gutierrez et al., 2015). The red algae, *Gracilaria corticata* and brown algae, *Sargassum glaucescens* were collected in the region of Persian Gulf, Queshm Island. The collected biomass was washed many times with tap water and then sun dried for 6 days. The dried biomass was chopped and milled to obtain the biosorbents in the size range of 0.5–1 mm. The biosorption efficiency of *Sargassum glaucescens* and *Gracilaria corticata* towards mercury removal was 95.1% and 90.0% (Esmaeili et al., 2015).

5.2. Pre-treated algae

The samples of *Padina* sp. procured from Phuket Marine Biological Center, Thailand were sun dried. The pre-treatment was done by mixing 20 g of algal biomass with 0.2 M calcium chloride solution for the contact time of 24 h with slow stirring. Using deionized water, the pre-treated biomass was washed several times to remove the excess calcium

associated with the algal biomass. Then the biosorbent was dried at 60 °C for 24 h and sieved to obtain particles in the size range of 0.300–0.600 mm (Kaewsarn and Yu, 2001). The brown algae *Cystoseira indica* was pre-treated with calcium chloride and used for the removal of lead from aqueous solution (Moghaddam et al., 2013). The yellowish green alga *Oedogonium hatei* sampled in a stream near Roorkee, India. The sampled biomass was cleaned by washing in running tap water and then with Milli-Q water. Using filter paper, the water content in the biomass was reduced and then sun dried for four days followed with oven drying. The prepared algal biomass was subjected to acid treatment of 0.1 M hydrochloric acid and the prepared mixture was agitated at 200 rpm for 8.0 h. The acid treated biomass was washed using physiological saline solution and oven dried at 60 °C. The dried material was ground and the particles were selected between the mesh sizes of 150 µm and 250 µm (Gupta et al., 2010). The brown algae *Sargassum bevanom* was sampled in the region of Persian Gulf in Bandar Boshehr, Iran. After cleaning with distilled water, the biomass was dried and subjected for acid treatment with 0.5 M hydrochloric acid. Then the material was washed using physiological saline solution, dried, sieved and assessed for the removal of hexavalent chromium aqueous solution and industrial wastewater. The adsorption capacity of acid treated biomass was 35.41 mg/g and the removal efficiency was about 90% (Javadian et al., 2013). The biomass of brown algae *Sargassum oligocystum* was collected in the Persian Gulf, Bushehr coast, Iran. The collected biomass was first washed using running tap water followed with deionized water. The washed biomass was subjected for physical pre-treatment by placing the algal biomass in a muffle furnace at 350 °C for 2 h. Then the carbonized material was grinded to obtain the particle size of 0.074 mm. The obtained adsorbent was tested for the removal of metal ions from aqueous solutions. The maximum adsorption capacity by the adsorbent towards mercury, cadmium and coppers ions was 60.25, 153.85 and 45.25 mg/g respectively (Delshab et al., 2016). The dried biomass of 2.5 g red algae *Jania ruben* was pre-treated with 17 mL of 36% formaldehyde and 33 mL of 0.1 M hydrochloric acid solutions. The content of the mixture was stirred for 1 h and then the biomass was filtered, washed with distilled water followed with 0.2 M sodium carbonate solution and finally using the deionized water. The prepared adsorbent was dried overnight at the temperature of 60 °C and after that at 110 °C for 2 h. The highest biosorption capacity of 774 mg/g lead uptake by the adsorbent was observed (Hanbali et al., 2014).

The effects of different chemical treatments of nitric acid, hydrochloric acid, sodium hydroxide and acetone on the algal biomass of *Gracilaria conferta*, *Eisenia bicyclis*, *Ulva lactuca*, *Sargassum fluitans*, *Cladophora prolitera*, *Padina pavonica*, and *Zostera marina* were performed. The metal ions such as lead, copper, zinc, cadmium chromium, manganese, nickel, cobalt and mercury were subjected for the biosorption studies. All the pre-treatments of biomass had showed the effective improved ability of metal ions binding and better biosorption capacity (Zhao et al., 1994). The biomass of *Gracilaria* waste and *Oedogonium* sp., was subjected under the effects of the different iron concentration and various pyrolysis temperatures for the removal of arsenic. Each biomass was exposed to ferric chloride solutions equivalent to 1.5, 4, 8 and 12.5 g Fe³⁺ per 100 mL and highest heating temperatures of 300, 450 and 750 °C respectively. The biosorbent from *Oedogonium* had a higher capacity towards arenic removal than the biosorbent produced using *Gracilaria* waste (Johansson et al., 2016). The brown algae *Pelvetia canaliculata* Ochrophyta was collected at the Northern coast region of Portugal. The collected biomass was sun dried, washed with deionized water and oven dried. The pre-treatment was performed by soaking 5.0 g of algae into 0.5 M of sodium chloride solution. The sodium loaded biomass was washed with deionized water until the pH attain to 6.0–6.5. Finally, the sodium pre-treated biomass was dried at 45 °C for 24 h. The prepared adsorbent was used for the removal of nickel ions and the maximum uptake capacity by sodium loaded algae was 100 mg/g (Bhatnagar et al., 2012). The *Sargassum* sp., were sampled in the region of Qeshm coast, Iran. The biomass was pre-

treated with magnesium nitrate for the removal of cobalt ions. After cleaning and drying, the samples were sieved to obtain an average of 0.7 mm particle size. With slow stirring, 10 g of biomass was mixed with 0.1 M magnesium nitrate hexahydrate for 24 h. The magnesium ions treated biomass was washed using deionized in such a way to attain stable solution pH and to remove excess magnesium ions from the biomass. The prepared biosorbent was dried overnight in hot air oven at 55 °C. The biosorbent showed uptake capacity of about 80.27 mg/g (Soleymani et al., 2015). Algal biomass of *Spirulina platensis* was used for the removal of hexavalent chromium with the pre-treatment of three different acids like sulphuric acid, nitric acid and hydrochloric acid. The results showed that hydrochloric acid modified biomass had better removal capacity of 5 mg/g, comparatively higher than the other acid pre-treatments (Hegde et al., 2016).

5.3. Immobilized algae

The biomass of *Sargassum duplicatum* was immobilized by silica gel through continuous method and used for the removal of copper, cadmium and lead ions from aqueous solutions. For the immobilization, 1 g of biomass with specific size of 0.03 mm was mixed with 3 M sulphuric acid. The acid mixed biomass was treated with Na-silicate solution in the ratio of 1:1, left to 1 h for the gel formation. The resultant gel left over night, then washed, oven dried, ground and sieved to 200 mesh size. The biosorption capacity of *Sargassum duplicatum* towards copper, cadmium and lead ions removal was 280.112, 130.513 and 113.660 µmol/g respectively (Suharso et al., 2010). The fine particles size < 125 µm of green algae *Ulva lactuca* was pre-treated with the saturated solution of calcium nitrate hexahydrate. The pre-treated algal biomass was added to the beaker containing 10 mL of an agar solution concentration of 20 g/L. The prepared suspension was transferred to a petri dish and allowed to solidify. The final matrix form was cut into the square size of 0.5 cm × 0.5 cm (Maria et al., 2012). The equal quantities of the solution of *Isochrysis galbana* algae and alginate were well mixed in a magnetic stirrer. Then the mixture of algal biomass and alginate was pumped using peristaltic pump into the solution of 0.5 M calcium chloride dihydrate. For the process of curing, the formed beads were stored in 0.25 M calcium chloride dihydrate solution at the temperature of 4 °C for overnight, after that washed with distilled water to remove the excess calcium chloride dihydrate. The prepared biosorbent was used for the removal of Cr(III) and the biosorption capacity was about 335.27 mg/g (Kadimpati et al., 2013). The brown alga *Cystoseira indica* collected along the coast of Chabahar, Iran was washed, dried and sieved to obtain particle size in the range of 1–2 mm. The prepared biomass sample of 10 g was treated with 0.1 M calcium chloride solution in 1000 mL for 12 h and agitated at 150 rpm. The prepared immobilized biosorbent was washed with deionized water in order to remove the excess calcium ions associated with the biosorbent and then dried in hot air oven at 60 °C for 24 h. The immobilized *Cystoseira indica* had greater affinity towards copper ions compared to other ions in case of single-ion biosorption study (Keshtkar et al., 2015). The immobilization of *Chlorella vulgaris* biomass performed through an entrapment into alginate matrix was produced by means of ionic polymerization in the calcium chloride solution. The prepared immobilized biomass was used for the removal of nickel ions and the biosorption capacity was about 25.6 mg/g (Rub et al., 2004). The brown algae *Fucus vesiculosus* biomass size of < 0.5 mm was treated with the 2% sodium alginate solution. The prepared mixture was dropped into 0.5 M calcium chloride using syringe at constant stirring. The final size of the beads was about 2.5 mm. In comparison of immobilized biomass towards the removal of three metal ions like cadmium, lead and copper, lead recovery is particularly effective (Mata et al., 2009).

Marine algae, *Gelidium* was immobilized by an organic polymer polyacrylonitrile and was employed the removal of copper ions. The maximum uptake capacity of about 13 mg/g was obtained (Vilar et al., 2008). 10 g of the biomass of *Sargassum* sp., in the size range of

65–212 µm was mixed to the 10% poly vinyl alcohol and stirred using magnetic stirrer at the temperature of 80 °C. Then the solution content was cooled to the room temperature and agitated to obtain the uniform solution. The mixture was transferred drop wise into liquid nitrogen by peristaltic pump at the flow rate of < 5 mL/min. The resultant beads were frozen approximately at –20 °C for 1–2 h. After that, the beads were transferred to 4 °C. The copper ions uptake rate was increased with an increase in the biomass concentration in the beads (Sheng et al., 2008). The *Chlamydomonas reinhardtii* was immobilized using calcium alginate for the sequestration of heavy metal ions from aqueous solutions. The biosorption capacity of mercury, cadmium, and lead ion by biosorbent was 89.5, 66.5, and 253.6 mg/g respectively (Bayramoglu et al., 2006). *Scenedesmus quadricauda* biomass of 1.33 g was mixed to the polymer mixture containing 3.5% poly vinyl alcohol and 1.0% sodium alginate. The content was agitated using the magnetic stirrer at the room temperature and time duration of 1 h. Then the solution was added drop wise into 0.1 M boric acid and 0.1 M calcium chloride. The prepared beads are approximately in the size of 2 mm. The results indicated that the immobilized algal beads had more biosorption capacity for the copper and cadmium ions than the control immobilized beads (Bayramoglu and Arica, 2011). The microalgae biomass *Isochrysis galbana* entrapped into alginate gel and used for the biosorption of trivalent chromium ions. The equal quantities of the algal and alginate solution were agitated using a magnetic stirrer at the room temperature. The prepared mixture was pumped using the peristaltic pump into the 0.5 M calcium chloride dihydrate solution. The prepared beads were subjected for curing by 0.25 M calcium chloride dihydrate solution. The maximum biosorption capacity of algal biomass towards trivalent chromium removal was found as 335.27 mg/g. About 75% of the removal of trivalent chromium took place in the first 2 h (Kadimpati et al., 2013). The *Enteromorpha* sp. particles size of < 0.25 was immobilized with the polymer of sodium alginate and polysulfone. The immobilization of biomass in polysulfone matrix was done by dissolving 10 g of polysulfone in 90 mL of N, N dimethyl formamide. The prepared suspension mixed with 5 g of algal biomass in a magnetic stirrer and transferred to 80% methanol solution by drop wise manner. The formed beads were washed with double distilled water in such a way to diffuse out the N, N dimethyl formamide and the resultant beads were air dried for 2–3 days at the room temperature. The maximum percentage removal of hexavalent chromium by *Enteromorpha* sp. immobilized in sodium alginate and polysulfone was 90.52% and 90.86% respectively (Rangabhashiyam et al., 2016a).

6. Factors affecting the biosorption process

The biosorption of toxic heavy metal ions using the algal biomass influenced mainly by the experimental parameters such as the biosorbent dosage, solution pH, contact time, initial metal ions concentration and temperature. The optimal conditions of the significant experimental parameters towards the removal of heavy metals by algal biomasses are listed in Table 3. The discussions of each parametric effect over the metal ions removal process through the algal biosorbents are as follows.

6.1. The effect of biosorbent dosage

The biosorbent dosage at a specified initial metal ion concentration determines the biosorption capacity and the removal efficiency of the algal biomass towards the heavy metal removal. The biosorbent dosage is mainly attributed to the metal binding sites on the biomass (Monteiro et al., 2012; Zaib et al., 2016). The increase of biosorbent dosage showed higher percentage removal of the metal ions and this was due to the availability of more number of active sites on the biosorbent surface. The decrease of the biosorption capacity of the algal biomass with an increase of biosorbent dosage may be because of the concentration gradient between the biosorbent and the biosorbate (Mohammad et al.,

Table 3

The optimal operational conditions for the biosorption of heavy metals by algal biomass.

Species of algae	Metal	Optimal biosorption conditions					References
		Algal dosage (g)	Initial solution pH	Time (min)	Initial metal concentration (mg/L)	Temperature (K)	
<i>Oscillatoria princeps</i>	Cd(II)	1.0	5.0	240	50	298	Sulaymon et al., 2013
<i>Ulva lactuca</i>	Pb(II)	0.2	5.0	240	130	293	Bulgariu and Bulgariu, 2012
<i>Sargassum glaucescens</i>	Ni(II)	1.0	6.0	120	30	313	Pahlavanzadeh et al., 2010
<i>Maugeotia genueflexa</i>	As(III)	4.0	6.0	60	10	293	Ahmet et al., 2011
<i>Cystoseira indica</i>	Cu(II)	1.0	5.0	300	100	298	Keshkar et al., 2015
<i>Sargassum angustifolium</i>	Cu(II)	0.4	6.0	60	150	315	Niad et al., 2014
<i>Porphyridium cruentum</i>	Hg(II)	0.25	7.0	120	10	298	Zaib et al., 2016
<i>Sargassum fusiforme</i>	Cu(II)	3.0	10.0	60	10	–	Huang and Lin, 2015
<i>Chlorella vulgaris</i>	Cd(II)	0.018	–	105	100	298	Cheng et al., 2016
<i>Enteromorpha</i> sp.	Cr(VI)	0.2	2.0	160	20	303	Rangabhashiyam et al., 2016b
<i>Halimeda gracilis</i>	Cu(II)	1.98	4.49	60.21	–	308.15	Jayakumar et al., 2015a, 2015b
<i>Scenedesmus quadricauda</i>	Cd(II)	0.2	5.0	60	10	–	Mirghaffari et al., 2015
<i>Spirogyra</i> sp.	Cr(VI)	1.0	4.0	120	–	303	Yaqub et al., 2012
<i>Cystoseira indica</i>	Co(II)	1.0	5.0	240	100	298	Akbari et al., 2015
<i>Caulerpa fastigiata</i>	Cd(II)	10	5.5	60	30	298	Sarada et al., 2014b
<i>Sargassum bevanom</i>	Cr(VI)	0.7	3.0	110	100	–	Javadian et al., 2013
<i>Sargassum muticum</i>	Ni(II)	0.5	3.0	–	10	293	Bermudez et al., 2011
<i>Sargassum ilicifolium</i>	Pb(II)	0.2	3.7	–	200	–	Tabaraki et al., 2014
<i>Undaria pinnatifida</i>	Zn(II)	0.1	4.0	120	–	293	Cazon et al., 2013
<i>Chondracanthus chamissoi</i>	Pb(II)	0.2	4.0	360	70	293	Yipmantin et al., 2011
<i>Spirulina platensis</i>	Cu(II)	0.05	7.0	90	100	310	Homaidan et al., 2014
<i>Pediastrum boryanum</i>	Cr(VI)	0.1	2.0	90	100	298	Ozer et al., 2012
<i>Microcystis aeruginosa</i>	Cd(II)	2.0	6.0	180	200	298	Wang et al., 2014
<i>Chlorella vulgaris</i>	Zn(II)	1.0	6.0	30	50	295	Aniko et al., 2014
<i>Hizikia fusiformis</i>	Ni(II)	0.03	4.0	180	5	293	Shin and Kim, 2014
<i>Sargassum myriocystum</i>	Cr(VI)	2.017	5.2	108	–	308.15	Jayakumar et al., 2015a, 2015b

2011; Sari and Tuzen, 2009). At the equilibrium condition, biosorption capacity of formaldehyde pre-treated *Cystoseira indica* towards cadmium, nickel, and lead ions removal decreased with biomass dosage increase from 0.006 to 0.48 g (Mohammad et al., 2011). The biosorbent dosage of raw and 0.1 M hydrochloric acid treated *Oedogonium hatei* had significant effect on the removal of nickel ions from aqueous solutions. The percentage removal of the nickel ions increased with an increase of the both types of *Oedogonium hatei* (Gupta et al., 2010). The influence of sodium chloride pre-treated *Cystoseira indica* dosage was investigated in the range of 1.0–4.0 g/L for the removal of copper and cobalt ions. The increase of the algal dosage showed decreased biosorption capacity on the each metal ions, which was due to presence of the unsaturated active sites on the biosorbent (Akbari et al., 2015). The algal biomass of *Ulva lactuca* and its activated carbon with the varying dosage of 0.2–1.0 g/L were analyzed for the removal of copper, trivalent chromium, cadmium and lead ions. The maximum uptake capacity of the biosorbents towards the metal ions removal was at the dosage 0.8 g/L. Beyond the dosage of 0.8 g/L, the biosorption capacity of the biosorbents was almost constant, this could be due to the agglomeration effect and the resultant decrease of the intercellular distance (Ibrahim et al., 2016). The biosorbent dosage in the biosorption process is proportional to the special binding area of the biosorbent. The influence of *Polysiphonia urceolata* and *Chondrus ocellatus* dosages of 0.4 to 4.0 g/L was analyzed on the removal of hexavalent chromium from aqueous solutions. The removal efficiency of the hexavalent chromium increased with an increase of biosorbent dosage, due to availability of greater surface area and larger pore volume. The negative effect at low biosorbent dosage was because of biosorbent saturation with the hexavalent chromium (Li et al., 2015).

6.2. The effect of the solution pH

One of the important critical parameter in the examination of the biosorption process is the initial solution pH of the biosorption system. The pH of the aqueous solution have influence over the solubility of metal ions, the concentration of the counter ions on the functional group of the biosorbent, metal ions binding site on the algal biomass

and the metal ion chemistry in the aqueous solutions (Cirik et al., 2012; Azza et al., 2013; Mustafa and Ahmet, 2010). The removal of copper and zinc ions was demonstrated as function of solution pH using calcium chloride pre-treated biomass of *Chaetomorpha linum*. The metal ions removal efficiency by the biomass increased with an increase in the solution pH from 2.0 to 5.0. The maximum removal was attained for both the metal ions at 5.0 solution pH due to the positively charged metals ions occupy the free binding sites on the biomass. At lower values of the solution pH, the higher concentration of hydrogen protons competes with these metal ions for the binding sites on the algal surface. Resulting in the protons saturation on the binding sites of the biomass functional group, forbids the further cation interaction. The decrease in biosorption efficiency at the higher solution pH values could be because of the anionic hydroxide complexes and their competition effects on the active sites of the biomass (Ajjabi and Choub, 2009). The removal of nickel, zinc and lead ions was analyzed using *Arthrospira platensis* and *Chlorella vulgaris*. The option of the zero point of charge was considered to select the optimum pH range for metal biosorption. The biosorbent surface gets positive charge when the pH value was less than the zero point of charge and gets negative charge at higher values than zero point of charge. The zero point of charge values for *Arthrospira platensis* and *Chlorella vulgaris* were estimated as 4.0 and 3.4, respectively. Further examination on the biosorption studies in the pH range 3.0 to 6.0 showed that the solution pH of 5.0 to 5.5 was the optimum for the biosorption experiments (Ferreira et al., 2011). In the biosorption of copper by *Spirulina platensis*, the percentage removal of copper ions by the biomass showed decreased effect in the pH range from 2.0 to 5.0 and also in above 10.0 pH. The neutral solution pH of 7.0 showed maximal removal efficiency of copper ions by the algal biomass. The biosorbate and biosorbent interactions in the aqueous solution is controlled by the solution pH through the different forms of metal ions existence in various solution pH and the presence of various functional groups in the biosorbent surface (Homaidan et al., 2014). The biomass of the algae biomass normally contains the alkali and alkaline earth metal ions, which are bound to the surface acidic functional groups. During the biosorption process, the solution pH and electrical conductivity of the aqueous solution was increased due to the

release of light metal ions. The study using Chlorophyta and Cyanophyta demonstrated that optimum solution pH for the biosorption of lead, cadmium, copper and arsenic ions are 3.0, 5.0, 4.0, and 5.0 respectively (Sulaymon et al., 2013). Solution pH ranges of 0.5 to 5 were considered for the biosorption analysis of hexavalent chromium using *Chlorella vulgaris*. The percentage removal of hexavalent chromium increased from 54.4% to 81.6% as the solution pH increased from 0.5 to 2.0. The solution pH affects the active site configurations and the structure of the biomass (Sibi, 2016). *Sargassum glaucescens* nanoparticle as biosorbent tested for the removal of nickel and cobalt from plant effluent in the pH range from 2.0 to 7.0. The maximum uptake capacity by the biosorbent towards both the metal ions was observed at the solution pH of 6.0. Other than the optimal solution pH, heavy metals with the higher redox potential undergo bioreduction, occurred by the supply of electrons resultant from the biomass reduction (Esmaeili and Beni, 2015). The removal of cadmium and lead with the biomass of *Scenedesmus quadricauda* showed positive effect by the initial solution pH increase from 2.0 to 5.0. At the optimal solution pH of 5.0, the maximum removal efficiency of cadmium and lead was 66% and 82% (Mirghaffari et al., 2015).

6.3. The effect of contact time

As the biosorption process proceeds, the biosorbent gets saturated with the biosorbate and then have a tendency for desorption process. At the equilibrium time, the rate of the biosorption will be equal to the rate of the desorption. Once the biosorption process reached the state of equilibrium, there will not be any further binding of the biosorbate on the biomass. The determination of the such equilibrium time of the biosorption process are important since the parameter plays vital role in the biosorption optimization (Mohammad et al., 2011; Zaib et al., 2016). The effect of contact time was performed on the removal of lead and cadmium using chemically modified algal biomass. The removal efficiency of 86.8% for lead at 80 min and 80.3% for cadmium at 60 min was attained (Khan et al., 2016). The biosorption of cadmium ions by *Sargassum angustifolium* revealed the two stage removal pattern. The first 30 min of rapid cadmium removal of > 90% of the initial metal ion concentration, followed by the next 15 min of the biosorption process attained equilibrium (Jafari et al., 2015). Fast biosorption profile of *Sargassum fusiforme* biomass for the removal of both mercury and copper was observed, which was the significant criteria for the selection of biosorbent in the removal process. The metal removal process was rapid at the contact time of first 60 min, since the biosorption process could carry out only on the biosorbent surface. Further, the increase of the biosorbent may also contribute in fast removal process because of increased area to volume ratio, resulting in the large contact area provided by the biomass for the binding of heavy metal ions (Huang and Lin, 2015). The assessment of biosorption equilibrium time for hexavalent chromium removal using the biomass of *Laminaria japonica*, *Undaria pinnatifida*, *Porphyra haitanensis*, and *Gracilaria lemaneiformis* was done with the contact time range from 5 to 120 min. The metal removal efficiency was rapid at the initial period of the biosorption process and then gradually reached equilibrium. The biomass of *Porphyra haitanensis* in the aqueous solution formed larger particles due to aggregation, resulting comparatively in lower performance (Jia et al., 2014). The biosorption of lead ions by *Caulerpa fastigiata* showed faster removal at initial stages of the process followed with slower removal and finally reached equilibrium. This could be because of the presence of more vacant sites for metal binding and the decline in biosorption removal may be due the repulsion between biosorbed lead ions on the biomass (Sarada et al., 2014a).

6.4. The effect of initial metal ions concentration

The biosorption of heavy metal ions from the aqueous solutions by means of the algal biomass highly depends on the initial metal ions

concentration. The process of biosorption increases at the initial period and with the further increase in initial metal ions concentration has no significant in the metal biosorption (Singh et al., 2010). The biosorption capacity of *Cystoseira indica* and *Nizimuddiniana zanardini* was investigated with the different initial concentrations of metal ions like cadmium, nickel and lead. The biosorption capacity of the algal biomasses towards the heavy metal removal was increased with an increase in the initial metal ion concentration. This may be because of the larger driving force provided by the increased metal ion concentration, which overcomes the mass transfer resistances exhibited between the biosorbent and the aqueous solution (Mohammad et al., 2011). Different concentrations for hexavalent chromium were analyzed for the removal process using modified brown algae *Sargassum bevanom*. The experimental results showed that the percentage removal of hexavalent chromium ions decreased from 89.64% to 45.08% with the increase of initial hexavalent chromium concentration from 100 mg/L to 550 mg/L. The decrease in percentage removal of the metal ion was due to the decrease in the biosorption sites, since the ratio of initial concentration of the metal ions to the available biosorption surface area was higher. Whereas, the biosorption capacity of algal biomass towards the hexavalent chromium removal increased from 12.88 mg/g to 35.41 mg/g. This may be due to the competitive effects of the metal ions for the available binding sites and represent that the initial metal concentration plays an important role in the adsorption capacity (Javadian et al., 2013). The effect of initial mercury ion concentration studied in the range from 2.5 to 500 mg/L with *Porphyridium cruentum*. The uptake capacity by the constant amount of algal biomass increased from 0.10 mg/g to 2.57 mg/g with the increase in initial metal ions concentration, nevertheless the percentage removal showed decreased effect (Zaib et al., 2016). The initial metal ions concentration of heavy metals like copper, zinc, cadmium, and mercury remarkably influenced over the biosorption process by the algal biomass of *Cladophora fracta*. The increase of the initial metal ion concentration caused the increase of the quantity of biosorbed metal ion per unit weight of algal biomass (Ji et al., 2012). The biomass of *Spirulina platensis* was employed for the biosorption of copper ions from the aqueous solution. With the biosorbent dosage of 0.05 g, the percentage removal increased from 47.65% to 90.61% for the initial copper ion concentration increase from 10 to 100 mg/L, whereas the negative effect was noticed at higher metal ion concentration of 150 and 200 mg/L. Results are due to the fully occupied biosorbent binding sites at higher copper ion concentrations (Homaidan et al., 2014).

6.5. The effect of temperature

In the biosorption process, the temperature parameter normally increases the sequestration of the biosorbate from the aqueous solution. The possible reasons for the enhanced removal with increasing temperature includes the increase of biosorbent active sites and its raised activity, enlargement of biosorbent pore, reduction in the diffusion boundary layer thickness around biosorbent, increased mobility of metal ions and higher biosorbent surface activity (Park et al., 2010; Rangabhashiyam and Selvaraju, 2015b). Most of the biosorptive removals of the metal ions are endothermic in nature and the higher temperature mostly increases the biosorptive removal of the metal ions (Veglio and Beolchini, 1997). The biomass of *Oedogonium hatei* was studied for the removal of hexavalent chromium from the aqueous solution with three different temperatures. The biosorption capacities was increased with an increase with the temperature represented endothermic nature of the biosorption process. The increased uptake capacities may be because of the enhanced active sites or the decreased mass transfer resistance of the metal ions (Gupta and Rastogi, 2009). The maximum removal of hexavalent chromium by *Sargassum muticum* biomass was found at the higher temperature of 323 K. The temperature of the biosorption process is a vital factor because of the metal biosorption mechanisms are dependent of temperature (Bermudez et al.,

2012). The parameteric effect of temperature on the biosorption seems to have lesser extent, when the process performed within the temperature range from 20 to 35 °C (Vijayaraghavan and Yun, 2008). The temperature effect on the biosorption of arsenic ions onto the biomass of *Maugeotia genulflexa* examined in the range from 293 to 323 K. The biosorption efficiency decreased from 96% to 60% with the temperature increase and represented the exothermic nature of the biosorption process. The decrease in the percentage removal of arsenic ions may be due to the desorption tendency of metal ions and the bond ruptures in the biosorbent active sites (Ahmet et al., 2011). The effect of temperature on the removal of nickel ions using *Oedogonium hatei* performed at three different temperatures of 298, 308 and 318 K respectively. The biosorption capacities of the biomasses showed decreased effect towards the metal ion removal, which represent the exothermic nature of the removal process. The negative effect may be because of the damage of biosorbent active sites otherwise the desorption tendency of metal ions from the biosorbent interface (Gupta et al., 2010). The biosorption process employing the biomass at the higher temperature may leads to the physical damage to the biosorbent. The removal of metal ions through biosorption process at room temperature was mostly advantageous (Park et al., 2010).

7. Biosorption isotherms

The biosorption isotherm describes the relation between biosorbate concentration in the equilibrium solution and amount of biosorbate adsorbed by unit mass of the biosorbent at constant temperature. Biosorption isotherms are very essential for the design of the biosorption systems. The data from the biosorption isotherm models gives information on the removal capacity of the biosorbent (Maciel et al., 2013; Liang et al., 2010). The most suitable biosorption isotherm model is indispensable in the attempt to explore novel potential biosorbents for an ideal biosorption system. The isotherm models are important in the prediction of biosorption parameters and useful in the comparison of various biosorbents under different process operating conditions (Anastopoulos and Kyzas, 2015).

Biosorption isotherm models are mostly used in the investigation over the removal studies of heavy metal from aqueous solution. In most of the metal biosorption process, the equilibrium data was best fitted with the isotherm models of two and three parameters (Rangabhashiyam et al., 2014b). Therefore, the isotherm models like Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Jovanovic, Flory–Huggins, Redlich–Peterson, Sips and Koble–Corrigan were considered in the further discussions. The best fitted biosorption isotherm models in various metal removals by algae are given in Table 4.

7.1. Langmuir model

The Langmuir biosorption isotherm model (Langmuir, 1916) describes quantitatively about the monolayer formation of biosorbate on the biosorbent outer surface. The model denotes an empirical equation describes the equilibrium distribution between a bulk liquid and a solid phase. The Langmuir isotherm was based on the biosorption and desorption rates, integrating the surface coverage net rate. The Langmuir adsorption isotherm was based on the hypothesis such as (1) biosorption on homogeneous monolayer surface, (2) no more biosorption takes place in the already occupied site, (3) the energy of biosorption is constant, (4) the intermolecular attractive forces drop rapidly with an increase of distance, (5) the biosorbent has limited uptake capacity, (6) all the biosorption sites are similar and energetically equal, and (7) no interaction between adsorbed species. The Langmuir biosorption isotherm model was effectively used for the various pollutants removal processes and this model is one of the most widely used isotherm model for the removal of heavy metal from the aqueous solutions (Rangabhashiyam et al., 2014b). The non-linear form of the Langmuir isotherm model represented as follows:

$$q_e = \frac{Q_0 b_L C_e}{1 + b_L C_e} \quad (1)$$

where q_e is the biosorption capacity at equilibrium (mg/g), Q_0 indicate the maximum uptake capacity of the biosorbent, b_L represent the Langmuir biosorption constant (L/mg) and C_e is the equilibrium metal ions concentration (mg/L).

The Langmuir isotherm model can be elucidated in terms of dimensionless constant separation factor, also called as equilibrium parameter (R_L) represented by

$$R_L = \frac{1}{(1 + b_L C_0)} \quad (2)$$

where C_0 is the initial concentration of the metal ions (mg/L) and the value of R_L represents the nature of the biosorption process. When the value of R_L lies between 0 and 1, indicate the favorable biosorption. The value of $R_L > 1$ represents the unfavorable biosorption, the value of R_L equal to 1 represents the linear biosorption and specifies the irreversible biosorption process in case of R_L value equal to 0.

7.2. Freundlich model

The Freundlich isotherm model (Freundlich and Helle, 1939) is an empirical equation based on the the non-ideal, reversible biosorption, infinite biosorbent binding site and extended to multilayer biosorption. Freundlich model is another form of the Langmuir isotherm model for biosorption on an amorphous surface. The amount of biosorbate bound on the biosorbent is the summation of all the biosorption active sites. This isotherm describes the surface heterogeneity and the exponential distribution of biosorbent active sites and its corresponding energies. The model was based on the assumption that the stronger binding sites on the biosorbent are first occupied, consequently the binding strength decline with an increase in the degree of biosorbent active site utilization. Freundlich isotherm model is commonly represented by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F represent the Freundlich isotherm constant (L/g) and n indicate the Freundlich exponent known as the biosorbent intensity, which gives information on whether the biosorption process is favorable or not. The slope ranges between the values of 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as biosorbent intensity value gets closer to zero. Whereas, the value of biosorbent intensity below unity implies chemisorption process and $1/n$ value above one specify the cooperative biosorption process (Haghseresht and Lu, 1998). If the value of biosorbent intensity is equal to 1, the biosorption process is linear. Henry's isotherm or one parameter isotherm model is valid for linear biosorption when the value of biosorbent intensity is equal to 1 (Al-Duri and McKay, 1996).

7.3. Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is an empirical model was used for the analysis of isotherms with high degree of regularity (Dubinin and Radushkevich, 1947). Unlike the Langmuir isotherm, this isotherm model does not assume the homogeneous biosorbent surface and constant biosorption potential. The Dubinin–Radushkevich isotherm model finds its application in verifying whether the metal biosorption process is physical or chemical (Dubinin, 1960). The isotherm of this model is as follows:

$$q_e = Q_m \exp^{-K\varepsilon^2} \quad (4)$$

where Q_m is the maximum biosorption capacity (mg/g), R denotes the gas constant (8.314 J/mol K), T represent the temperature (K). The mean biosorption energy E (kJ/mol) can be calculated using K values through the following equation.

Table 4

Biosorption isotherm, kinetic and thermodynamic data of the metal ions biosorption using algae.

Species of algae	Metal ions	Model		Thermodynamic parameters			References
		Isotherm	Kinetic	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	
<i>Ulothrix cylindricum</i>	As(III)	Langmuir	Pseudo-second-order	–20.6	–30.9	–35.8	Tuzen et al., 2009
<i>Padina pavonica</i>	Al(III)	Langmuir	Pseudo-second-order	–15.43	45.96	0.21	Sari and Tuzen, 2009
<i>Niznuddiniana zanardini</i>	Ni(II)	Langmuir	Pseudo-second-order	–17.558	11.823	0.999	Pahlavanzadeh et al., 2010
<i>Maugeotia genulflexa</i>	As(III)	Langmuir	Pseudo-second-order	–18.39	–29.69	–38.42	Ahmet et al., 2011
<i>Ceramium virgatum</i>	Cd(II)	Langmuir	Pseudo-second-order	–19.5	–31.8	–42.4	Sari and Tuzen, 2008a, 2008b
<i>Gracilaria caudata</i>	Ni(II)	Langmuir, Freundlich	Pseudo-second-order, Intraparticle diffusion	–	–	–	Bermudez et al., 2011
<i>Laminaria japonica</i>	Cu(II)	Langmuir	Pseudo-second-order	–17.89	15.89	115.33	Wang et al., 2009
<i>Oedogonium hatei</i>	Ni(II)	Langmuir, Freundlich	Pseudo-first-order, Pseudo-second-order	–20.236	–7.927	0.0413	Gupta et al., 2010
<i>Spirulina platensis</i>	Cd(II)	Langmuir	Pseudo-second-order, Intraparticle diffusion	–	–	–	Celekli and Bozkurt, 2011
<i>Microcystis novacekii</i>	Pb(II)	Langmuir	–	–	–	–	Ribeiro et al., 2010
<i>Sargassum bevanom</i>	Cr(VI)	Langmuir, Freundlich	Pseudo-second-order	–5.256	28.656	0.115	Javadian et al., 2013
<i>Cystoseira indica</i>	Cd(II)	Freundlich	Pseudo-second-order	–	–	–	Mohammad et al., 2011
<i>Maugeotia genulflexa</i>	As(III)	Langmuir	Pseudo-second-order	–18.39	–29.69	–38.42	Ahmet et al., 2011
<i>Gracilaria verrucosa</i>	Cr(VI)	Sips, Redlich-Peterson	Pseudo-first-order	–0.008	12.98	0.043	Ata et al., 2012
<i>Ulva lactuca</i>	Pb(II)	Langmuir	Pseudo-second-order	–	–	–	Maria et al., 2012
<i>Oedogonium hatei</i>	Cr(VI)	Langmuir, Freundlich	Pseudo-first-order	–19.880	2.639	0.075	Gupta and Rastogi, 2009
<i>Cystoseira indicia</i>	Cu(II)	Langmuir, Temkin	Pseudo-second-order	–15.067	12.244	0.092	Akbari et al., 2015
<i>Chlorella vulgaris</i>	Cd(II)	Sips	Pseudo-second-order	–	–	–	Cheng et al., 2016
<i>Cystoseira indica</i>	Ni(II)	Freundlich	Pseudo-second-order	–	–	–	Mohammad et al., 2011
<i>Micractinium reisseri</i>	Cu(II)	Langmuir	Pseudo-second-order	–32.88	–15.80	0.058	Lee et al., 2016

$$E = \frac{1}{\sqrt{2K}} \quad (5)$$

The mean biosorption energy provides important information regarding the nature of biosorption process. The physical adsorption dominates in the biosorption process, if the mean biosorption energy value is < 8 kJ/mol. In case of the mean biosorption energy value > 16 kJ/mol signify the chemisorption and ion-exchange mechanism will predominant if the mean biosorption energy lies between 8 and 16 kJ/mol (Helfferich, 1962).

7.4. Temkin isotherm model

The Temkin isotherm model (Temkin and Pyzhev, 1940) considers the biosorbent–biosorbate interactions. Not taking in account of the extreme low and large value of concentrations, the model assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to biosorbent–biosorbate interactions. The biosorption described through the even distribution of binding energies up to a certain maximum binding energy. The model also assumes that the decline in the biosorption heat is linear rather than logarithmic as implied in the Freundlich biosorption isotherm model. The Temkin isotherm commonly represented in the following form

$$q_e = B_T \ln(A_T C_e) \quad (6)$$

where, $B_T = (RT)/b_T$, b_T is the heat biosorption constant (J/mol), A_T represent the equilibrium binding constant (L/g) related to the maximum binding energy, T , represent the absolute temperature (K) and R denotes the universal gas constant (8.314 J/mol K).

7.5. Jovanovic isotherm model

The assumption of the biosorption surface considered in this model is similar to that used in the Langmuir isotherm model, except the possibility of some mechanical contacts between the biosorbing and desorbing molecules. The Jovanovic isotherm model represents another approximation for the monolayer localized biosorption without any

lateral interactions. This isotherm model is similar to that of the Langmuir model (Jovanovic, 1969). The expression of the Jovanovic Isotherm model is expressed as follows

$$q_e = q_{mj} (1 - e^{-(K_j C_e)}) \quad (7)$$

where K_j indicates the Jovanovic isotherm constant (L/g), q_{mj} is the maximum biosorption capacity in Jovanovic model (mg/g).

7.6. Flory–Huggins isotherm model

The Flory–Huggins model (Horsfall and Spiff, 2005) demonstrates on the degree of surface coverage characteristics of the biosorbate on the biosorbent, which gives information regarding the feasibility and spontaneous nature of the biosorption process. The equation of the Flory–Huggins model is as follows:

$$\frac{Q}{C_0} = K_{FH} (1 - Q)^{n_{FH}} \quad (8)$$

where Q denotes the degree of surface coverage, K_{FH} specify the equilibrium constant and used to calculate the spontaneity of Gibbs free energy, n_{FH} represent the model exponent. Using the values of the biosorbate initial and equilibrium concentration, the degree of surface coverage can be calculated using the below equation

$$Q = 1 - \frac{C_e}{C_0} \quad (9)$$

7.7. Redlich–Peterson isotherm model

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) contains three parameters and the model includes the features of both the biosorption isotherm model like Langmuir and Freundlich. The model may be used to describe the biosorption equilibrium over a broad range of biosorbate concentrations. The equation of the model given as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^g} \quad (10)$$

where K_{RP} (L/g) and a_{RP} (L/mg) are the Redlich–Peterson isotherm model constants. The value of exponent g mentioned in the Eq. (10), lies between 0 and 1. When the value of g equal to 1, the Redlich–Peterson equation becomes the Langmuir equation and when the value equal to 0, the model becomes the Henry's law.

7.8. Sips isotherm model

The Sips isotherm model (Sips, 1948) is the resultant of the combined form of Langmuir and Freundlich isotherm models, find its importance in the prediction of heterogeneous biosorption systems. Sips isotherm model solved the problem encountered in continuing increase of the biosorbed amount with concentration increase in the Freundlich equation. At the low concentration of the biosorbate the Sips isotherm model reduces to Freundlich isotherm and at higher concentrations, the model predicts the monolayer biosorption capacity of the Langmuir isotherm isotherm. The Sips isotherm model is mainly based on the biosorption parameter of solution pH, initial metal ions concentrations and temperature (Marin et al., 2007). The simplified form of Sips isotherm model can be expressed as:

$$q_e = \frac{q_{ms} K_s C_e^{m_s}}{1 + K_s C_e^{m_s}} \quad (11)$$

where q_{ms} is the Sips maximum adsorption capacity (mg/g), K_s indicate the Sips isotherm model isotherm constant (L/g) and m_s represent the Sips model exponent, the value limited from 0 to 1.

7.9. Koble–Corrigan isotherm model

The Koble–Corrigan model (Koble and Corrigan, 1952) is an empirical isotherm equation used for representing the equilibrium biosorption data and generally applied for the heterogeneous biosorbent surface. The model includes the features of both Langmuir and Freundlich isotherm models in one equation. The model represented as follows:

$$q_e = \frac{a C_e^n}{1 + b C_e^n} \quad (12)$$

where a , b and n denotes are the parameters of the Koble–Corrigan isotherm model.

8. Biosorption kinetics

The biosorption kinetics is helpful in understanding the metal ions removal process using the biosorbents in terms of the rate constant. The residence time of biosorbate is an important factor, since the biosorption rate has its effects on the solid–liquid interface. The kinetics parameters provide noteworthy information regarding the controlling mechanism of biosorption process such as mass transfer, chemical reaction and diffusion control, which are vital in the designing and modeling of the biosorption process (Gupta and Babu, 2009). Table 4 shows the kinetic models followed by the various algal metal biosorption systems. Biosorption kinetic models such as pseudo-first-order, pseudo-second-order, intra-particle diffusion, Elovich and Boyd kinetic model were discussed in the following section.

8.1. Pseudo-first-order kinetic model

The Pseudo-first-order Lagergren equation (Lagergren, 1898) is the first kinetic model applied for the sorption of liquid/solid system based on the solid capacity. The pseudo-first-order kinetic model is widely used in the biosorption of biosorbate from the aqueous solution. The linearized form of pseudo-first-order rate equation expressed as follows

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (13)$$

where q_e and q represents the amounts of metal ions biosorbed (mg/g) at equilibrium and at any time t . k_1 (1/min) is the pseudo-first-order kinetic model rate constant. In most of the metal biosorption process, the pseudo-first-order kinetic model does not fit to the entire range of the contact time and normally pertinent only at the initial stage of biosorption process (Ho and McKay, 1998).

8.2. Pseudo-second-order kinetic model

The biosorption kinetics described by a pseudo-second-order kinetic model (Ho and McKay, 1999) predicts the biosorption behavior over the entire time of the process. The assumption of the model includes the rate limiting factor of the chemisorption involving the valence forces by means of electrons sharing between the amino group and metal ions (Ho, 2006). The linearized-integral form of the pseudo-second-order kinetic model is given as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

where k_2 denotes the pseudo-second-order rate constant (g/mg min).

8.3. Intraparticle diffusion model

The intraparticle diffusion model (Weber and Morris, 1962) provides the insights into the mechanisms and rate controlling steps affecting the kinetics of the biosorption process. According to this model, the process of biosorption carries out with three distinct stages of external mass diffusion, intraparticle diffusion and biosorption on interior of the porous biosorbent. The first and second stage are the slower steps, whereas the third stage is very fast and cannot account for the consideration in rate limiting step (Meghna and Monoj, 2013). The intraparticle diffusion model represented using the following equation:

$$q_t = k_{id} t^{1/2} + C \quad (15)$$

where k_{id} indicate the intraparticle diffusion rate constant (mg/g min^{1/2}), the C value denotes the thickness of the boundary layer (mg/g).

8.4. Elovich kinetic model

The Elovich kinetic equation (Wu et al., 2009) is a rate equation based on the biosorption capacity. The model considered the assumption that the biosorbent surface energetically heterogeneous and neither desorption or interactions between the biosorbed species could largely affect the biosorption kinetics at low surface coverage. The model generally expressed as

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (16)$$

where α indicate the initial biosorption rate constant (mg/g min) and β represent the desorption constant related to the extent of surface coverage and to the activation energy for the chemisorption (g/mg).

8.5. Boyd kinetic model

The Boyd model (Boyd et al., 1947) used to check whether the biosorption proceeded via an external film diffusion or intraparticle diffusion mechanism. The Boyd kinetic model can be expressed in the following form:

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (17)$$

$$F = \frac{q}{q_e} \quad (18)$$

F denotes the fractional attainment of equilibrium at any time t , where Bt is a mathematical function of F . By substituting the expression of F in Eq. (17) and by further rearrangement, the following equation was obtained.

$$Bt = -0.4977 - \ln\left(1 - \frac{q}{q_e}\right) \quad (19)$$

Using the value of B , the effective diffusion coefficient can be found through the following relation

$$B = \frac{\pi^2 D_i}{r^2} \quad (20)$$

where D_i represents the effective diffusion coefficient of metal ions in the biosorbent phase (m^2/s) and r denotes the radius of the biosorbent particles (μm).

9. Thermodynamics

The temperature dependence in the biosorptive removal of heavy metal ions from the aqueous solutions is associated with thermodynamic parameters like Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The thermodynamic parameters value is an indication of spontaneity, randomness and exothermic or endothermic nature of the biosorption process (Rangabhashiyam et al., 2016b). The thermodynamic parameters values of different algal biosorption systems are listed in Table 4. Thermodynamic parameters can be calculated according to the following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (21)$$

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (22)$$

where Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) represents the thermodynamic parameters constants. T denotes the absolute temperature (K) and R is the gas constant (8.314 J/mol K) and K_c is the distribution coefficient for biosorption and can be found using the following equation:

$$K_c = q_e/C_e \quad (23)$$

10. Mechanisms of metal ions biosorption and instrumental techniques

The interaction of metal ions with algal biosorbent is a complex process. The metal biosorption by inactive biomass is a physico-chemical passive process, which includes the possible mechanisms such as physical adsorption, ion exchange complexation and precipitation (Sud et al., 2008; Gadd, 2009). The possible mechanisms over the removal of heavy metal ions by algal biomass are illustrated in Fig. 4. In order to understand the biosorption mechanism, it is essential to analyze the

factors such as the metal ions properties, structural property of the biosorbent surface and the biosorption process parameters (Michalak et al., 2013).

Biosorbent surface consists of various functional groups, which plays an important role in the metal binding mechanisms. The intensity of the functional group distribution varied according to kind, number, affinity and distribution on the biopolymers. The algal biomass constituents of alginate, sulfate, fucoidan, cellulose and sulfated galactans are mainly responsible for the heavy metal biosorption (Celekli and Bozkurt, 2011; Davis et al., 2003). Solution pH determines the participation of different functional groups in the metal ion binding process. The initial solution pH ranges of 2.0–5.0, 5.0–9.0 and 9.0–12.0 represents the functional group of carboxyl, carboxyl and phosphate and hydroxyl (or amine) respectively. The protons and the light metal ions like Na^+ , K^+ , Mg^{2+} , Ca^{2+} naturally associated with algal functional groups, exchanged with metal ions during the biosorption process (Chojnacka et al., 2005; Davis et al., 2003).

Different instrumental techniques are available for the elucidation of biosorption mechanism of heavy metal. The scanning electron microscope analysis provides topography on the surface feature of the algal biosorbent. Energy-dispersive X-ray spectroscopic technique used to find out the elemental composition of the biosorbent surface before and after binding of the metal ions. Scanning electron microscope and energy-dispersive X-ray spectroscopic analysis used in the study of hexavalent chromium biosorption by *Enteromorpha* sp., in order to obtain the surface morphology, element analysis and chemical characterization of metal ion on the algal biomass (Rangabhashiyam et al., 2016b). Fourier transform infrared spectroscopy technique helpful to understand the functional groups interactions with metal ions. Fourier transform infrared spectroscopy technique applied to the algal biosorbent and metal loaded biosorbent, the changes in absorption of different bands reveals the functional groups participation in metal biosorption process or the appearance of newbands for modified algae (Shin and Kim, 2014). X-ray photoelectron spectroscopy technique find its application in finding the composition of elements, and the metal ion oxidation state bound to the algal biosorbent and its ligand effects over the transition-metal complexes which occurs within the biosorbent surface region. X-ray absorption spectroscopy used in the assessment of the oxidation state of metal bound on the biosorbent and the coordination environment of metal ion in the biosorption system. X-ray powder diffractometer used to determine the amorphous or crystallographic nature of the biosorbent as well as the chemical composition and structure of the native and metal-loaded biosorbent. Atomic absorption spectrophotometer used to analyze the metal ion concentration in the aqueous phase of the biosorption medium. The influence of the pretreatment methods on the native algal biomass checked through the measurement of biosorbent surface area by means of the surface area analyzer. Thermogravimetric analyzer used in the evaluation of thermal stability of biosorbent and provides information on the suitable

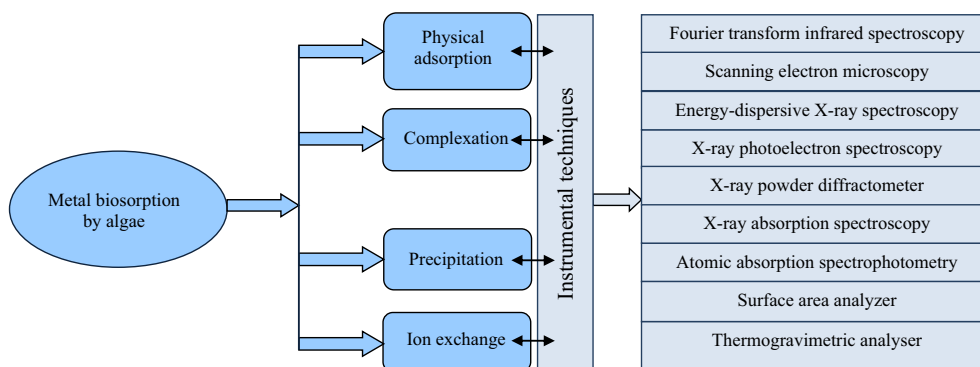


Fig. 4. Possible mechanisms of heavy metal removal by algae and different instrumental techniques significance in biosorption mechanism studies.

temperature range for the biosorbent pretreatment (Park et al., 2010).

11. Conclusions

In the present review, the application of algal biomass for the removal of heavy metal ions has been reviewed extensively. Biosorption using algae recognized as effective, economic and eco-friendly approach for the removal of metal ions. A wide variety of algal biosorbents in the raw, pre-treated and immobilized form for the removal of various heavy metal ions from aqueous environment were presented. The effects of process parameters such as algal dosage, pH, contact time, initial metal ions concentration and temperature were examined on the heavy metal removal process. The biosorption isotherm models, kinetic models and thermodynamic analysis of different metals biosorption by algae reviewed. In most of the studies, the Langmuir isotherm model better fitted the biosorption experimental data. The kinetic data of most of the reported studies followed the pseudo-second-order model, specifies the chemisorption process. Thermodynamics data analysis reveals the biosorption process as spontaneous nature in most of the cases. The biosorption mechanism extremely related to the functional group distribution on the algal biosorbent. Although several researches was conducted with the use of algal based biosorbents in heavy metal removal, still researches are needs to be performed for the commercial application. The further approaches are requires in the directions of multicomponent pollutants analysis, mechanistic modeling, pilot scale studies with industrial effluents, metal recovery, biosorbent regeneration and modeling investigation.

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