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Sequestration of toxic Cr(VI) ions from industrial wastewater using waste biomass: A review

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ABSTRACT

Heavy metal pollution is one of the most pressing environmental problems today. Several metals such as chromium, mercury, lead, copper, cadmium, zinc and nickel are considered as a highly toxic heavy metals. These metals are carcinogenic and pose a severe threat to the ecosystem and living organisms in it. Among various heavy metals, Cr(VI) is of particular interest because it is commonly found in the wastewater. Therefore, the removal of chromium is essential for environmental protection. Many conventional technologies have been developed for the removal of heavy metals from aqueous solutions such as membrane separation, ion exchange, filtration, precipitation, liquid–liquid extraction, solid–liquid extraction, reverse osmosis, etc. However, most of these are not economically feasible. Biosorption is a promising alternative biotechnological innovation for the removal of heavy metals from aqueous effluents. Biosorption method of wastewater treatment is highly competent and ecofriendly. A range of materials that act as biosorbent such as fungi, bacteria, algae, activated carbon, agro wastes, etc., have been used for the removal of heavy metals from aqueous solutions. The parameters influencing the removal of chromium, kinetics, mechanism, isotherms and thermodynamic study details were discussed in this article. This study encompasses an overview of past research and current development of the biosorption field for the effective removal of Cr(VI) ions from aqueous effluents.

Keywords: Biosorption; Cr(VI) ions; Heavy metals; Isotherm; Kinetics; Mechanism

1. Introduction

Nowadays, continuous contamination of surface and ground water is a serious environmental problem. Wastewaters containing heavy metals have been leaking into the environment in large quantities. Industrial and municipal wastewaters commonly contain heavy metals. The rapid development in a diverse range of industries including fertilizer, mining operations, fuel production, metal plating facilities, paper, pesticide, iron and steel, tanneries, electroplating, battery, electro-osmosis, aerospace and atomic energy, photography, metal surface treating, electrolysis and leather industries, etc., proves to be the major source for the introduction of heavy metals into various divisions of the environment including water, soil and air. Heavy metals such as chromium (Cr), copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni) and mercury (Hg) are the major primary pollutants due to their mobility in water streams. Moreover, they are toxic, carcinogenic, non-biodegradable, lead to bioaccumulation, bioaugmentation and cause serious health problems to human beings including skin irritations, problems in nervous system, kidney impairment, liver damage, vomiting, anemia, headache and weakness of muscles. Table 1 shows the maximum contamination level, source and effects of various heavy metal ion contaminations. Amongst

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Table 1
Source, effects and maximum contamination level of various heavy metal ion contaminations

S. No	Industry	Heavy metal	Toxicity	MCL (mg/L)
1	Electroplating, paints and pigments, electronics, mining, fertilizers, sewage sludge, landfill leachate, leather, photography and tannery	Chromium (Cr)	lung cancer, bone cancer, diarrhea, damage of kidney, liver, nervous system, skin irritation, dermatitis, mutagenicity and carcinogenicity	0.05
2	Mining, electroplating, alloy and steels, sewage sludge, paper and pulp, landfill leachate, tannery	Copper (Cu)	Allergies, anaemia, diabetes, kidney disorder, liver damage	0.25
3	Fertilizers, batteries, electronics, mining, alloy and steels, sewage sludge, paper and pulp, landfill leachate	Cadmium (Cd)	Kidney damage, human carcinogen, weight loss, hupertension, pulmonary fibrosis	0.01
4	Paints and pigments, batteries, electronics, fertilizers, alloy and steels, sewage sludge, paper and pulp, landfill leachate	Lead (Pb)	Damages in nervous system, circulatory system, kidney damage, Alzheimer's disease, decreased bone growth	0.006
5	Batteries, electroplating, paints and pigments, mining, fertilizers, alloy and steels, sewage sludge, paper and pulp, landfill leachate	Zinc (Zn)	Neuronal disorder, respiratory disorders, lethargy, depression	0.80
6	Alloy and steels, batteries, electroplating, electronics, mining, sewage sludge, paper and pulp, landfill leachate	Nickel (Ni)	Dermatitis, asthma, cancer risk, respiratory disorders, neuronal disorder, metal fume fever	0.20
7	Electronics, sewage sludge, batteries, landfill leachate	Mercury (Hg)	Damages in immune system, digestive system, lungs cancer, skin and eye infection, nervous system and circulatory system problem	0.00003

MCL - Maximum Contamination Level.

these metals, hexavalent chromium Cr(VI) is considered to be the most significant toxic pollutant by US Environmental Protection Agency [1–3]. Cr(VI) is a highly toxic metal liberated from several industries as a result of various processes including metal finishing, mineral processing, electroplating, steel manufacturing, pesticide application, leather tanning, dyeing, photography industries and chromate production [4,5]. Normally chromium exists as Cr(VI) and Cr(III) ions. Both Cr(VI) and Cr(III) ions have low solubility in water. However, Cr(VI) ions is more toxic when compared to Cr(III) ions. Exposure to Cr(VI) causes several health effects in humans such as lung cancer, bone cancer, diarrhea, damage of kidney, liver, nervous system, skin irritation and dermatitis. It is also associated with changes in plant morphology and diminishes the plant growth [6–8]. Industrial wastewater normally contains chromium metal in the range of 500 to 270,000 µg l^{-1}. It could enter into the groundwater in the range of 50 to 700 µg l^{-1} [9,10]. The legal limits of chromium concentration for drinking water and surface water is 50 µg l^{-1} and 100 µg l^{-1} respectively [11,12]. Therefore, controlling the discharge limit value of anthropogenic chromium and developing effective methods to remove chromium especially Cr(VI) is critical to human health and the ecological system [13].

Several conventional treatment methods have been applied for the removal of Cr(VI) from industrially polluted aqueous solutions, such as membrane separation [14], ion exchange [15], ultrafiltration [16], chemical precipitation [17], chelation [18], electrodialysis [19], reverse osmosis [20]. These conventional technologies used for the removal of heavy metals from effluent wastewater have several drawbacks such as high installation cost, time consuming running, expensive maintenance, low efficiency of performance at low metal concentration and issues with disposal of sludge. Therefore, there exists a need for development of low cost adsorbent materials and an economical method for the removal of Cr(VI) metal from aqueous solution [21–24]. Adsorption is a conventionally adopted technology for removing heavy metals from aqueous solutions. Biosorption technology has some major advantages like effectiveness of the sequestration of toxic heavy metals at very low concentrations, easy operation, minimization of biological sludge, no additional nutrient requirement, prospect of metal recovery and moreover the biosorbent material is cheap [25,26]. Table 2 shows the comparison of conventional technologies for the removal of Cr(VI) ions from contaminated water. The living and dead microbial cells have been used as an adsorbent for the removal of heavy metals from aqueous solution. Bacteria [27], fungi [28], agro wastes [26], algae [29], seaweeds [30], yeast and other polysaccharide materials [31] are some of the biosorbents that are being used for the removal of Cr(VI) ions from wastewater. Among these, low cost agricultural waste can preferably be used as the adsorbent materials for the effective removal of Cr(VI) ions from effluent water [26]. Many reviews can be referred to demonstrate the application of low cost adsorbents on the removal of heavy metals and they clearly indicate that the agricultural waste biomass is cost-effective and showed high removal efficiency compared to activated carbon. Agricultural waste such as sawdust [32], pinus

Table 2
Comparison of conventional technologies for the removal of Cr(VI) ions from contaminated water

Cr(VI) ion removal from contaminated water			
S. No	Types – treatment technologies	Advantages	Disadvantages
1	Ion exchange	Selective removal of metal ion Less number of metal ions removed	Cost expensive (Synthetic resins), large scale application Less number of metal ions removed High maintenance and operational cost
2	Membrane filtration	Metal dye selective Small space requirements	Membrane fouling, capital cost, maintenance, Limited flow rates, less efficiency at lower metal ion concentration High maintenance and operational cost
3	Coagulation/Floccculation	Dewatering characteristics	More sludge settling, cost expensive reagents, Chemical consumption
4	Flotation	Low retention time	High maintenance and operational cost Initial capital cost
5	Electrochemical treatment	No chemical consumption	Requirement of filtration process for flocs Cost effective and running cost
6	Chemical precipitation	Simple operation	Large amount of sludge containing metals Cost effective, high chemical requirement, parameters have to be monitored during this technique which is problematic
7	Chelation/complexation	High separation selectivity	High maintenance and operational cost
8	Adsorption using activated carbon	High efficiency of metal ion removal Fast kinetics Extensive range of target pollutants	High cost of activated carbon Performance depends upon the adsorbent
9	Biosorption	Cost inexpensive, metal recovery possible, no additional nutrient requirement, high removal efficiency, regeneration of biosorbents, minimization of chemical and biological sludge	Early saturation

bark [33], coconut husk [34], cellulosic materials [35], palm kernel husk [36], peanut skins [37], peanut hull [38], maple [39], hazelnut shells [40], coffee and tea waste [41], palm fruit bunch [42], modified sugar beet pulp [43], maize leaf [44], modified sunflower stalk [45], charcoal [46], modified lignin [47], banana and orange peels [48], wool fibers [49], modified bark [50], tea leaves [51], apple wastes [52], rice hulls [53], modified corncobs [54] and coffee grounds [55] were used as adsorbent materials for the removal of heavy metals from aqueous solutions. Thus the low-cost and huge availability of biosorbents would make the process of biosorption economically feasible.

Batch adsorption studies on the removal of Cr(VI) ions from aqueous solution can be carried out by measuring the parameters such as initial metal ion concentration, temperature, pH, contact time and adsorbent dose. The adsorption isotherm, kinetics and thermodynamic parameters have been discussed to explain the adsorption process. There are several models used to describe the equilibrium, kinetics and thermodynamic study of biosorption. They include the one, two, three, four and five parameter models such as Henry's law, modified Langmuir model-1, modified Langmuir model-2, Dubinin-Radushkevich, Temkin, Langmuir, Freundlich, Redlich-peterson, Sips, Fritz-Schlunder, Radke-Prausnitz, Toth model, Jossens, Weber-van Vilet and Baudu model of adsorption isotherms. The adsorption kinetics can be evaluated using the pseudo-first order kinetics, pseudo-second order kinetics and Elovich kinetic model. The thermodynamic parameters of Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be evaluated to perform the thermodynamic analysis.

The aim of this review article is to investigate biosorbents for the removal of Cr(VI) ions from aqueous solutions. The effects of parameters such as choice of solution, pH, temperature, biomass loading and metal ion concentration were studied. The adsorption mechanism, isotherm and kinetics characteristics and thermodynamic studies were discussed as well as the development of biosorbents for future needs was also investigated.

2. Conventional methods

Several technologies have been developed and used for the removal of toxic Cr(VI) from effluent water. Each technology has its own advantages and disadvantages.

Biosorption is the advanced alternate technology for the efficient removal of Cr(VI) from the aqueous solution. In recent times, many low cost biosorbent materials have been investigated and used for the removal of heavy metals and found to be economically suitable.

2.1. Membrane filtration

Membrane filtration technology has been used for the removal of unwanted particles present in the water streams [56–58]. Membrane filtration works under the pressure-driven separation principle which is dependent on separation limit and diameter. There are four membrane processes which are used in wastewater treatment for the efficient removal of heavy metals from the aqueous solution, namely ultrafiltration, microfiltration, nanofiltration and reverse osmosis [59–61]. Membrane separation has few advantages over other conventional technologies such as perfect retention, being free of fine particles and pathogens, being able to provide a pretreatment to the superior nanofiltration/reverse osmosis process and to act as process feedstock in industrial wastewater. However, this technology is expensive and economically nonviable because of high operational costs and maintenance [62–66].

2.1.1. Ultrafiltration

Ultrafiltration (UF) is a promising methodology for the separation process. UF is works at low transmembranic pressure for the removal of dissolved substances. These membranes are capable of handling high flux and are free from microbes. They're pore size ranges between 0.001–0.02 microns. Since some metals are smaller in size than the pores of the UF membranes they pass through the membranes [67,68]. So, for effective removal of these metals, micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) are introduced. In MEUF the removal efficiency is altered by various parameters such as metal concentration and pH. PEUF is used in the removal of heavy metals from the industrial outflow streams [69]. A polymeric binding agent which is soluble in water is added to target the heavy metal ions forming a macromolecular component [70]. Fouling is a major problem associated with the UF technique, though it can be prevented by pre-treatment of the feed. However, this increases the overall working cost [71].

2.1.2. Microfiltration

Microfiltration (MF) has been widely applied in water treatment. MF has a sterilizing filter cartridge in the size of 0.22 micron, which provide bacterial removal in the biotechnological applications. MF membranes are made of a homogeneous pore structure through the membrane cross section [72,73]. MF may have an advantage over the UF where feed particles create a pre-coat on the membrane surface. The main drawback of MF is the formation of a cake layer on the surface of the membrane due to the concentration polarization. This becomes a hindrance on permeate movement and thereby decreases permeate flux.

2.1.3. Nanofiltration

Nanofiltration is an advanced membrane technology and is effective for the removal of heavy metals. NF membranes have a non-porous thin skin layer which provides a high permeability character. NF process possess the property in intermediate of ultrafiltration and reverse osmosis. NF processes consume less energy and results in high removal of pollutants [74–75]. The NF membranes keep possession of divalent and higher-valence ions and let monovalent ions pass through these membranes [76]. The major problem in NF is the formation of bio fouling on the membrane and this alters the quality of the outflow, also increases the pressure drop along the membrane [77]. Another advantage of UF over NF is that, NF could additionally be used in treatment of final effluent for disinfection [78].

2.1.4. Reverse osmosis

Reverse osmosis (RO) technology has many applications in the treatment of waste water. It gives a clear permeate leaving a reverse osmosis concentrate. This RO concentrate will have a high level of organic concentration [79–80]. As the permeate obtained is very pure it is widely in practice in recent days. The cationic compounds i.e. metals are removed by providing a high hydrostatic pressure on the feed over the membrane. Polyamide when used as a skin material for RO membrane resulted in complete removal of Cu(II) and Ni(II) metals. It also shows that the rejection rate of metal ions increases with the increase in the transmembranic pressure [56]. RO is more efficient in removing heavy metals when compared to UF and NF. Since the RO membranes have fine pores they are easily prone to fouling by the suspended particles. To prevent this fouling the feed water must undergo some pretreatment process to control its turbidity level [81]. This increases the operational cost of the overall process hence it has some defects by default.

2.1.5. Electro dialysis

Electrodialysis (ED) is one among the common membrane separation process in which the solution carrying ionized species are allowed to pass across ion exchange membrane with the help of an electric potential. This electric potential difference acts as a driving force to assist the separation of ionized species [82]. The most widely used membranes are cation-exchange and anion-exchange membranes [74]. When the solution is brought in contact with the membrane, anions drift toward anode and similarly cations toward the cathode, crossing the anion-exchange and cation-exchange membranes [56]. In electrodialysis, cell performance can be enhanced by increasing voltage, temperature and also by using a membrane with higher ion exchange capacity [83]. It can also diminish the consumption of expensive chemical reagents (acid, alkali) utilized for regeneration of ion-exchange filters [84]. Though it has several advantages, it cannot process inorganic effluents with metal concentration above 1000 mg l^{-1} and is more appropriate only for concentration below 20 mg l^{-1} [56].

2.2. Flotation

Flotation process is an important process in the removal of heavy metals from industrial waste water. The metals are separated from the liquid with the help of bond formation over the bubbles generated. In flotation process, the suspended particles/metals get attached to the air bubbles generated. These air bubbles are less dense than water and make the cluster of suspended particles to raise to the surface of the feed water. Many types of flotation process such as dissolved air flotation, precipitate flotation and ion flotation are available for the separation of metals [74,85,86]. Once the cluster is formed, they are removed from the top surface of the water. In the case of ion flotation, the removal efficiency can the increased by maintaining a favorable pH condition. In precipitate flotation chemical reagents are used to form precipitate which aid in the removal of heavy metals [61]. Flotation consumes more energy thus requires more operational cost and it also involves intense mechanical operations hence not suitable for areas where maintenance work is neglected.

2.3. Coagulation and flocculation

Coagulation and flocculation are mostly employed after the completion of sedimentation and filtration for the removal of heavy metals from wastewaters [74]. Coagulation involves the destabilization of colloidal particles resulting in agglomeration of floccules known as flocculation, to afford the removal of heavy metals by sedimentation [87,88]. This method mostly requires pH adjustments and addition of coagulating agents such as ferric/alum salts to diminish the repulsive force between particles [89]. It is suitable to treat inorganic effluents with a metal concentration below 100 mg l^{-1} or above 1000 mg l^{-1}. The separation of heavy metals by this method can be achieved within a narrow range of coagulant with optimum coagulant concentrations [90]. In spite of its benefits, the high operational cost due to chemical utilization restricts its wide usage.

2.4. Ion exchange

Ion exchange technology seems to be very effective method for the removal of heavy metals from water stream. Ion exchange is a physical separation process in which the ions in solution are transferred to a solid matrix [91–94]. Ion exchange resin can be classified on the basis of functional groups as anion exchange resin, cationic exchange resin and chelating exchange resin [95,96]. Ion exchange resins having specific metal uptake capacity are being used during ion exchange. The resins may be either synthetic or natural. Synthetic resins are majorly used because of their supreme metal removal capacities from the aqueous solution [97–99]. Naturally occurring silicate minerals called as zeolites play a vital role in ion exchange process. Zeolites are widely used due to their selective heavy metal recovery capability and low cost. Selectivity, effective removal, low sludge volume production and recovery of targeted metals are some of the main advantages of this technology over other conventional technologies. However, resins need to be recharged for the selective removal of heavy metals from aqueous solution which can raise the cost of whole unit process, so this technology is not economically feasible. [100–102].

2.5. Chemical precipitation

Chemical precipitation is the most widely used technique for the removal of heavy metals from wastewater due to its simplicity and inexpensive in nature. Several heavy metals such as Zn^{2+}, Pb^{2+}, Cr^{3+}, Hg^{2+}, Cu^{2+}, Cd^{2+} and Mn^{2+} can be removed by using the chemical precipitation method [103,104]. Generally, in the precipitation processes, the chemicals added react with metals to form either suspended or dissolved precipitates in solution called solid precipitates [105,106]. These solid precipitates can be separated from the water solution using sedimentation and filtration process. Ferrous sulfate ($Fe(SO_4)_3$, calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH) are most used chemicals for the precipitation of heavy metals from wastewater [107,108]. By adding the hydroxides (OH^-) or carbonates (CO^{3-}) or sulfates (S^{2-}) to the wastewater, the soluble heavy metals get converted into insoluble precipitates. The solubility of the metal compounds mainly depends on the pH of the solution. If the pH of the solution is alkaline, the solubility of metal is very low. Hydroxide precipitation is a commonly used chemical precipitation technique because of its low cost and ease of pH control [109]. The main drawback of hydrogen precipitation is generation of large volume of sludge which further causes disposal problems. Sulfide precipitation is the most suitable technique for the removal of heavy metals from wastewater, because the solubility of metal sulfide precipitation is low compare to hydroxide precipitation [110]. Ferrous sulfate and calcium hydroxide ($Ca(OH)_2$) can be used for the precipitation of chromium metal from wastewater solution. By using ($Fe(SO_4)_3$ and ($Ca(OH)_2$), the Cr(VI) gets converted into Cr(III) [111]. However, Chemical precipitation technique can be used to remove the metals at high concentrations and low concentration of metals was settled down in the wastewater solution.

2.6. Electrochemical treatment

Electrochemical treatment methods have also been actively used for the removal of metals from wastewater streams. These technologies enforce the adsorption of metal ions onto the cathode surface [112,113]. But these treatment technologies have several disadvantages such as i) requires large capital cost in maintenance ii) needs to be operated over a long period of time and iii) requirement of huge amount of electrical supply [114,115]. Due to these disadvantages, these ascertained electrochemical treatment technologies namely, electroflotation, electrodeposition and electrocoagulation have not been widely used for the wastewater treatment process.

3. Adsorption

The conventional methods for the removal of heavy metals have many drawbacks as discussed earlier such as i) economically expensive – high operational cost and high maintenance cost, ii) ineffective removal of heavy metals and iii) disposal problem of metal sludge. Therefore, the adsorption technique is most preferable for the removal of Cr(VI) ions from aqueous solutions. Adsorption has several advantages over conventional technologies including the low cost and high efficiency of removal of heavy metals and dyes from the aqueous solution.

3.1. Activated carbon and carbon nanotubes

Activated carbon is most widely used adsorbent for the removal of heavy metals from aqueous solution due to its characteristics such as huge surface areas, large volume of micropores and mesopores structure, high thermal stability, various functional groups present on the surface helping it to be more effective [116–119]. These specific characteristics could enhance the use of activated carbons for the removal of organic and inorganic contaminants from the wastewater streams. Cr(VI) ions have been removed by using diverse types of activated carbons such as hazelnut activated carbons [120], dust coal activated carbons [121], coconut shell activated carbons [122], wood activated carbons [121] and sawdust activated carbons [123]. Activated carbon was prepared by two activation methods: physical and chemical. Of the two methods, chemical activation has some advantages over physical activation, such as larger surface area, lower activation temperature and higher yield. Many chemical agents such as $ZnCl_2$, $FeCl_3$ and phosphoric acid were used for the chemical activation (activated carbon preparation) [124–126]. Carbon nanotubes (CNTs) have been generally used in several fields such as energy storage devices, fabrication of semiconductors, sensors, catalysts and wastewater treatment [127,128]. In wastewater treatment technologies, CNTs play an important role in the removal of heavy metals. Many studies report that variety of adsorbents has been used for adsorption process. Each adsorbent has some characteristics for the removal of heavy metals. Moreover, these adsorbents can be used for the Cr(VI) removal at higher concentration, compared to that of CNTs which have specific characteristics such as carbonaceous adsorbents for the Cr(VI) removal at low concentrations. CNTs can be formed by using two methods leading to formation of: i) single-walled carbon nanotubes (SWNTs) ii) multi-walled carbon nanotubes (MWNTs) [129,130]. CNTs have large surface area and that can be discriminated by graphite layers, which enhance the adsorption capacities. However, Activated carbon methodology and carbon nanotubes were efficient in the removal of heavy metals but economically cost effective process, more sludge production and disposal problems.

3.2. Biosorption

Biosorption is a more suitable and promising alternate technology for the removal of Cr(VI) metals contaminants from aqueous solutions. Biosorption has good potential and capability for adsorption and advantages over the conventional methods, activated carbon and carbon nanotubes, because of its specific features such as higher efficiency in the removal of heavy metals at low concentrations, lower cost of adsorbents and possible recovery of sludge [131–134]. Biosorbents were described based on three factors: i) microbial adsorbent ii) non living biomass and iii) algal biomass.

3.2.1. Microbial adsorbent

Microbial adsorbent in aquatic environment plays an important role in the removal of Cr(VI) metals from aqueous solution. The contaminant or pollutant removal efficiency of biosorption technology can be improved by using the microbial biomass. Due to the porous structure of its surface, the metals from aquatic solutions can easily be adsorbed onto the surface of the microorganism [135,136]. In wastewater treatment, diverse microbial bacteria have been used as biosorbent for the removal of heavy metals from aqueous solutions (Table 3) (*Bacillus.* sp [137], *Amycolatopis.* sp [138], *Enterobacter.* sp [139], *Pseudomonas aeruginosa* [140], *Streptomyces rimosus* [141], *Escherichia coli* [142], *Pseudomonas sp* [143], *Acinetobacter haemolyticus* [144], *Sphaerotilus natans* [145], *Lactobacillus sp* [146], *Bacillus cereus* [147], *Aeromonas caviae* [148], *Corynebacterium glutamicum* [149], *Phormidium* sp [150], *Staphylococcus xylosus* [151], *Chroococcus* sp [152], *Nostoc muscorum* [153]). Several researchers have reported that fungi biomass have been utilized for the sequestration of heavy metals from contaminated water (Table 4). The variety of fungi biomass used for biosorption process include *Aspergillus Niger* [154], *Rhizopus oryzae* [155], *Saccharomyces cerevisiae* [156], *Lentinus edodes* [157], *Fomes fomentarius* [158], *Phellinus igniarius* [158], *Agaricus bisporus* [159], *Auricularia polytricha* [160], *Trametes versicolor* [161], *Rhizopus arrhizus* [162], *Penicillium* sp [163], *Aspergillus flavus* [164], *Candida intermedia* [165], *Penicillium janthinellum* [166], *Fusarium* sp [167]. Yeast has also been used as adsorbent for the removal of heavy metals from aqueous solution. The main reason is the presence of cytoplasm in the yeast, Cytoplasm organelles in living cells have high adsorption capacity i.e. interact with metals and bind with metals which are present in the wastewater [168].

3.2.2. Algal biomass

Algae are natural biomass that are most extensively used for the removal of Cr(VI) ions from an aqueous environment. Algae have numerous advantages such as low cost, high adsorption capacity, renewable biomass and more availability [169]. A large number of functional groups are present on the surface of algae and these characteristics will enhance the adsorption capacity of algae [170]. In wastewater treatment, a variety of algae have been used for the removal of heavy metals (Table 5) (*Caulerpa lentillifera* [170,171], *Turbinaria ornate* [172], *Ulothrix zonata* [172], *Grateloupia lithophila* [173], *Spirulina platensis* [174], *Pleurotus eous* [175], *Ulva lactuca* [176], *Sargassum wightii* [177], *Spirogyra* [178], *Fucas spirali* [179], *Pilayella littoralis* [180], *Cystoseira indica* [181], *Scenedesmus obliquus* [182], *Spirogyra* sp [183]).

3.2.3. Agricultural biomass

Nowadays, the conversion of agricultural wastes into the low cost adsorbents is a beneficial alternative

Table 3
Microbial adsorbent (bacteria) used for the removal of Cr(VI) ions from contaminated water

Optimum conditions									
S. No	Microbial adsorbent	Metal	Percentage removal	Metal concentration (mg/L)	pH	Contact time	Temperature (°C)	Best fit model	Reference
1	*Pseudomonas* sp	Cr(VI)	87	5	7.0	48 h	30	–	[143]
2	*Enterobacter.* sp	Cr(VI)	–	–	7.0	20 h	37	–	[139]
3	*Bacillus.* sp	Cr(VI)	96	60	6.5	48 h	37	–	[137]
4	*Pseudomonas aeruginosa*	Cr(VI)	80	2	6.0–8.0	120 h	30–40	–	[140]
5	*Phormidium* sp	Cr(VI)	–	100	2	–	25	Langmuir	[150]
6	*Nostoc muscorum*	Cr(VI)	80	100	3	2 h	25	Langmuir & Freundlich	[153]
7	*Corynebacterium glutamicum*	Cr(VI)	87	50	3	15	–	Langmuir	[149]
8	*Chroococcus* sp	Cr(VI)	70	20	3	30 min	26	Langmuir & Freundlich	[152]
9	*Streptomyces rimosus*	Cr(VI)	–	100	6.0	90 min	37	Langmuir and Freundlich	[141]
10	*Acinetobacter haemolyticus*	Cr(VI)	88	70	–	36 h	–	–	[144]
11	*Staphylococcus xylosus*	Cr(VI)	89	5	3	2 h	–	Langmuir	[151]

Table 4
Microbial adsorbent (fungi) used for the removal of Cr(VI) ions from contaminated water

Optimum conditions									
S. No	Microbial adsorbent	Metal	Percentage removal	Metal concentration (mg/L)	pH	Contact time	Temperature (°C)	Best fit model	Reference
1	*Penicillium* sp	Cr(VI)	–	50	1.0	150 min	28	–	[163]
2	*Rhizopus oryzae*	Cr(VI)	91.15	400	7.0	72 h	37	–	[155]
3	*Aspergillus niger*	Cr(VI)	–	400	1.0	48 h	50	Langmuir	[154]
4	*Agaricus bisporus*	Cr(VI)	–	50	1.0	1 h	20	Freundlich	[159]
6	*Penicillium janthinellum*	Cr(VI)	86.61	30	2.0	1 h	25	Langmuir & Freundlich	[166]
7	*Rhizopus arrhizus*	Cr(VI)	–	25	2.0	72 h	25	Langmuir-Freundlich	[162]
8	*Lentinus edodes*	Cr(VI)	69	100	4.0	24 h	25	Langmuir	[157]
9	*Fusarium* sp	Cr(VI)	92	50	2.0	2 h	30	Freundlich	[167]
10	*Candida intermedia*	Cr(VI)	–	10	4.0	5 h	28	–	[165]

technology for the removal of toxic Cr(VI) ions from the aqueous solutions. Agricultural wastes containing the components such as cellulose, lignin, proteins, starch, simple sugars, lipids, hydrocarbons and water possibly increase the adsorption capacity of agricultural biomass for the removal of heavy metals from aqueous effluents [184–186]. Agricultural wastes have several advantages such as low cost, renewable nature, easy availability and higher potential for removal various pollutants. Variety of agricultural wastes have been used for the adsorption process such as Sugarcane bagasse [187], Maize bran [188], rice husk [189], peanut hull [190], tea and coffee waste [41], pinus bark [33], corncobs [54], modified bark [191], modified lignin [47], modified sugar beet pulp [43], maize leaf [44], chemically modified cotton [192], sunflower stem [193], Pistachio hull [194], charcoal [46], apple wastes [52], Rubber seed shell [195], sawdusts [196], rice husk carbon [197], orange peel [198], palm

Table 5
Microbial adsorbent (algae) used for the removal of heavy metal ions from contaminated water

Optimum conditions									
S. No	Microbial adsorbent	Metal	Percentage removal	Metal concentration (mg/L)	pH	Contact time	Temperature (°C)	Best fit model	Reference
1	*Spirogyra*	Cr(VI)	70	40	3.0	–	25	–	[178]
2	*Pleurotus eous*	Cr(VI)	21.6	5	4.5	9 h	25	–	[175]
3	*Grateloupia lithophila*	Cr(VI)	78.19	–	7.0	60 h	–	–	[173]
4	*Sargassum wightii*	Cr(VI)	85.4	50	4.5	12 h	–	Freundlich	[177]
5	*Spirulina platensis*	Cr(VI)	78	50	7.0	1 h	25	Langmuir	[174]
6	*Cystoseira indica*	Cr(VI)	–	30	3.0	2 h	–	Dubinin-Radushkevich	[181]
7	*Ulva lactuca*	Cr(VI)	92	30	4.0	2 h	27	Langmuir	[176]

Table 6
Agricultural biomass used for the removal of heavy metal ions from contaminated water

Optimum conditions									
S. No	Microbial adsorbent	Metal	Percentage removal	Metal concentration (mg/L)	pH	Contact time	Temperature (oC)	Best fit model	Reference
1	Modified wheat bran	Cr(VI)	90	200	2.2	3 h	27	Freundlich	[201]
2	Peanut hull	Cr(VI)	47	30	2.0	7 h	25	Langmuir	[190]
3	Rubber seed shell	Cr(VI)	90	–	2.0	2 h	27	Freundlich	[195]
4	Pistachio hull	Cr(VI)	–	50	2.0	1 h	28	Langmuir	[194]
5	Rice husk carbon	Cr(VI)	76.63	250	2.0	3 h	25	Langmuir	[197]
6	Sunflower stem	Cr(VI)	76.5	50	2.0	3 h	26	Langmuir	[193]
7	Hazelnut shell	Cr(VI)	88.4	–	3.5	2 h	26	Langmuir	[200]
8	Maize bran	Cr(VI)	–	200	2.0	2 h	40	Langmuir	[188]
9	Sugarcane bagasse	Cr(VI)	92	50	2.0	1 h	25	Langmuir	[187]
10	Charcoal	Cr(VI)	81	100	2.0	2 h	30	Langmuir	[46]

oil fruit shell [199], hazelnut shell [200], modified wheat bran [201], cassava waste [202] and different agricultural byproducts (Table 6).

3.2.4. Industrial wastes

Generally, Industrial activities engender huge amount of solid wastes as by-products. Solid wastes are available at free of cost and could be used as adsorbents for the removal of heavy metals from wastewater effluents. If the solid wastes could possibly be used as low-cost adsorbents, it will provide several advantages to environmental pollution such as i) volume of solid wastes could be partly reduced ii) development of low-cost adsorbents (solid wastes) for the adsorption process iii) more availability of adsorbents and iv) possible solution for sludge disposal problems. Different industrial wastes such as fly ash [203], aluminium industry – redmud [204], steel industry – blast furnace slag [205], paper industry [206], fertilizer industry [207], leather industry wastes [208] have been extensively used to remove the toxic heavy metals from contaminated water.

4. Factors affecting heavy metals adsorption

The biosorption capacity for the uptake of Cr(VI) ions from liquid solution depends upon diverse factors such as initial metal concentration, solution pH, temperature, adsorbent dosage, agitation rate and ionic strength.

4.1. Effect of initial metal concentration

The biosorption process depends on several characteristics such as i) type of metals ii) functional groups present on the surface of the adsorbent iii) binding competence of functional groups with the metals present on the liquid phase. Several research works have developed and carried out investigation to determine the effect of initial Cr(VI) ions concentration on the uptake of metal from liquid phase to the surface of the adsorbent. Several experimental results stated that the maximum adsorption capacity of the adsorbent increases as the initial metal concentration increases. Higher amount of initial metal concentrations presents in the liquid solution signify that more metals available for the adsorption process and also since the process mainly depends on the number of active sites present on the surface of the adsorbents. The driving force made by the initial metal concentration plays an important role on the adsorption of metal onto the active sites of the adsorbents. The driving force has been increased with the increase in the initial metal concentration due to the concentration polarization, and its overcome of all mass transfer resistance of heavy metals [209–218]. On the contrary, the removal efficiency of the adsorbent decreases gradually as the initial concentration increases, due to the saturation of active sites on the surface of the adsorbents and the lower rate of transporting metals from liquid solution to the surface of the adsorbents. Thereby, adsorbing almost the same amount of solute [219–224].

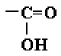
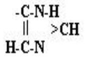
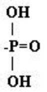
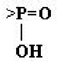
4.2. Effect of temperature

Many of the biosorption research have investigated the effect of temperature on uptake of Cr(VI) ions. Temperature of the solution plays a significant role for the removal of heavy metals from aqueous solutions. The influence of temperature on the Cr(VI) ions adsorption process is majorly classified into two ways i) exothermic and ii) endothermic process. Several research studies have investigated that the Cr(VI) ions uptake is inversely proportional to the temperature which means that the percentage removal of Cr(VI) metals decreases with increase in temperature. It has been recognized that the biosorption process is exothermic in nature, due to the deterioration of adsorptive forces between the metals and the active sites on the surface of the adsorbents, the damage of active adsorption sites of the adsorbents or the adsorbed metals fugitive from the active sites of the adsorbents to the liquid solution [216,217,225,226]. Many research studies have stated that the Cr(VI) ions adsorption is increased with an increase in the temperature which means that higher temperature enhances the removal of heavy metals onto the adsorbents. They attributed that the biosorption processes are endothermic in nature, due to the rise of active sites on the surface of the adsorbents and the decrease of boundary layer thickness that surrounds the adsorbent [227–229,224].

4.3. Effect of pH

The pH of the solution is an important process parameter for the removal of heavy metals from aqueous solution. The solution pH plays a significant role in controlling the biosorption of Cr(VI) ions. The solution pH can affect the redox reactions, complexation by organic or inorganic ligands, precipitation, solution chemistry of the heavy metals and the adsorption process based on the functional groups present on the surface of the adsorbents. Table 7 shows the functional groups and its structural formula for the biosorption. The solution pH changes the ionization state of the functional groups such as carboxyl, amino groups and phosphate and the solubility of metals. Several research studies have reported that as the pH of the solution increases, the percentage removal of Cr(VI) ions increase and then decreases on further increase in solution pH. At low pH value, the surface charge of the adsorbent is positively charged, its attracts the Cr(VI) ions from the solution due to the high electrostatic interaction. At high pH values, the Cr(VI) ions adsorption decreases due to the formation of metal hydroxide complexes [230].

Table 7
Functional groups and its structural formula for the biosorption

S. No	Binding groups	Structural formula	Present in selected biomass
1	Carboxyl	>C=O	Peptide pond
2	Hydroxyl	–OH	Polysaccharide, Amino acid, Uronic acid
3	Sulfhydryl	–SH	Amino acid
4	Amine	$-NH_2$	Amino acid, Chitosan
5	Amide	 $\begin{array}{l}-C=O\\ \quad\,|\\ \quad OH\end{array}$	Amino acid
6	Imine	=NH	Amino acid
7	Imidazole	 $\begin{array}{l}-C-N-H\\ \;\;\,\| \qquad >CH\\ H-C-N\end{array}$	Amino acid
8	Phosphate		Phospholipids
9	Phosphodiester	 $\begin{array}{l}OH\\ \,|\\ -P=O\\ \,|\\ OH\end{array}$  $\begin{array}{l}>P=O\\ \quad\,|\\ \quad OH\end{array}$	Lipopolysaccharide, Teichoic acid

4.4. Effect of biosorbent dose

Applying an optimum adsorbent dose strongly influences the removal of Cr(VI) ions from aqueous solution in a batch adsorption system. Several research studies have investigated and stated that the percentage removal of Cr(VI) ions increases with increase in the adsorbent dosage. By increasing adsorbent dose, more active sites are made available for the binding of metal ions on the surface of adsorbents. Conversely, the percentage removal of metal ions from liquid phase gradually decreases with increase of adsorbent dosage [231,232]. They attributed this to the overlapping of active sites i.e. unavailability of active sites for the ligand formation with metal ions. At low dosage, the adsorption of Cr(VI) ions is quickly approached and the active sites of adsorbents gets saturation quickly. After the equilibrium is attained, the percentage removal of Cr(VI) is gradually decreased, due to the unavailability of active sites on the surface of the adsorbents [194,233].

4.5. Effect of contact time

The effect of contact time plays an important role in the removal of Cr(VI) ions from aqueous solution. Several research studies have reported that the percentage removal of Cr(VI) ions has increased with the increase in contact time for all initial metal of concentrations. The maximum adsorption is attained at 30 min. After that, the adsorption of Cr(VI) metal has increased gradually for all concentrations which clearly indicates that the active sites of adsorbents get saturated quickly. The adsorption of Cr(VI) ions reaches the equilibrium condition at the time of 120 min. This helps describe that the higher and faster binding between the adsorbents and the high concentration of Cr(VI) ions in the liquid solution takes place. After the equilibrium is reached, the percentage removal of Cr(VI) gradually decreases, due to the unavailability of active sites on the surface of the adsorbents [234–237].

5. Equilibrium, kinetics and thermodynamic studies of Cr(VI) ions adsorption

The adsorption equilibrium experimental data has been fitted with several adsorption isotherm models to determine the interaction behaviour between the adsorbents and the solutes. Adsorption isotherm studies can be used to find the best isotherm model for the adsorption process. The adsorption isotherm model can be explained by the following models; one, two, three, four and five parameter models such as Langmuir, Freundlich, Henry's law, modified Langmuir model-1, modified Langmuir model-2, Dubinin-Radushkevich, Temkin, Langmuir, Freundlich, Redlich-peterson, Sips, Fritz-Schlunder, Radke-Prausnitz, Tóth model, Jossens, Weber-van Vilet and Baudu model.

One parameter model

Henry's Law model can be given as follows [238]

$$q_e = KC_e \tag{1}$$

where q_e is the amount of metal ions adsorbed onto adsorbent at equilibrium (mg g^{-1}), C_e is the concentration of metal ions in the liquid solution at equilibrium (mg l^{-1}) and K is the Henry's constant.

Two parameter model

Henry's Law model can be given as follows

$$q_e = KC_e + m \tag{2}$$

where K is the Henry's constant.

The Langmuir isotherm model can be given as follows [239]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where K_L is the Langmuir constant related to the affinity of the metal ions to the adsorbent (L mg^{-1}) and q_m is the maximum monolayer adsorption capacity (mg g^{-1}).

The Freundlich model can be given as follows [240,241]

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant ((mg g^{-1})(L mg^{-1})$^{1/n}$) used to measure the adsorption capacity and n is the Freundlich exponent which is used to measure the intensity of adsorption. The consequence of n is given as follows: n = 1 (linear); $n > 1$ (physical process); $n < 1$ (chemical process).

Modified Langmuir – 1 model equation can be given as follows [242]

$$q_e = \frac{bT^{-n}C_e}{1 + bC_e} \tag{5}$$

where T is the temperature (in Kelvin) and b is the constant related to the free energy of adsorption (expressed as, L mg^{-1}).

Modified Langmuir – 2 model equation can be given as follows [243]

$$q_e = \frac{bC_e}{1 + bc_e}\left(\frac{1 + \sigma^2(1 - bC_e)}{2(1 + bC_e)^2}\right) \tag{6}$$

where q_e and C_e represent their usual connotations and σ is the isotherm constants related to the degree of sorption.

Dubinin-Radushkevich (D-R) isotherm model can be given as follows [244]

$$q_e = q_{m,D} \exp\left[-\beta\left(\mathrm{RT}\ln\left(1 + \frac{1}{C_e}\right)^2\right)\right] \tag{7}$$

where $q_{m,D}$ is the Dubinin-Radushkevich monolayer adsorption capacity (mg/g) and β is a constant related to adsorption energy.

Temkin isotherm model can be given as follows [245]

$$q_e = \frac{RT}{b}(\ln AC_e) \tag{8}$$

where A and b are the Temkin isotherm constants.

Three parameter model

Langmuir-Freundlich isotherm model equation is given by [246]

$$q_e = \frac{q_{mLF}(K_{LF}C_e)^{mLF}}{1 + (K_{LF}C_e)^{mLF}} \tag{9}$$

where q_{mLF} is the Langmuir-Freundlich maximum adsorption capacity (mg g^{-1}), K_{LF} is the equilibrium constant and mLF is the Freundlich heterogenecity parameter lie between 0 to 1.

Fritz-Schlunder model equation is given by [247]

$$q_e = \frac{q_{mFS}K_{FS}C_e}{1 + q_{mFS}C_e^{\alpha}} \tag{10}$$

where q_{mLS} is the Fritz-Schlunder maximum adsorption capacity (mg g^{-1}), K_{FS} is the Fritz-Schlunder equilibrium constant (L mg^{-1}) and mFS is the Fritz-Schlunder model exponent.

Radke-Prausnitz model equation is given by [248]

$$q_e = \frac{q_{mRP}K_{RP}C_e}{(1 + K_{RP}C_e)^{mRP}} \tag{11}$$

where q_{mRP} is the Radke-Prausnitz maximum adsorption capacity (mg g^{-1}), K_{RP} is the Radke-Prausnitz equilibrium constant and mRP is the Radke-Prausnitz model exponent.

Toth model equation is given by [249]

$$q_e = \frac{q_{mT} C_e}{\left(\frac{1}{K_T} + C_e{}^{mT}\right)^{\frac{1}{mT}}} \tag{12}$$

where q_{mT} is the Toth maximum adsorption capacity (mg g^{-1}), K_T is the Toth equilibrium constant and mT is the Toth model exponent.

Four parameter model

The Fritz - Schlunder model is given by [247]

$$q_e = \frac{AC_e^{\alpha}}{(1 + BC_e^{\beta})} \tag{13}$$

where A and B are the Fritz-Schlunder parameters, α and β are the Fritz-Schlunder equation components.

Baudu model is given by [250]

$$q_e = \frac{q_m b_o C_e^{(1+x+y)}}{1 + b_o C_e{}^{(1+x)}} \tag{14}$$

where q_m is the Baudu maximum adsorption capacity (mg g^{-1}), x and y are the Baudu parameters and b_o is the equilibrium constant.

Five parameter model

The Fritz - Schlunder model is given by [247]

$$q_e = \frac{q_{mFSS} K_1 C_e^{m_1}}{1 + K_2 C_e{}^{m_2}} \tag{15}$$

where q_{mFSS} is the Fritz-Schlunder maximum adsorption capacity (mg g^{-1}). K_1, K_2, m_1 and m_2 are the Fritz-Schlunder parameters.

The adsorption isotherm parameters, correlation coefficient (R^2), sum of squared errors (SSE) and root mean square errors (RMSE) values for the above said adsorption isotherm models were calculated by using the non-linear regression analysis. The higher correlation coefficient values (R^2) and low error values can be used to predict the best adsorption isotherm model for the particular adsorbent-adsorbate system. The isotherm model depends on several factors such as whether the adsorbent surface is homogeneous or heterogeneous.

Adsorption kinetics is very important for designing an adsorption system. Adsorption kinetic studies can be used to determine the adsorption rate of Cr(VI) ions from the aqueous solutions. This information can also be helpful to understand the rate controlling mechanism in the removal of metal ions by the adsorbent which may be of either film diffusion or surface diffusion or particle diffusion or adsorption or all may together. Adsorption kinetic models such as pseudo-first order, pseudo-second order, Elovich kinetic and other diffusion models were widely used to illustrate the adsorption of metal ions from a liquid phase to the solid phase (adsorbent). Table 8 shows the kinetic models for the adsorption of Cr(VI) by several adsorbent materials. The data obtained by employing the kinetic models have been used to understand the complex dynamics of the adsorption process and to develop, characterize and enhance the adsorption capacity of the adsorbent material for industrial applications. The non-linear regression analysis has been used to determine the kinetic parameters, correlation coefficient values (R^2) and error values (SSE, RMSE) using MATLAB R2009a software. The best fitted adsorption kinetic model was determined by three factors such as (i) based on high correlation coefficient values (R^2), (ii) low error values and (iii) the predicted adsorption capacity (q_e, cal) from the various kinetic models were compared with experimental adsorption capacity (q_e, exp) and the results were concluded by the kinetic model that closely matched the experimental adsorption capacity (q_e, exp) was considered to be the best fitted kinetic model for the adsorption process. Several researchers reported that the adsorption kinetics of Cr(VI) ions follows the pseudo-first order kinetics and pseudo-second order kinetics model. Table 9 shows the diffusion models to study the adsorption process. Diffusion methods extensively influence the adsorption kinetics, many research papers stated that the film diffusion and pore diffusion play a significant role in the interaction between the adsorbate and the adsorbent. Adsorption of metal ions from liquid phase to the active sites of the adsorbent material is a complex process which includes the following stages. (i) the transfer of metal ions from the aqueous solution to the liquid-solid interface due to the convection (ii) the diffusion of metal ions into the boundary layer that surrounds the solid particles which is known as film diffusion (iii) the diffusion of metal ions on the surface of the adsorbent material known as surface diffusion (iv) the diffusion of metal ions on the interior of the adsorbent material known as pore diffusion (v) Finally, the metals ions were absorbed by the active sites of the adsorbent material and is known as equilibrium reaction.

Pseudo-first order kinetic model equation is given as follows [262,263]

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{16}$$

where k_1 is the pseudo-first order kinetic rate constant (min^{-1}), t is the time (min).

Pseudo-second order kinetic model equation is given as follows [264,265]

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{17}$$

where t is the time (min), k_2 is the pseudo-second order kinetic rate constant (g mg^{-1}min^{-1})

The Elovich kinetic model equation is given as follows

$$q_t = (1 + \beta_E)\ln(1 + \alpha_E \beta_E t) \tag{18}$$

where β_E (g mg^{-1}) is the desorption constant related to the activation energy of chemosorption and α_E is the initial adsorption rate mg (g·min)$^{-1}$.

Table 8a
Reaction kinetic models for the adsorption of Cr(VI) by several adsorbent materials

S. No	Fitted Kinetic model	Non-linear equation	Linear equation	Model parameters	Adsorbent materials	Reference
1	Pseudo first order	$q_t = q_e(1-e^{-k_1 t})$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	q_e, k_1	Rice husk Fungal biomass Tea factory waste *Tamarindus indica* *Nostoc muscorum*	[251] [252] [253] [254] [153]
2	Pseudo second order	$q_t = \frac{q_e^2 k_2 t}{(1+q_e k_2 t)}$	$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}$	q_e, k_2	Activated carbon Fly ash Fungai *Agaricus bisporus* Dried *Rhizopus arrhizus* Brown and Red macroalga *Mucor hiemalis* *Aspergillus niger* Tamarind seeds	[255] [256] [159] [162] [257] [258] [259] [183]
3	Elovich	$q_t = \left(\frac{1}{\beta_e}\right)\ln\left(\alpha\beta_e t + 1\right)$	$q_t = \frac{\ln(\alpha\beta_e)}{\beta_e} + \frac{\ln t}{\beta_e}$	α, β_e	Tea fungus	[252]

Table 8b
Diffusion models to study the adsorption process

S. No	Model	Equation	Model parameters	Reference
1	Intraparticle	$q_t = k_{id}t^{0.5}$	k_{id}	[260]
2	Film surface diffusion	$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_r}{\partial r}\right)$	D_s	[261]
3	Film mass transfer coefficient	$\frac{dq_t}{dt} = -\frac{V}{m}\frac{dc_b}{dt} = \frac{3k_f}{R\rho_p}\left(c_b - c_s\right)$	k_f	[261]
4	Surface diffusion coefficient	$\frac{q_t}{q_s} = 1 - \frac{6}{\pi^2}\sum_{i=1}^{\infty}\frac{1}{i^2}\exp\left(-\frac{D_s i^2 \pi^2 t}{R^2}\right)$	D_s	[261]
5	Reichenburg equation	$-\ln\left(1-\frac{q_t}{q_s}\right) \approx \ln\frac{\pi^2}{6} + \frac{D_s \pi^2 t}{R^2}$	D_s	[261]
6	Linear driving force	$\frac{dq_t}{dt} \approx \frac{\pi^2 D_s}{R^2}\left(q_s - q_t\right)$	D_s	[261]

The intraparticle diffusion model can be given as follows [260]

$$q_t = k_p t^{1/2} + C \tag{19}$$

where q_t is the adsorption capacity at time t (mg g^{-1}), k_p is the intraparticle diffusion rate constant, (mg g^{-1} min$^{-1/2}$), t is the time (min), and C is the intercept.

Film surface diffusion model can be given as follows [261]

$$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q_r}{\partial r}\right) \tag{20}$$

With the initial and boundary conditions

$$t = 0,\; q_r = 0 \tag{21}$$

Table 9
Presence of metal binding groups of different microorganisms

S. No	Microorganism	Metal binding groups
1	Bacteria	N-acetylglucosamine (NAG) N-acetylmuramic acid (NAM)
2	Fungi	Chitin (β-(1,4)-linked-N-Acetylglucosamine) Chitosan (poly- β-(1,4)-linked-N-Acetylglucosamine) glycans (glucans, mannans) Mannoproteins Inorganic ions, Poly-phosphates Lipids and proteins
3	Algae	Carboxylates, amines Imidazoles, phosphates, Sulfhydryls, sulfates and hydroxyls

$$r = 0,\ \frac{\partial q_r}{\partial r} = 0 \tag{22}$$

$$r = R,\ \rho_p D_s \frac{\partial q_r}{\partial r} = k_f\left(c_b - c_s\right) \tag{23}$$

where R is the adsorbent radius, r is the radial coordinate, D_s is the surface diffusion coefficient, q_r is the adsorbed phase concentration at r, k_f is the film mass transfer coefficient, c_s is the liquid phase concentration at the adsorbent surface, ρ_p is the adsorbent particle density. There are two key parameters in the film surface diffusion model are the film mass transfer coefficient k_f and the surface diffusion coefficient D_s.

Film mass transfer coefficient can be given as follows [261]

$$\frac{dq_t}{dt} = -\frac{V}{m}\frac{dc_b}{dt} = \frac{3k_f}{R\rho_p}\left(c_b - c_s\right) \tag{24}$$

where k_f is the film mass transfer coefficient, R is the adsorbent radius, c_s is the liquid phase concentration at the adsorbent surface, c_b is the adsorbent phase concentration at the adsorbent surface q_s, ρ_p is the adsorbent particle density.

Surface diffusion coefficient can be given as follows [261]

$$\frac{q_t}{q_s} = 1 - \frac{6}{\pi^2}\sum_{i=1}^{\infty}\frac{1}{i^2}\exp\left(-\frac{D_s i^2 \pi^2 t}{R^2}\right) \tag{25}$$

where D_s is the surface diffusion coefficient, R is the adsorbent radius. At long adsorption time, Eq. (25) can obtain

$$\frac{q_t}{q_s} \approx 1 - \frac{6}{\pi^2}\exp\left(-\frac{D_s \pi^2 t}{R^2}\right) \tag{26}$$

Eq. (26) can be written as

$$-\ln\left(1 - \frac{q_t}{q_s}\right) \approx \ln\frac{\pi^2}{6} + \frac{D_s \pi^2 t}{R^2} \tag{27}$$

which is known as Reichenburg equation used for Boyd plot at the late adsorption time (near-equilibrium). Eq. (26) can also be written as

$$\frac{dq_t}{dt} \approx \frac{\pi^2 D_s}{R^2}\left(q_s - q_t\right) \tag{28}$$

which is known as linear driving force for intraparticle mass transfer.

The adsorption kinetic models and diffusion models can be used to determine the rate limiting step in the biosorption of heavy metals, which engages the valence forces through the movement of electrons or ions from the solute to the adsorbent.

Furthermore, the thermodynamic study can be used to determine the magnitude of the parameter change due to the transfer of metal ions from the liquid solution to the surface of the adsorbents in the adsorption process. The thermodynamic parameters such as enthalpy (ΔH^o, kJ mol^{-1}), entropy (ΔS^o, kJ mol^{-1}) and Gibbs free energy (ΔG^o, kJ mol^{-1}) can be further used to explain the adsorption process. The thermodynamic parameters can be calculated from the following equations [266]

$$K_c = \frac{C_{Ae}}{C_e} \tag{29}$$

$$\Delta G^\circ = -RT \ln K_c \tag{30}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{31}$$

$$\log K_c \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{32}$$

where C_e is the equilibrium concentration in solution (mg l^{-1}), C_{Ae} is the amount of metal ion adsorbed on the adsorbent per litre of solution at equilibrium (mg l^{-1}), R is the gas constant (8.314 KJ mol^{-1}), T is the temperature (K) and K_c is the equilibrium constant. The values of ΔH^o and ΔS^o were calculated from the slope and the intercept of the plot of log K_c vs. 1 T^{-1}.

6. Biosorption mechanism

Many researchers have tested and reported the sequestration of heavy metals from aqueous solution using several treatment methodologies. These conventional methods have many disadvantages such as high installation and cost expensive, process complexity, time consuming, low efficiency in performance at low metal concentration and problems associated with the disposal of sludge. Adsorption by microorganisms or microbial aggregates is called as biosorption. Biosorption is a promising emerging alternate technology for the effective removal of heavy metals from the contaminated water. Biosorption technology has several advantages such as low cost, easy operation, reuse of sludge thereby reducing disposal issues, removal of heavy metals at low concentrations. The biosorption mechanism can be influenced by several factors such as type of biosorbent (living or non-living), types of biomaterials, chemical interaction between the metal solution and the adsorbents, metal ion concentration, pH, contact time, adsorbent dosage and temperature. The mechanism of biosorption process may be classified according to dependence on the cell's metabolism which is called metabolism dependent and non-metabolism dependent. Metabolism dependent is the process of metal uptake by physio-chemical interaction between the solid phase (adsorbent; biosorbent) and liquid phase (solvent; water). The liquid phase which contains the dissolved species (adsorbate; metal ions). The cell wall of different microorganism consists of polysaccharides, proteins and lipids which offers a number of active sites capable of binding metal ions. These cell wall compositions majorly consists of several potential metal binding groups such as carboxyl, hydroxyl, aldehydes, ketones, alcohol, amyl and ether. These functional groups have unique surface chemistry which attracts the metal ions from the liquid phase. This type of biosorption is called as non-metabolism dependent. Variety of microbial materials such as bacterial, fungal, algal mass, yeast and agricultural wastes have been employed as the biosorbent material for the adsorption process. Microbial aggregates have complex surface structure, formed from micro and meso-microbes and have different shapes such as filamentous, oval, spherical, sheet and irregular. Under the favorable conditions, the microbial aggregates will espouse the dense structure and have some special features such as adhesion and flocculation, which enhance the microbial adsorbent activity to adsorb the metal ions from the aqueous solution. The types and amount of metal ion binding on biosorbent material will differ for each microorganism because of differences in the cell wall composition among the different group of microorganisms. Cell wall of bacteria majorly consists of peptidoglycan which is made up of a polysaccharide backbone consisting of N-acetylglucosamine (NAG) and N-acetylmuramic acid (NAM) residues. Peptidoglycan is responsible for the firmness of the bacterial cell wall and for the determination of the cell shape. Normally, fungai cell wall is flexible which is made up of glycosamine polymer chitin, chitosan, inorganic ions, proteins and polysaccharides. Many negatively charged functional groups were present on the cell wall of fungai species such as carboxyl, hydroxyl, sulphate, phosphate and amino groups. Interestingly, these negative groups possibly bind the positive chromium ions which was present in the liquid solutions. Algae cell wall consists of potential metal binding groups such as carboxylates, phosphates, sulphates and sulfhydryls. Table 10 shows that presence of metal binding groups of different microorganisms. Generally, adsorbent (biosorbent material) has higher affinity which attracts the sorbate species. The adsorption of metal ions from the solvent to biosorbent material continues till the equilibrium condition will establish. Biosorption can be classified into two types such as i) passive mode and ii) active mode. In passive mode, the dead or inactive cells are used for the sequestration of metals from aqueous solutions. Passive mode mainly embraces the cell wall and primarily depends on the functional groups present on the surface of the adsorbent. In passive mode, the uptake of metal ions takes place immediately and reaching the equilibrium within 30–40 min. In active mode, the living cells are used for the removal of heavy metals. In active mode, the metal biosorption process can be done by two steps. Step 1: metal ions are adsorbed to the surface of biomass which can be done by interaction between the functional groups were present on the surface of the biomass and metal ions. Step 2: Metal ions penetrate the cell membrane and enter into the cells. In step two process, before the penetration, the metal ions are come across the cell wall of biosorbent material. Active mode is metabolism-dependent and is associated with metal transport and deposition [267]. The sequestration of metals from aqueous solutions can be determined according to the following mechanism i) Extracellular accumulation ii) cell surface sorption/precipitation and iii) intracellular accumulation.

6.1. Extracellular accumulation

Extracellular polymeric substances (EPS) such as soluble peptide, polysaccharides, glucoprotein and lipopolysaccharide can be produced from prokaryotic (bacteria, archaea) and eukaryotic (algae, fungi) microorganisms. EPS substances have an extensive quantity of anion functional groups which can adsorb the metal ions from the aqueous solutions. Several research studies have investigated the effect of EPS on the biosorption of metals by using bacteria and fungi [268,269]. These results showed that the metal adsorbed on the surface of the cells because of the existence of EPS. The percentage removal of metal is increased due to the increase in the amount of EPS excreted.

6.2. Cell surface precipitation

In the cellular structure, cell wall is the first major component for the binding of metal ions. Metal adsorption on the cell wall can be processed by two mechanism i) physiochemical inorganic deposition ii) stoichiometric interaction between the metals in the solution and the functional groups present on the surface of the cell wall (adsorbent). Many researchers have investigated that the functional groups such as carboxyl, hydroxyl, sulfhydryl, amine, amide, imine, imidazole, phosphate and phosphodiester play an important role in the adsorption of metals from the aqueous solution [270,271]. The protein and the carbohydrate present on the cell wall, partially purified products such as chitin, mannan and glucan also contribute significantly towards the removal of heavy metals from aqueous solutions.

6.3. Intracellular accumulation

In the extracellular accumulation, the presence of high concentration of metal ions could easily penetrate into the cell wall and the membrane of the cell (biosorbent). The cell wall can be disrupted by two forces; natural force (autolysis) and artificial force (mechanical force, alkali treatment process). Intracellular accumulation is an energy driven process and is dependent on active metabolism [272]. Metal ions are transported or precipitated within the cell by active metabolism. After the precipitation of metals in the cell, the metal ions are cubicled into different subcellular organelles (vacuole and mitochondria). The compartmentalized metal ions can further be detoxified by reduction, oxidation, demethylation or methylation [273].

7. Immobilization of microorganism

Microorganism or whole cell immobilization is the technique of imprisonment of cell in a distinct support or matrix. In biosorption technology, the free cells (biosorbent material) can be effectively used for adsorption of metal ions in batch experimentation but have some limitations in industrial applications which are not suitable for column packing in industrial application. Because, freely suspended microbial cells have low mechanical strength, difficulty in sequestering biomass and small particle size. Remarkably, free cells can easily have disintegrated due to high pressures and therefore, excessive hydrostatic pressures are required to generate suitable flowrates [274,275]. These problems can be rectified by applying immobilizing cell system. Immobilization of cell is the well-developed method for the utilization of several important functional groups from microbial biomass. Microbial biomass has been immobilized by using several inert materials such as calcium-alginate, gelatin, silica, polyacrylamide, glutaraldehyde, polymethane, polysulfone and polyurethane. The inert materials immobilize the cells by holding it permanently or temporarily. Example: A natural polymer derived from the cell wall of microorganisms such as bacteria, fungai and algae can be immobilized by using the most commonly used inert material (calcium alginate). They are inert and have good water holding capacity. Immobilization of microbial biomass offers several advantages such as superior reuse, continuous usage, saving in cost investment, more stability, high biomass loading, minimal clogging in continuous flow systems and cell organelles will be more active for a long period of time [276]. Noticeably, immobilized microbial biomass packed in adsorption column, which are effective for continuous removal of heavy metal ions from contaminated liquid. Immobilization of microbial biomass can be performed by several methods such as adsorption, covalent bonding, entrapment, cell to cell cross linking and encapsulation. After the adsorption process, desorption of metal ions from immobilized microbial biomass can be executed by using inorganic salts such as NaCl and $Ca(NO_3)_2$.

8. Future research needs

In the past years, most of the research have been done based on the batch adsorption experimental studies but with limited application in column studies. The batch adsorption experiment is limited to the laboratory level application and is not applicable at industrial scale. Different types of adsorbents with or without modification procedures have been tested for the effective removal of heavy metal ions from water/wastewater. But these fail to provide higher adsorption capacity, good regeneration ability, low cost, etc. Therefore, more attention should be given towards improving the adsorption capacity, cost-effectiveness and regeneration ability. The solution is to ascertain and design column experimentation using selective surface modification procedures to increase the adsorption properties of the targeted metal ions from the wastewater. In column studies, full-scale and pilot-scale studies should be performed with surface modified adsorbents and immobilized microbial biomass to ensure their potential on a commercial scale. The synthesized adsorbent material is applied for the specific and multiple removal of targeted pollutants and effective metal uptake from the wastewater. Immobilization of cell is the well-developed method for the utilization of several important functional groups from microbial biomass to attain the higher removal of metal ions and better reuse of microbial biomass. Further research needs to be done in the future on the development of fixed bed columns to estimate the removal efficiency and investigate the enhancement of the adsorption capacity of the adsorbent material through selective surface modification procedures which can positively bring about the effective adsorption of metal ions from the wastewater. These results could be used for design the column experimental setup at an industrial scale.

9. Conclusion

The review article has majorly focused on the low-cost agricultural adsorbents that could be effectively used for the sequestration of Cr(VI) ions from aqueous solution. Adsorption process is a surface phenomenon, and depends on several factors such as functional groups present on the surface of the adsorbents, chemical interaction between the adsorbent and the toxic metals present in the liquid solution, wastewater pH and metal ion concentration. Several isotherms, kinetics, diffusion and thermodynamic models have been used to predict the interaction behavior between the adsorbent and the adsorbate, adsorption rate and mechanism. It is important to note that the selective and specific surface modified agricultural waste and immobilized microbial biomass could have better and enhanced adsorption capacity through greater surface area, porosity and higher availability of active sites over other natural adsorbents. This review article has showed that the Cr(VI) ions adsorption capacity of several biosorbents is in the following order: activated carbon > agricultural biomass > micro algal > fungal > bacterial > yeast > industrial waste. The literature study reveals that the selective surface modification process could have a potential for a breakthrough in this wastewater treatment technology. Finally, it has been suggested that the low cost surface modified adsorbent and immobilized microbial biomass have been successfully used repeatedly in the batch and column experimental studies for the effective removal of toxic metal ions from the wastewater.

References

[1] Y. Pang, G.M. Zeng, L. Tang, Y. Zhang, Y.Y. Liu, X.X. Lei, Z. Li, J.C. Zhang, G.X. Xie, PEI-grafted magnetic porous powder for highly effective adsorption of heavy metal ions, Desalination, 281 (2011) 278–284.

[2] K.K. Krishnani, S. Srinives, B.C. Mohapatra, V.M. Boddu, J. Hao, X. Meng, A. Mulchandani, Hexavalent chromium removal mechanism using conducting polymers, J. Hazard. Mater., 99–106 (2013) 252–253.

[3] L. Tang, Y. Fang, Y. Pang, G. Zeng, J. Wang, Y. Zhou, Y. Deng, G. Yang, Y. Cai, J. Chen, Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline–magnetic mesoporous silica composite, Chem. Eng. J., 254 (2014) 302–312.

[4] M.R. Samania, S.M. Borgheib, A. Oladc, M.J. Chaichid, Removal of chromium from aqueous solution using polyaniline–poly ethylene glycol composite, J. Hazard. Mater., 184 (2010) 248–254.

[5] M. Avila, T. Burks, F. Akhtar, M. Gothelid, P.C. Lansaker, M.S. Toprak, M. Muhammed, A. Uheida, Surface functionalized nanofibers for the removal of chromium(VI) from aqueous solutions, Chem. Eng. J., 245 (2014) 201–209.

[6] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, Bioresour. Technol., 97 (2006) 15–20.

[7] R.M. Schneider, C.F. Cavalin, M.A.S.D. Barros, C.R.G. Tavares, Adsorption of chromium ions in activated carbon, Chem. Eng. J., 132 (2007) 355–362.

[8] P. Lakshmipathiraj, G.B. Raju, M.R. Basariya, S. Parvathy, S. Prabhakar, Removal of Cr(VI) by electrochemical reduction, Sep. Purif. Technol., 60 (2008) 96–102.

[9] C. Oze, D.K. Bird, S. Fendorf, Genesis of hexavalent chromium from natural sources in soil and groundwater, Proc. Natl. Acad. Sci. USA., 104 (2007) 6544–6549.

[10] C. Jung, J. Heo, J. Han, N. Her, S.J. Lee, J. Oh, J. Ryu, Y. Yoon, Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, Sep. Purif. Technol., 106 (2013) 63–71.

[11] US Environmental Protection Agency (USEPA), Environmental pollution control alternatives: drinking water treatment for small communities, USEPA, Washington, DC 1990.

[12] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, J. Hazard. Mater., 123 (2005) 223–231.

[13] N. Zaitseva, V. Zaitsev, A. Walcarius, Chromium(VI) removal via reduction–sorption on bi-functional silica adsorbents, J. Hazard. Mater., 250 (2013) 454–461.

[14] C.V. Gherasim, G. Bourceanu, R.I. Olariu, C. Arsene, A novel polymer inclusion membrane applied in chromium (VI) separation from aqueous solutions, J. Hazard. Mater., 197 (2011) 244–253.

[15] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere, 56 (2004) 91–106.

[16] J.L-. Aguirre, V. Garcia, E. Pongracz, R.L. Keiski, The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments, Desalination, 240 (2009) 262–269.

[17] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electro-chemical precipitation process, Water Sci. Technol., 34 (1996) 109–116.

[18] B. Gao, Y. Gao, Y. Li, Preparation and chelation adsorption property of composite chelating material poly(amidoxime)/SiO_2 towards heavy metal ions, Chem. Eng. J., 158 (2010) 542–549.

[19] C.V. Gherasim, J. Krivcik, P. Mikulasek, Investigation of batch electrodialysis process for removal of lead ions from aqueous solutions, Chem. Eng. J., 256 (2014) 324–334.

[20] L. Lin, X. Xu, C. Papelis, T.Y. Cath, P. Xu, Sorption of metals and metalloids from reverse osmosis concentrate on drinking water treatment solids, Sep. Purif. Technol., 134 (2014) 37–45.

[21] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Resour., 33 (1999) 2469–2479.

[22] A. Chakir, J. Bessiere, K.El. Kacemi, B. Marouf, A comparative study of the removal of trivalent chromium from aqueous solutions by bentonite and expanded perlite, J. Hazard. Mater., B95 (2002) 29–46.

[23] I.G. Abid, K. Galai, M.T. Ayadi, Retention of chromium(III) and cadmium (II) from aqueous solution by illitic clay as a low cost adsorbent, Desalination, 256 (2010) 190–195.

[24] K.J. Cronje, K. Chetty, M. Carsky, J.N. Sahu, B.C. Meikap, Optimization of chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride, Desalination, 275 (2011) 276–284.

[25] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of heavy metals, Res. J. Chem. Environ., 7 (2003) 71–79.

[26] A. Demirbas, Heavy metal adsorption onto agro based waste materials: A review, J. Hazard. Mater., 157 (2008) 220–229.

[27] Y. Sahin, A. Ozturk, Biosorption of chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*, Proc. Biochem., 40 (2005) 1895–1901.

[28] R.I. Acosta, X. Rodriguez, C. Gutierrez, G. Moctezuma, Biosorption of chromium(VI) from aqueous solutions onto fungal biomass, Bioinorg. Chem. Appl., 2 (2004) 1–7.

[29] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium (VI) from aqueous solution by green algae Spirogyra species, Water Res., 35 (2001) 4079–4085.

[30] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weeds: kinetics and mechanism studies, J. Hazard. Mater., 152 (2008) 100–112.

[31] J. Wang, C. Chen, Biosorbents for heavy metals removal and their future, Biotechnol. Adv., 27 (2009) 195–226.

[32] M.A. Zarraa, A study on the removal of chromium (VI) from waste solution by adsorption on to sawdust in stirred vessels, Adsorpt. Sci. Technol., 12 (1995) 129–138.

[33] J. Freer, J. Baeza, H. Maturana, G. Palma, Removal and recovery of uranium by modified Pinus Equilib D. Don bark, J. Chem. Technol. Biotechnol., 46 (1989) 41–48.

[34] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of Cr(VI) from solution by coconut husk and palm pressed fibres, Environ. Technol., 14 (1993) 277–282.

[35] B. Acemioglu, M.H. Alma, Equilibrium studies on the adsorption of Cu(II) from aqueous solution onto cellulose, J. Coll. Interf. Sci., 243 (2001) 81–83.

[36] J.A. Omgbu, V.I. Iweanya, Dynamic sorption of Pb^{2+} and Zn^{2+} with Palm (*Eleasis guineensis*) kernel husk, J. Chem. Educ., 67 (1990) 800–801.

[37] J.M. Randall, F.W. Reuter, A.C. Waiss, Removal of cupric ions from solution with peanut Skins, J. Appl. Polym. Sci., 19 (1975) 1563–1571.

[38] P.D Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage., 22 (2002) 471–480.

[39] Y. Bin, Adsorption of copper and lead from industrial wastewater by maple sawdust, Thesis, Lamar University, Beaumont, USA, 1995.

[40] E. Demirbas, Adsorption of Cobalt (II) from aqueous solution onto activated carbon prepared from hazelnut shells, Adsorpt. Sci. Technol., 21 (2003) 951–963.

[41] Y. Orhan, H. Buyukgungor, The removal of heavy metals by using agricultural wastes, Water Sci. Technol., 28 (1993) 247–255.

[42] M.M. Nassar, The kinetics of basic dyes removal using palm fruit bunch, Adsorpt. Sci. Technol., 15 (1997) 609–617.

[43] Z. Reddad, C. Gerente, Y. Andres, M.C. Ralet, J.F. Thibault, P.L. Cloirec, Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp, Carbohydr. Polym., 49 (2002) 23–31.

[44] V.M. Vucurovic, R.N. Razmovski, U.D. Miljic. V.S. Puskas, Removal of cationic and anionic azo dyes from aqueous solutions by adsorption on maize stem tissue, J. Taiwan. Inst. Chem. Eng., 45 (2014) 1700–1708.

[45] A. Hashem, A.A-. Okeil, A.El-. Shafie, M.El-. Sakhawy, Grafting of high α-cellulose pulp extracted from sunflower stalks for removal of Hg (II) from aqueous solution, Polym. Plast. Technol. Eng., 45 (2006) 135–141.

[46] M. Dakiky, M. Khamis, A. Manassra, M. Mereb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6, (2002) 533–561.

[47] A. Demirbas, Adsorption of Cr(III) and Cr(VI) ions in aqueous solutions onto modified lignin, Energy Sources, 27 (2005) 1449–1455.

[48] G. Annadurai, R.S. Juang, D.L. Lee, Adsorption of heavy metals from water using banana and orange peels. Water Sci. Technol., 47 (2002) 185–190.

[49] D. Balkose, H. Baltacioglu, Adsorption of heavy metal cations from aqueous solutions by wool fibers, J. Chem. Technol. Biotechnol., 54 (1992) 393–397.

[50] J.M. Randall, E. Hautala, A.C. Waiss, J.L. Tschernitz, Modified barks as scavengers for heavy metal ions, Forest. Prod. J., 26 (1976) 46–50.

[51] T.W. Tee, R.M. Khan, Removal of lead, cadmium and zinc by waste tea leaves, Environ. Technol. Lett., 9 (1988) 1223–1232.

[52] E. Maranon, H. Sastre, Heavy metal removal in packed beds using apple wastes, Bioresour. Technol., 38 (1991) 39–43.

[53] K.S. Low, C.K. Lee, A.Y. Ng, Column study on the sorption of Cr(VI) using quaternized rice hulls, Bioresour., Technol., 68 (1999) 205–208.

[54] T. Vaughan, C.W. Seo, W.E. Marshall, Removal of selected metal ions from aqueous solution using modified corncobs, Bioresour. Technol., 78 (2001) 133–139.

[55] G. Macchi, D. Marani, G. Tirivanti, Uptake of mercury by exhausted coffee grounds. Environ. Technol. Lett., 7 (1986) 431–444.

[56] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J., 118 (2006) 83–98.

[57] G. Pearce, Introduction to membranes: Filtration for water and wastewater treatment, Filtr Separat, 44 (2007) 24–27.

[58] N.L. Le, S.P. Nunes, Materials and membrane technologies for water and energy sustainability, Sustainable Mater. Technol., 7 (2016) 1–28.

[59] J.Y. Seo, A. Vogelpohl, Membrane choice for wastewater treatment using external cross flow tubular membrane filtration, Desalination, 249 (2009) 197–204.

[60] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavymetals removal from industrial wastewater, Desalination, 256 (2010) 90–93.

[61] M. Bilal, J.A. Shah, T. Ashfaq, S.M.H. Gardazi, A.A. Tahir, A. Pervez, H. Haroon, Q. Mahmood, Waste biomass adsorbents for copper removal from industrial wastewater – A review, J. Hazard. Mater., 263 (2013) 322–333.

[62] D. Jeison, J.B.V. Lier, Bio-layer management in anaerobic membrane bioreactor for wastewater treatment, Water Sci. Technol., 54 (2006) 81–86.

[63] T.A. Mohammed, A.H. Birima, M.J.M.M. Noor, S.A. Muyibi, A. Idrid, Evaluation of using membrane bioreactor for treating municipal wastewater at different operating conditions, Desalination, 221 (2008) 502–510.

[64] Y. Wang, K.W. Ong, M.W.D. Brannock, G.L. Leslie, Evaluation of membrane bioreactor performance via residence time distribution: effects of membrane configuration and mixing, Water Sci. Technol., 57 (2008) 353–359.

[65] K. Mohammed, O. Sahu, Biosorption and membrane technology for reduction and recovery of chromium from tannery industry wastewater, Environmental Technology and Innovation, 4 (2015) 150–158.

[66] S. Habibi, A. Nematollahzadeh, S.A. Mousavi, Nano-scale modification of polysulfone membrane matrix and the surface for the separation of chromium ions from water, Chem. Eng. J., 267 (2015) 306–316.

[67] Y. Bao, X. Yan, W. Du, X. Xie, Z. Pan, J. Zhou, L. Li, Application of amine-functionalized MCM-41 modified ultrafiltration membrane to remove chromium(VI) and copper(II), Chem. Eng. J., 281 (2015) 460–467.

[68] Z. Yao, S. Du, Y. Zhang, B. Zhu, L. Zhu, A.E. John, Positively charged membrane for removing low concentration Cr(VI) in ultrafiltration process, J. Water Process Eng., 8 (2015) 99–107.

[69] Y. Huang, D. Wu, X. Wang, W. Huang, D. Lawless, X. Feng, Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation, Sep. Purif. Technol., 158 (2016) 124–136.

[70] D. Purkayastha, U. Mishra, S. Biswas, A comprehensive review on Cd(II) removal from aqueous solution, J. Water Process Eng., 2 (2014) 105–128.

[71] X. Shi, G. Tal, N.P. Hankins, V. Gitis, Fouling and cleaning of ultrafiltration membranes: A review, J. Water Process Eng., 1 (2014) 121–138.

[72] D. Vasanth, G. Pugazhenthi, R. Uppaluri, Biomass assisted microfiltration of chromium(VI) using baker's yeast by ceramic membrane prepared from low cost raw materials, Desalination, 285 (2012) 239–244.

[73] S.M. Doke, G.D. Yadav, Process efficacy and novelty of titania membrane prepared by polymeric sol-gel method in removal of chromium(VI) by surfactant enhanced microfiltration, Chem. Eng. J., 255 (2014) 483–491.

[74] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage., 92 (2011) 407–418.

[75] Z. Li, T. Li, L. An, P. Fu, C. Gao, Z. Zhang, Highly efficient chromium(VI) adsorption with nanofibrous filter paper prepared through electrospinning chitosan/polymethyl methacrylate composite, Carbohydr. Polym., 137 (2016) 119–126.

[76] Y. Zhang, S. Shao, W. Yu, F. Yang, X. Xu, Study on recycling alkali from the wastewater of textile mercerization process by nanofiltration, IERI Procedia., 9 (2014) 71–76.

[77] A.J.C. Semiao, G. Gazzola, O. Habimana, R. Heffernan, C. Murphy, E. Casey, Understanding the mechanisms of biofouling on nanofiltration membranes: Effect of the bioflim structure on solute removal, Procedia Eng., 44 (2012) 1557–1560.

[78] T. Wintgens, M. Gallenkemper, T. Melin, Endocrine disrupter removal from wastewater using membrane bioreactor and nanofiltration technology, Desalination, 146 (2002) 387–391.

[79] X. Wei, P. Gu, G. Zhang, Reverse osmosis concentrate treatment by a PAC countercurrent four stage adsorption/MF hybrid process, Desalination, 352 (2014) 18–26.

[80] J.S. George, A. Ramos, H.J. Shipley, Tanning facility wastewater treatment: Analysis of physical-chemical and reverse osmosis methods, J. Environ. Chem. Eng., 3 (2015) 969–976.

[81] P. Bhattacharya, A. Roy, S. Sarkar, S. Ghosh, S. Majumdar, S. Chakraborty, S. Mandal, A. Mukhopadhyay, S. Bandyopadhyay, Combination technology of ceramic microfiltration and reverse osmosis for tannery wastewater recovery, Water Research and Industry, 3 (2013) 48–62.

[82] A. Mahmoud, A.F.A. Hoadley, An evaluation of a hybrid ion exchange electrodialysis process in the recovery of heavy metals from simulated dilute industrial wastewater, Water Res., 46 (2012) 3364–3376.

[83] M.A. Barakat, New trends in removing heavy metals from industrial wastewater. Arab. J. Chem., 4 (2011) 361–377.

[84] V.V. Slesarenko, Electrodialysis and reverse osmosis membrane plants at power stations, Desalination, 158 (2003) 303–311.

[85] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: A review, Bioresour. Technol., 99 (2008) 6709–6724.

[86] B. Merzouk, B. Gourich, A. Sekki, K. Madani, M. Chibane, Removal turbidity and separation of heavy metals using electrocoagulation-electroflotation technique: a case study, J. Hazard. Mater., 164 (2009) 215–222.

[87] N. Tran, P. Drogui, J.F. Blais, G. Mercier, Phosphorus removal from spiked municipal wastewater using either electrochemical coagulation or chemical coagulation as tertiary treatment, Sep. Purif. Technol., 95 (2012) 16–25.

[88] S. Aoudj, A. Khelifa, N. Drouiche, R. Belkada, D. Miroud, Simultaneous removal of chromium(VI) and fluoride by electrocoagulation-electroflotation: Application of a hybrid Fe-Al anode, Chem. Eng. J., 267 (2015) 153–162.

[89] B. Merzouk, B. Gourich, K. Madani, Ch. Vial, A. Sekki, Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continous electrocoagulation. A comparative study, Desalination, 272 (2011) 246–253.

[90] S.S. Hamdan, M.H. El-Naas, Characterization of the removal of chromium(VI) from groundwater by electrocoagulation, J. Ind. Eng. Chem., 20 (2014) 2775–2781.

[91] L. Metcalf, H.P. Eddy, Wastewater Engineering: Treatment, Disposal, and Reuse, McGraw-Hill, NewYork., (1991) 740–741.

[92] S.A. Abo-Farha, A.Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, Removal of some heavy metal cations by synthetic resin purolite C100, J. Hazard. Mater., 169 (2009) 190–194.

[93] N. Kamakura, T. Inui, M. Kitano, T. Nakamura, Determination of chromium(III), chromium(VI) and chromium(III) acetylacetonate in water by ion-exchange disk extraction/metal furnace atomic absorption spectrometry, Spectrochim. Acta B, 93 (2014) 28–33.

[94] T.M. Zewail, N.S. Yousef, Kinetic study on heavy metal ions removal by ion exchange in batch conical air spouted bed, Alexandria Eng. J., 54 (2015) 83–90.

[95] I.H. Lee, Y. Kuan, J.M. Chern, Equilibrium and kinetics of heavy metal ion exchange. J. Chin. Inst. Chem. Eng., 38 (2007) 71–84.

[96] B. Alyuz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater., 167 (2009) 482–488.

[97] S.A. Cavaco, S. Fernandes, M.M. Quina, L.M. Ferreira, Removal of chromiumfrom electroplating industry effluents by ion exchange resins, J. Hazard. Mater., 144 (2007) 634–638.

[98] H. Li, J. Li, Z. Chi, W. Ke, Kinetic and equilibrium studies of chromium (III) removal from aqueous solution by IRN-77 cation-exchange resin, Procedia Environ. Sci., 16 (2012) 646–655.

[99] H.Y. Li, C. Li, M. Zhang, K. Wang, B. Xie, Removal of V(V) from aqueous Cr(VI)-bearing solution using anion exchange resin: Equilibrium and kinetics in batch studies, Hydrometallurgy, (2015) (Article in press).

[100] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Equilibrium and kinetic ionexchange studies of Pb2+, Cr3+, Fe3+and Cu2+on natural clinoptilolite, Water Res., 36 (2002) 2784–2792.

[101] V.J. Inglezakis, A.A. Zorpas, M.D. Loizidou, H.P. Grigoropoulou, The effect of competitive cations and anions on ion exchange of heavy metals, Sep. Purif. Technol., 46 (2005) 202–207.

[102] T. Motsi, N.A. Rowson, M.J.H. Simmons, Adsorption of heavy metals from acidmine drainage by natural zeolite, Int. J. Miner. Process., 92 (2009) 42–48.

[103] A.H.M. Veeken, S. de Vries, A. Van der Mark, W.H. Rulkens, Selective precipitation of heavy metals as controlled by a sulfide-selective electrode, Sep. Sci. Technol., 38 (2003) 1–19.

[104] N. Reynier, L. Coudert, J.F. Blais, G. Mercier, S. Besner, Treatment of contaminated soil leachate by precipitation, adsorption and ion exchange, J. Environ. Chem. Eng., 3 (2015) 977–985.

[105] S. Golbaz, A.J. Jafari, M. Rafiee, R.R. Kalantary, Separate and simultaneous removal of phenol, chromium and cyanide from aqueous solution by coagulation/precipitation: mechanisms and theory, Chem. Eng. J., 253 (2014) 251–257.

[106] D. Wang, S. He, C. Shan, Y. Ye, H. Ma, X. Zhang, Z. Weiming, B. Pan, Chromium speciation in tannery effluent after alkaline precipitation: isolation and characterization, J. Hazard. Mater., 316 (2016) 169–177.

[107] E. Alvarez-Ayuso, A. Garcia-Sanchez, X. Querol, Purification of metal electro-plating waste waters using zeolites, Water Res., 37 (2003) 4855–4862.

[108] Q.Y. Chen, Z. Luo, C. Hills, G. Xue, M. Tyrer, Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon oxide, Water Res., 43 (2009) 2605–2614.

[109] J.L. Huisman, G. Schouten, C. Schultz, Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry, Hydrometallurgy, 83 (2006) 106–113.

[110] S.A. Mirbagheri, S.N. Hosseini, Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse, Desalination, 171 (2004) 85–93.

[111] A. Ozverdi, M. Erdem, Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption from aqueous solutions by pyrite and synthetic iron sulphide, J. Hazard. Mater., 137 (2006) 626–632.

[112] Y.X. Liu, D.X. Yuan, J.M. Yan, Q.L. Li, T. Ouyang, Electrochemical removal of chromium from aqueous solutions using electrodes of stainless steel nets coated with single wall carbon nanotubes, J. Hazard. Mater., 186 (2011) 473–480.

[113] C. Liu, N. Fiol, J. Poch, I. Villaescusa, A new technology for the treatment of chromium electroplating wastewater based on biosorption, J. Water Process Eng., 11 (2016) 143–151.

[114] L.K. Wang, Y.T. Hung, N.K. Shammas, Advanced physiochemical treatment technologies. Handbook of Environmental Engineering. 5. Humana Press, Totowa, New Jersey (2007).

[115] I. Heidmann, W. Calmano, Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminium electrocoagulation, J. Hazard. Mater., 152 (2008) 934–941.

[116] Q. Liu, T. Zheng, P. Wang, J. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chem. Eng. J., 219 (2013) 499–511.

[117] M. Karnib, A. Kabbani, H. Holail, Z. Olama, Heavy metals removal using activated carbon, silica and silica activated carbon composite, Energy Procedia, 50 (2014) 113–120.

[118] O.G. Apul, T. Karanfil, Adsorption of synthetic organic contaminants by carbon nanotubes: A critical review, Water Res., 68 (2015) 34–55.

[119] M.J. Ahmed, Application of agricultural based activated carbons by microwave and conventional activations for basic dye adsorption: review, J. Environ. Chem. Eng., 4 (2016) 89–99.

[120] M. Kobya, Adsorption kinetic and equilibrium studies of Cr(VI) by hazelnut shell activated carbon, Adsorpt. Sci. Technol., 22 (2004) 51–64.

[121] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol., 74 (1999) 111–122.

[122] Z.A. Aluthman, R. Ali, M. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J., 184 (2012) 238–247.

[123] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawbust, Chem. Eng. J., 81 (2001) 95–105.

[124] M. Al Bahri, L. Calvo, M.A. Gilarranz, J.J. Rodriguez, Activated carbon from grape seeds upon chemical activation with phosphoric acid: Application to the adsorption of diuron from water, Chem. Eng. J., 203 (2012) 348–356.

[125] Z.A. Aluthman, M. Naushad, R. Ali, Kinetic, equilibrium isotherm and thermodynamic studies of Cr(VI) adsorption onto low-cost adsorbent developed from peanut shell activated with phosphoric acid, Environ. Sci. Pollut. Res., 20 (2012) 3351–3365.

[126] S.K. Theydan, M.J. Ahmed, Adsorption of methylene blue onto biomass-based activated carbon by $FeCl_3$ activation: equilibrium, kinetics, and thermodynamic studies, J. Anal. Appl. Pyrolysis, 97 (2012) 116–122.

[127] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by mutiwalled carbon nanotubes, Carbon, 41 (2003) 2787–2792.

[128] H. Hyung, J. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, Environ. Sci. Technol., 42 (2008) 4416–4421.

[129] L. Ji, Y. Shao, Z. Xu, S. Zheng, D. Zhu, Adsorption of monoaromatic compounds and pharmaceutical antibiotics on carbon nanotubes activated by KOH etching, Environ. Sci. Technol., 44 (2010) 6429–6436.

[130] L. Joseph, Q. Zaib, I.A. Khan, N.D. Berge, Y. Park, N.B. Saleh, Y. Yoom, Removal of bisphenol A and 17 a-ethinyl estradiol from landfill leachate using singlewalled carbon nanotubes, Water Res., 45 (2011) 4056–4068.

[131] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-a review, Bioresour. Technol., 99 (2008) 6017–6027.

[132] F. Kaczala, M. Marques, W. Hogland, Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto *Pinus sylvestris* sawdust, Bioresour. Technol., 100 (2009) 235–243.

[133] O.S. Amudaa, F.E. Adelowoa, M.O. Ologunde, Kinetics and equilibrium studies of adsorption of chromium(VI) ion from industrial wastewater using *Chrysophtllum albidum* (Sapotaceae) seed shells, Colloid Surf., 68 (2009) 184–192.

[134] A. Abdolali, W.S. Guo, H.H. Ngo, S.S. Chen, N.C. Nguyen, K.L. Tung, Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review, Bioresour. Technol., 160 (2014) 57–66.

[135] J.H. Joo, S.H.A. Hassan, S.E. Oh, Comparative study of biosorption of Zn^{2+} by *Pseudomonas aeruginosa* and *Bacillus cereus*, Int. Biodeter. Biodegr., 64 (2010) 734–741.

[136] Y. Wu, T. Li, L. Yang, Mechanisms of removing pollutants from aqueous solutions by microorganisms and their aggregates: A review, Bioresour. Technol., 107 (2012) 10–18.

[137] S. Murugavelh, K. Mohanty, Isolation, Identification and characterization of Cr(VI) reducing *Bacillus cereus* from chromium contaminated soil, Chem. Eng. J., 230 (2013) 1–9.

[138] V.H. Albarracin, B. Winik, E. Kothe, M.J. Amoroso, C.M. Abate, Copper bioaccumulation by the actinobacterium *Amycolatopsis* sp. AB0, J. Basic Microbiol., 48 (2008) 323–330.

[139] Z. Rahman, V.P. Singh, Cr(VI) reduction by *Enterobacter* sp. DU17 isolated from the tannery waste dump site and characterization of the bacterium and the Cr(VI) reductase, Int. Biodeter. Biodegr., 91 (2014) 97–103.

[140] M. Oves, M.S. Khan, A. Zaidi, Chromium reducing and plant growth promoting novel strain *Pseudomonas aeruginosa* OSG41 enhance chickpea growth in chromium amended soils, Eur. J. Soil Biol., 56 (2013) 72–83.

[141] A. Chergui, M.Z. Bakhti, A. Chahboub, S. Haddoum, A. Selatnia, G.A. Junter, Simultaneous biosorption of Cu^{2+}, Zn^{2+} and Cr^{6+} from aqueous solution by *Streptomyces rimosus* biomass, Desalination, 206 (2007) 179–184.

[142] S. Ravikumar, I.K. Yoo, S. Lee, S. Hong, Construction of copper removing bacteria through the integration of two component system and cell surface display, Appl. Biochem. Biotechnol., 165 (2011) 1674–1681.

[143] R. Bakiyaraj, L. Baskaran, A.L. Chidambaram, T. Mahakavi, M.S. kumar, Bioremediation of chromium by *Bacillus subtilis* and *Pseudomonas aeruginosa*, Int. J. Curr. Microbiol. App. Sci., 3 (2014) 715–719.

[144] Z.A. Zakaria, Z. Zakaria, S. Surif, W.A. Ahmad, Hexavalent chromium reduction by *Acinetobacter haemolyticus* isolated from heavy-metal contaminated wastewater, J. Hazard. Mater., 146 (2007) 30–38.

[145] F. Beolchini, F. Pagnanelli, L. Toro, F. Veglio, Ionic strength effect on copper biosorption by *Sphaerotilus natans*: equilibrium study and dynamic modeling in membrane reactor, Water Res., 40 (2006) 144–152.

[146] S. Schut, S. Zauner, G. Hampel, H. Konig, H. Claus, Biosorption of copper by wine relevant lactobacilli, Int. J. Food Microbiol., 145 (2011) 126–131.

[147] J.H. Pan, R.X. Liu, H.X. Tang, Surface reaction of *Bacillus cereus* biomass and its biosorption for lead and copper ions, J. Environ. Sci., 19 (2007) 403–408.

[148] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*, Colloid Surface A., 242 (2004) 93–104.

[149] D. Park, Y.S. Yun, J.Y. Kim, J.M. Park, How to study Cr (VI) biosorption: Use of fermentation waste for detoxifying Cr (VI) in aqueous solution, Chem. Eng. J., 136 (2008) 173–179.

[150] Z. Aksu, S. Ertugrul, G. Donmez, Single and binary chromium (VI) and remazol balck B biosorption properties of *Phormidium* sp, J. Hazard. Mater., 168 (2009) 310–318.

[151] M. Ziagova, G. Dimitriadis, D. Aslanidou, X. Papaioannou, E.L. Tzannetaki, M.L. Kyriakides, Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosus* and *Pseudomonas* sp. in single and binary mixtures, Bioresour. Technol., 98 (2007) 2859–2865.

[152] K. Anjana, A. Kaushik, B. Kiran, R. Nisha, Biosorption of Cr(VI) by immobilized biomass of two indigenous strains of cyanobacteria isolated from metal contaminated soil, J. Hazard. Mater., 148 (2007) 383–386.

[153] V.K. Gupta, A. Rastogi, Sorption and desorption studies of chromium(VI) from nonviable cyanobacterium *Nostoc muscorum* biomass, J. Hazard. Mater., 154 (2008) 347–354.

[154] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Biosorption of Cr (VI) onto marine *Aspergillus niger*: experimental studies and pseudo-second order kinetics, World J. Microbiol. Biotechnol., 25 (2009) 1413–1421.

[155] M. Sukumar, Reduction of hexavalent chromium by *Rhizopus oryzae*, Afr. J. Environ. Sci. Technol., 4 (2010) 412–418.

[156] C. Cojocaru, M. Diaconu, I. Cretescu, J. Vasic, Biosorption of copper(II) ions from aqua solutions using dried yeast biomass, Colloid Surface A., 335 (2009) 181–188.

[157] G.Q. Chen, G.M. Zeng, X. Tu, C.G. Niu, G.H. Huang, W. Jiang, Application of a by-product of *Lentinus edodes* to the bioremediation of chromate contaminated water, J. Hazard. Mater., 135 (2006) 249–255.

[158] N.S. Maurya, A.K. Mittal, P. Cornel, E. Rother, Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH, Bioresour. Technol., 97 (2006) 512–521.

[159] N. Ertugay, Y.K. Bayhan, Biosorption of Cr (VI) from aqueous solution by biomass of *Agaricus bisporus*, J. Hazard Mater., 154 (2008) 432–439.

[160] R. Pan, L. Cao, H. Huang, R. Zhang, Y. Mo, Biosorption of Cd, Cu, Pb and Zn from aqueous solutions by the fruiting bodies of jelly fungi (*Tremella fuciformis* and *Auricularia polytricha*), Appl. Microbiol. Biotechnol., 88 (2010) 997–1005.

[161] T. Sahan, H. Ceylan, N. Sahiner, N. Aktas, Optimization of removal conditions of copper ions from aqueous solutions by *Trametes versicolor*, Bioresour. Technol., 101 (2010) 4520–4526.

[162] Z. Aksu, E. Balibek, Chromium (VI) biosorption by dried *Rhizopus arrhizus*: effect of salt (NaCl) concentration on equilibrium and kinetic parameters, J. Hazard. Mater., 145 (2007) 210–220.

[163] I. Acosta-Rodriguez, D.L. Arevalo-Rangel, J.F. Cardenas-Gonzalez, M.G. Moctezuma-Zarate, V.M. Martinez-Juarez, Hexavalent Chromium (VI) removal by penicillium sp. IA-01, Advances in Bioremediation of Wastewater and Polluted Soil, 9 (2015) 2165–2167.

[164] K.K. Deepa, M. Sathishkumar, A.R. Binupriya, G.S. Murugesan, K. Swaminathan, S.E. Yun, Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*, Chemosphere, 62 (2006) 833–840.

[165] M. Pas, R. Milacic, K. Draslar, N. Pollak, P. Raspor, Uptake of chromium(III) and chromium(VI) compounds in the yeast cell structure, Biometals, 17 (2004) 25–33.

[166] R. Kumar, N.R. Bishnoi, G.K. Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chem. Eng. J., 135 (2008) 202–208.

[167] M. Sen, M.G. Dastidar, P.K. Roychoudhury, Biosorption of chromium (VI) by non-living *Fusarium* sp Isolated from soil, Practice Periodical of Hazardous, Toxic and Radioactive Waste Management, 9 (2005) 147–151.

[168] R. Han, H. Li, Y. Li, J. Zhang, H. Xaio, J. Shi, Biosorption of copper and lead ions by waste beer yeast, J. Hazard. Mater., 137 (2006) 1569–1576.

[169] N.R. Bishnoi, A. Pant, Garima, Biosorption of copper from aqueous solution using algal biomass, J. Sci. Ind. Res., 113 (2004) 813–816.

[170] R. Apiratikul, P. Pavasant, Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*, Bioresour. Technol., 99 (2008) 2766–2777.

[171] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, Bioresour. Technol., 97 (2006) 2321–2329.

[172] Y. Nuhoglu, E. Malkoc, A. Gurses, N. Canpolat, The removal of Cu(II) from aqueous solutions by *Ulothrix zonata*, Bioresour. Technol., 85 (2002) 331–333.

[173] N. Tamilselvan, J. Hemachandran, T. Thirumalai, C.V. Sharma, K. Kannabiran, E. David, Biosorption of heavy metals from aqueous solution by *Gracilaria corticata varcartecala* and *Grateloupia lithophila*, J. Coastal Life Medicine, 1 (2013) 102–107.

[174] E. Finocchio, A. Lodi, C. Solisio, A. Converti, Chromium(VI) removal by methylated biomass of *spirulina platensis*: The effect of methylation process, Chem. Eng. J., 156 (2010) 264–269.
[175] S.R. Suseem, M.A. Saral, Biosorption of heavy metals using mushroom *Pleurotus eous*, J. Chem. Pharm. Res., 6 (2014) 2163–2168.
[176] A. El-Sikaily, A.E. Nemr, A. Khaled, O. Abdelwehab, Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon, J. Hazard. Mater., 148 (2007) 216–228.
[177] S. Abirami, S. Srisudha, P. Gunasekaran, Biosorption of chromium from tannery effluent using biomass of *Sargussum wightii* (Greville), Int. J. Pharma Bio Sci., 3 (2012) 584–595.
[178] R.Gh. Mostafaii, H. Sayyaf, L. Iranshahi, A.Gh. Mosavi, E. Asemam, Evaluation and optimization of chromium removal from synthetic aqueous solutions by powdered *spirogyra*, Quarterly of International Archives of Health Sciences, 2 (2015) 57–61.
[179] V. Murphy, H. Hughes, P. Mcloughlin, Comparative study of chromium biosorption by red, green and brown seeweed biomass, Chemosphere, 70 (2008) 1128–1134.
[180] E.V.M. Carrilho, T.R. Gilbert, Assessing metal sorption on the marine alga *Pilayella littoralis,* J. Environ. Monit., 2 (2000) 410–415.
[181] S. Basha, Z.V.P. Murthy, B. Jha, Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*, Chem. Eng. J., 137 (2008) 480–488.
[182] G.C. Donmez, Z. Aksu, A. Ozturk, T. Kutsal, A comparative study on heavy metal biosorption characteristics of some algae, Proc. Biochem., 34 (1999) 885–892.
[183] S. Gupta, B.V. Babu, Utilization of waste product (tamarind seeds) for the removal of Cr (VI) from aqueous solutions: Equilibrium, kinetics, and regeneration studies, J. Environ. Manage., 90 (2009) 3013–3022.
[184] M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from selected agricultural by-products and evaluation of their physical, chemical and adsorption properties, Bioresour. Technol., 71 (2000) 113–123.
[185] S. Qaiser, A.R. Saleemi, M.M. Ahmad, Heavy metal uptake by agro based waste materials, Environ. Biotechnol., 10 (2007) 409–416.
[186] A. Bhatnagar, M. Sillanpaa, Utilization of agro industrial and municipal waste materials as potential adsorbents for water treatment – A review, Chem. Eng. J., 157 (2010) 277–296.
[187] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, J. Hazard. Mater., 140 (2007) 60–68.
[188] S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, Removal of Cr(VI) from aqueous solutions using agricultural waste 'maize bran', J. Hazard. Mater., 152 (2008) 356–365.
[189] K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddu, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater., 153 (2008) 1222–1234.
[190] Z.A. AL-Othman, R. Ali, Mu. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J., 184 (2012) 238–247.
[191] J.M. Randall, Variation in effectiveness of barks as scavengers for heavy metal ions, Forest Prod. J., 27 (1977) 51–56.
[192] E.J. Roberts, S.P. Rowland, Removal of mercury from aqueous solution by nitrogen containing chemically modified cotton, Environ. Sci. Technol., 7 (1973) 552–555.
[193] M. Jain, V.K. Garg, K. Kadirvelu, Chromium(VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste, J. Hazard. Mater., 162 (2009) 365–372.
[194] B. Moussavi, B. Barikbin, Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass, Chem. Eng. J., 162 (2010) 893–900.
[195] B. Sunil, M. Das, M. Thomas, T.V. Mathew, K.C. Philip, Adsorptive removal of Cr(VI) from aqueous solution using rubber seed shell charcoal, J. Ind. Pollut. Contr., 28 (2012) 137–144.
[196] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, Water. Res., 22 (1998) 3085–3091.
[197] M. Bansal, D. Singh, V.K. Garg, A comparative study for the removal of hexavalent chromium from aqueous solution by agricultural wastes' carbons, J. Hazard. Mater., 171 (2009) 83–92.
[198] N.C. Feng, X.Y. Guo, S. Liang, Kinetic and thermodynamic studies on biosorption of Cu(II) by chemically modified orange peel, Trans. Nonferrous Met. Soc. China, 19 (2009) 1365–1370.
[199] M.A. Hossain, N.H. Ngo, W.S. Guo, T.V. Nguyen, Palm oil fruit shells as biosorbent for copper removal from water and wastewater: experiments and sorption models, Bioresour. Technol., 113 (2012) 97–101.
[200] E. Pehlivan, T. Altun, Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell, J. Hazard. Mater., 155 (2008) 378–384.
[201] K. Kaya, E. Pehlivan, C. Schmidt, M. Bahadir, Use of modified wheat bran for the removal of chromium(VI) from aqueous solutions, Food Chem., 158 (2014) 112–117.
[202] M. Jr. Horsfall, A.A. Abia, Sorption of cadmium(II) and zinc(II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta* Cranz), Water Res., 37 (2003) 4913–4923.
[203] I.J. Alinnor, Adsorption of heavy metal ions from aqueous solution by fly ash, Fuel, 86 (2007) 853–857.
[204] H.S. Altundogan, S. Altundogan, F. Tumen, M. Bildik, Arsenic adsorption from aqueous solutions by activated red mud, Waste Manage., 22 (2002) 357–363.
[205] S.R. Kanel, H. Choi, J.Y. Kim, S. Vigneswaran, W.G. Shim, Removal of arsenic(III) from groundwater using low-cost industrial by-products blast furnace slag, Water Qual. Res. J. Can., 41 (2006) 130–139.
[206] A. Bhatnagar, A.K. Minocha, B.H. Jeon, J.M. Park, G. Lee, Adsorption of orange G dye on paper mill sludge: equilibrium and kinetic modeling, Free. Environ. Bull., 16 (2007) 99–103.
[207] I.D. Mall, V.C. Srivastava, G.V.A. Kumar, I.M. Mishra, Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution, Colloids Surf. A. Physicochem. Eng. Asp., 278 (2006) 175–187.
[208] D.Q.L. Oliveira, M. Goncalves, L.C.A. Oliveira, L.R.G. Guilherme, Removal of As(V) and Cr(VI) from aqueous solutions using solid waste from leather industry, J. Hazard. Mater., 151 (2008) 280–284.
[209] D. Wu, Y. Sui, S. He, X. Wang, C. Li, H. Kong, Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash, J. Hazard. Mater., 155 (2008) 415–423.
[210] S. Coruh, O.N. Ergun, Ni^{2+} removal from aqueous solutions using conditioned clinoptilolites: kinetics and isotherm studies, Environ. Prog. Sustain. Energy, 28 (2009) 162–172.
[211] B. Erdem. A. Ozcan, O. Gok, A.S. Ozcan, Immobilization of 2,2′-dipyridyl onto bentonite and its adsorption behavior of copper(II) ions, J. Hazard. Mater., 163 (2009) 418–426.
[212] C.O. Ijagbemi, M.H. Baek, D.S. Kim, Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, J. Hazard. Mater., 166 (2009) 538–546.
[213] D.H.K. Reddy, D.K.V. Ramana, K. Seshaiah, A.V.R. Reddy, Biosorption of lead from aqueous solutions using chemically modified *Moringa oleifera* tree leaves, Chem. Eng. J., 162 (2010) 626–634.
[214] J. Wang, C. Chen, Research advances in heavy metal removal by biosorption, Acta Scien. Circum., 30 (2010) 673–701.
[215] G.M. Taha, A.E. Arifien, S.El. nahas, Removal efficiency of potato peels as a new biosorbent materials for uptake of Pb(II), Cd(II) and Zn(II) from the aqueous solutions, J. Solid Waste Technol. Manage., 37 (2011) 128–140.
[216] M.N. Sahmoune, K. Louhab, A. Boukhair, Advanced biosorbents materials for removal of chromium from water and wastewaters, Environ. Prog. Sust. Energy, 30 (2011) 284–293.
[217] P.S. Kumar, S. Ramalingam, V. Sathyaselvabala, S.D. Kirupha, A. Murugesan, S. Sivanesan, Removal of Cd(II) from aqueous solution by agricultural waste cashew nut shell, Korean J. Chem. Eng., 29 (2012) 756–768.

[218] M. Abbas, S. Kaddour, M. Trari, Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon, J. Ind. Eng. Chem., 20 (2014) 745–751.

[219] A.R. Bhanupriya, M. Sathishkumar, D. Kavitha, K. Swaminathan, S.E. Yun, S.P. Mun, Experimental and isothermal studies on sorption of Congo red by modified mycelial biomass of wood rotting fungus, Clean, 35 (2007) 143–150.

[220] K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, K. Ueda, Adsorption of platinum (IV), palladium (II) and gold (III) from aqueous solutions on l-lysine modified crosslinked chitosan resin, J. Hazard. Mater., 146 (2007) 39–50.

[221] N. Kannan, T. Veemaraj, Batch adsorption dynamics and equilibrium studies for the removal of Cd(II) ions from aqueous solution using jack fruit seed and commercial activated carbons - a comparative study, Electron. J. Environ. Agric. Food Chem., 9 (2010) 327–336.

[222] M.A. Ashraf, A. Wajid, K. Mahmood, M.J. Maah, I. Yusoff, Low cost biosorbent banana peel (*Musa sapientum*) for the removal of heavy metals, Sci. Res. Essays, 6 (2011) 4055–4064.

[223] J. Kumar, C. Balomajumder, P. Mondal, Application of agro-based biomasses for zinc removal from wastewater - a review, Clean - Soil Air Water, 39 (2011) 641–652.

[224] A.K. Giri, R. Patel, S. Mandal, Removal of Cr(VI) from aqueous solution by *Eichhornia crassipes* root biomass-derived activated carbon, Chem. Eng. J., 185 (2012) 71–81.

[225] G.F. Coelho, A.C.G. Jr Goncalves C.R.T. Tarley, J. Casarin, H. Nacke, M.A. Francziskowski, Removal of metal ions Cd(II), Pb(II) and Cr(III) from water by the cashew nut shell *Anacardium occidentale* L, Ecol. Eng., 73 (2014) 514–525.

[226] N. Talreja, D. Kumar, N. Verma, Removal of hexavalent chromium from water using Fe-grown carbon nanofibers containing porous carbon microbeads, J. Water Process. Eng., 3 (2014) 34–45

[227] B. Volesky, Biosorption of heavy metals, CRC Press, Boca Raton. 1990.

[228] A.K. Meena, K. Kadirvelu, G.K. Mishra, R. Chitra, P.N. Nagar, Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica), J. Hazard. Mater., 150 (2008) 604–611.

[229] D. Park, Y. Yun, J.M. Park, The past, present and future trends of biosorption, Biotechnol. Bioprocess Eng., 15 (2010) 86–102.

[230] A. Saravanan, P.S. Kumar, B. Preetha, Optimization of process parameters for the removal of chromium(VI) and nickel(II) from aqueous solutions by mixed adsorbents (custard apple seeds and *Aspergillus niger*) using response surface methodology, Desalin. Water Treat., (2015) 1–14.

[231] N. Das, Recovery of precious metals through biosorption – a review, Hydrometallurgy 103 (2010) 180–189.

[232] X. Liang, Y. Zang, Y. Xu, X. Tan, W. Hou, L. Wang, Y. Sun, Sorption of metal cations on layered double hydroxides, Colloids Surf. A Physiochem. Eng. Asp., 433 (2013) 122–131.

[233] L. Ramrakhiani, R. Majumder, S. Khowala, Removal of hexavalent chromium by heat inactivated fungal biomass of *Termitomyces clypeatus*: surface characterization and mechanism of biosorption, Chem. Eng., J. 171 (2011) 1060–1068.

[234] R.S. Vieira, M.L.M. Oliveira, E. Guibal, E. Rodriguez-Castellon, M.M. Beppu, Copper, mercury and chromium adsorption on natural and crosslinked chitosan films: an XPS investigation of mechanism, Colloids Surf. A Physiochem. Eng. Asp., 374 (2011) 108–114.

[235] Y. Wen, Z. Tanga, Y. Chen, Y. Gu, Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent, Chem. Eng. J., 175 (2011) 110–116.

[236] R.M. Nthumbi, J.C. Ngila, B. Moodley, A. Kindness, L. Petrick, Application of chitosan/polyacrylamide nanofibres for removal of chromate and phosphate in water, Phys. Chem. Earth, 50–52 (2012) 243–251.

[237] A. Adamczuk, D. Kolodynska, Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan, Chem. Eng. J., 274 (2015) 200–212.

[238] D.M. Ruthven, Principles of adsorption and adsorption processes, John willey & sons, (1984) 43–45.

[239] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Amer. Chem. Soc., 40 (1918) 1361–1403.

[240] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.

[241] A. Dabrowski, Adsorption from theory to practice, Adv. Coll. Int. Sci., 93 (2001) 135–224.

[242] R.T. Yang, S.J. Doong, Gas separation by pressure swing adsorption: A pore diffusion model for bulk separation, Amer. Inst. Chem. Eng., 31 (1985) 1829–1842.

[243] J.A. O'Brien, A.L. Myers, Physical adsorption of gases on heterogeneous surfaces series expansion of isotherms using central moments of the adsorption energy distribution, J. Chem. Soc. Faraday Trans., 80 (1984) 1467–1477.

[244] M. Akhtar, S.M. Hasany, M.I. Bhanger, S. Iqbal, Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions, Chemosphere, 66 (2007) 1829–1838.

[245] C. Aharoni, F.C. Tompkins, Kinetics of adsorption and desorption and the Elovich equation, in: D.D. Eley, H. Pines, P.B. Weisz (Eds). Advances in catalysis and related subjects, Academic Press, Newyork (1970) 21–22.

[246] R. Sips, On the structure of a catalyst surface, J. Chem. Phys., 16 (1948) 490–495.

[247] W. Fritz, E.U. Schlunder, Simultaneous adsorption equilibria of organic solutes in dilute aqueous solution on activated carbon, Chem. Eng. Sci., 29 (1974) 1279–1282.

[248] C.J. Radke, J.M. Praunsitz, E.U. Fritz, A.L. Myers, Thermodynamics of multi-solute adsorption from dilute aqueous solutions, Chem. Eng. Sci., 33 (1978) 1097–1106.

[249] J. Toth, Calculation of the BET-compatible surface area from any type I isotherms measured above the critical temperature, J. Coll. Interf. Sci., 225 (2000) 378–383.

[250] M. Baudu, Etude des interactions solute-fibres de charbon actif, Application et regeneration, Ph.D Thesis, Universite. De. Rennes. I. (1990).

[251] E.I. El-Shafey, Behaviour of reduction sorption of Chromium(VI) from an aqueous solution on a modified sorbent from rice husk, Water Air Soil Poll., 163 (2005) 81–102.

[252] R. Razmovski, M. Sciban, Biosorption of Cr (VI) and Cu (II) by waste tea fungal biomass, Ecol. Eng., 34 (2008) 170–186.

[253] E. Malkoc, Y. Nuhoglu, Potential of tea factory waste for chromium (VI) removal from aqueous solutions: Thermodynamic and kinetic studies, Sep. Purif. Technol., 54 (2007) 291–298.

[254] A.J. Priya, S.R. Gajulapalli, K. Abburi, V.M. Boddu, Biosorption of Chromium, Copper and Nickel Ions by *Tamarindus Indica* Fruit Nut Testa, Bioremediat. J., 12 (2008) 145–155.

[255] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water SA, 30 (2004) 533–540.

[256] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr (VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J., 137 (2008) 529–541.

[257] X.S. Wang, Z.Z. Li, C. Sun, Removal of Cr(VI) from aqueous solution by low-cost biosorbents: marine macroalgae and agricultural by-products, J. Hazard Mater., 153 (2008) 1176–118.

[258] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J., 23 (2005) 185–192.

[259] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, Chem. Eng. J., 145 (2009) 489–495.

[260] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div. Am. Soc. Civ. Eng., 89 (1963) 31–60.

[261] C. Yao, T. Chen, A new simplified method for estimating film mass transfer and surface diffusion coefficients from batch adsorption kinetic data, Chem. Eng. J., 265 (2015) 93–99.

[262] S. Lagergren About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl., 24 (1898) 1–39.

[263] W. Cheng, S. Wang, L. Lu, W. Gong, X. Liu, B. Gao, H. Zhang, Removal of malachite green (MG) from aqueous solutions by native and heat treated anaerobic granular sludge, Biochem. Eng. J., 39 (2008) 538–546.
[264] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Proc. Biochem., 34 (1999) 451–465.
[265] M.S. Ozacar, I.A.S. Engil, H. Turkmenler, Equilibrium and kinetic data and adsorption mechanism for adsorption of lead onto valonia tannin resin, Chem. Eng. J., 143 (2008) 32–42.
[266] S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, Biochem. Eng. J., 44 (2009) 19–41.
[267] J. Wang, C. Can, Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review, Biotechnol. Adv., 24 (2006) 427–451.
[268] Y. Liu, M.C. Lam, H.H.P. Fang, Adsorption of heavy metals by EPS of activated sludge, Water Sci. Technol., 43 (2001) 59–66.
[269] H.C. Flemming, J. Wingender, Relevance of microbial extracellular polymeric substances (EPSs)-Part II: Technical aspects, Water Sci. Technol., 43 (2003) 9–16.
[270] Z.Y. Lin, J.K. Fu, J.M. Wu, Y.Y. Liu, H. Cheng, Preliminary study on the mechanism of non-enzymatic bioreduction of precious metal ions, Acta Phys. Chim. Sin., 17 (2001) 477–480.
[271] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res., 37 (2003) 4311–4330.
[272] M.E. Portnoy, P.J. Schmidt, R.S. Rogers, Metal transporters that contribute copper to metallochaperones in *Saccharomyces cerevisiae*, Mol. Genet. Genomics, 265 (2011) 873–882.
[273] M.G. Vijver, C.A.M.V. Gestel, R.P. Lanno, N.M. Van Straalen, W.J.G.M. Peijnenburg, Internal metal sequestration and its ecotoxicological relevance: a review, Environ. Sci. Technol., 38 (2004) 4705–4712.
[274] P. Rajendran, J. Muthukrishnan, P. Gunasekaran, Microbes in heavy metal remediation, Indian J. Exp. Biol., 41 (2003) 935–944.
[275] N. Das, R. Vimala, P. Karthika, Biosorption of heavy metals – An overview, Indian J. Biotechnology 7 (2008) 159–169.
[276] R. Gupta, P. Ahuja, S. Khan, R.K. Saxena, H. Mohapatra, Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solution, Curr. Sci., 78 (2000) 967–973.