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Reduction and biosorption of hexavalent chromium ions from wastewaters: a review

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Chromium contamination is one of the most serious environmental concerns faced by the world today. Chromium contamination can cause a variety of health problems. Research focussing on the reduction or eradication of hexavalent chromium has evoked the interest of scientists in recent years. The applicability of several types of microorganisms for hexavalent chromium reduction and biosorption is highlighted in this review. The type of microorganism growth determines the optimal pH and temperature for Cr(VI) reduction. Culture medium for Cr(VI) reduction must be chosen carefully since it is significantly reliant on the functional group present; as with *Aspergillus niger* and *Aspergillus parasiticus,* culture with tannic acid has a lower Cr(VI) removal efficiency than culture for *Bacillus* sp. Having glucose, the Cr(VI) removal efficiency improves substantially. The application of dead cells is more efficient for reduction and biosorption of Cr(VI) as dead cells require less maintenance. A brief discussion of several types of chromium removal methods from wastewater streams is also included in the review.

Keywords: Biosorption; Chromium reduction; Hexavalent chromium; Microorganisms; Bioreduction; Wastewater treatment.

INTRODUCTION

Chromium (Cr) is found in abundance in the crust of the earth. Cr is mostly utilized in tanning of leather, dyes and paints, ceramic ware and glass, fungicides, for the manufacturing of several catalysts, in photography, chrome alloys, chrome plating, corrosion control, wood preservation and manufacturing of refractory materials. Chromium exists as Cr(III) and Cr(VI) in the aquatic environment. When compared to trivalent chromium, hexavalent chromium is hundred times more hazardous and transportable. Because it causes cancer and mutations in humans, Cr(VI) is one of the most dangerous environmental contaminants [1]. Contamination of underlying aquifers and vadose zones has resulted in improper Cr metal disposal at sites in semiarid and arid locations [2]. Most of the industrial effluents contain Cr(VI) and these effluents are almost impossible to be removed from wastewater using conventional wastewater treatment systems [3].

Methods including coagulation, precipitation, filtration, adsorption, ion exchange, membrane technology, electrodialysis, and biological removal are the few ways for removing chromium from wastewater. Majority of the traditional methods for the removal of Cr(VI) are not economically viable and have certain difficulties in developing countries [4]. From the past research, it has been found that microorganisms can be used to reduce Cr(VI) to Cr(III) in an alternative approach. Bioaccumulation, chromate reduction, chromate efflux, and biosorption have all been ascribed to microorganisms such as bacteria, fungi, and yeast for chromium bioremediation [5]. This study focuses on reducing hexavalent chromium to trivalent chromium utilizing various microorganisms such as bacteria, fungi, and yeast, as well as hexavalent chromium biosorption.

Chromium removal techniques from contaminated wastewater

Human health is known to be jeopardized by Cr(VI) ions. Skin rashes, ulcers, respiratory difficulties, renal damage, liver dysfunction, cancer, and even death can be caused by these ions [6-8]. As a result, the removal of these ions is critical for maintaining human health. There are several techniques through which Cr(VI) is removed from contaminated wastewater like adsorption, coagulation, membrane technology, precipitation, filtration, ion exchange, electrodialysis and biological removal which are being summarized in Table 1 along with benefits and drawbacks of the main approaches for chromium removal from water.

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Table 1. Summary of different methods for Cr removal from water

Method	Advantages	Limitations	References
Adsorption	Depending on pH adsorption, media can adsorb either cationic or anionic Cr ions. Adsorbent can be regenerated. Activated carbon is effective in removing both Cr (III) and Cr (VI).	Difficult to get optimum pH to remove both cation and anion. Also, they have low capacity Activated carbon is expensive. Carbon nanotubes get disposed in water and pose a risk to aquatic life and humans.	[9-16]
Coagulation	Conventional coagulation is an efficient method for removing Cr (III) with a fast response time. Redox-assisted coagulation (RAC) with Fe (II) is >99% effective for removal of Cr (VI).	For the removal of Cr (VI), conventional coagulation uses a two-stage procedure that generates a large amount of sludge. RAC is affected by the settleability of the floc and filterability of the precipitated particles.	[17-19]
Membrane Filtration	Reverse osmosis is 90–100% effective for the removal of Cr (VI) and Cr (III). Polymer enhanced ultrafiltration has high removal efficiency and high binding selectivity.	Reverse osmosis needs high investment and operational costs. Difficult to find suitable polymers to achieve complexation with metal ions, in polymer enhanced ultrafiltration.	[20-24]
Chemical Precipitation	The solubilities of metal sulfide precipitates are lower than hydroxide precipitates and sulfide precipitates are not amphoteric. Sulfide potentially reduces Cr (VI) and precipitates Cr in one step.	Hydroxide precipitation generates large volumes of relatively low-density sludge Sulfide precipitants in acidic conditions can result in the evolution of toxic H_2S fumes. Also, the process is relatively expensive.	[25-28]
Ion Exchange	High treatment capacity and fast kinetics. Suitable for small and large installations. Variety of specific resins are available for removing specific contaminants	More research into the industrial application of zeolites is required. Resin fouling and removal efficiency is affected by the presence of other ions in water.	[29-33]
Biological Removal	Biosorbents are characteristic of broad sources, low cost and rapid adsorption.	The separation of biosorbents is difficult after adsorption At acidic pH, certain biological removal methods are not suitable for drinking water treatment applications.	[34, 35]

Reduction of hexavalent chromium by using microorganisms

Bacillus sp. isolation from chromium waste was investigated by Liu *et al*. [1] for its ability to reduce Cr(VI). Among the five isolated bacteria, two were recognized as *Bacillus* sp., namely XW-2 and XW-4. But XW-4 was selected for the Cr(VI) reduction experiments because XW-4 isolates have lower concentration as compared to XW-2 after 3 days.

They investigated the influence of Cr(VI) on cell growth and discovered that the higher the Cr(VI) concentration, the stronger is the effect on cell growth as compared with the lower concentration. They also examined the effects of pH and temperature and discovered that the best initial pH value was 9 when changing pH from 4 to 11. Three different temperatures, 37°C, 47°C, and 20°C, were used to reduce Cr(VI).

The absorption and reduction of Cr(VI) by two fungi were investigated by Shugaba *et al*. [2]. They used two fungi i.e, *Aspergillus niger* and *Aspergillus parasiticus* which are isolated from the landfill. It was shown that the Cr(VI) concentration decreases with growth time. The authors found that subsequent to the growth of 96 hours the solution became completely colourless and the removal of Cr(VI) was achieved at 96.3% and 91.6% after 96 hours in *Aspergillus niger* and *Aspergillus parasiticus* cultures.

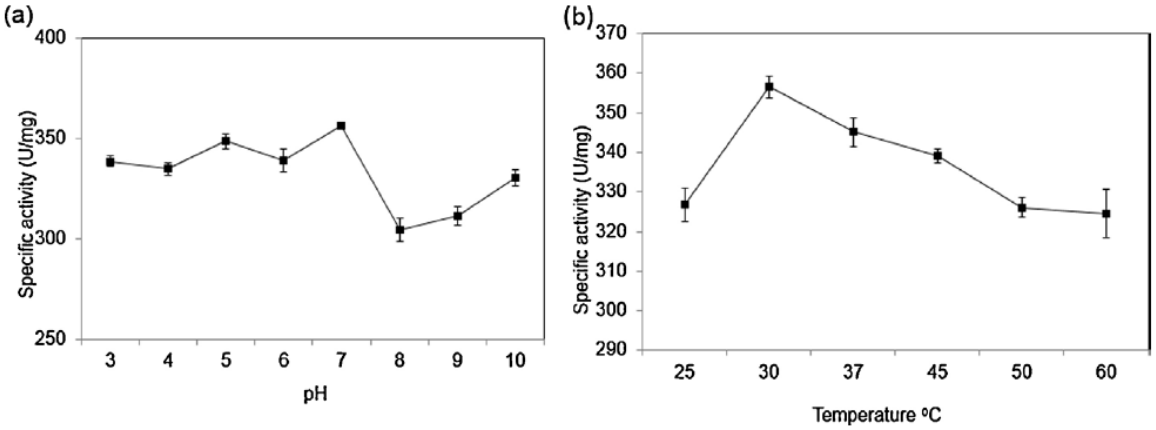


Figure 1. (a) Effect of pH on chromate reductase activity in B. *methylotrophicus*. (b) Effect of temperature on chromate reductase activity in *B. methylotrophicus* [5].

Donmez and Kocberber [3] used enhanced microbial cultures made from molasses and NaCl-containing medium to investigate the bioaccumulation of hexavalent chromium. They prepared the enriched cultures with the help of sodium chloride, molasses and Cr(VI) for better bioaccumulation efficiency. The authors found that the percentage of uptake yield of mixed cultures increased from 95 to 99 percent after 5 days for all samples of NaCl concentration and pH values. The optimum pH values were 7, 8 and 9 in a solution containing 2%, 4% and 6% NaCl, respectively. At pH 7, maximal Cr uptake was 87.5 mg/g at a higher NaCl concentration (6 percent w/v), whereas initial Cr concentration was 83.6 mg/L.

Mala *et al*. [5] investigated the chromium bioremediation potential of an inducible chromate reductase with extracellular activity in *Bacillus methylotrophicus*. The authors utilized four *Bacillus* strains for chromate reduction in various media, all of which were obtained from tannery sludge. *Bacillus methylotrophicus*, for example, reduced chromate 95 M Cr(VI) to 7.14 M Cr(VI) after 48 hours. They created five different assay mixtures, including the standard assay system, TCA (tricarboxylic acid) addition prior to incubation, heat-inactivated enzyme, no added enzyme, and no added NADPH (nicotinamide adenine dinucleotide phosphate), and discovered that the percentage of residual Cr(VI) in the standard assay system is significantly lower than in the other four systems. The authors studied the effect of pH and temperature, as shown in Figure 1. Except for Na^+ and Ca^{2+}, all metal ions enhanced chromate reductase activity which was estimated using a Lineweaver–Burk plot, and the values of K_m and V_{max} derived from the graph are 86.5 µM and 59.89 µM, respectively, which suggest that the reaction rate using $K_2Cr_2O_7$ as substrate is feasible. Fukuda *et al.* [36] investigated the removal of Cr(VI) from chromium deposits by chromate-resistant fungi *in vitro* and in contaminated soils. Seven fungal isolates were used for reducing the chromium concentration at nearly neutral pH and strongly acidic pH. They identified only three fungal isolates by using a morphology study, i.e, *Aspergillus* sp. N2, *Penicillium* sp. N3 and *Pencillium* sp. N5. These three isolates reduced higher chromium concentrations as compared to others. In strongly acidic pH 3 *Aspergillus* sp. N2 and *Penicillium* sp. N3 are reducing 50% of chromium concentration and *Penicillium* sp. N5 is reducing chromium concentration by nearly 30%. The authors found that the higher the initial concentration of chromium in growth media the slower will be the Cr(VI) removal. Fernandez *et al.* [37] explored the removal efficiency of Cr^{6+} by indigenous yeasts, i.e. *Pichia jadinni* M9 and *Pichia anomala* M10 isolated from textile factory effluent. There is a very slight effect on the growth of cells at concentrations of 26, 52 and 78 µg mL^{-1} and the indigenous yeasts survive the Cr^{6+} concentration 104 µg mL^{-1} and have no effect on cells growth. They found that the optimum temperature is 30°C, optimum pH is 7, optimum agitation speed is 150 and 250 rpm and optimum initial Cr^{6+} concentration is 26 µg mL^{-1} where the chromium is removed by both the cultures *Pichia jadinni* M9 and *Pichia anomala* M10.

The decrease of Cr(VI) by *Bacillus coagulans* isolated from polluted soils was investigated by Philip *et al.* [38]. They isolated *Bacillus coagulans* from contaminated soils and compared it with *Pseudomonas aeruginosa* and *Bacillus circulans* from garden soil and found that *Bacillus coagulans* (8.30 mg/L) showed the highest Cr(VI) reduction as compared to the *Pseudomonas aeruginosa* (20.48 mg/L) and *Bacillus circulans* (38.80 mg/L) when initial concentration was 104 mg/L. Malate showed

the highest Cr(VI) reduction as compared to the other three electron donors, i.e. citrate, succinate and glucose. Cr(VI) had an optimal pH of 7. The presence of nitrates and sulfates had no influence on the decrease of Cr(VI). Garbisu *et al.* [39] evaluated the aerobic chromate reduction by *Bacillus subtilis.* The latter have been cultured in agar media and were able to reduce Cr(VI) to Cr(III) at a concentration varying from 0.1 to 1 mM K_2CrO_4. They studied the effect of sodium nitrate and metabolic poisons and found that chromate reduction was independent of sodium nitrate which had no effect on growth and reduction of chromate. Metabolic poisons had inhibited the growth and chromate reduction. Effects of kanamycin and low temperature were studied and it was found that kanamycin cultures have not reduced the chromate as fast as compared to the control cultures and at low temperature 4°C inhibited the chromate reduction, as shown in Figure 2.

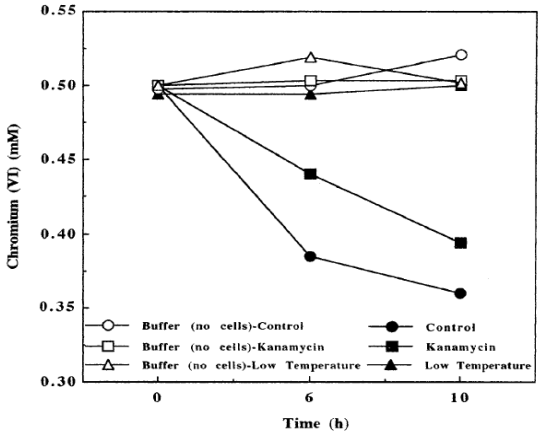


Figure 2. Effect of kanamycin and low temperature on the decrease in Cr(VI) in the supernatant fraction of cultures of *B. subtilis* resting cells [39].

Ganguli and Tripathi [40] used chromate-reducing *Pseudomonas aeruginosa* A2Chr to study the bioremediation of hazardous chromium from electroplating effluent in two bioreactors. In batch culture - dialysis bioreactor and rotating biological contactor, they compared *Pseudomonas aeruginosa* A2Chr's chromate-reducing capabilities. They had cultured two media, succinate minimal medium and electroplating effluent and varied the Cr(VI) concentration 10-100 mg/L. The study found that the highest Cr(VI) reduction occurred at 10 mg/L and the rotating biological contractor showed the highest Cr(VI) reduction as compared to the batch culture and dialysis bioreactor at 100 mg/L Cr(VI) concentration. Park *et al.* [41] evaluated the elimination of Cr(VI) by *Aspergillus niger* dead fungal biomass. They found that Cr(VI) to Cr(III) reduction occurred when no Cr(III) was in the solution at first but gradually emerged in an aqueous solution when Cr(VI) was reduced to Cr(III). They investigated the X-ray photoelectron spectroscopy and desorption of this dead fungal biomass and discovered that much of the chromium linked to the biomass was trivalent. They also noticed that if the temperature increases then the percentage of adsorption increases but pH followed the opposite trend by increasing the pH then the percentage of adsorption decreases.

Biosorption of hexavalent chromium by using bioadsorbent

Bankar *et al.* [4] explored the adsorption of Cr(VI) ions from aqueous solution onto two *Yarrowia lipolytica* marine isolates, namely NCIM 3589 and NCIM 3590. They studied the effect of sea salt and cell biomass on Cr(VI) adsorption and noticed that adding sea salt decreases the adsorption capacity and increasing the biomass percentage it also starts decreasing the adsorption capacity. They also conducted a surface morphology study of cell loaded with Cr(VI) by SEM-EDS and ED-XRF to notice the presence of chromium (VI) as shown in Figure 3.

Bai and Abraham [42] investigated *Rhizopus nigricans'* capacity to biosorb Cr(VI) from aqueous solution. The highest adsorption capacity was achieved at optimum pH 2; that is 99.8%. Optimum agitation speed is 120 rpm for higher adsorption efficiency. By increasing the initial Cr(VI) ion concentration from 50 to 400 mg/L the adsorption efficiency starts decreasing. Adsorption capacity starts increasing by increasing the contact time but if more than 75% Cr(VI) is removed within 30 minutes then it takes a long time for complete removal of Cr(VI) which is approximately 8 hours.

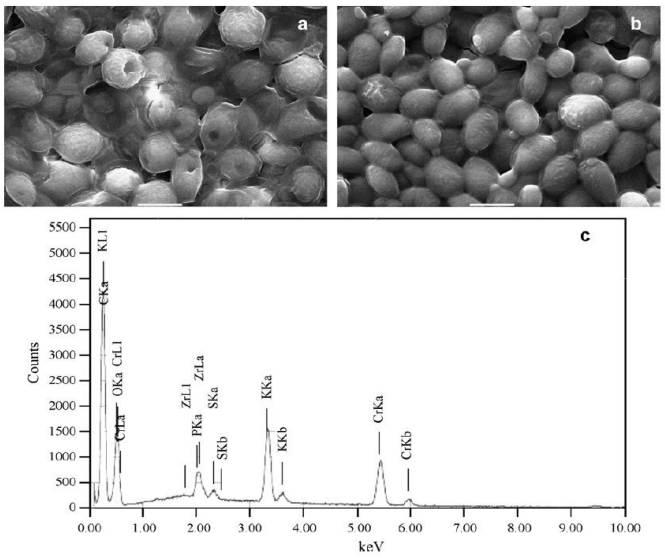
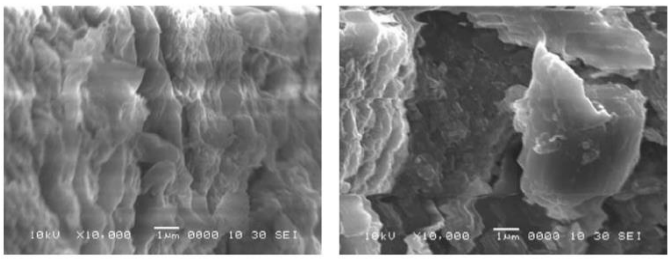


Figure 3. SEM analysis of *Y. lipolytica* (a) NCIM 3589 and (b) NCIM 3590 after Cr (VI) biosorption (c) Representative energy dispersive X-ray spectrum of SEM images indicating the presence of Cr [4].

Figure 4. SEM micrographs of the *Chlorella pyrenoidosa* before (b) and after (a) of biosorption [43] .



(b) (a)

Rezaei [43] has studied the biosorption of chromium by using dried *Spirulina*. He observed that by increasing the contact time, adsorbent dose, agitation speed and temperature the percentage of biosorption also increases. Optimum contact time, adsorbent dose, agitation speed, temperature and pH are 120 min, 0.1 g, 120 rpm, 25°C and 5, respectively. He analyzed the Langmuir and Freundlich isotherms for adsorption and found that the results are in accordance with these two models. Kinetic modeling was studied by using pseudo-first and second order rate but adsorption of chromium by *Spirulina* followed second order kinetics. Finally, he also performed SEM analysis of bio-adsorbent as shown in Figure 4.

Balan *et al.* [44] conducted batch sorption studies with *Sphagnum* moss peat as a sorbent to investigate the elimination process of chromium(III) from aqueous solutions. They found that moss peat treated with sodium chloride showed a higher reduction of Cr(III) as compared to chromium nitrate. They investigated the Langmuir model which shows a higher sorption capacity as compared to others. The sorption capacity of Langmuir is 18.62 mg Cr(III)/g of peat. Mean free sorption energy binding the Cr(III) on peat through an ion exchange mechanism is in the range of 10.9 to 12.9 kJ mol^{-1}. The production of varied metal ions based on alginate bentonite bio-composites for Cr(VI) sorption was investigated by Gopalakannan *et al.* [45]. They synthesized the bio-composites by dispersing bentonite in an alginate biopolymer and crosslinked with calcium chloride (Ca^{2+}), cerium nitrate (Ce^{3+}) and zirconium oxychloride (Zr^{4+}). They also used SEM to characterize the synthesized biocomposites and noticed that some changes take place in the synthesized bio-composites after Cr(VI) is sorbed by bio-composites as shown in Figure 5. They have found that optimum contact time is 60 min, optimum dosage is 0.1 g, optimum pH is 2, the presence of co-ions shows less influence on sorption capacities except for HCO_3^-.

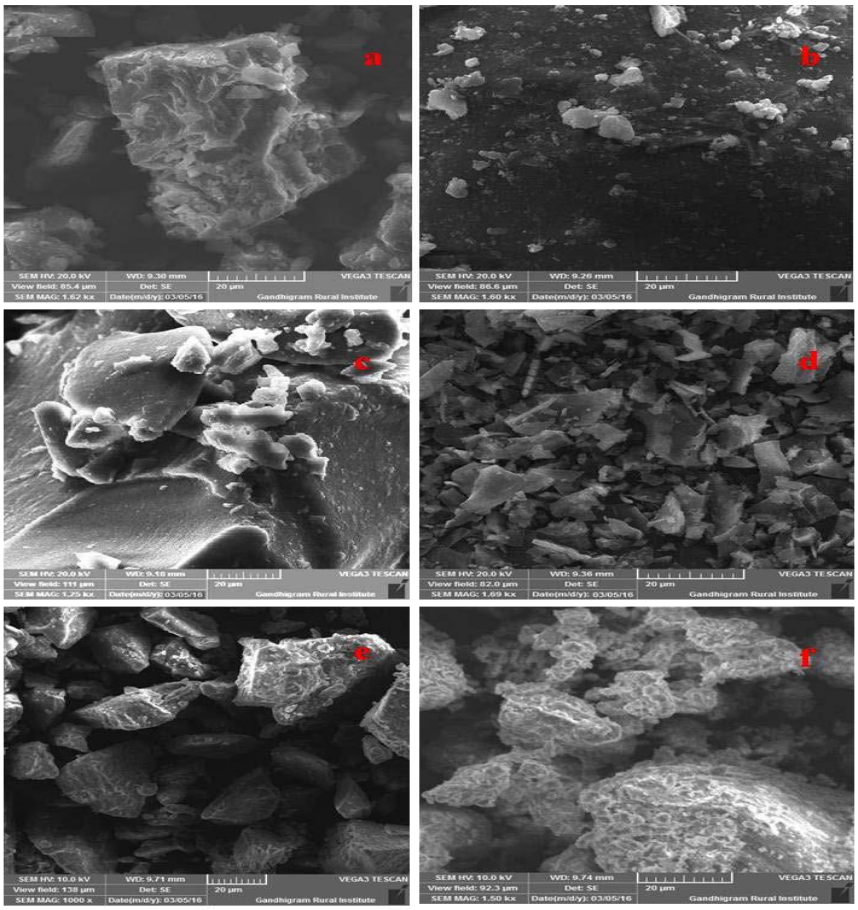


Figure 5. SEM images of (a) Calcium-alginate biopolymer, (b) Chromium sorbed calcium-alginate biopolymer composite, (c) Cesium-alginate biopolymer, (d) Chromium sorbed cesium-alginate biopolymer composite, (e) Zirconium-alginate biopolymer, (f) Chromium sorbed zirconium-alginate biopolymer composite [45].

The authors found that Langmuir isotherm best fits the Cr(VI) sorption and also noticed that all three bio-composites followed pseudo-second order kinetics. Pan *et al*. [46] investigated the use of amino-functionalized alkaline clay combined with a cationic polymer as adsorbent for removing Cr(VI) from aqueous solution. The cationic polymer was prepared through the method of atom transfer radical polymerization by using acrylamide (AM) and dimethyl aminoethyl methacrylate (DMAEMA) monomers and using CuBr/2,2ˈ-bipyridine (BPY) and 4Br-PER as an initiator. According to the authors, the optimum value of pH is 4 which shows a high adsorption capacity, i.e. 102 mg/g and by increasing the contact time the adsorption capacity also starts increasing. Maximum adsorption capacity is 102 mg/g in 100 min. Then they fitted the equilibrium data in two isotherm models, i.e. Langmuir and Freundlich adsorption isotherm and noticed that Langmuir isotherm which is the best-fit isotherm, had an adsorption capacity of 137.9 mg/g at 30°C. Mala *et al*. [47] had studied the biosorption and bioaccumulation of chromium by *Aspergillus niger* MTCC 2594. They had taken a spent chrome liquor from the leather industry. They identified the Cr(III) and Cr(VI) content in spent chrome liquor from two different processes. Similarly, they also prepared a biomass (*Aspergillus niger*) by harvesting for 72 hours at room temperature. The Cr(VI) and Cr(III) levels found in spent chrome liquor were higher and above the permissible limit. Then they studied the bioaccumulation of Cr(VI) and Cr(III) and found that 75%-78% accumulation takes place by the end of 24-36 hours. According to the research, in contrast to the Langmuir isotherm, the data matched better the Freundlich isotherm. Ucun *et al*.[48] examined the biosorption of Cr(VI) from aqueous solution by *Pinus sylvestris* cone biomass. They discovered that as pH decreases from 7 to 1, initial Cr(VI) concentration increases from 50 to 300 mg/L, the biosorption efficiency decreases. The research group also used the Freundlich isotherm to study the adsorption and discovered that the data fit well in this model, indicating a high adsorption capacity.

Soya cake was used to investigate Cr adsorption and Cr(VI) reduction to Cr(III) in aqueous solutions by Daneshvar *et al*. [49]. Adsorption and reduction

efficiency decreased as the pH increased. In the temperature parameter, adsorption and reduction efficiency is increasing as the temperature increased. The optimum condition for the reduction of Cr(VI) to Cr(III) is pH=1, T=25°C, time=5 h and soya mass is 0.7 g. The optimum condition for the adsorption of Cr(VI) is pH=1, T=20°C, time=1 h and soya mass is 30 g. They also concluded that the Langmuir and Freundlich isotherms did not explain the adsorption data well. Aksu *et al*. [50] explored the adsorption of Cr(VI) ions by dead cells of *C. Vulgaris* and *Z. Ramigera*. The study had shown that for the adsorption of Cr(VI) by dead cells, optimal temperature and pH range are 25-50°C and 1-2, respectively. The authors also found that when the metal ion concentration increases, the adsorption capabilities decrease. In case of cell concentration, efficiency of adsorption starts increasing by increasing the biomass concentration but the rate of adsorption is very slow.

The absorption of chromium cations and anions by milled peat was investigated by Dean and Tobin [51]. They looked at Cr(VI) and Cr(III) absorption by biomass at different pH levels, such as 2, 4, and 7, and used MINEQL to predict Cr(VI) and Cr(III) speciation. Finally, they compared both. The research group found that the uptake of Cr(VI) and Cr(III) increased by increasing the concentration of the solution and maximum uptake of Cr(VI) and Cr(III) is 0.58 and 0.27 mmol/g at pH 2 and 4. The researchers also found the speciation of Cr(VI) and Cr(III) by MINEQL at different pH 2, 4 and 7 and predominant species at pH 2, 4 and 7 in Cr(VI) is $HCrO_4^-$ at pH 2 and 4 but at pH 7 predominant species is CrO_4^{2-}. They also found that the predominant species at pH 4 for Cr(III) is 50% Cr^{3-} and 50% $Cr(OH)^{2+}$. Predominant species at pH 2 is Cr^3 and predominant species at pH 7 is $Cr(OH)^{2+}$. Prakasham *et al.* [52] explored how free and immobilized *Rhizopus arrhizus* adsorbed chromium (VI) from synthetic effluent and chromium solution. Immobilization of *Rhizopus arrhizus* was done with the help of alginate. All the experiments were conducted at pH 2. They discovered that the effectiveness of adsorption improved as contact time increased for both free and immobilised biomass. At 2-8 hours; 46.50-63.54% and 50.63-73.98% Cr(VI) was adsorbed for immobilized and free biomass. However, when the initial chromium ion concentration raises, the adsorption capacity of both free and immobilized biomass decreases. At 50-300 mg/L initial chromium concentration residual chromium left was 0.57-69.21 mg/L and 0.79-61.6 mg/L for free and immobilized biomass. They also studied the adsorption isotherm on these data and found that the data showed a low intensity of biosorption less than 1, 0.187 and 0.23 for free and immobilized biomass.

Sag and Kutsal [53] investigated the need for adsorption of isotherms in the study of chromium adsorption on *Z. ramigera*. The research group explored the influence of pH and temperature isotherm in two models, i.e. Langmuir and Freundlich isotherm. The authors varied the pH from 0.5-4 and temperature 25-35°C and then finally found out that the optimum pH and the temperature is 2 and 25°C in the eradication process of chromium from aqueous solution. Dakiky *et al*. [54] researched on the selective adsorption of chromium (VI) in industrial wastewater using low-cost, widely available adsorbents. The authors used a variety of adsorbents such as wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, and charcoal for the experiment. They discovered that as the adsorbent concentration and contact duration rose, so did the percentage of Cr(VI) removal. Wool showed the highest removal efficiency, that is 81.3% at 16 g/L concentration of adsorbent. Almond shell showed the lowest removal efficiency, that is 19.8% at 8 g/L adsorbent concentration. When the pH was raised from 1 to 8, the removal efficiency of Cr(VI) began to decline. The best pH, contact duration, temperature, and adsorbent dose were 2, 2 hours, 30°C, and 8 g/L, respectively. In comparison to the other adsorbents, it was apparent that wool is the best adsorbent for removing Cr(VI). Kiran *et al.* [55] researched the biosorption of Cr(VI) in the presence of salts by a natural isolate of *Lyngbya putealis* (HH-15). They noticed that by increasing the pH from 2 to 10, Cr(VI) uptake started decreasing. Cr(VI) uptake started increasing by increasing the contact time from 5-180 minutes and metal ion concentration from 10-100 mg/L. Optimum pH, contact time and metal ion concentration was 3, 120 min and 50 mg/L. They also found that their experimental data were in accordance with both pseudo-first and second order kinetics. Das and Guha [56] have studied the biosorption of chromium by *Termitomyces clypeatus*. They have tested different strains of fungi to eliminate chromium but *Termitomyces clypeatus* had shown a great potential for the elimination of chromium and adsorption percentage of live and dead *Termitomyces clypeatus* biomass is 91±2.1 and 62±2.0. But they have taken live *Termitomyces clypeatus* biomass for further studies. They noticed that the adsorption value increased by increasing the pH of that solution from 2 to 3 but after that equilibrium was obtained, and the optimum value of pH was 3. They examined the adsorption isotherm

by using two models, i.e. Langmuir and Freundlich isotherm and noticed that Langmuir model fits better as compared to Freundlich. The coefficient of regression, r^2 value for Langmuir and Freundlich is 0.998 and 0.965, respectively. They also analyzed this model by using χ^2- square test and found that χ^2 value for Langmuir and Freundlich is 5.03 and 18.53, respectively.

Park *et al.* [41] investigated the biosorption of Cr(VI) by chemically treated *Ecklonia* sp. biomass. They had taken *Ecklonia* sp. and treated it with various alkalis, acids, organic solvents, and other chemicals and noticed that the treatment of biomass with acids showed the best performance as compared to the other treatments like alkalis, organic solvents, etc. By using FTIR spectroscopy they discovered that carboxyl and amino groups were connected to chromium biosorption and that methylation of the amino group reduced the removal rate of Cr(VI) while amination of the carboxyl group enhances the removal rate of Cr(VI). Kratochvil *et al.* [57] investigated how seaweed biosorbent may remove trivalent and hexavalent chromium. They discovered that pH 4 and 2 are the best for removing Cr(III) and Cr(VI). They also studied the desorption mechanism, and found that after 2 to 24 hours, about 40 to 70 percent of the total chromium was recovered. Basha *et al.* [58] tested the biosorption of Cr(VI) by using *Cystoseira indica,* a scientifically formulated seaweed. They have used *Cystoseira indica* as a bioadsorbent and chemically modified it by oxidation with potassium permanganate (CB3), crosslinking agent epichlorohydrin (CB1, CB2) and distilled water (RB). The research group also noticed that by increasing the contact time and initial Cr(VI) ion concentration the Cr(VI) uptake started increasing. But they also found that the percentage of adsorption started decreasing in case of increasing the initial Cr(VI) ion concentration. They have found that by increasing the pH from 1 to 3 the Cr(VI) uptake started increasing but, above pH 3 Cr(VI) uptake started decreasing. Optimum pH, contact time, and solid/liquid ratio is 3, 180 min and 0.5 g/L.

Suksabye *et al.* [59] researched the use of coir pith to remove chromium from electroplating effluent. They used adsorbents made of coir pith and activated carbon to remove chromium from electroplating effluent. The authors have found that by increasing the contact time (5 min-24 hours), adsorbent dosage (5-45 g/L) and temperature (15-60°C) the efficiency of adsorption also increased in both cases, but coir pith had shown better result as compared to the activated carbon. They discovered that pH played a significant part in the adsorption of chromium, and that raising the pH from 2 to 10 decreased the effectiveness of adsorption in both situations. Coir pith had shown the maximum adsorption efficiency and chromium uptake - that is 99.99% and 317.65 mg/g at solution pH 2. Optimum contact time, adsorbent dosage, pH and temperature were 18 hours, 20 g/L, 2 and 30°C. The elimination of Cr(VI) from aqueous solutions by a surplus agricultural waste – rice straw was investigated by Gao *et al.* [60]. They discovered that raising the initial Cr(VI) ion concentration (40-200 mg/L) and temperature (27-47°C) increased the percentage of adsorption. At the same time, by increasing the pH (2-6) and straw particle sizes (150-380 μm) the removal percentage of Cr(VI) started decreasing. Optimum pH, temperature, initial Cr(VI) ion concentration and straw particle sizes were 2, 47°C, 100 mg/L, and less than 150 μm. They have also noticed that rice straw reduces the Cr(VI) to Cr(III) and studied the effect of NO_3^- and SO_4^{2-}on Cr(VI) removal. They had found that Langmuir data well fitted these experimental data and Langmuir showed the highest sorption capacity that is 3.15 mg/g as compared to the Freundlich model, 1.397 mg/g.

Han *et al.* [61] investigated the biosorption and bioreduction of Cr(VI) by *Chlorella miniata*, a microalgal isolate. The kinetics and equilibrium of Cr(VI) removal indicated that increasing Cr(VI) concentration from 50 to 200 g/L increases Cr(VI) absorption, whereas raising pH from 1-4 decreases Cr(VI) removal percentage. The amount of biomass present had an important impact on the decrease and adsorption of Cr(VI). As biomass concentration rises from 1 to 5 g/L, the percent of Cr(VI) removed rises as well. The ideal pH and biomass concentrations were 2 and 2 g/L, respectively. They also conducted a desorption study using 0.5 M NaOH, 0.5 M HCL, and deionized water, finding that the majority of the Cr(VI) was converted to Cr(III) and that 0.5 M NaOH had a better potential for total chromium recovery than 0.5 M HCL and deionized water. They have found that biosorption-bioreduction model had a higher value of R^2 as compared to the direct bioreduction model.

Using the green alga *Ulva Lactuca* and its activated carbon, EL-Sikaily *et al.* [62] researched the eradication of chromium from aqueous solution, wastewater, and saline water. They had found that by enhancing the biosorption time and adsorbent dose the removal efficiency of chromium also increases for both adsorbents and at the same time by increasing the pH and metal ion concentration the removal efficiency of chromium starts decreasing for both adsorbents. Optimum pH was 1. According to the authors the Langmuir model complemented the experimental data as compared to other models.

According to the Langmuir model, the highest adsorption capacity of activated carbon and green alga *Ulva Lactuca* was 112.36 and 10.61 mg/g, respectively. They also discovered that the pseudo-second order model matched the actual data. Activated carbon and green alga had shown the maximum removal and uptake of chromium which was 100 %, 59.55% and 96.52 mg/g, 10.5 mg/g from synthetic seawater. The biosorption of Cr(VI) from aqueous solutions by green algae *Spirogyra* species was tested by Gupta *et al*. [63]. They assessed pH, contact duration, and adsorbent dosage, as well as other variables in Cr(VI) adsorption. The initial concentration of Cr(VI) was changed from 1 to 25 mg/L. The authors have found that adsorption capacity basically depended upon the pH. They have also noticed that by increasing the pH from 1-5 the removal of Cr(VI) started decreasing and at the same time by increasing the contact time (0-200 min) and adsorbent dose (1-25 g/L) the removal of Cr(VI) started increasing. The research group used the Langmuir model to study the adsorption isotherm and discovered that the maximum removal of Cr(VI) from aqueous solution was 14.7×10^3 mg/kg biomass at pH 2 with an initial Cr(VI) concentration of 5 mg/L and a contact duration of 120 minutes. *Spirogyra* species, a kind of green algae, showed the capacity to extract Cr(VI) from industrial wastewaters. Comparison of biosorption capacities of Cr(VI) removal with different adsorbents is being tabulated in Table 2.

Table 2. Comparison of biosorption capacities of Cr(VI) removal with different adsorbents

Adsorbent	Kinetics	Sorption-Isotherm Model	Optimum pH	Sorption Capacity, mg/g	Reference
Tamarindus Indica	First order	Freundlich	2	90	[64]
Phanera vahilii fruit biomass based activated carbon	Pseudo-second order	Freundlich	2	159.1-278.5	[10]
Heat-treated microalgae *Chlamydomonas reinhardtii*	Second order	Langmuir	2	25.6	[65]
Rhizopus nigricans	Langergren model	Langmuir and Freundlich	2	47	[66]
Dunaliella species	Pseudo-second order	Langmuir and Freundlich	2	45.5-58.3	[67]
Spirulina platensis	Initially zero order followed by first order	Langmuir and Freundlich	1.5	148.64	[68]
Chlorella vulgaris				140	
Acid-treated green alga *Oedogonium hatei*	Pseudo-first order	Langmuir and Freundlich	2	35.2	[69]
Date pit and olive stone	Pseudo-second order	Freundlich	2	82.63 and 53.31	[70]
Banana peel dust	Pseudo-first and pseudo-second order	Langmuir	1	26.46	[71]
Bacillus cereus	Pseudo-second order	Langmuir and Freundlich	2	86	[72]
Luffa cylindrica activated carbon	Pseudo-first order	Freundlich	8	188.50	[73]
Sulfuric acid activated strychnine tree fruit shell	Pseudo-second order	Langmuir and Freundlich	2	100	[74]
Phosphoric acid activated strychnine tree fruit shell				142.85	

CONCLUSION

Hexavalent chromium is a very lethal, known carcinogen that is classified as a major environmental contaminant. This review focuses on the chemistry of employing microbes to treat Cr(VI)-containing wastes. There is ample literature available to demonstrate the role of microbes in Cr (VI) biosorption and reduction. A broad range of microorganisms including bacteria, fungi, yeasts, and many more have demonstrated efficient reduction under a variety of conditions, including pH, temperature, contact time, agitation, nutritional medium, initial Cr concentration, adsorbent dose and many more, as described in the literature. Cr(VI) can be adsorbed by attaching to the functional mass of certain living or dead cells. Bacteria, fungi, plants, algae, and other microbes highlight the feasibility to bioreduce or biosorb Cr(VI) due to their diverse life cycles. In these findings with the removal of potentially hazardous metal such as Cr(VI), as presented in this review, the application of microbes to adsorb or reduce Cr(VI) is considered to be a developing, low-cost biotechnological approach.

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