Removal of Cadmium, Lead and Hexavalent Chromium from Wastewater

Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

By

Veer Singh

School of Biochemical Engineering
Indian Institute of Technology
(Banaras Hindu University)
Varanasi – 221005
India

Roll No. 17011503 **2021**

CHAPTER 9

Chapter 9

9.1 Disposal of used adsorbent

The safe disposal of used adsorbent is need of sustainable environmental and proper waste management policy. The adsorbent waste can be used for production of value added products on the basis of its properties. In case there is no leaching of heavy metal ions from the saturated adsorbent, it can be used for manufacturing bricks and can be burnt as fuel for energy production [Nag et al., 2017; Dadwal and Mishra, 2017].

9.2 Comparative heavy metal removal

In the present work, we have used FeRH, CMNPs, ChCLP, bacterial isolate and *Pleurotus florida* for the removal of heavy metal ions. FeRH was prepared for adsorption-cum-reduction of lethal Cr (VI) to less toxic and partially soluble Cr (III). Additionally, bacterial isolate and *Pleurotus florida* were used in the live form for removal of heavy metal ions. Hence, heavy metal removal efficiency of FeRH, bacterial isolate and *Pleurotus florida* could not be compared with CMNPs and ChCLP. CMNPs were synthesized through the green route using curcumin and *Citrus limetta* peel extract. CMNPs showed high Cr (VI), Cd (II) and Pb (II) removal efficiency up to 92.19 %, 98.01 %, 94.40% at 100 mg/L initial metal ion solution and 1 g/L CMNPs dosage. *Citrus limetta* was coated with chitosan polymer for removal of Cr (VI), Cd (II) and Pb (II). Results showed that chitosan coated *Citrus limetta* peels biomass has Cr (VI), Cd (II), and Pb (II) removal efficiency up to 99.34 % Cr (VI), 99.92 % Cd (II), 99.58 % Pb (II). The heavy metal removal efficiency of CMNPs and ChCLP biosorbents was compared at similar conditions. The comparative heavy metal removal efficiency is shown in Table 9.1.

Table 9.1 Comparative heavy metal removal capacity

Absorbent	Heavy metal	Adsorbent dosage (g/L)	Initial metal ion concentration (mg/L)	Removal efficiency (%)

CMNPs	Cr (VI)	2	100	98.93
	Cd (II)	2	100	98.07
	Pb (II)	2	100	98.27
ChCLP	Cr (VI)	2	100	63.11
	Cd (II)	2	100	69.41
	Pb (II)	2	100	67.43

CMNPs showed better heavy metal removal efficiency than ChCLP as shown in Table 9.1. Hence, CMNP was used in column study for removal of Cr (VI), Cd (II) and Pb (II).

9.3 Column study

The removal of Cr (VI), Cd (II) and Pb (II) was observed in the continuous column study. The effect of flow rate on the heavy metal removal was investigated by varying the flow rate of the metal ion solution at 10 ml/min, 20 ml/min and 30 ml/min, other parameters such as initial metal ion concentration (100 mg/L) and bed height remain constant. The effect of flow rate on the removal of Cr (VI), Cd (II) and Pb (II) is shown in Figures 9.1, 9.2 and 9.3.

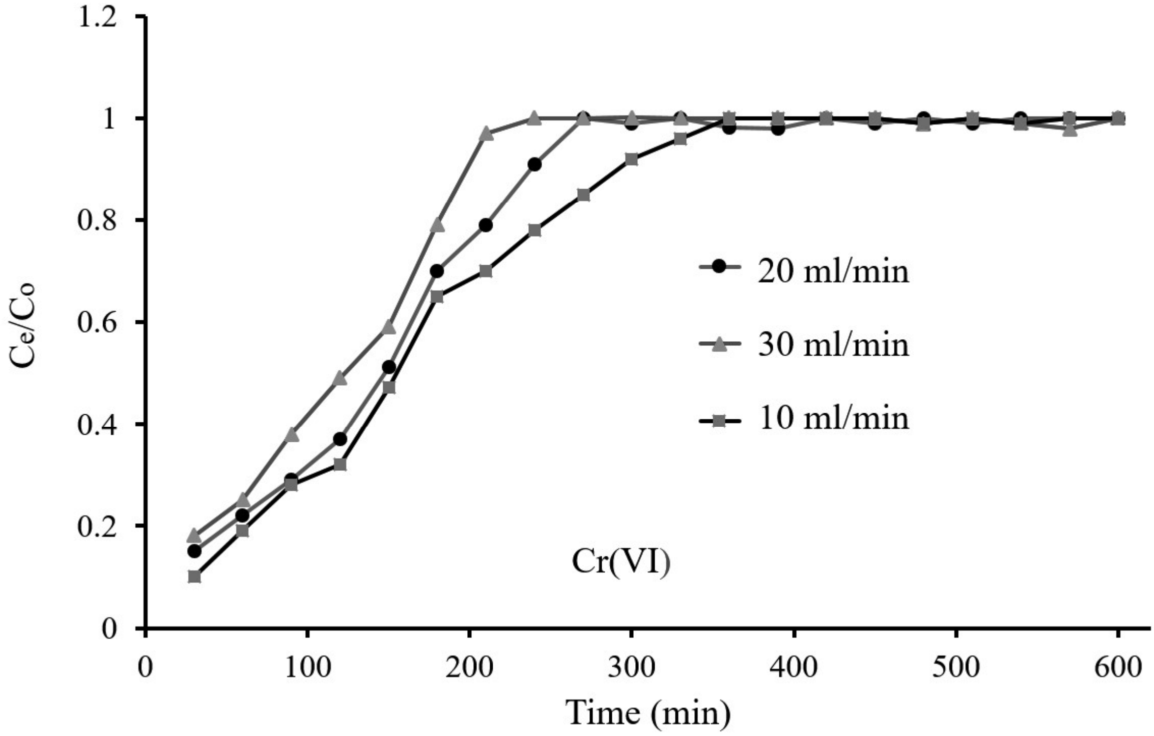

Figure 9.1 Breakthrough curves of Cr (VI) removal at flow rate 10, 20 and 30 ml/min

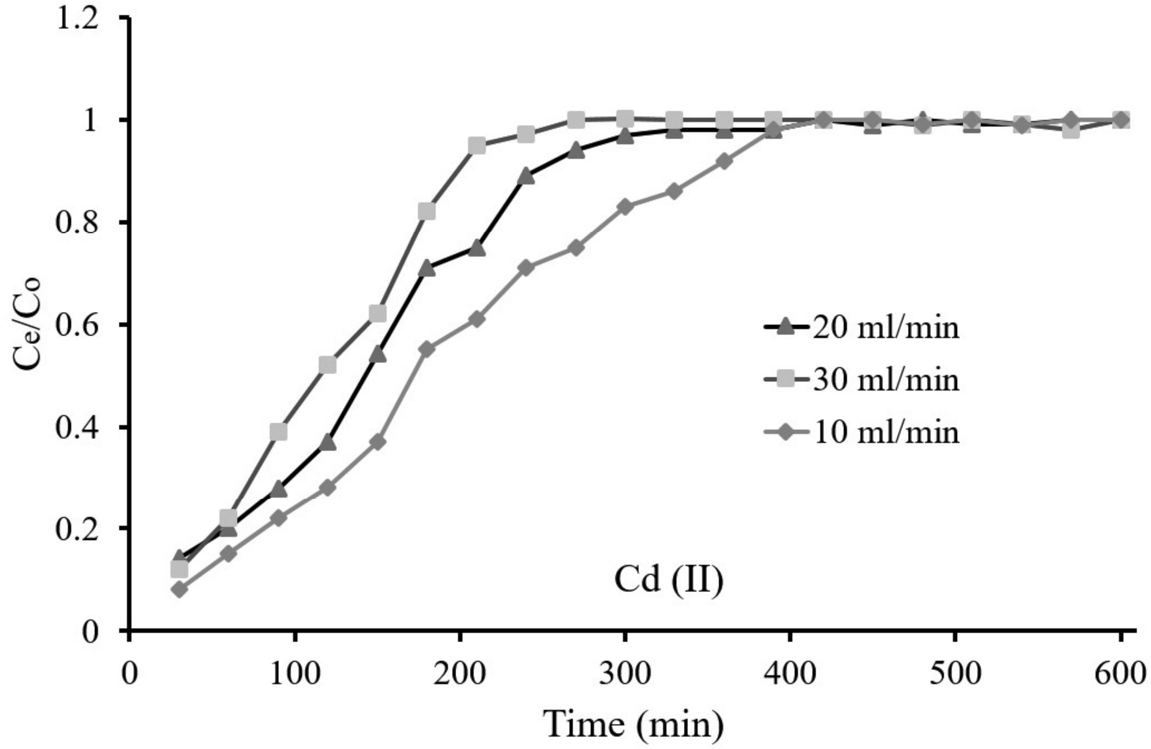

Figure 9.2 Breakthrough curves of Cd (II) removal at flow rate 10, 20 and 30 ml/min

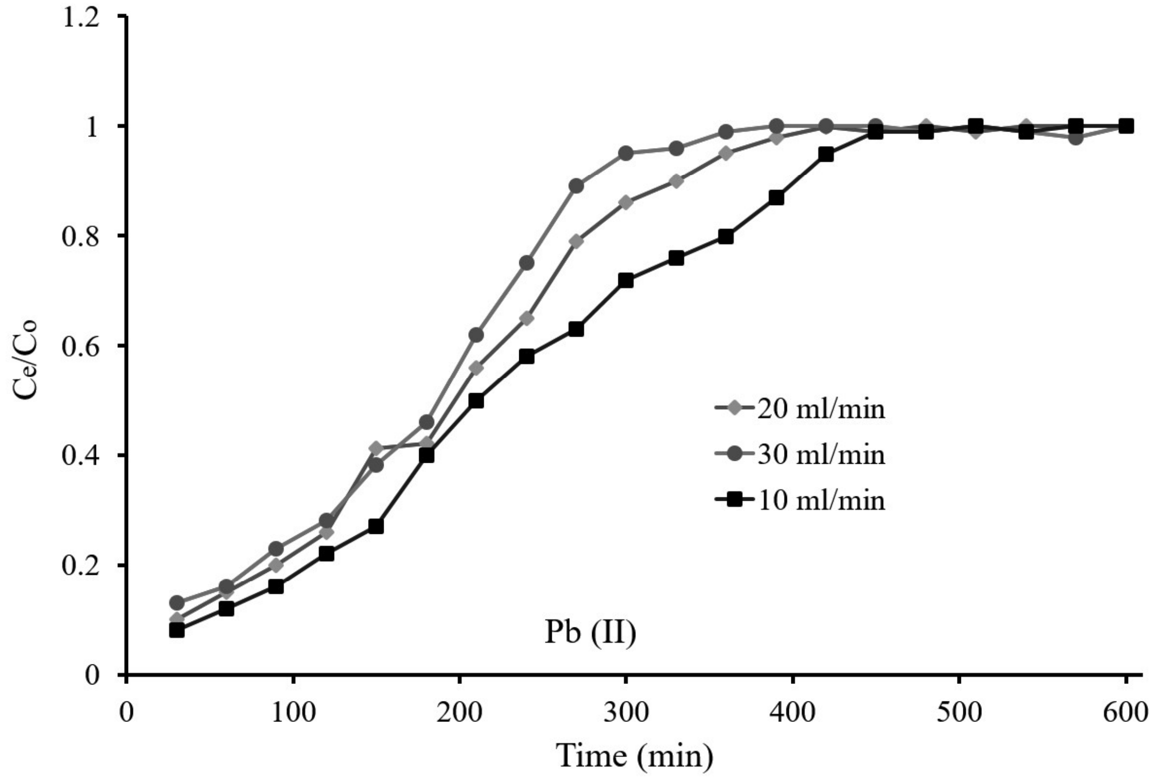

Figure 9.3 Breakthrough curves of Pb (II) removal at flow rate 10, 20 and 30 ml/min

A quick breakthrough was observed for the highest flow rate (30 ml/min) of metal ion solutions. At a lower flow rate of the solution, the contact time between the adsorbent and metal ions was higher which results in a slower breakthrough curve. At a higher flow rate, the heavy metal ions leave the bed before the attainment of equilibrium which is responsible for the quicker breakthrough curve at a higher flow rate. Fiol et al., 2006 investigated Cr (VI) removal by using grape stalk wastes encapsulated in calcium alginate beads in a packed bed column and reported similar observation. Mohanta et al., 2021 investigated heavy metal removal by activated charcoal derived from *Sapindus trifoliat* fruit biomass in a continuous fixed-bed column and reported similar observations. Srivastava et al., 2020 investigated heavy metal removal by fix bed column and reported the quick breakthrough point at higher flow rate and delayed breakthrough at lower flow rate.

9.4 Recommendations for future studies

Present study showed interesting results in terms of Cr (VI), Cd (II) and Pb (II) removal from liquid phase. However, in future, the potential of adsorbents and bacterial isolate can be explored for the removal of other toxic metal ions such as As, Ni, Hg and Cu. Advanced technical duty/ assessment tools such as life cycle assessment, exergo-environmental and exergoeconomic investigation of large-scale wastewater treatment plant can also be done in future to develop cost effective, energy saving and eco-friendly system. Additionally, the molecular mechanism of heavy metal removal and comparative transcriptomic analysis may be also consider in future research plans.

9.5 Life Cycle Assessment Theoretical Study for the Removal of Cadmium, Lead and Hexavalent Chromium from Wastewater

9.5.1 Life Cycle Assessment (LCA) framework of the study

Biosorption is an eco-friendly and inexpensive method which is applied for the extraction of metal ions from heavy metal contaminated water [Jobby et al., 2018]. A variety of biomaterials like rice and wheat husk, activated carbon, lignite, agro-waste, banana and *citrus limetta* peels, and green synthesized nanoparticles are considered as an active biosorbent for extraction of toxic metallic pollutants [Gadd, 2007]. A LCA study explained in Figure 9.4, the system boundary shows the remove heavy metal ions such as Cr (VI), Cd (II), and Pb (II) from industrially contaminated wastewater using agrowaste as activated biosorption materials i.e., rice husk, *Citrus limetta* peels, and MnO_2 nanoparticles respectively. During the production of activated biosorbents, and use in contaminates removal from wastewater a very minimal amount of energy has been consumed, therefor minimal loss of energy has been reported. Whereas during the treatment of wastewater the activated biosorbents material will be recycled to used again in the heavy metal ion contamination removal of another batch of wastewater. The life cycle of biosorbents is shown in Figure 9.4.

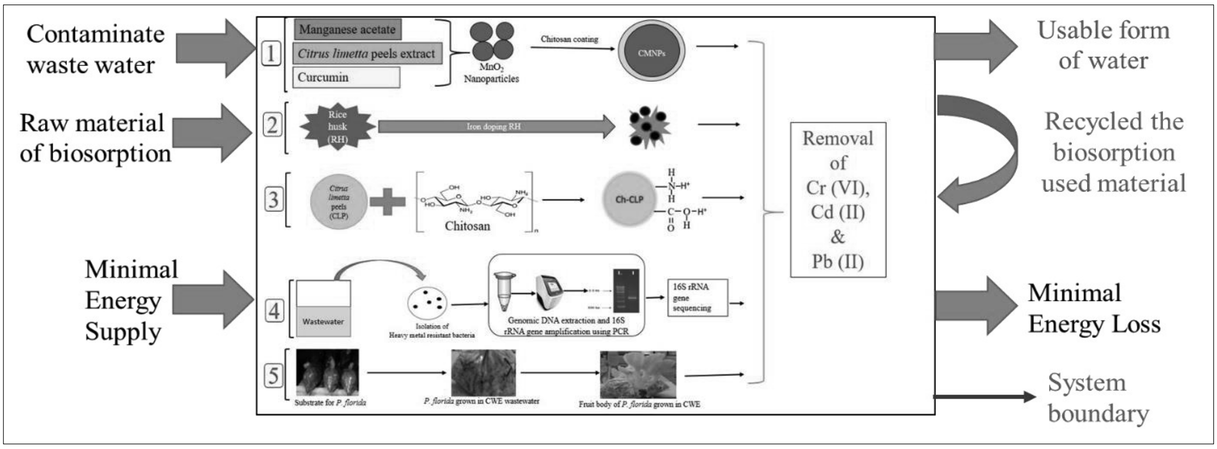

Figure 9.4. System boundary describing life cycle of production, use and recycle of the biosorbent corresponds to Cr (VI), Cd (II), and Pb (II) removal from contaminated wastewater system.

Rice husk is one of the widely available agricultural waste generated in large amounts worldwide. It is a good source of carbon (C) and silica (Si) which actively participate in the adsorption of heavy metals. Thereby, rice husk has been widely applied for the extraction of toxic metal ions like Cr (VI) from wastewater [Bansal et al., 2009; Gaikwad et al., 2020]. *Citrus limetta* is very common in the India and other countries such as Brazil, China, United States and Mexico (https://www.worldatlas.com/articles/the-world-s-top-citrus-producing-countries.html). Several food industries use *citrus limetta* for the production of fruit juices, jellies, jams and squashes. These industries also generate massive amount of *citrus limetta peels* (CLP) as a waste. Several type of nanomaterials made up of silver, iron, gold, grapheme and other polymer have been synthesized for the adsorption of heavy metals. Among these nanomaterials, manganese dioxide (MnO_2) is considered as an inexpensive and effective nano-adsorbent [Singh et al., 2021a]. Green synthesis of MnO_2 from several plant extract is considered as an eco-friendly, inexpensive and effective nano-adsorbent compared to other nanoparticle prepared from physiochemical methods [Gnanasangeetha et al., 2013]. Curcumin extract obtained from turmeric powder act as efficient stabilizing agent that provides stability and prevent the accumulation of nanomaterials in an aqueous medium [Souri et al., 2019; Abdelgawad et al., 2017].

The toxicity of Cr (VI) can be minimized through the reduction process. The reduced form Cr (III) is less toxic and easily adsorbed as compared to Cr (VI) on the adsorbent surface due to less solubility in water [Bandara et al., 2020]. Several chemical compounds such as sodium dithionite, hydrogen peroxide and Ferrous sulfate have been used as reducing agents for Cr (VI) [Gao and Liu, 2017]. Among these, ferrous ions are considered as an eco-friendly and effective reducing agent. Research has demonstrated the adsorption-cum-reduction of Cr (VI) by using ferrous ion-doped adsorbent.

Artificial neural network (ANN) is a data-driven modelling technique. It has been commonly applied for adsorption study [Chowdhury, 2013; Khonde and Pandharipande, 2012; Ullah et al., 2020]. Singha et al., 2014 studied ANN modelling for adsorption of Cr (VI) and authors reported enhanced predictability of Cr (VI) percentage removal. The molecular dynamics of heavy metal adsorption have played a significant role in understanding the behaviour and mechanism of adsorption. The molecular dynamics has been studied by determining dimensionless numbers [Biswas et al., 2005] which are also applied for scaling-up and designing for continuous reactors system for wastewater treatment [Chong and Hernandez, 2018; Hua et al., 2018].

The living microbes like bacteria and fungi are considered an effective remediating agents. This is due to high metal tolerance properties of fungi (*Pleurotus florida*) and bacteria. Several functional groups on the bacterial surface and cell wall receptors are actively involved in the accumulation of heavy metal ions inside the bacterial cell [Gadd, 2007].

The reduction of Cr (VI) from rice husk waste doped with ferrous ions (FeRH), chitosan coated MnO_2 nanoparticles (CMNPs) and chitosan coated *Citrus limetta* peels (ChCLPs). The heavy metal uptake efficiency of FeRH, CMNPs and ChCLPs for Cr (VI), Cd (II) and Pb (II) were determined in both single metal ion and ternary metal ion system. Biosorption behavior was estimated using kinetic, thermodynamics and several isotherm studies. Also, the heavy metal resistant bacterial strain was isolated from wastewater of Baliya Nala, Singrauli, Madhya Pradesh, India and heavy metal removal efficiency was evaluated at various concentrations of Cr (VI), Cd (II) and Pb (II) in both single and ternary metal ion system. The heavy metal removal efficiency of fungi *Pleurotus florida* was also investigated. *Pleurotus florida* was grown on the coal washery effluent (CWE) exposed paddy straw substrate and the removal of heavy metal ions from the contaminated substrate was analyzed. Finally, to show the applicability of FeRH, CMNPs, ChCLPs, bacterial isolate and *Pleurotus florida* and comparative study with other adsorbents, bacteria and fungi has been done. The guidelines of permissible limits of discharge of Cr (VI), Cd (II) and Pb (II) as demarcated by WHO, USEPA and CPCB, India have been satisfied in the present work.

This study has been framed in four phases which can be categorized as aim and possibility description, inventory study, impact exploration, and improvement evaluation. The outcome of regression trend forecast of cancer, liver and kidney failure and skin problems are explored as the community health impact of Cr (VI) whereas, logistic regression model has been analyzed for improvement evaluation through this assessment framework which has been explained below (Figure 9.5).

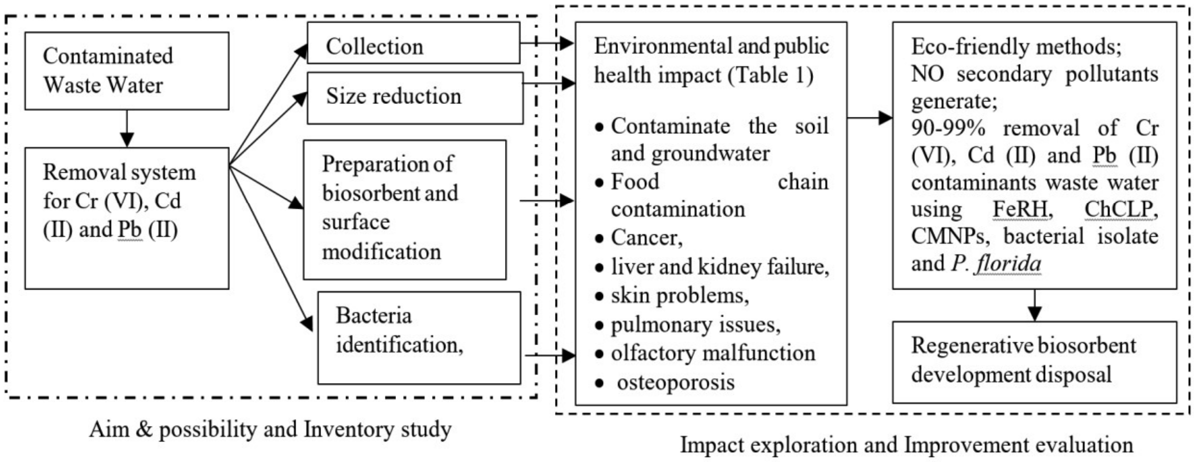

Figure 9.5. Life cycle Assessment four stages procedure

9.5.2 Aim and possibility description

The aim of the study to development a cost-effective, recyclable and effective biosorbent for simultaneous removal of Cr (VI), Cd (II) and Pb (II) from wastewater. The LCA four stage procedure study helps to define the environmental impacts accompanying during waste water handling, production, use, and recycling (Figure 9.5).

9.5.3 Inventory study

Inventory study includes collection biomass, preparation and surface modification of biosorbent, isolation and characterization of bacteria, cultivation of mushroom, and removal of heavy metal using synthetic adsorbent. The inventory study requires the considerable type of data which includes:

- Collection biomass and preparation of biosorbent
- Surface modification of biosorbent
- Isolation and characterization of heavy metal resistant bacterial isolate
- The characterization of biosorbents by using SEM-EDX, XPS, AFM, FTIR, BET and Ultimate- Proximate were used.
- Cultivation of P. florida in coal washery effluent (CWE) wastewater
- Heavy metal removal, regeneration of biosorbent and safe disposal of used biosorbent

The environmental contamination is defined as elevated concentration of unwanted materials in the air, water and soil beyond the permissible limit. It is also defined as undesirable change in the natural environment which shows harmful effects on both animals and plants [Wong, 2012]. Leather tanning, chrome plating, batteries industries, pigment industries and chemical (fertilizers, pesticides and insecticides) used in agriculture field add pollutants in the environment. Inorganic pollutants such as heavy metal ions originate from natural or anthropogenic activities [Wong, 2012]. Heavy metal such as Cr (VI), Cd (II) and Pb (II) toxicity is enormous as it possesses an ability of bio-accumulation in the vital organs of the living organisms and is accountable for nausea, diarrhea, kidney damage, cancers, respiratory disorders and several other health issues [Saha et al., 2010; Saha et al., 2013]. The heavy metals and their hazardous impact are listed in Table 9.2.

Table 9.2. Heavy metals and its hazardous impact on community health

Environmental pollutants	**Source of different pollutants (belongs to**	**Environmental and Health hazards**	**References**

	different type of waste)		
Cr (VI)	Mining industry, leather industry, chrome plating, coal mining, etc	• Soil and groundwater are found contaminated at the active and unrestricted industrial sites, they required environmental remediation and restriction. • Several types of cancer, liver and kidney failure, skin problems, etc	Wong, 2012, Saha et al., 2010; Saha et al., 2013
Cd (II)	Steel industry, phosphate fertilizer plant, zinc production and coal mining	• Soil and groundwater are found contaminated at the active and unrestricted industrial sites, they required environmental remediation and restriction. • Cancer in lungs, kidneys, prostate and stomach, disturbance in pulmonary function,	Wong, 2012; Cheng et al., 2021

		decrease in olfactory function and bone mineral density and osteoporosis	
Pb (II)	Batteries manufacturing, glass industries and pharmaceutical industrial	• Soil and groundwater are found contaminated at the active and unrestricted industrial sites, they required environmental remediation and restriction. • Damages in liver, kidney malfunctioning, cardiac failure and neurological impairment, The initial stage of Pb (II) toxicity includes headache, memory loss and dullness	Wong, 2012; Yang et al., 2010

Traditional techniques like adsorption mediated by chemical adsorbents, membrane filtration, and chemical reduction have been practiced in past [Gaikwad et al., 2020]. However, majority of these approaches are exclusive as they require tremendous volume of chemicals, equipment and also produce toxic ancillary chemical waste. Hence, development of effective, inexpensive and eco-friendly metal ion adsorbent which not only adsorbs but also reduces highly toxic form of heavy metals into less toxic heavy metal ions is the need of the hour. Agro-waste such as sawdust, sunflower husk, sugar cane bagasse, wheat bran, rice husk, Jatropha oil cake and coconut husk have been applied for adsorption of Cr (VI) from metal contaminated water, soil etc. Activated carbon synthesized from various biomasses has also shown encouraging results in Cr (VI) adsorption [Gaikwad et al., 2018]. Among these, rice husk, *Citrus limetta* peels and MnO_2 nanoparticles have been reported as an effective and cost-effective adsorbents for adsorbing heavy metals from aqueous phase. The modified adsorbents FeRH, CMNPs, ChCLP, isolated bacterial strain and *P. florida* are considered as cost effective, eco-friendly and effective method for removal of Cr (VI), Cd (II) and Pb (II) from contaminated water [Bansal et al., 2009].

9.5.4 Improvement evaluation

In the present work, iron ions were doped on the rice husk for adsorption-cum-reduction of lethal Cr (VI) to less toxic and partially soluble Cr (III). Energy dispersive X-ray analysis and X-ray photoelectric spectroscopy disclosed the effective doping of iron on rice husk and significant reduction of Cr (VI) into Cr (III). The maximal removal of Cr (VI) was found to be 81.56 % for iron doped which was much higher than uncoated (43.28 %) rice husk. Chitosan coated MnO_2 nanoparticles (CMNPs) were synthesized through green route using curcumin and *Citrus limetta* peel extract. X-ray photoelectron spectroscopic analysis of chromium loaded nanoparticles confirmed the biosorption of Cr (VI), Cd (II) and Pb (II) onto biosorbent surface. Chitosan coated MnO_2 nanoparticles showed high Cr (VI), Cd (II) and Pb (II) removal efficiency upto 92.19 %, 98.01 %, 94.40% at 100 mg/L initial metal ion solution and 1 g/L biosorbent dosage in a single metal ion system. In the ternary metal ion system, biosorbent was able to removal 53.90 % Cr (VI), 48.09 % Cd (II) and 57.96 % Pb (II) in the ternary metal ion system. *Citrus limetta* was coated with chitosan polymer for removal of Cr (VI), Cd (II) and Pb (II). Energy dispersive X-ray and elemental mapping indicated the homogeneous distribution of Cr (VI), Pb (II) and Cd (II) together with other major elements like carbon, nitrogen and oxygen which are considered as a major elemental constituent of chitosan and play a significant role in heavy metal biosorption as well as Cr (VI) biotransformation. Results showed that chitosan coated *Citrus limetta* peels biomass has Cr (VI), Cd (II), and Pb (II) removal efficiency up to 99.34 % Cr (VI), 99.92 % Cd (II), 99.58 % Pb (II) in single metal ion system and 56.19 % Cr (VI), 62.29 % Pb (II), 68.29 % Cd (II) in the ternary metal ion system at 100 mg/L initial metal ion concentration and 10 g/L chitosan coated *Citrus limetta* peels biomass. A combination of two batch reactors in series was capable in removing 100 % heavy metal ions in single and ternary metal ion system. FeRH, CMNPs and ChCLP also showed high regeneration capacity and can be used over several biosorption cycles for the removal of Cd (II), Cr (VI) and Pb (II).

A heavy metal tolerance bacteria was isolated from the wastewater collected from Baliya Nala (drain) Singrauli, Madhya Pradesh, India wherein coal mining units discharge their effluents after treatment. The bacterial isolate showed maximum sequence similarity with the *Microbacterium paraoxydans* and it was submitted to the NCBI GenBank under the accession no. MN650647. The bacterial isolate showed a maximum heavy metal ion removal efficiency of 99.96 % Cr (VI), 94.96 % Pb (II), 84.96 % Cd (II) at 50 mg/L for single metal ion system and 91.62 % Cr (VI), 89.29 % Pb (II), 83.29 % Cd (II) at 50 mg/L of each metal ions in the ternary metal ion system.

Additionally, bioremediation of heavy metal ions from the coal washery effluent by *Pleurotus florida* was investigated. Metal ion concentration in the fruit body and substrate (paddy straw) was determined by inductively coupled plasma optical emission spectrometry. The maximum heavy metal uptake capacity of *Pleurotus florida* was found as 10.65, 1.12, 13.46, 3.0, 1.21, 19.11, 0.47 and 0.23µg/g for Pb, Cr, Cd, Zn, As, Mn, Ni and Ti, respectively. The maximum heavy metal removal from substrate (paddy straw) was found 99.53 % (Cd), 70.85 % (Cr), 77.77 % (Ni), 76.23 % (Zn), 42.63 % (Mn), 52.10 % (Pb), 49.07 % (Ti) and 51.66 % (As). The negatively charged rough surface, high amount of carbon and oxygen in biomass and the induced production of intracellular metal stress markers on exposure to heavy metals illustrated the immense bioaccumulation ability of *Pleurotus florida* in coal washery effluent. On the basis of present work, we concluded that biosorbents developed were inexpensive, non-toxic and highly effective for the removal of hexavalent chromium, cadmium and lead.

The LCA study for the removal of Cr (VI), Cd (II) and Pb (II) from contaminated wastewater helps to define the environmental impacts accompanying during handling, production, use, and recycling. There is minimum energy input and energy loss during heavy metal removal study, using FeRH, ChCLP, CMNPs, bacterial isolate and *P. florida*. Even the modified biosorbents material will be recycled and reused wastewater treatment. Hence, theoretical LCA study has been performed.