CHAPTER 1

Introduction

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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]. The environmental pollutants are categorized in the several classes such as organic and inorganic pollutants, and microbial contaminations [Nathanson, 2021]. Organic pollutants can be defined as naturally occurring biodegradable substances and anthropogenic activities. Few examples of these pollutants are food and agro-waste, polycyclic aromatic hydrocarbons (PAHs), domestic and dairy waste products and polychlorinated biphenyls (PCBs) [El-Shahawi et al., 2010]. Biological pollution is generally caused by bacteria, viruses, moulds, mites, cockroaches, pollen and fungi [Tran et al., 2020]. The pollution caused by human beings impacts on the terrestrial and aquatic ecosystem [Elliott, 2003]. 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 are natural occurring elements having higher density as compared to water [Fergusson, 1990]. The metallic pollutants have top thoughtfulness among the researchers due to their high toxic behaviour. Trace amount of these substances naturally occur in ecosystems. However, few metal ions have higher toxicity level even at low concentrations [Herawati et al., 2000]. Chromium (Cr), Arsenic (As), Lead (Pb), Iron (Fe), Cadmium (Cd), Nickel (Ni), Mercury (Hg) and Cobalt (Co) metallic ions are toxic even in less quantity [Wu et al., 2016]. Nevertheless, Cr, Co, Zn, Fe, Mo, K, and Cu metals are also involved in the several metabolic activities and considered as essential metal ions for growth of living organisms. These heavy metals become lethal when their intake is in excess and are not metabolized by body and accumulated in the intra or extracellular space of body organs [Briffa et al., 2020; Flora and Pachauri, 2010]. Heavy metals can easily enter in the living system due to their high solubility in the water [Singh et al., 2011]. Heavy metals have been found in the body parts of fishes captured from the metal contaminated aquatic system [Sobhanardakani et al., 2016]. Heavy metals enter into the human body via food chain [Barakat, 2011]. The effluent emanating from tanneries, battery manufacturing unit, glass, paint and metal plating industries, pigment and steel productions cause heavy metal pollution in the terrestrial and aquatic ecosystems [Rai et al., 2008]. Coal has important application in the energy sector and considered as major energy source in India, China, Nepal, Pakistan and other countries. It is easy available and inexpensive source of energy compared to other energy sources. These features make it priority choice for several industries. During coal processing, large volume of toxic substances is released as coal washery effluent (CWE) including heavy metal ions like Cd (II), Cr (VI) and Pb (II) which massively contaminates natural environment [Ghose, 1999].

Agency for Toxic Substances and Disease Registry (ATSDR), USA has defined the toxicity ranking of several substances on the basis their toxicity. According to ATSDR, Pb (II), Cd (II) and Cr (VI) have 3rd, 7th, and 17th rank, respectively (https://www.atsdr.cdc.gov/toxprofiledocs/index.html). Toxic effect of these metal ions depends on the factors such as level and route of exposure, rate of emission, oxidative state of metallic species and period of exposure [Valavanidis and Vlachogianni, 2010].

Hexavalent chromium [Cr (VI)] has seventh rank in the ATSDR [ATSDR, 2019]. It is considered as a priority carcinogen which is generated from several anthropogenic activities like tanning of leathers, pigment and rubber production, paint manufacturing, production of anticorrosion agent and from processing of coal [Owlad et al., 2009; Shi et al., 2011]. Cr (VI) is 100 times more toxic as compared to Cr (III). High solubility in water and higher oxidative state of Cr (VI) make it more lethal. The Central Pollution Control Board (CPCB), India has defined maximum allowable concentration Cr (VI) in effluent of industrial units as 1.0-2.0 mg/L (CPCB, 2000). Cr (VI) enters into to human body and causes cancer, liver and kidney damage, and difficulties in respiration [Peterson-Roth et al., 2005]. World health organization (WHO) has recommended permissible limit up to 0.05 mg/L of Cr (VI) in drinking water [Singh et al., 2020].

According to ATSDR's toxicity ranking Pb (II) is considered as second most toxic element [ATSDR, 2019]. The main routes of Pb (II) exposure are contaminated food, water and Pb (II) contaminated dust in air. The Pb (II) toxicity is generally associated with damages in liver, kidney malfunctioning, cardiac failure and neurological impairment (Flora et al., 2006). The initial stage of Pb (II) toxicity includes headache, memory loss and dullness [CDC, 2002]. It is also responsible for disturbance in the synthesis of RBCs and also cause anemia. Pb (II) also considered as potential carcinogen which cause several types of cancer [Jarup, 2003]. WHO has recommended permissible limit up to 0.01 mg of Pb (II) per liter in drinking water [Ayeni, 2014].

Cd (II) exposer mainly occurs through intake of contaminated food, water, working in a Cd (II) contaminated area and smoking of cigarettes [Paschal et al., 2000]. Industrial processes such as steel industry, phosphate fertilizer plant, zinc production and coal mining are responsible for Cd (II) contamination into the environment. A study reported that the Cd (II) concentration was higher in the fishes than the maximum limit. This higher Cd (II) concentration in the fish's samples was due to discharge of effluent from various industries into the aquatic environment [Sobhanardakani, 2017]. United States Environmental Protection Agency (USEPA) has decided the upper allowable limit of Cd (II) in the water as 0.005 mg/L and beyond this limit of Cd (II) in the drinking water causes several harmful effect on human health [Onuegbu et al., 2013; USEPA, 2018]. Cd (II) toxicity is generally associated with cancer in lungs, kidneys, prostate and stomach, disturbance in pulmonary function, decrease in olfactory function and bone mineral density and osteoporosis [USEPA, 2018].

Therefore, it is very needful to eliminate heavy metal contamination before releasing industrial effluent into the aquatic ecosystem [Li et al., 2020a]. There are several technologies like reverse osmosis, membrane filtration, ion-exchange, solvent extraction, precipitation, flocculation, electro-dialysis and coagulation for heavy metal extraction from aqueous medium [Ali and Hashe, 2007]. These methods are expensive, partially effective at trace amount of metal solution in wastewater and also generate secondary chemical sludge [Ahalya et al., 2003; Fang et al., 2019; Wang and Chen, 2006]. These methods are also unable to complete reduction of lethal Cr (VI) to less toxic Cr (III) [Jin et al., 2017]. On the other hand, biological methods like bioaccumulation, bio-conversion/ bio-transformation of more to less toxic form and biosorption of heavy metals from water are considered as eco-friendly and inexpensive methods [Igiri et al., 2018]. The advantages and limitations of some important heavy metal removal methods are discussed in Table 1.1.

Table 1.1 The advantage and limitations of the heavy metal removal method

Methods	Advantage	Limitations	References
Oxidation	A rapid process for heavy metal removal	Expensive and generation of by product	Ariffin et al., 2017
Ion exchange	Effective removal of the wide range of heavy metals	Adsorbents require regeneration or disposal	Ariffin et al., 2017, Al-Enezi et al., 2004
Chemical precipitation	An effective method for removal of heavy metals	Production of a large amount of sludge	Djedidi et al., 2009; Fu and Wang, 2011, Ariffin et al., 2017

Adsorption	Flexibility and simplicity of method design, and insensitivity to toxic metals	Regeneration required after adsorption	Ariffin et al., 2017; Perumal et al., 2022
Membrane filtration	An effective method for removal of heavy metal ions	High operation cost and concentrated sludge production	Blocher et al., 2003; Ariffin et al., 2017
Photochemical	No production of sludge	Formation of by products	Ariffin et al., 2017; Makhatova et al., 2020
Coagulation/ flocculation	Economically feasible	Formation of large particles and production of sludge	Jaradat et al., 2021; Ariffin et al., 2017
Electrochemical coagulation	Economically feasible	A large amount of sludge production	Hu et al., 2021; Ariffin et al., 2017
Biological treatment	Eco-friendly, inexpensive and effective removal of heavy metals	Biological methods are yet to be established and commercialized	Ariffin et al., 2017; Agnello et al., 2016; Verma et al., 2017

Bioremediation methods such as biosorption, bio-reduction, bioaccumulation, mycoremediation, bacterial bioremediation and phytoremediation have been tremendously applied for elimination of heavy metal ions from the wastewater [Sharma et al., 2018].

Biosorption is an eco-friendly and inexpensive method which is applied for extraction of metal ions from heavy metal contaminated water [Jobby et al., 2018]. 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, 2008]. Rice husk is one of the widely available agriculture waste generated in large amount worldwide. It is good source of carbon (C) and silica (Si) which actively participate in adsorption of heavy metals. Thereby, rice husk has been widely applied for 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. *Citrus limetta* peels are the good source of carbon, oxygen, and hydrogen [Poonam and Kumar, 2020]. Nowadays, nanoparticles are considered as effective adsorbent for extraction of toxic metallic pollutants due to its small size and large surface area [Zhang et al., 2020a]. Nanoparticle has also applications in the field of medical, pharmaceutical, drug delivery, biofuel production and agriculture [Kumar et al., 2015]. 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 provide stability and prevent accumulation of nanomaterials in aqueous medium [Souri et al., 2019; Abdelgawad et al., 2017].

The toxicity of Cr (VI) can be minimized through 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 agent for Cr (VI) [Gao and Liu, 2017]. Among these, ferrous ions are considered as an eco-friendly and effective reducing agent. Researches have demonstrated the adsorption-cum-reduction of Cr (VI) by using ferrous ion doped adsorbent. Wang et al., 2020 performed adsorption elimination of Cr (VI) by using ferrous ion modified activated carbon. Successful elimination of Cr (VI) from aqueous medium was also reported by Verma et al, 2015. Authors used iron ion modified aerogels as an adsorbent for Cr (VI) removal. This iron ion doped adsorbent also played an important role in the extraction of other metal ions like Cd and Pb (II) from contaminated water [Phuengprasop et al., 2011]. Some biopolymer like chitosan were also used for adsorbent surface modification. Chitosan is generally produced from few arthropods such as crabs and fungi, etc [Kumar, 2000]. It has several functional groups in its structure which have important role in the heavy metal adsorption [Youssef et al., 2018; Kaveeshwar et al. 2018].

Artificial neural network (ANN) is a data-driven modeling 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 modeling 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 the understanding the behavior and mechanism of adsorption. The molecular dynamics has been studied by determining dimensionless numbers [Biswas et al., 2005] which are also applied for scalingup 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 as 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]. Metal ions present in the intracellular either associate with metallothionein proteins or get transformed into less toxic form. Antioxidant system of fungal cell minimize the heavy metal toxicity and help in the intracellular accumulation of metal ions [Zafar et al., 2007]. Bacteria use several metabolic pathways for uptake heavy metal ions within cell. Bacteria either utilize heavy metal ions as electron acceptor or detoxify it by producing soluble enzymes [Ahemad 2015]. Reactive oxygen species (ROS) are produced as an intermediate component during reduction of Cr (VI) into Cr (III) (Kubrak et al. 2010). ROS is highly reactive which damages the cell organelles and such heavy metals can be neutralized by bacterial cell antioxidant system [Kumar et al. 2013]. Thus, antioxidant activity of bacterial and fungal cell actively participates in the detoxification of metal toxicity and bioremediation [Joutey et al. 2015].

This research work focusses on the preparation of inexpensive, recyclable and effective biosorbent for simultaneous sorption of Cr (VI), Cd (II) and Pb (II) and 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 study. 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 concentration 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 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.