ABSTRACT

Presently more than half billion people are underprivileged and deprived of fresh water, clean air, soil and pure food. Contamination of aquatic streams due to release of toxic metal ions is a stern issue demanding global concern. Toxic metals such as Cr (VI), Cd (II), Pb (II), Zn (II), Ni (II) and many more are being released in natural aquatic systems by various small and large scale industries such as tanneries, electroplating, galvanizing, pigment and dyes, metallurgical, paint, refining and metal processing etc. The average daily discharge of wastewater from these industries is approximately 1500 m³/day/industry posing big challenge to the aquatic environment. Metals once discharged into the environment remain for years due to their property of persistence and they slowly crawl into the food chain causing various health hazards such as chronic pulmonary problems, skeletal deformity, renal damage, hypertension, irritation of the skin, ulceration, nausea, vomiting, diarrhea and many more.

The existing conventional treatment methods applied for the removal of heavy metals from aquatic environment are chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation recovery. However, these conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, and production of secondary sludge and further the disposal of sludge is a costly affair. Another promising technology is adsorption of heavy metals by activated carbon for treating domestic and industrial waste water, but the high cost of activated carbon and its loss during the regeneration restricts its application. Due to inherent limitations and drawbacks of conventional treatment methods, there was an urgency to swing from synthetic chemical based technology intensive options, towards environmentally sustainable, economically feasible and technically viable alternatives. Since 1990’s the adsorption of heavy metal ions
by low cost renewable organic materials has gained momentum. The utilization of seaweeds, moulds, yeasts, and other dead microbial biomass for removal of heavy metals has been explored. Although many advantages have been found in the process of using microbes for biosorption but limitations such as need of maintaining particular environmental conditions with respect to temperature and high selectivity of the biosorbents for particular metal ions hinders its applications for industrial purposes.

In yesteryears attention has been diverted towards the agricultural biomass particularly those containing cellulose with potential metal biosorption capacity. The basic components of the agricultural waste biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complextation and helps for the sequestering of heavy metals. Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and being effective seem to be viable option for heavy metal remediation. Studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, *Cassia fistula* leaves, maize corn cob, Jatropha de-oiled cake, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, cotton stalks etc has been tried. These promising agricultural waste biomass are used for the removal of metal ions either in their natural form or after some physical or chemical modification. The major advantages of using agricultural waste biomass over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, no requirement of temperature specific conditions, regeneration of biosorbents and possibility of metal recovery.
In the present investigation various leguminocellulosic agricultural waste biomass viz; *Arachis hypogea* shells (AHS), *Acacia saligna* pods (ASP) and *Delbergia sisso* pods (DSP) have been selected as biosorbents for the removal of toxic heavy metal ions such as Ni (II), Cr (VI), Pb (II) and Cd (II) from simulated and industrial effluents in batch and fixed bed column mode. Selected biosorbents were used in natural, carbonized and the immobilized form for the sequestering of heavy metal ions.

The biosorbents have been selected on the bases of easy availability and no cost. The biosorbents were collected from the local area and after preliminary treatments were used to get in natural form, carbonized form (heating the biosorbents at 800°C for 2 hours) and Immobilized form (mixing with polymer sodium alginate and converting in the form of beads). The characterization of biosorbents was carried out by FT-IR, SEM and XRD studies.

Sequestering of heavy metals using selected biosorbents such as Ni (II), Cr (VI), Cd (II) and Pb (II) was investigated in batch mode. The various process parameters such as pH, adsorbent dose, initial metal ion concentration, stirring speed and contact time were considered for batch studies. All batch experiments were performed in triplicates and mean values are reported. The metal ion concentration was analyzed spectrophotometrically (Shimadzu 1800) and by using Thermo Orion Ion selective meter 920 A.

Fixed bed column studies were carried out on immobilized biosorbents for removal of heavy metal ions. The various column hydraulics affecting the removal efficiency were initial metal ion concentration, bed height and flow rate. Regeneration efficiency and breakthrough time were calculated to explore the complete exhaustion time and reusability of the column to investigate practical utilization at industrial scale.

Removal of Cr (VI) was investigated in batch adsorption experiments by varying pH (2-7), adsorbent dose (25-1500 mg/100 ml), stirring speed (50-300 rpm), initial metal ion
concentration (5-500 mg/l) and contact time (5-120 min) by all the three forms of biosorbents viz; natural, immobilized and carbonized. Maximum removal efficiency was observed at pH 2 and a sharp decline in removal efficiency was observed as pH was increased. Optimized parameters obtained for Cr (VI) removal by natural and immobilized form of biosorbents were adsorbent dose (1.5 g/100 ml), contact time (60 min), stirring speed (250 rpm) and initial metal ion concentration (50 mg/l). Removal efficiency of 95 %, 92% and 92% was found by the natural form of biosorbents and slightly higher with immobilized biosorbents.

In case of a carbonized form of biosorbents the optimized conditions were adsorbent dose (0.5 g/100 ml), contact time (30 min), stirring speed (150 rpm) and initial metal ion concentration (50 mg/l). Complete phasing out of heavy metals was achieved by a carbonized form of biosorbents (AHSC, DSPC and ASPC).

Studies on sequestering of Ni (II) were carried out in batch mode by using biosorbents in natural, immobilized and carbonized forms by varying pH (2-7), adsorbent dose (25-1500 mg/100 ml), stirring speed (50-300 rpm), initial metal ion concentration (5-500 mg/l) and contact time (5-120 min). Optimized parameters obtained for Ni (II) removal by natural and immobilized form of biosorbents were adsorbent dose (1.5 g/100 ml), contact time (60 min), stirring speed (250 rpm) and initial metal ion concentration (50 mg/l) at pH 6.0. In case of a carbonized form of biosorbents the optimized conditions were adsorbent dose (0.5 g/100 ml), contact time (30 min), stirring speed (150 rpm) and initial metal ion concentration (50 mg/l) at pH 6.0. Maximum removal efficiency was observed with a carbonized form of biosorbents, followed by immobilized form and then natural form.

Similarly studies were carried out for the removal of Pb (II) and Cd (II) metal ion from simulated solutions and were subject to variation of process controlling parameters such as pH (2-7), adsorbent dose (25-1500 mg/100 ml), stirring speed (50-300 rpm), initial metal ion concentration (5-500 mg/l) and contact time (5-120 min). The adsorption for Pb (II) was
found to be 84 %, 76 % and 70 % with natural form of *Arachis hypogea* shells, *Delbergia sissoo* pods and *Acacia saligna* pods respectively at 6.0 pH. Removal efficiency was enhanced to 90 %, 94 % and 98 % by a carbonized form of biosorbents. Maximum adsorption efficiency of Cd (II) was found to be 95 %, 78 % and 82 % for *Arachis hypogea* shells, *Delbergia sissoo* pods and *Acacia saligna* pods respectively in natural form and almost complete removal of Cd (II) was observed using immobilized and carbonized form.

Classical adsorption models such as Langmuir and Freundlich models were used to describe the equilibrium established between adsorbed metal ions on the biomass and metal ions remaining in solution at a constant temperature. The experimental results obtained for the adsorption of selected heavy metals on biosorbents under predefined conditions of pH, adsorbent dose and stirring speed obeyed the Freundlich adsorption isotherm. Value of n near unity or more supports the good fit of model. The good fit of Intraparticle diffusion and Pseudo second order kinetic studies was observed.

Fixed bed column studies using immobilized biosorbents were carried out for the sequestering of Cr (VI), Ni (II), Cd (II) and Pb (II). The effect of variation in bed height (12 cm and 17 cm), initial metal ion concentration (50 mg/l and 100 mg/l) and feed flow rate (1.5 ml/min and 3.0 ml/min) on removal efficiency was investigated. Optimized conditions obtained from a set of experiments were 17 cm bed height, 1.5 ml/min flow rate and initial metal ion concentration of 50 mg/l. Maximum adsorption capacity was found to be 14 mg/g, 15.5 mg/g and 15.75 mg/g with immobilized ASP, DSP and AHS respectively, with breakthrough time of 640 min, 730 min and 780 min respectively for removal of Cr (VI).

Maximum adsorption capacity was found to be 13.5 mg/g, 13.5 mg/g and 12 mg/g with immobilized ASP, DSP and AHS respectively, with breakthrough time of 540 min, 540 min and 480 min respectively for Ni (II) from aqueous solutions. Maximum adsorption capacity was found to be 13.5 mg/g to 15 mg/g, respectively by immobilized form of biosorbents at
breakthrough time of 420 min to 600 min at bed height (17 cm), feed flow rate (1.5 ml/min) and initial metal ion concentration (50 mg/l) in case of Pb (II) and Cd (II).

FT-IR studies reveal the plausible contribution of many functional groups such as –OH, OCH₃, C=O etc. for the binding of metal ions. The major shifts in the peaks assigned to these groups after loaded with metal ions signifies the involvement of complexation along with other process such as chemisorptions, adsorption on the surface and pores, ion exchange and diffusion. XRD study suggests the biosorbents were converted into semi crystalline powder on carbonization. The size of the biosorbent was found at nano-scale in carbonized form as compared to micro-scale in natural form, thus leading to increased surface area available. Enhanced removal efficiency in immobilized biosorbents may be due to uniform distribution of binding sites on surface of beads and reduced rate of desorption of metal ions back to solution.

The industrial effluents were collected from the nearby tannery and chrome plating industries and were characterized for analyzing the concentration of various heavy metals such as Ni (II), Cr (VI), Cd (II), Zn (II) and Pb (II). The results gauged from simulated solutions were employed to the industrial effluent to explore the potential of biosorbents for practical suitability. Significantly high removal efficiency was observed revealing the capability of biosorbents for the removal of heavy metals from industrial effluents.

The results of biosorption capacity of selected biosorbents (ASP, DSP and AHS) for the sequestering of Ni (II), Cr (VI), Cd (II) and Pb (II) from simulated as well as industrial effluents has demonstrated the potential of biosorbents. Thus biosorption technology using leguminocellulosic waste biomass offers paradigm shift from chemical intensive approach to greener solutions.