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Introduction

1.1 General introduction

Rapid industrialization has subjected the environment to immense stress which is manifested in the form of degradation of several ecosystems due to the accumulation of various toxic pollutants such as the heavy metals. Heavy metal contamination is prevalent in the aqueous streams of industries such as, textiles, paper and pulp, tanneries, chlor-alkali, electroplating, fertilizers, battery manufacturing units, dying and mining operations (Manzoor *et al.* 2013). Heavy metal ions like Pb(II), Cu(II), Cd(II), As(III), Co(II), Ni(II), Zn(II), Cr(II), Hg(II), Mn(II) are the major pollutants present in waste water (Barbarinde *et al.* 2006) and unlike the organic pollutants, these metals are characteristically noxious, non-biodegradable and persistent and tend to accumulate in living organisms resulting in occurrence of diseases and disorders (Bailey *et al*. 1999; Bilal *et al.* 2013). Most metals are carcinogenic and can interfere with the normal growth and development of the embryo. Metal toxicity can also lead to nervous disorder, organ failure, diminished growth and oxidative stress (Nagjyoti *et al.* 2010; Lee *et al.* 2012). The factors like the metal species, pH of the aquatic system, concentrations and solubility of the metal ions, as well as the type of waste

water, influences the toxicity of metals (Chipasa, 2003). The heavy metals from the environment gets incorporated in the food chain and is eventually consumed by human beings (Lin *et al.* 2000) The human physiology is incompetent in processing and disposal of metals and as a result, the metal ions are deposited in the living tissues causing detrimental changes to the body (Gavrilescu, 2004; WHO 2007). Table 1.1 illustrates some deleterious effects of heavy metals on human health.

For the protection of the environment as well as for the maintenance of the overall constitution of the ecosystem, it has become imperative that the industrial effluents containing these contaminants must be essentially treated so that the trace quantities of metal ions can also be effectively removed (Harvey and Chantawong, 2001). Several physical, chemical and biological techniques have been designed and adopted over the years for the treatment of waste water. The conventionally operated techniques include ion-exchange (Alyuz and Veli, 2009), membrane filtration (Shaalan *et al.* 2001), electrolysis (Abou-Shady *et al.* 2012), coagulation (Song *et al.* 2006), floatation (Mavrov *et al.* 2003), adsorption (Hegazi, 2013). Among all the above mentioned methods, adsorption is likely to be the most efficient as it provides rapid results, is simple in design, effectual at low concentrations and is highly cost-effective (Aksu and Yener, 2001). Moreover it has metal regeneration capability and the adsorbents can also be reused (Demirbas, 2008).

Currently, the focus has shifted towards the utilization of different adsorbents for the removal of pollutants from the industrial wastes. Large quantities of natural materials available locally or a particular waste material arising from industrial or agricultural practices may be expended as a potential adsorbent (Bailey, 1999). Biosorption has emerged as a practical approach towards removal of pernicious heavy metals from water and waste water at low concentrations. It involves application of inactive waste biomass for removal of heavy metals from aqueous solutions (Jain *et al.* 2016).

These include wood (Poots *et al.* 1978), pine bark (Al-Asheh and Duvnjak, 1997), peanut shells (Wafwoyo *et al.* 1999), hazelnut shell (Cimino *et al.* 2000), rice husk (Mishra *et al.* 1997), grape bagasse (Farinella *et al.* 2008), heartwood powder of *Areca catechu* (Chakravarty *et al.* 2011), seeds of *Ziziphus spina-Christi* (Omri and Benzina, 2012). Extensive investigation on use of microorganisms as biosorbents has also been carried out. Microorganisms due to their diverse properties like growth in different conditions, pH, temperature and characteristic cell wall organization have played an important role in removal of heavy metals from aqueous media (Munoz *et al.* 2012).

The present study is undertaken with the purpose of exploring the dimension of biosorption of heavy metals using seeds of *Adenanthera pavonina* (red sandalwood) tree. These seeds are copiously available in the loacality, are inexpensive untapped plant materials and have high surface area and sorptive properties which make it an appropriate biosorbent. The seeds of *Adenanthera pavonina* are examined to understand its potentiality to adsorb selected metal ions viz. Pb(II), Cu(II) and Cd(II), from simulated waste water solutions. The biosorption experiments are conducted in batches to determine the percentage removal of heavy metals for single ion solutions of each metal as well as in combinations in binary and ternary metal ion solutions. In order to understand the efficiency of the powdered seeds of *Adenanthera pavonina* (PSAP) to remove heavy metal ions in real environmental conditions, adsorption experiments are also conducted using actual industrial waste water.

The current work analyses the removal of heavy metals under various experimental conditions. The effect of pH, adsorbent dose, initial metal ion concentration and contact duration are primarily studied in order to establish the optimum conditions necessary for the

Table 1.1 Hazardous effects of heavy metals on human health

Heavy metals	Effects	References
Pb(II)	Seizure and mental retardation, encephalopathy, reduction in production of haemoglobin	Quaiser *et al.* 2007; Arief *et al.* 2008
Cu(II)	Insomnia, liver damage, Wilson's disease	Kurniawan *et al.* 2006b
Cd(II)	Renal disorder, kidney damage, cancer, hypertension, bone demineralization	Arief *et al.* 2008, Purkayastha *et al.* 2014
Cr(III)	Cancer, allergic skin reactions	Vilar *et al.* 2007
Cr(VI)	Carcinogenic, adversely potential to modify the DNA transcription process, headache, nausea, epigastric pain, haemorrhage, severe diarrhea	Quaiser *et al.* 2007; Arief *et al.* 2008
Zn(II)	Depression, lethargy, neurological effects (seizures and ataxia)	Hlihor and Gavrilescu (2009)
Ni(II)	Dermatitis, chronic asthma, coughing, bronchial haemorrhage, gastrointestinal distress, nausea, weakness and dizziness	Vilar *et al.* 2007, Arief *et al.* 2008, Dahiya *et al.* 2008
As(III)	Vomiting, esophageal and abdominal pain, cancer, dermatological diseases	Shafique *et al.* 2012

removal of heavy metals, Pb(II), Cu(II) and Cd(II). Based on these optimized values, the removal experiments are conducted for the binary and ternary solutions as well as for the industrial waste water. Statistically acceptable Plackett-Burman design is created to carry out the biosorption of metal ions in a three metal mixture and the results are tested using Analysis of Variance (ANOVA) and Student's t-test.

Adsorption/biosorption equilibria provide a valid foundation to the analysis and designing of adsorption/biosorption process. Similarly, the mechanism of adsorption and identification of the rate-controlling steps is done by exploiting the adsorption kinetic models (Febrianto *et al.* 2009). In the current study the experimental data are tested with the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the isotherm constants are determined to understand the efficacy of biosorption. The pseudo first-order,

pseudo second-order, Elovich kinetic model and the intra-particle diffusion model are studied in order to understand the adsorption kinetics in removal of Pb(II), Cu(II) and Cd(II) by PSAP.

1.2 Aims and objectives

Adenanthera pavonina (red sandalwood) is widely available in low elevations of north-east India and is endemic to south-east Asia. The seeds of *Adenanthera pavonina* trees are chosen as biosorbent for the current study. The adsorbent characteristics of the seeds have not yet been reported in literature. Thus with the goal of sustaining ecological and social health, it is indispensible to pursue and contribute a realistic and economical approach to remove heavy metals. Hence, the seeds of *Adenanthera pavonina* demonstrate as a locally available, environmentally friendly, and cost effective adsorbent.

The current study aims at scrutinizing the potentiality of the *Adenanthera pavonina* seeds in removal of heavy metals from simulated waste water. In order to achieve the above mentioned aim, the following objectives are adopted.

i. To characterize the biosorbent using procedures like determination pH_{pzc}, determination of moisture content, CHNS analysis, FTIR spectroscopy, FESEM-EDX analysis and estimation of BET surface area, pore size and pore volume, in order to understand the structural, morphological and elemental information of the biosorbent.

ii. Study the biosorption characteristics of the metal ions from their aqueous solutions over a range of contact time, initial metal ion concentrations, biosorbent dose and solution pH at room temperature, using batch experiments.

iii. Study of the adsorption isotherm models (Langmuir adsorption isotherm, Freundlich adsorption isotherm, Temkin adsorption isotherm and Dubinin-Radushkevich adsorption isotherm) to determine the maximum adsorption capacity of the biosorbent for each metal.

iv. Study of adsorption kinetics of the adsorbed metal ions using Lagergren's pseudo-first order, McKay and Ho's pseudo-second order, Elovich, and Weber and Morris's intra-particle diffusion models.

v. Analysis of the competitive biosorption in binary and ternary metal ion solutions.

vi. Study biosorption of metal ions from industrial waste water on the surface of the biosorbent.

1.3 Significance of the study

With the rampant industrialization in modern era and simultaneous production of wide range of chemical compounds, the quality of the environment has degraded worldwide. Heavy metals, unlike organic pollutants, are substantially non-biodegradable and have a tendency to accumulate in living organisms. Heavy metals are released from mining and electroplating industries and also from tanneries, thereby contaminate the freshwater and marine ecosystems. In recent times, heavy metals are considered to be most important pollutants in surface and ground water (Gavrilescu, 2004; Brinza *et al*., 2009; Baysal *et al*., 2009). All aerobic and anaerobic organisms require trace quantities of heavy metals as essential minerals. But it has been proven that consumption of these heavy metals beyond a recommended concentration can critically affect human physiology. Since human body is incapable of processing and disposing heavy metals, these gradually accumulate in different

tissues and internal organs of the body which can trigger adverse reactions and consequential damage to the body (Gavrilescu, 2004). The contamination of different water bodies with heavy metals and the exposure of aquatic organisms, including fishes, to these harmful pollutants, is a serious issue as heavy metals on being incorporated in the food chain can bio magnify due to absence of bio degradation of these elements. As a result the problem demands continuous surveillance and monitoring of the aquatic ecosystems. Keeping in view the toxicological impacts of heavy metals on the living biota, it is of paramount importance that sector specific methods and technologies must be adopted so as that waste water effluents are treated before being discharged into the environment. Since the conventional technologies for removal of heavy metals from water and waste water suffer from numerous disadvantages, biosorption on the other hand, proves to be a very feasible alternative technique for sequestering heavy metal ions. Thus the current study focuses on exploring the possibilities of *Adenanthera pavonina* seeds as a potential and economical technique for heavy metal removal from waste water.

1.4 Organization of the thesis

The thesis is sequentially arranged into six chapters. The arrangement of the research work is as follows.

Chapter 1 delineates a framework of the study and highlights the need for the removal of heavy metal ions (Pb, Cu, Cd) from the waste water using different biosorbents. This chapter also presents the aims and objectives of the thesis along with the thesis organization.

Chapter 2 provides information about the various dimensions of heavy metal contamination and toxicity. The chapter also focuses on the different conventional as well as novel technologies available for sequestration of heavy metals from their aqueous solutions. This chapter extends a profound description of the several theories that form the basis for the

interpretation of the experimental results. An overview of the related knowledge on biosorption processes is also given in chapter 2.

Chapter 3 elucidates the biological characteristics of the *Adenanthera pavonina* plants as well as their role in the environment from regional, national and global perspective. The chapter also includes a description on the chemical composition of the *Adenanthera pavonina* seed oil.

Chapter 4 refers to the methodology adopted to accomplish the biosorption experiments in batch system. The analytical procedures adopted for the characterization of the biosorbent (powdered seeds of *Adenanthera pavonina*, PSAP) are also incorporated here.

Chapter 5 furnishes the results obtained from the biosorption experiments operated under different experimental conditions along with the valid discussion and explanations. The detailed report on the characterization of the biosorbent is also presented in this chapter along with the adsorption equilibrium and kinetic models obtained for each metal ion studied. At the end of the chapter a brief report on cost estimation of the biosorbent is also included.

Chapter 6 showcases the comprehensive conclusions that are drawn on the basis of the findings obtained in the previous chapter. Recommendations for future research are also suggested in this chapter.

At the end of the disquisition, a list of reference of the closely related studies is included.