REMOVAL OF HEAVY METAL IONS FROM SYNTHETIC WASTEWATER USING LOW COST BIOSORBENTS

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Certificate

This is to certify that the project work embodied in this dissertation entitled **“Removal of Heavy Metal Ions from Synthetic Wastewater using Low Cost Biosorbents”** has been carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma of any other institute or university.

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…… Dedicated to

My Parents

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CHAPTER-I

INTRODUCTION

1. Introduction and Literature Review

Survival of living being cannot be imagined without water. It sustains life and is available in large quantity as the free gift of nature. Water considered as an abundant renewable resource, is now becoming an inadequate resource (Mehta, 2007). On this planet water is not evenly distributed. Fresh water is only 3% of the total water available on earth out of that only 0.01% is available for human consumption (Hinrichsen and Tacio, 2002). Fresh water is available as surface water and groundwater. Groundwater contributes only 0.6% of the total water resources on the earth, and is a preferred source of drinking water in rural as well as urban areas in India (Meenakshi and Maheshwari, 2006).

Various geogenic and anthropogenic sources are responsible for ground and surface water pollution (Kass et al., 2005; Amina et al., 2004; Oren et al., 2004; Anwar, 2003). Geometric increase in population, rapid urbanization, industrialization, agricultural development and modern technology have impacted adversely on quality and quantity of water in India (CPCB, 2010). Depletion of available freshwater resources, declining ground water levels and deteriorating water quality are important factors, raising several challenges in India to manage water resources. The annual per capita availability of renewable freshwater in the country has decreased from 6042 cubic meters in 1947 to 1845 cubic meters in 2000 (CPCB, 2010). More and more ground water resources are depleting and polluting too much surface water, without pondering over future (CPCB, 2010).

The main anthropogenic sources of water pollution in India include textiles, pharmaceuticals, ceramics, petrochemicals, food, steel, oil mills, sugar, fertilizer, and leather tanning industries (Sial et al., 2006). Various contaminants including fluoride, chloride, arsenic, nitrate, sulfate, pesticides, dyes and heavy metals have been reported in water from different parts of India (Liu et al., 2005; Charles et al., 2005; Muhammad et al., 2004; Rukah et al., 2004; Mulligan et al., 2001).

Groundwater contamination due to the high nitrate concentration has become a significant environmental problem in many parts of the world (Rao, 2006; Rivett et al., 2007; Roy et al., 2007). As per the BIS standard for drinking water, the maximum permissible limit of nitrate is 45 mg/L. The main anthropogenic sources of nitrate are sewage effluents and excessive dose of nitrogenous fertilizers from cropping system (Suthar, 2009). The most common impact of nitrate ingestion on health is a type of blood disorder called "Methemoglobinemia" commonly known as blue baby syndrome (Suthar et al., 2009). A high level of nitrate in water is one of the reasons that resulted in increased risk for respiratory tract infections in children (Gupta et al., 2000; Weyer et al., 2001). Ground water level of nitrate (>45 mg/L) has been reported from Andhra Pradesh, Bihar, Delhi, Haryana, Orissa, Punjab (CGWB, 2008).

Iron is commonly available in water either as a soluble ferrous iron or the insoluble ferric iron. The BIS permissible limit of iron in drinking water is <1.0 mg/L. High concentration of iron (>1.0 mg/L) in ground water has been found in many states including Andhra Pradesh, Assam, Bihar, Chhattisgarh, Goa, Gujarat, Haryana, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Manipur, Meghalaya, Orissa, Punjab, Rajasthan, Tamil Nadu, Tripura, Uttar Pradesh, West Bengal and Andaman & Nicobar (CGWB, March 2008).

Arsenic is a naturally occurring trace element found in rocks, soil and water. Arsenic has been recognized as a toxic element and is considered a human health hazard. The BIS permissible limit of arsenic in ground water is 0.01 mg/L (BIS, 1991; Mohan and Pittman, 2007). Continuous consumption of arsenic contaminated water can cause various health disorders including birth complications and cancer (Li et al., 2008; Tokar et al., 2011). In India ~10 million people are at risk on account of arsenic contamination (Ghosh et al., 2007). In West Bengal, 79 blocks in 8 districts have been affected with arsenic contamination. The most affected areas are the eastern side of Bhagirathi river in the districts of Malda, Murshidabad, Nadia, North 24 Parganas and South 24 Parganas and western side of the districts of Howrah, Hugli and Bardhman (CGWB, 2008). Apart from West Bengal, arsenic contamination in ground water has been found in Bihar, Uttar Pradesh, Assam and Chhattisgarh (CGWB, 2008). Over exposure to arsenic may cause a decrease in production of white and red blood cells, gastrointestinal irritation, disruption in the heart rhythm, damage blood vessels and cause "pins and needles" sensation in hands and feet (Abernathy et al., 2003).

The ground water having chloride concentration >1000 mg/L is not suitable for drinking purposes. High values of chloride (>1000 mg/L) are reported in Andhra Pradesh, Delhi, Gujarat, Rajasthan and Tamil Nadu (CGWB, 2008).

Fluoride is essential as well as harmful for human being. Most of the fluoride found in groundwater is naturally occurring from the breakdown of rocks and soils or weathering and deposition of atmospheric particles (Jagtap et al., 2012). BIS has recommended 1.0 mg/L as desirable limit and 1.5 mg/L as permissible limit in drinking water. Its excessive intake causes fluorosis. Fluorosis is prevalent in 17 states of India including Assam (0.2–18.1 mg/L), Andhra Pradesh (0.11–20.0 mg/L), Bihar (0.6–8.0 mg/L), Delhi(0.4–10.0 mg/L), Gujarat (1.58–31.0 mg/L), Haryana (0.17–24.7 mg/L), Jammu and Kashmir (0.05–4.21 mg/L), Karnataka (0.2–18.0 mg/L), Kerala (0.2–2.5 mg/L), Maharashtra (0.11–10.2 mg/L), Madhya Pradesh (0.08–4.2 mg/L), Orrissa (0.6–5.7 mg/L), Punjab (0.44–6.0 mg/L), Rajasthan (All the 32 districts 0.2–37.0 mg/L), Tamilnadu (1.5–5.0 mg/L), Uttar Pradesh (Unnao, Agra, Meerut, Mathura, Aligarh, Raibareli, Allahabad 0.12–8.9 mg/L), and West Bengal (Birbhum, Bhardaman, Bankura 1.5–13.0 mg/L) (Susheela, 1999).

In addition to the above geogenic sources, anthropogenic activities also make ground water contaminated. Some of the sources included dyes, phenol, heavy metal, pesticides, PAH, pharmaceutical industries (Verma et al., 2012; Ji et al., 2012).

Wastewater containing dyes causes several problems because of its high toxicity and possible accumulation in the environment. The main sources are textile, dyeing and finishing industries that liberate dyes into the water. Most of these dyes are synthetic in nature and are classified on the basis of their chemical structures as azo, anthraquinone, triphenylmethane and phthalocyanine derivatives. Most of these dyes contain aromatic rings, which have carcinogenic and mutagenic effects (Robinoson et al., 2001; Mittal et al., 2006). There are about 10,000 garment manufacturers and 2100 bleaching and dyeing industries in India. Majority of them are concentrated in Tamil Nadu, Punjab and Gujarat (Ravikumar and Dutta, 1996). Gujarat is one of the most industrialized states in India and has many traditional textile units. It is a major producer of chemicals, polymers, fertilizers, dyes and dye intermediates, synthetic resins, paints and inks. Gujarat accounts for 20% of the chemicals manufactured in India. In this state more than 750 units are engaged in the manufacturing of dyestuffs (Rathi, 2002).

Heavy metals are extremely toxic. These are found in soil, surface and groundwater due to anthropogenic activities include discharged of industrialized wastewater without any treatment into natural ecosystems including rivers, lakes, and other water bodies (Larison et al., 2000). Consequently, heavy metals pose a potential threat to various terrestrial and aquatic organisms including human health (Hsu et al., 2006; Wei et al., 2010).

Chromium, lead, cadmium, nickel are the important heavy metals found in ground and surface water in India (Saha et al., 2006). The main anthropogenic sources of chromium are electroplating, metal finishing, magnetic tapes, pigments, leather tanning, chemical manufacturing, brass, electrical & electronic equipment and catalysis industries (Mohan et al., 2006). The permissible limit and desirable limits of chromium in drinking water is 0.05 mg/L (BIS, 2003). India is a leading leather manufacturing country. Kanpur, one of India's most polluted cities possesses more than 60 tanneries situated on the bank of pious river the Ganga. Tanning process requires a lot of water and most of the untreated waste is discharged into local groundwater and the Ganges River (Mohan et al., 2006). The wastewaters produced from these units are the main source of chromium contamination in Kanpur and nearby areas.

The major sources of lead pollution in natural waters include the discharge of waste from acid battery manufacturing, metal plating and finishing, printing, metallurgical alloying, lead mining, ceramics and glass industries (Jalali et al., 2002; Patel et al., 2006). Lead in general is responsible for metabolic poison and enzyme inhibiton (King et al., 2007). The anthropogenic emission of lead is at least 100 times higher than natural emissions (Patel et al., 2006). High concentrations of lead (13–545 $\mu g\ g^{-1}$) have been found in Chhattisgarh state of central India.

The main constraints that inhibit the better management of the water quality in India are unpredicted rainfall, uneven geographic distribution of surface water resources, overuse of ground water, salinisation of water and partially treated and untreated wastewater from urban settlements (CPCB, 2010). These environmental challenges may be mitigated through four broad approaches including improving efficiencies and minimizing losses of water, recharging groundwater aquifers, abatement and treatment of water pollution and reuse and recycling of wastewater (CPCB, 2010). In most parts of the country, wastewater from domestic and industrial sources is hardly treated. This wastewater contains high amount of organic and inorganic pollutants. Poor environmental management systems, especially in thermal power stations, chemicals, metals and minerals, leather processing and sugar mills, have lead to discharge of highly toxic and organic wastewater (CPCB, 2010).

The enforcement of regulations in discharge of industrial wastewater and limited extraction of groundwater needs to be strengthened, while more incentives are required for treating wastewater and its reuse and recycling to be enforced (CPCB, 2010). Non-biodegradability, persistency and accumulation in multiple factor at higher trophic level made heavy metals pollution is a serious concern in the environment and this required attention (CPCB, 2010).

Various methods were used to treat water having metal ions concentration. These include filtration (Zouboulis et al., 2002), solvent extraction (Lee et al., 2000), activated sludge (Bromley-Challenor et al., 2000), bacterial treatment (La Para et al., 2000), irradiation by nuclear radiations (Rela et al., 2000; Basfar et al., 2002), ultrasonic treatment (Suzuki et al., 2000), and magnetic separation (Karapinar, 2003). These wastewater treatments technologies are significant in water treatement but they produce other harmful effects in various manners. Although traditional methods have better efficiency to remove heavy metals but these methods are expensive and even ineffective and expensive in the concentration range of 1-100 mg/ L (Ceribasi and Yetis, 2001). The comparative evaluation of traditional methods is shown in table 1.1.

Adsorption method to remove heavy metals has been widely used. Some selective adsorbents to remediate heavy metals include red mud (Gupta et al., 2001), coal (Lakatos et al., 2002), photocatalyst beads (Idris et al., 2010), nanoparticles (Liu et al., 2010; Yuan et al., 2010), multi-walled carbon nanotubes (Pillay et al., 2009), biomass (Sharma et al., 2009) and activated carbon fabric cloth (Mohan et al., 2005). Activated carbon is considered to be the most appropriate option for metal remediation from wastewater. Despite the above facts activated carbon is expensive to use in daily practices.

Low cost biosorbents have gained momentum to remediate proteins, steroids, pharmaceuticals, drugs, precious metal and radioactive element (Sag et al., 2001; Tsezos, 2003; Tsuruta, 2004). These biosorbent can be used either in living or nonliving forms and has drawn worldwide attention (Wase and Forester, 1997).

Table 1.1 Advantages and disadvantages of traditional metal removal technologies (Source- Volesky, 2000; O'Connell et al., 2008)

Methods	Advantages	Disadvantages
Chemical precipitation and filtration	-Simple -Inexpensive -Removal of almost all metals	-At higher concentration difficult separation processes -Production of large amount of sludge
Chemical coagulation	-Sludge settling -Dewatering	-High cost -High amount of chemical consumption
Chemical oxidation or reduction	-Mineralization	-Slow rate in biological system
Electrochemical treatment	-Recovery of metals -Metal selective -No consumption of chemicals -Ultra pure metals can be achieved	-Expensive at high concentration -High capital costand running cost -Initial solution pH and current density
Reverse osmosis	-Pure effluent	-At high pressure scaling of membrane
Ion exchange	-Recovery of metals -Metal selective -High regeneration of material	-Resin is expensive -Less number of metal ions removed
Adsorption	-Conventional sorbent carbon -High efficiency	-Not for metals -Cost of activated carbon
Membrane process and ultrafilteration	-Less chemical consumption -High efficiency	-Expensive and generation of sludge -High initial and running cost -Low flow rates -Percent removal decrease in the presence of other metals

Biosorption is described as the removal of contaminants by the passive (not metabolically controlled) binding to non-living biomass from an aqueous solution (Davis et al., 2003). The biosorbents possess metal-sequestering property and can be used effectively and efficiently to decrease the concentration of toxic ions in solution. It can also effectively sequester dissolved metal ions with high efficiency and therefore it is well suited for the treatment of high volume and low concentration complex wastewaters (Wang and Chen, 2006). The biosorption is considered to be the most perspective way to clean environment at low capital cost. Its non-invasiveness, minimum operational cost, easy implementation and high acceptance in public draw their attention to use at worldwide levels (Wase and Forester, 1997). Uptake of metals by living materials is called bioaccumulation but the same uptake by dead biomass is called biosorption. The major differences between biosorption and bioaccumulation are given in Table 1.2.

Table 1.2 Differences between biosorption and bioaccumulation

(Source- Chojnacka, 2010)

Biosorption	**Bioaccumulation**
Passive process	Active process
Dead biomass	Live biomass
Metals are bounded with cellular surface	Metals are bound with cellular surface and interior
adsorption	absorption
Reversible process	Partially reversible process
Nutrients are not required	Nutrients are required
Single stage process	Double stage process

A variety of biosorbents including algae, fungi, yeast, moss, bacteria and agricultural wastes are used to sequester heavy metals from water and wastewater (Davis et al., 2003; Wang and Chen 2006; Davis et al., 2006; Varma et al., 2006; Ahluwalia and Goyal, 2007). Major biosorbents used in remediation of metals and dye are hazelnut shells, peanut hulls, walnut shells, and green coconut shells (Johns et al., 1998;

Kurniawan et al., 2006). Maple sawdust, oak, black locust, *Cassia fistula* biomasses were used for the removal of nickel (Hanif et al., 2007; Sciban et al., 2006; Shukla et al., 2005). Mustard oil cake was used to remediate nickel, copper, zinc, chromium, mangenese, cadmium, and lead (Ajmal et al., 2005). The other biosorbent used for various contaminants are *Rhizopus oryzae* biomass for dye rhodamine B, sugar-beet pulp pectin gels for heavy metals and Boston ivy leaf powder for ammonia (Das et al., 2006; Mata et al., 2009; Liu et al., 2010). Some commercial available biosorbents are AlgaSORB^{TM}, B.V. Sorbex AMT-Bioclaim^{TM}, Bio-Fix, RAHCO, Bio-Beads (Park et. al., 2010).

Some of the important studies related to the present investigation are discussed in the subsequent paragraphs.

Akar et al. (2009) investigated, agro-waste product (waste of *Phaseolus vulgaris L.*) to remediate reactive textile dye from aqueous solutions. The batch biosorption experiments have been conducted at various pH, biosorbent dosage, contact time and temperature. Biosorption efficiency of Brazilian pine-fruit shell towards reactive red 194 textile dye removal from aqueous solution was studied by Lima et al., (2008). The effects of shaking time, dose and pH on biosorption capacity have been investigated. In acidic pH region (pH 2.0) the biosorption was favorable. The equilibrium data were fitted to Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models. *Arundo donax L.* (hydrophyte) reed based anion exchange resin was used for nitrate removal from aqueous solution by Xu et al., (2012). The maximum adsorption capacity (Q_{MAX}) for nitrate was 44.61 mg/g.

Artificial neural network (ANN) model was applied by Giri et al., (2011) to explore the removal efficiency of *Bacillus cereus* for arsenic from aqueous solution. The maximum biosorption of arsenic (III) was 85.24% at pH 7.5, equilibrium time of 90 minutes, biosorbent dose of 6 g/L. The experimental data was used to train a back propagation (BP) learning algorithm having 4-7-1 architecture. The model used tangent sigmoid function. 75% of data was taken as training and 25% for testing. High degree of correlation (R^2 = 0.986) was reported between experimental and modeled data. A mathematical model was used to develop the biosorption phenomenon of lead, cadmium, and zinc transport through porous fiber matrice in lignocellulosic material (chemically modified hemp fibers) by Pejic et al., (2011). These results showed that the biosorption process was fast at the beginning and became slow over a period of time. This may be due to electrostatic repulsive interactions between ions into the fibers. The effective diffusion coefficients of metal ions through the fibers, and the effectiveness of sorption were determined by a mathematical model based on the second Fick's law. Proposed mathematical model optimized the complex process of biosorption in better way through porous fiber matrices.

Biomatrix prepared from rice husk was studied by Krishnani et al., (2008). Biomatrix was prepared by partial alkali digestion of rice husk. This matrix efficiently removed Ni, Zn, Cd, Mn, Co, Cu, Hg, and Pb in single and mixed metal solutions. Adsorption followed both Langmuir and Freundlich isotherm models. This was probably due to the real heterogeneous nature of the surface sites involved in the metals uptake. It was concluded that biomatrix has calcium, magnesium OH and COOH groups in the lignocellulosic materials and ion exchange is the dominating mechanism. Yun et al. (2001) investigated protonated brown algae (Ecklonia) biomass for biosorption of Cr^{3+}. Carboxyl groups present in the biomass were responsible for binding of trivalent chromium in the pH range of 1.0 - 5.0.

Microalga (*Chlorella miniata*) was used to remediate chromium (Han et al., 2007). Experiments were conducted to determine the mechanism and uptake capacity of Cr^{6+}. The capacity of total Cr [$Cr^{3+}$and Cr^{6+}] was maximum at an initial pH of 3.0. FTIR analysis confirmed the presence of amino groups on the algal biomass was the major adsorption site for Cr^{6+} biosorption in acidic pH while the reduced Cr^{3+} was mainly sequestered by carboxylate groups. Dried *Fucus vesiculosus, Fucus spiralis, Ulva linza, Ulva compressa, Ulva intestinalis,Ulva lactuca, Palmaria palmate and Polysiphonia lanosa* were utilized for chromium biosorption by Murphy et al., (2008). The metal sorption was pH dependent. The maximum sorption for $Cr^{3+}$and Cr^{6+}occured at pH 4.5 and pH 2.0 respectively. The equilibrium time required for Cr^{6+} and Cr^{3+} binding were 180 and 120 minutes respectively. The highest removal efficiency for both Cr^{3+} and Cr^{6+}

was observed for *Palmaria palmate* (red sea weed). Chromium binding capacity of ulva species was due to amino, carboxyl, sulphonate and hydroxyl groups.

Chromium biosorption mechanism is a complex process due to the presence of different compounds in biomaterials. Park et al., (2008) used XAS and XPS to determine the chromium binding groups during Cr^{6+} biosorption on brown seaweeds (Ecklonia) and it was established that Cr^{6+} had an octahedral geometrical arrangement during binding. The bond distance between chromium and oxygen was 1.97-1.99 Å. Oxygen containing groups, carboxylic and phenolic groups helped in Cr^{3+} binding. Cr^{3+} formed because of Cr^{6+} reduction by biomass (Park et al., 2008).

The different aquatic weeds reed mat (*Cannomois Vvirgata*), water lettuce (*Pistia stratiotes*), arrow-leaved tear thumb (*Polygonum sagittatum*), lotus flower (*Nelumbo nucifera*), green taro (*Colocasia esculenta*), water lily flower (*Nymphaea sp.*), water hyacinth (*Eichornia crassipes*), and mangrove leaves (*Rhizophora mangle L*) were utilized for $Cr^{3+}$and Cr^{6+} removal (Elangovan et al., 2008). The kinetic and equilibrium experiments confirmed that mangrove leaves had Cr^{6+} removal capacity of 8.87 mg/g followed by water lily flower (8.44 mg/g). The maximum adsorption capacity by reed mat was 7.18 mg/g. Cr^{6+} was reduced to Cr^{3+} by tannin, phenolic compounds and different functional groups present in the biosorbent. Treatment with acids significantly increased Cr^{6+} removal capacity of all the biosorbents while alkali treatment reduced the Cr^{6+} removal capacities.

Zvinowanda et al. (2009) investigated maize tassel as an alternative adsorbent for Cr^{6+} removal. Experiments have been carried out to find the effects of pH, temperature, contact time, initial metal ion concentration and adsorbent dose on Cr^{6+} adsorption in batch methods. The maximum removal occurred at ~pH 2.0 and at 25 ºC (equilibrium time of 1 hour). Maize tassel showed high percentage of Al, Mg and Si. These compounds may be responsible for the tough elastic properties exhibited by the tassel powder (Zvinowanda et al., 2009). The immense potential of maize tassel could be an alternative adsorbent for toxic metal ions remediation. Cinnamon bark (*Cinnamonum zeylanicum*) biosorbent was explored for chromium remediation by Zainal (2010). The batch experiments have been carried out to know the potentiality of this biosobent for chromium removal. The optimum pH was 2.0 while equilibrium time was two hours. The biosorption data were well fitted to Dubinin-Radushkevich (D-R), Freundlich and Tempkin adsorption isotherm model. The maximum adsorption capacity was 12.49 mg/g.

The waste biomass of seaweed *Kappaphycus alvarezii* was also used as potential biosorbent for chromium removal (Kang et al., 2011) at pH 3. The maximum sorption capacity was 0.86 mg/g. Langmuir, Freundlich and BET isotherms models were applied to find mechanisms. Ion exchange coupled with a complexation was the dominating mechanism. In the presence of copper and cadmium, the removal capacity was suppressed.

Peanut shells were explored to remove chromium from water (Krowiak et al., 2011). Several mathematical models were applied to determine the biosorption mechanisms. Langmuir model fitted the data well. Pseudo-second order kinetic model best fit the data. Complete biosorption occurred at an equilibrium time of 20 minutes. The maximum adsorption capacity of peanut shells was 27.86 mg/g.

Durian shell waste, a potential biosorbent was investigated by Kurniawan et al., (2011) for Cr^{6+} removal from wastewater. The study was carried out at different temperatures, pH and doses to determine maximum removal of chromium. Langmuir and Freundlich isotherm models were used to fit the data. The maximum biosorption capacity of durian shell was 117 mg/g. The biosorption process onto durian shell surface was spontaneous, irreversible and endothermic in nature. It was concluded that chemisorption was the dominating mechanism. Sorptive potential of sunflower (*Helianthus annus*) stem for Cr^{3+} from aqueous solution was studied by Malik et al., (2005). The 180-300 µm mesh size was used. The surface area of $2m^2/g$ was measured by BET method. In the presence of other ions, sorption capacity decreased. The equilibrium time for the reaction was 10 minutes. The proximate analysis of high density sunflower stem (180–300 µm) revealed that sunflower stem is composed of substantial amount of cellulose, hemicelluloses and lignin. The potential binding sites in the cells were carbohydrate, amine, hydroxyl, and other functional groups. Ion exchange and surface complexation were proposed as a possible mechanism. Kinetics data followed Reichenberg and Lagergren equations over the entire agitation time, while Morris–Weber equation followed partially up to 10 minutes. The D–R, Freundlich and Langmuir isotherm models well fitted the sorption data. Bisulphate, citrate, molybdate, Fe^{2+}, Fe^{3+} and Y^{3+} ions caused decrease in sorption capacity. The negative enthalpy and free energy confirmed the exothermic and spontaneous nature of the process.

Eichhornia crassipes, an aquatic submerged plant successfully remediate chromium from water (Mohanty et al., 2006). Its roots and stem were used for chromium removal. The biosorbent was characterized using FTIR. Hydroxyl groups were mainly responsible for the chromium binding in the pH range of 1–5. Initial part of the metal adsorption was governed by the diffusion process. The overall adsorption rate was best described by pseudo-second-order rate equation. The sorption data were well fitted by Freundlich model. *E. crassipesis* can be used to efficiently remove chromium for wastewater. Eucalyptus bark (EB) was used for chromium removal from wastewater (Sarin and Pant, 2006). Wastewater collected from metal finishing industry was also treated. The optimum pH for removal was ~2.0. Maximum removal capacity of EB was 45 mg/g. The isotherm data well fitted the Freundlich model. Kinetic data followed first order Lagergren model. The negative values of Gibbs free energy confirmed the feasibility and spontaneous nature of the process. The potential of low cost agro-based materials including *Tamarindus indica* seeds (TS), crushed coconut shells (CS), almond shells (AS), ground nut shellz (GS) and walnut shells (WS) were investigated for Cr^{6+} removal (Agarwal et al., 2006). Hexavalent chromium sorption capacity (q_e) followed the sequence q_e (TS) > q_e (WS) > q_e (AS) > q_e (GS) > q_e (CS). Sorption kinetic data followed first order kinetic model in all the cases. The equilibrium time was 150 minutes. Sorption data were well fitted to Freundlich isotherm model. Maximum desorption of Cr^{6+} was achieved by NaOH in downflow column mode. Native and acid treated algae (Pithophora) was explored for metal binding capacity (Priya et al., 2007). Experiments were carried out to determine Cr^{6+} removal at different pHs, amount of adsorbent and adsorbate concentration. The maximum removal occurred at pH 2.The adsorption capacities of native and acid treated algae were 434.10 and 666.21 mg/g respectively.

Singh et al. (2008) reported that *Cassia marginata* seed gum can remediate hexavalent chromium from water. Biosorbent *Cassia marginata* seed gum-graft poly (methyl methacrylate) was synthesized using microwave irradiation in the absence of any radical initiator or catalyst. Biosorbent synthesis was controlled by varying the amount of methyl methacrylate, microwave irradiation intensity and exposure time. Adsorbent characterization was performed using FTIR, XRD, TGA, and SEM. The sorption study was performed to determine the optimum pH, dose and concentration. The effect of electrolyte was also studied. pH 1.0 was the optimum value at which maximum removal of Cr^{6+} occurred .The adsorption capacity was 16.94 mg/g at an adsorbent dose of 5 g/L and at 30 °C. Freundlich and Langmuir isotherm models were applied. The adsorbent was also tested to treat industrial wastewater to efficiently remove Cr^{6+}.

Six different types of biosorbents namely rice husk, neem leaves, coconut shells, rice straw, rice bran and hyacinth roots were tested for removal of Cr^{6+} from aqueous solution (Singh et al., 2011). Except for rice husk, the optimum pH was 2.0 for all biosorbents. The optimum pH for rice husk was 1.5. The equilibrium time for all the adsorbent was in the range of 3-6 hrs. All adsorbents follow pseudo-second order rate model. Interaction between Cr^{6+} ions and natural adsorbents were chemical in nature. The adsorption process was endothermic and spontaneous in nature. Surface functional groups namely O–H, aliphatic C–H, unsaturated alkenes, aromatic $C–NO_2$, carboxylate anion, Si–O groups, $–SO_3$ and sulphonic acid groups were responsible for Cr^{6+} uptake. Rice husk, neem leaves and coconut shells adsorption data were best fitted to Langmuir isotherm model while rice straw, rice bran and hyacinth roots followed the Freundlich adsorption isotherm model. The seeds of various plant species can be used as an adsorbent for metal removal. The seeds of Nirmali plant were used as a biosorbent for chromium remediation by Lakshmipathiraj et al., (2011). Dried powered Nirmali seeds have binding potential for chromium metal. The major functional groups responsible for chromium adsorption were OH and COOH. The zeta potential was 1.50. The maximum removal of Cr^{6+} occurred at pH 1.0. The adsorption equilibrium was achieved within 4 minutes. The maximum removal capacity was 59 mg/g for Cr^{6+}. Interferences of anions on adsorptive capacity were insignificant. Adsorption followed pseudo second order rate equation. Free energy of the reaction was measured to be very high. Chemical and electrostatic interactions were the dominating mechanisms.

Duckweed (*Wolffia globosa*) (Upatham et al., 2002), saltbush (*Atriplex canescens*) (Sawalha et al., 2006), marine algal (*Padina boergesenli*) (Thirunavukkarasu and Palanivelu, 2007), moss (*Hylocomium splendens*) (Sari et al., 2008), walnut, hazelnut and almond shells (Pehlivan and Altun, 2008), *Agaricus bisporus* (Ertugay and Bayhan, 2008), waste tea fungal (Razmovski and Sciban, 2008), green algae (*Cladophora albida*) (Deng et al., 2009), pistachio hull waste (Moussavi and Barikbin, 2010) were also used for chromium remediation. The biosorption capacity of fungus (*Rhizopus nigricans)* for removal of lead in aqueous solution was 83.5 mg/g (Kojeg and Pavko, 2001).

Lalang (*Imperata cylindrica*) one of the worst weed of the world was utilized for lead adsorption (Hanafiah et al., 2006a). Sodium hydroxide treated Lalang was utilized by Hanafiah et al., (2006a). The optimum pH was in the range of 4.0 to 5.0. Pseudo-second order kinetic model was the best fitted model. The maximum adsorption capacities of NaOH treated and untreated *Imperata cylindrica* were 13.50 and 5.89 mg/g respectively (Hanafiah et al., 2007). Faster equilibrium time (20 minutes) was found for treated *Imperata cylindrica* versus untreated *Imperata cylindrica* (120 minutes).

Ashraf et al. (2010) reported fruiting buds of mango plant for lead removal in single and binary metal solution. 255-355 µm particle size was used in the experiment. The adsorption capacity was 24.4 mg/g at an initial adsorbate concentration of 147.41 mg/L. Ozer and Pirincci, (2006) studied the removal of lead by sulfuric acid treated wheat bran. Maximum lead removal of 82.8% was achieved at pH 6.0 after 2 hrs of contact time. Langmuir, Freundlich and Redlich-Peterson models were applied to determine the maximum adsorption capacity of wheat bran. Adsorption isotherm fitted well to the Redlich-Peterson isotherm models than Langmuir and Freundlich isotherm models. The sorption was endothermic in nature.

Wong et al. (2003a) used carboxylic acids (citric acid, salicylic acid, tartaric acid, oxalic acid, mandelic acid, malic and nitrilotriacetic acid) treated rice husk for heavy metals removal. Maximum adsorption capacity (108 mg/g) was achieved by tartaric acid treated rice husk for lead. The reduction in the uptake capacity was found in case of rice husk esterified with tartaric acid. The adsorption of Pb by tartaric acid modified rice husk was also studied in the presence of chelators. It was found that higher molar ratios of chelators such as nitrilo triacetic acid (NTA) and ethylenediamine tetraacetic acid (EDTA) caused decrease in adsorption of Pb. Say et al. (2001) investigated the removal of lead by dry fungal biomass (*Phanerochaete chryosporium)*. The equilibrium time for metal uptake was 6 hrs. The uptake capacity was 85.9 mg/g. The separation factor lied between 0-1 indicated favourable sorption reaction. The Langmiur and Freundlich adsorption models were applied.

Green leaves of *Syzygium cumini L*. were used as biosorbent for lead removal (King et al., 2007). Experiments have been carried out in a batch adsorption system as a function of pH, concentration, and adsorbent size. The Langmuir, Freundlich, Redlich-Peterson and Temkin adsorption models were applied to describe the sorption data. Biosorption isothermal data were well interpreted by the Langmuir model followed by Temkin models. The maximum adsorption capacity was 32.47 mg/g.

Zhang et al. (2006) compared the properties of polyurethane immobilised Sphagnum moss, the brown seaweed (*Ascophyllum nodosum*), sunflower waste and whole maize plant for the biosorption of lead in continuous flow packed columns.The biosorption capacities of seaweed, sunflower waste, Sphagnum moss, and maize were 117.3 mg/g, 33.2 mg/g, 32.5 mg/g and 2.3 mg/g respectively. The uptake capacity increased with rise in pH. The optimum pH was 5.0. The data followed Langmuir isotherm and the pseudo second-order kinetic models. The biosorption was endothermic in nature. The ability of cork wastes to remove lead from aqueous solutions has been studied by Mesas et al., (2011). The influence of the aqueous pH and the initial metal concentration on the metal uptake were investigated. Cork has been proved to be an efficient biomaterial for heavy metal separation. The maximum sorption was found at pH 5.0, FTIR and SEM were carried out to determine the modification in the chemical structure and morphology. The kinetic study indicated that adsorption occurred by both film and intraparticle diffusion. The different sorption models were also applied. The P-factor approach based on the Langmuir model provided the best correlation for the metal cork system.

Vázquez et al. (2012) studied chestnut (*Castanea sativa*) shell for lead removal. Shells were modified using 4% NaOH aqueous solution at 25 °C for 4 hrs. Alkali treatment enhanced the adsorptive capacity. The alkali pre-treated chestnut shells were characterized before and after adsorption using scanning electron microscopy (SEM). Kinetic data followed the pseudo-second order model while the equilibrium data were best fitted by Sips and Freundlich models. Carboxyl and hydroxyl functional groups were involved in metal adsorption. *Citrus limetta* fruit peels treated with alkali were used for lead biosorption (Suryavanshi and Shukla, 2010). The alkali treated biomass enhanced the adsorption capacity up to 87%. The optimum pH for maximum adsorption capacity was 4.5. The biosorption capacity was 630 mg/g. Adsorption data were fitted by Langmuir and Dubinin-Radushkevich (D-R) models.

Various other biosorbents utilized for lead and chromium removal were reviewed by Kapoor and Virraghaavan, (1995), Davis et al., (2003), Farooq et al., (2010), Das (2010), Vijayaraghavan and Yun (2008), Aksu (2005), Volesky (2007).

Biosorption has emerged in the last few decades as a modern water treatment technology that can provide rapid and efficient removal of pollutants from aqueous wastewater. To the best of our knowledge, very less attention has been given towards the development of Nirmali seeds powder and Pongamia pods powder biosorbents for heavy metals remediation. Thus, in the present proposal, attempts were made to develop Nirmali seeds powder and Pongamia pods powder biosorbents for the removal of lead and chromium from water and wastewater.

1.1 Objective of the study

Biosorption is an effective way for removal of contaminants from water at low capital cost. Biosorbents have some remarkable properties that make them suitable for water remediation. These are readily available, have high removal efficiency, having low cost, easy implementation and can be regenerated and reused.

Study was carried out to investigate the feasibility of Nirmali seeds powder and Pongamia pods powder for chromium and lead removal from water and wastewater.

The specific objectives of the study were:

- To select biosorbents
- Chemical and physical processing of biosorbents
- To characterise biosorbents (e.g. surface area and pore properties, pH_{PZC}, elemental analyses, XRD, IR, SEM, EDX, EDXRF, TEM)
- To optimize the process for the remediation of lead and chromium using developed biosorbents
- Modelling and sorption studies using Langmuir and Freundlich isotherm models
- To study the kinetics of removal process using various kinetic model at different temperature, dose and concentrations
- Application of developed biosorbents to contaminated groundwater for lead and chromium removal

CHAPTER-II

MATERIALS AND METHODS

2. Materials and Methods

2.1. Biosorbents sampling and preparation

Biosorbents used in the study were *Pongamia pinnata* (Pongamia or Karanj) and *Strychnos potatorum Linn.* (Nirmali). Nirmali is commonly found in southern and central part of India, Srilanka and Burma. This tree is known as Nirmali or clearing nut tree because it was commonly used as coagulant for water purification in ancient time in India (Jayaram et al., 2009; Lakshmipathiraj et al., 2011; Yin et al., 2010).

Pongamia tree is found in the foothills of the Himalaya, Andaman, across Indo-China and in Northern Australia. The tree can be found in tidal mudflats and even in salty water. The mature tree can tolerate drought, wind, fire and frost (Krishen, 2006). The woody pods are green at early stage but it looks straw yellow or grey brown on ripening. Pods are ~5 cm long and oval in shape. The seeds have medicinal values. Oil obtained from seeds is used for the treatment of scabies, herpes and many other diseases. Every part of the tree including flowers, leaves, seeds and even ash have medicinal values as Pongam (Karanj) oil is used for many purposes as lubricant, soap making and as pesticide (Krishen, 2006).

The biosorbent Pongamia was collected from Jawaharlal Nehru University (J.N.U.), New Delhi, India. The seeds from pods were removed manually and the seed-less pods were grounded. Nirmali biosorbent was purchased from grocery market, Khari Baoli, Chandni Chowk, old Delhi, India. Both the biomasses were dried in sunlight to remove moisture content. After drying in sunlight, samples were grounded. The grinding was carried out in a commercial in grinder located at Khari Baoli, Chandni Chowk, old Delhi, India.

The powdered samples were sieved into different mesh sizes (30-50 BSS mesh). The particle size of 30-50 mesh was used in the whole study. The powdered material (30-50 mesh) was washed several times with doubly distilled water until a constant pH value was observed. Initial pH was 4.6 which changed to a constant value of pH 5.0 after multiple washing. Absorbance of filtrates was also recorded at the time of washing to check if any color was leached out. Scanning was performed in the UV-Visible scale of 700-200 cm^{-1}.Almost flat spectrum without any peak was recorded in case of both the adsorbents. Biosorbents were finally washed with ethyl alcohol and dried at 70 ^{o}C for 48 hrs in an oven (Digital hot air oven, Scientech Instruments, India). The biosorbents were stored in airtight polyjars in vacuum for further studies.

2.2. Experimental procedure

2.2.1. Reagents and equipments

The pH values of the solutions were measured using a pH meter (model EUTECH, pH 510). The initial pH value for sorption experiments of pH study (chromium 2-10; lead 2-6) was adjusted using reagent grade dilute HNO_3 (0.1N) and NaOH (0.1N). Lead and chromium concentrations in the samples were determined using atomic absorption spectrophotometer model Aanalyst 400, Perkin Elmer with an air-acetylene flame and Pb and Cr hollow cathode lamps. The characteristic wavelengths for lead and chromium analysis were 281.31 nm and 357.87 nm respectively. Mettler Toledo balance, model AB 265-S/FACT was used for weight measurements. The magnetic stirrer model SPINIT, Tarsons India was used for stirring of solutions during pH adjustment.

2.2.2. Preparation of stock solutions

Stock solutions of chromium and lead (1000 mg/L) were prepared by dissolving the required amounts of $K_2Cr_2O_7$ and $Pb(NO_3)_2$ in doubly distilled water of (pH ~ 3-4). The working solution (chromium 1-100 mg/L; lead 1-1000 mg/L) of different concentration range for sorption study was prepared by using stock solution.

2.3. Material characterization

2.3.1. Transmission electron microscopy

Samples of powdered dry biomass were fixed in glutaraldehyde (2.5%) and kept overnight in vacuum desiccators for better penetration of fixative solvents. These fixed samples were then washed thrice with PBS [(phosphate buffer (0.1 M) pH 7.2)] with an interval of 1 hr between each washing. Plant samples were post fixed in 1% osmium tetraoxide (OsO_4) in 0.1 M phosphate buffer for 2 hrs at 4 °C. Samples were washed again by using phosphate buffer. The fixed plant samples were dehydrated in acetone (50-70%) for 1hr in series of solution 50% acetone, 70% acetone, 90% acetone and 95% acetone (Handbook to Electron Microscopy, Electron Microscope Facility, Department of

Anatomy AIIMS, New Delhi). Final dehydration was done by dry acetone. After dehydration, samples were washed by toluene at room temperature for 2 hrs. The dehydrated samples were infiltrated with toluene and araldite mixtures in different ratio at room temperature (25 °C) and finally samples were infiltrated with pure araldite mixture at a temperature of 50 °C for 2 hrs.

The next step of sample preparation is embedding. Samples were embedded in pure araldite (Epoxy Resin Araldite (M) CY 212) mixture in capsular form for 3 hrs. Polymerization of resin having specimen blocks in capsular form was accomplished in an oven at a temperature of 50 °C overnight. The temperature was then raised to 60 °C for 48 hrs.

Section cutting is the most important step of sample preparation and was done by glass knife (made from Belgium glass strip). The specimen blocks were trimmed by hand with a razor blade. The semi thin 1 µ sections were cut by using ultra-microtome. The semi-thin sections of specimens were stained with methylene blue dye and viewed under light microscope. The selected sections were re-trimmed with glass knife in proper region to get ultra thin sections (70-90 nm). These ultra thin sections (200 mesh) were mounted on copper grid. The sections were primarily stained with saturated solution of urinyl acetate. The secondary staining was done by lead nitrate. The sample specimens were viewed under JEOL 2100F microscope to know the internal biomass morphology.

2.3.2. Scanning electron microscopy and energy dispersive analysis

The surface physical morphology of biosorbents was examined using a Scanning electron microscope (SEM) (model Zeiss, EVO 40 accelerating voltage 10,000 V, working distance 9900 µm and emission current 13,300 nA). Dried samples were sprinkled over a double stick carbon tape. In, SEM the samples were coated with a thin layer of gold and mounted on an aluminium stub using a double stick carbon tape. Gold coating was done to convert the non-conductive samples into conductive. The SEM/EDX analysis gave the elemental composition of the sample. The sintered pellet was used in energy dispersive analysis by X-ray (EDX) using the same electron microscope in conjunction with a BRUKER EDX system.

2.3.3. Energy dispersive X-Ray fluorescence

EDXRF was carried out on energy dispersive X-ray fluorescence spectrometer (model PANalytical Epsilon 5) was used to analyse the chemical composition of the biomass. Insmart System (INSMART XRF 40) was used to prepare the samples. Samples were mixed with boric acid and cellulose powder to make the pellet. The pellets were prepared by applying pressure of 5 ton. The size of prepared pellet was 34mm and exposure area was 8 mm.

2.3.4. Fourier transform infrared spectroscopy

The FT-IR spectra were recorded on a Varian spectrometer (model 7000 FTIR, Varian) to identify the functional groups present in the biomass. It was mixed with potassium bromide in the ratio 1:20 to make a homogenous mixture by using pestle-mortar, it was then placed on a steel dye at a pressure of 10 ton generated by hydraulic press (Spectrachrom Instruments, CAP-15T). The scanning range 500 cm^{-1}- 4000 cm^{-1} was used for the analysis of the sample.

2.3.5. X-ray powder diffraction

The PANalytical X-ray diffractometer (X'Pert PRO) was used to obtain the X-ray diffraction (XRD) patterns of biomass powders using Cu-Kα (X=1.54Å) at 45 kV and 40 mA. The samples were scanned from 5.0250-89.9750° (2θ, where θ is the angle of diffraction) at the of speed of 2° $min.^{-1}$

2.3.6. CHNS Analysis

Carbon, hydrogen, nitrogen and sulphur were analyzed using CHNS Analyzer (model LECO CHNS-932). It determines the presence of carbon, hydrogen, nitrogen and sulphur in terms of weight percent. The carrier gas used in the combustion reactor was helium with a flow rate of 80 ml min^{-1}. Ultra pure oxygen with a flow rate of 20 ml min-^{1} was used as fuel gas. The front furnace temperature was set at 980 °C and the GC oven temperature was 115°C. However, the actual combustion temperature of reactor reached up to 1800 °C. For analysis, oven dried samples were weighed in tin capsules. The capsules were sealed using tweezer. The sealed tin capsules were rolled compactly to avoid air entry. The samples were placed in the auto-sampler for analysis.

2.3.7. Surface area measurements

Quantachrome surface area analyzer (model Autosorb-1) was used to determine the N_2 adsorption isotherms. About 0.15 g of sample was out-gassed at 250 ºC for 12 hrs, prior to conducting adsorption measurements. The mercury density (ρ_{Hg}) (equation 1) was measured by obtaining the sample volumes by excluding the volume of mercury from the volume of a previously calibrated glass cell. This was done by using a Quantachrome Poremaster mercury porosimeter. The helium density (ρ_{He}) was measured in a Quantachrome Stereopycnometer, using ~3.0 g of sample (equation 2).

$$\rho_{Hg} = M/V_s \tag{1}$$

$$\rho_{He} = M/V_s' \tag{2}$$

where, M is the mass of the sample, V_s is the volume of the sample and V_s' is the volume of the sample inaccessible to helium.

Specific surface areas (S_{BET}) were evaluated by applying the BET equation from the N_2 adsorption isotherms. The relative pressure (p/p^0) range was between 0.05 and 0.35, and a_m (i.e., the average area occupied by a molecule of N_2 in the monolayer) to be 16.2 $Å^2$. The adsorption isotherms were also used to obtain the macro-pore (V_{ma}), meso-pore volumes (V_{me}) and micro-pore volumes (V_{mi}). The micro-pore volumes (W_0) were obtained by Dubinin-Radushkevich equation (Dubinin, 1975 and Dubinin, 1968).

$$\log W = \log W_0 - D\log^2\left(\frac{p^0}{p}\right) \tag{3}$$

where W is the micro-pore volume that has been filled with liquid N_2 when the relative pressure is p/p^0 and W_0 is the total micro-pore volume. D is a constant characteristic of the micro-pore structure of the adsorbent. V_{ma}, V_{me}, V_{mi} and W_0 were expressed as liquid volumes. The total pore volume (V_T) was calculated using the equation (4)

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \tag{4}$$

2.3.8. Zero point charge (pH_{PZC}) measurement

The zero point charge (pH_{PZC}) of the biosorbents (Pongamia pods powder and Nirmali seeds powder) were also measured (Not and Schwarz, 1989). At different pH 2, 4, 6, 8, and 10 pHpzc was measured using 0.01 M NaCl aqueous solutions. These pH values (2, 4, 6, 8, 10) were adjusted with either a 0.1N HCl or a 0.1N NaOH aqueous solution. Samples (0.01g) were brought into contact with these solutions (5 mL of each) and the system was stirred for 48 hrs. The supernatant was then decanted and its pH was measured.

2.3.9. Sorption Procedure

The sieved and dried biomass were added to metal solution in 50 mL beakers and placed in water bath shakers (model MSW275, Macro Scientific, India & RC51000, Scientech). The sample solutions were filtered by using Whatman filter paper no.1.

Batch sorption studies were performed to obtain the rate and equilibrium data for lead and chromium adsorption on biosorbents.

2.3.9.1 Effect of Solution pH

The pH experiment was performed to determine the optimum pH. Known amount of adsorbent was added into 50 ml of adsorbate with initial concentrations (lead-50 mg/L, chromium-10 mg/L) in the pH range of (pH 2- 10. for chromium and pH 2-6 for lead). The pH of metal ions solution was adjusted using 0.1 N HNO_3 and 0.1 N NaOH. The flasks were placed in water bath shaker for 48 hrs at 25 ^{o}C.

The metal uptake by the adsorbent phase was calculated by the difference between the initial metal concentration of the solution and the equilibrium metal concentration in solution using the following mass balance equation.

$$q_e = (C_o - C_e)V/W \qquad (5)$$

Where, C_o and C_e are initial and equilibrium metal concentrations (mg/L); V is the volume (L) of adsorbate and W is the weight (g) of the adsorbent.

2.3.9.2 Kinetic studies and modeling

Kinetic studies were performed to determine the effect of contact time, temperature, concentrations and dose on biosorbents.

2.3.9.2.1 Effect of dose

Different amount of biosorbents (2, 4, 10 g/L) were taken for both the biosorbents to know the optimum dose.

2.3.9.2.2 Effect of Temperature

To determine the effect of temperature on the adsorption of metal ions, known amount of adsorbent was added to 50 ml of metal ion solution. Experiments were carried out at 25, 35 and 45 ^{o}C.

2.3.9.2.3 Effect of Contact Time

To determine the effect of contact time on the metal ions adsorption, known amount of adsorbent was added into 50 ml of metal ions solution at an optimum pH. Experiments were carried out at different time intervals i.e. 1, 2, 4, 5, 6, 24, and 48 hrs at fixed amount of dose and concentration.

2.3.9.2.4 Effect of Concentration

To determine the effect of initial metal concentration, 10-80 mg/L (chromium) and 100-500 mg/L (lead) were taken to investigate the concentration effect. The fixed amount of adsorbents was added to 50 ml of metal solution.

Modeling-

Pseudo first order kinetic model-

A simple adsorption kinetic model, the pseudo-first-order equation suggested by Lagergen (Lagergren, 1898).

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \qquad (6)$$

or

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \qquad \text{(Non linear form)}$$

where k_1 (min^{-1}) is the first order adsorption rate constant, q_e and q_t are the amounts of adsorbate adsorbed at equilibrium and at time “t” respectively.

Pseudo second order kinetic model-

The pseudo second order is influenced by the amount of adsorbate on adsorbent's surface and the amount of adsorbate adsorbed at equilibrium (Ho et al., 1999). The rate is directly proportional to the number of active sites on the adsorbent's surface. The pseudo second order equation can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

$$\text{Rate} = k_2 q_e^2$$

Rate constant (k_2) and q_e values were determined from the plots at different temperatures and concentrations.

2.3.9.3. Sorption studies and modeling

Models would be helpful in predicting the adsorption data when it is used at large scale. Studies were conducted at different temperatures 25 ^{o}, 35 ^{o} and 45 ^{o}C to obtain equilibrium isotherms.

Freundlich isotherm

The Freundlich model describes the equilibrium on heterogeneous surfaces It does not indicate a finite sorbent uptake capacity. It should only be applied in the low to intermediate concentration range. The nonlinear Freundlich equation is

$$q_e = k_f C_e^{1/n} \qquad (8)$$

where qe is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium solute concentration in the solution (mg/L), constant k_F indicates the biosorbent's relative adsorption capacity (mg/g) and 1/n is the constant representing adsorption intensity.

Langmuir isotherm

The Langmuir adsorption isotherm describes the adsorbent surface as homogeneous on an assumption that all the adsorption sites have equal adsorbate affinity. It also assumes that adsorption at one site does not affect adsorption at an adjacent site. The Langmuir adsorption isotherm is not the mechanistic approach instead, it provides information on uptake capabilities and equilibrium behavior (Do, 1998). The nonlinear Langmuir equation is

$$q_e = \frac{Q^0 b c_e}{1 + b c_e} \qquad (9)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the solute equilibrium concentration in solution in mg/L, Q° is the monolayer adsorption capacity (mg/g) and b is constant related to the net enthalpy, H, of adsorption ($b \propto e^{-\Delta H/RT}$).

2.3.9.4. Applications of biosorbents in actual ground water sample treatment

The biosorption efficiency of Pongamia pods powder and Nirmali seeds powder in real waste water was investigated by collecting ground water from Mathura district of Uttar Pradesh, India. Real water/wastewater systems contain a complex mixture of ions. The pH of the water (50 mL) was adjusted using HNO_3 to 2.0 for chromium and 4.0 for lead before applying biosorbents. A predetermined amount (10 g/L) of biosorbents was added to each sample. After 48 hrs, the samples were filtered and the chromium and lead concentrations were measured by AAS.

CHAPTER-III

RESULTS AND DISCUSSIONS (I)

3. Results and Discussion

3.1. Characterization of biosorbents

3.1.1. Surface area (S_{BET}), pore volumes, density and pH_{PZC}

Surface area provides important information about sorption procedure. Surface area is an important property of powdered material. Large surface area is preferable for sorption. The data showed that Pongamia pods powder has negligible surface area but Nirmali seeds powder has 0.6 m^2g^{-1}. The pore size area is also an important aspect to the accessibility of sorbate molecules to the sorption surface. Macro pore in case of Nirmali seeds powder is more than that of Pongamia pods powder. W_0 is also negligible in both biosorbents.

pH_{PZC} values are given in Table 3.1. The PZC is the pH where the net surface charge is zero (Mohan et al., 2011). At this value the net charge becomes zero due to neutralization effect of H_3O^+ and OH^-. It is usually determined in relation to an electrolyte's pH and the PZC value is assigned to a given substrate or colloidal particle. In other words, PZC is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface of adsorbent. The pH_{PZC} values for Nirmali seeds powder and Pongamia seeds powder are 4.4 and 6.0 respectively (Table 3.1).

3.1.2. Elemental analyses

The elemental analyses of Nirmali seeds powder and Pongamia pods powder are given in Table 3.2. From analysis, it is clear that both biosorbents have high carbon and hydrogen while nitrogen and sulphur are present in very small amount. Nirmali seeds powder and Pongamia pods powder have almost same weight percent of carbon.

3.1.3 X-ray powder diffraction (XRD)

The XRD patterns of Nirmali seeds powder and Pongamia pods powder are presented in Figure 3.1 (a, b). The XRD pattern of Nirmali seeds powder shows two broad peaks. The peaks centered at $2\theta = 72.634$ and 72.815 may be due to silica and calcite respectively. Similar results were reported earlier for *Cassia grandis* and *Cassia marginata* (Singh et al., 2008 and Singh et al., 2007).

The XRD pattern of Pongamia pods powder is presented in Figure 3.1(b). The peak centered at $2\theta = 72.634^o$ may be assigned to calcite (X'Pert HighScore, Philips analytical B. V.). Peak observed at $2\theta = 21.869^o$ may be assigned to silica. Similar peaks in the 2 θ range of 15^o to 35^o diffraction angles were reported for the presence of silica in rice husk (Kamath and Proctor, 1998; Dell et al., 2001; Tarley et al., 2004).

3.1.4. Infrared spectroscopy (FTIR)

The identification of various forms of different constituents in Nirmali seeds powder and Pongamia pods powder has been carried out with the help of FTIR spectroscopy. The FTIR spectra of Nirmali seeds powder (neat and chromium loaded) and Pongamia pods powder are given in Figure 3.2 (a, b). Nirmali seeds powder [Figure 3.2 (a)] shows weak and broad peaks in the region of 1056-3410 cm^{-1}. Approximate FTIR band assignment in case of Nirmali seeds powder indicated the presence of alcohols, carboxylic acid, C-H, C=O and O-H stretching modes (Jayaram et al., 2009; Lakshmipathiraj et al., 2011). The band appeared at 1458 cm^{-1} in unloaded Nirmali seeds powder shifted to 1373 cm^{-1} when loaded with chromium. Furthermore, the band at 3410 cm^{-1} was also shifted to 3423 cm^{-1} after chromium adsorption. The band assignments are given in Table 3.3.

Similarly, in Pongamia pods powder various absorption bands appeared at 1056.98, 1458.18, 1652.99, 2362.79, 2926.00 and 3410.13 are assigned to C-O, C-H, C=O, NH_2, C-H and O-H bonds respectively (Elangovan et al., 2008).

3.1.5. Scanning electron microscopy (SEM) and energy dispersive analysis (EDX)

SEM micrographs of powdered Nirmali seeds are shown in Figure 3.3 (A-F). Micrographs show various types of morphological structures. These included hexagonal tubes like structure [(Figure 3.3 (B)], fibrous structure [Figure 3.3 (C)] and the honeycomb like structure [Figure 3.3 (A)]. Similar SEM micrographs of Nirmali seeds powder were reported earlier (Lakshmipathiraj et al., 2011; Stojanovic et al., 2011).

Figure 3.5 (A-F) represent the micrographs of powdered pods of Pongamia. It has open tubule-like structure [Figure 3.5 (B)]. It is clear that the pod powder is highly fibrous in structure and has rough texture [Figure 3.5 (D)]. Plant vessels of horizontal as well as vertical orientation were also visible [Figure 3.5 (D-E)]. These vessels were open and have many cavities on their external surface. These structures may also contribute to the absorption capacity of the material.

The SEM/EDX analysis spectra of Nirmali seeds powder and Pongamia seeds powder are given in figures 3.4 (A-B) and 3.6 (A-B) respectively. Nirmali seeds powder contain high percentage of oxygen than Pongamia, but less carbon. Calcium is present in Nirmali seeds powder which is absent in Pongamia pods powder. Yb is present in both the biosorbents but higher amount is seen in Pongamia pods powder.

3.1.6. Energy dispersive analysis and X-ray fluorescence analysis (EDXRF)

The EDXRF analysis spectra of Nirmali seeds powder [Figure 3.7 (A-B)] and Pongamia pods powder [Figure 3.8] summarizes their elemental composition. Major elements present in Nirmali seeds powder are Ca, Yb, Fe, S, Si, Ti, Zn while Pongamia pods powder shows the presence of Ca, Si, P, S, Mn, Fe. Same elements were confirmed using SEM/EDX.

3.1.7. Transmission electron microscopy (TEM)

TEM micrographs of Nirmali seeds powder are shown in Figure 3.9 (A-F). Cell wall like structure appears in Figure 3.9 (E) while irregular structure of different sizes appears in Figure 3.9 (D) (Riahi et al., 2009). At low resolution [Figure 3.9(A)] spherical shapes of the particles are clearly visible but at higher magnification these particles get associated and forms sheet like structure.

TEM micrographs of Pongamia pods powder are shown in Figure 3.10 (A-D). The cells appeared in micrograph are irregular in shape and size. These cells get associated and form globular structure [Figure 3.10 (D)].

Table: 3.1 Surface area (S_{BET}), pore volumes, density and zero point charge values for Nirmali seeds powder and Pongamia pods powder

Adsorbents	S_{BET} (m^2g^{-1})	V_{ma} ($cm^3\ g^{-1}$)	V_{me} ($cm^3\ g^{-1}$)	W_0 ($cm^3\ g^{-1}$)	ρ_{Hg} ($g\ cm^{-3}$)	ρ_{He} ($g\ cm^{-3}$)	pH_{PZC}
Nirmali seeds powder	0.6	0.22	0.00	0.001	1.04	1.27	4.4
Pongamia pods powder	0.0	0.18	0.08	0.000	0.8	1.35	6.0

Table: 3.2 Elemental analyses of Nirmali seeds powder and Pongamia pods powder

Adsorbents	C (Wt %)	H (Wt %)	N (Wt %)	S (Wt %)
Nirmali seeds powder	46.375	7.0885	1.434	0.0725
Pongamia pods powder	45.58	6.3965	0.8195	0.0245

Table: 3.3 FTIR spectral analysis of Nirmali seeds powder and Pongamia pods powder

Wave number (cm^{-1})				
Pongamia pods powder	Nirmali seeds powder		Functional group	References
Neat	Neat	Loaded		
1056.98	1056.98	1056.98	C-O stretching vibration of alcohols and carboxylic acid	Jayaram et al., 2009; Lakshmipathiraj et al., 2011; Elangovan et al., 2008
1458.18	1458.18	1373.31	Vibration of C-H	
1652.99	1652.99	1652.99	C=O stretching vibration of hydrogen bonded hydroxyl group, amide	
2362.79	-	-	NH_2 stretch	
2926.00	2926	2934	Stretching vibrations of C-H	
3410.13	3410.13	3423	Stretching vibration of hydrogen bonded hydroxyl group	

Table: 3.4 EDXRF analysis of Nirmali seeds powder and Pongamia pods powder

Adsorbents	**Elements**																		
	Mg (ppm)	Si (ppm)	P (ppm)	S (ppm)	Cl (ppm)	K (ppm)	Ca %	Ti (ppm)	V (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Sr (ppm)	Yb %	W (ppm)	Pt (ppm)	Pb (ppm)
Nirmali seeds powder	206.76	1447.49	126.74	659.78	102.86	176.21	0.25	116.27	5.251	36.411	1022.98	144.63	108.240	6.914	39.156	0.351	280.615	9.761	30.657
Pongamia pods powder	-	188.77	61.00	241.36	-	30.139	0.21	-	-	3.30	31.76	11.37	8.7	-	35.445	1556.66	-	-	-

Table: 3.5 SEMEDX elemental analysis of Nirmali seeds powder and Pongamia pods powder

Adsorbents	**Elements (wt.%)**			
	Carbon	Oxygen	Calcium	Ytterbium
Nirmali seeds powder	38.37	55.34	0.16	0.40
Pongamia pods powder	41.3	49.39	-	2.24

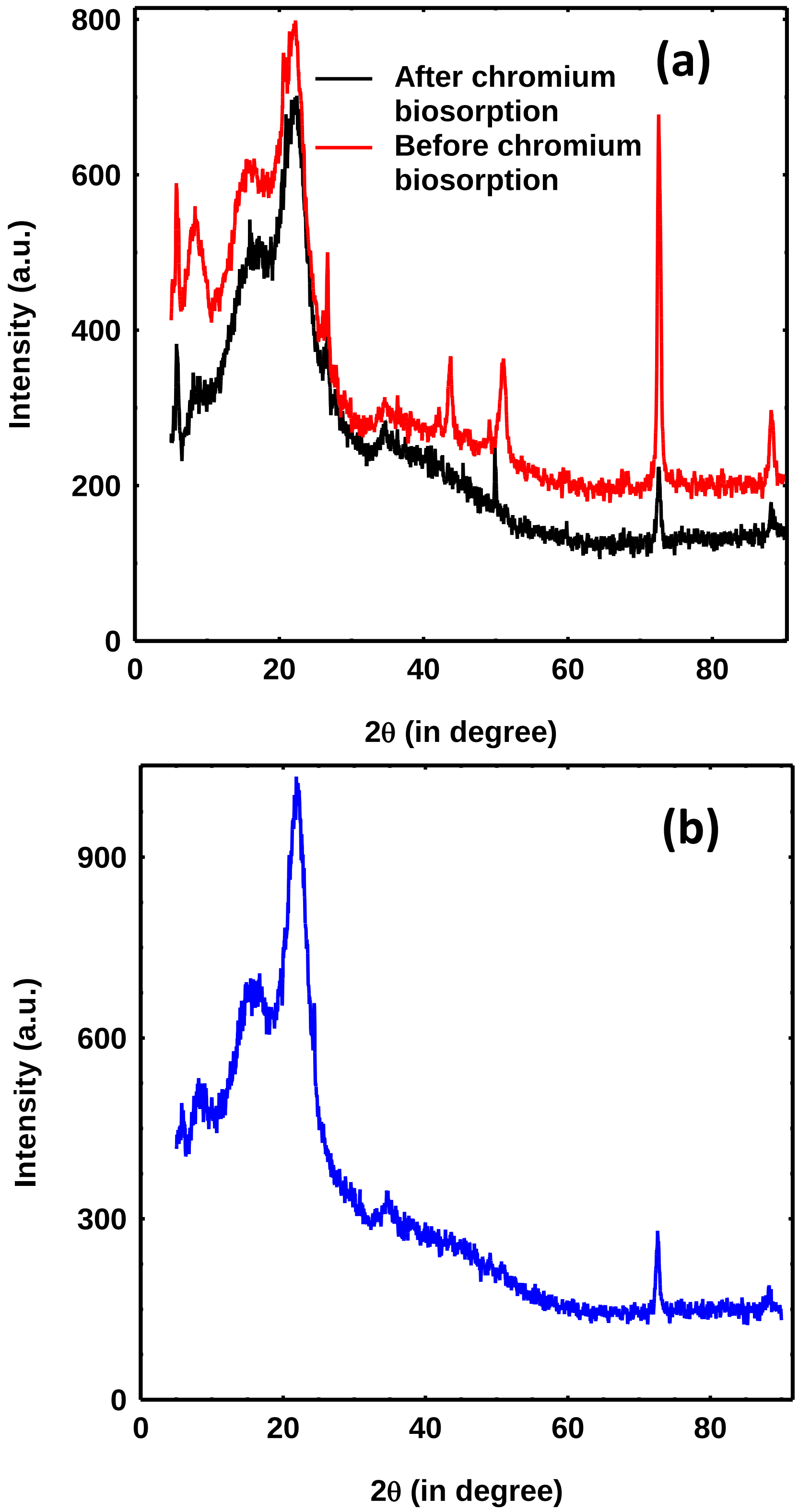

Figure 3.1 XRD spectra of (a) Nirmali seeds powder before and after chromium biosorption and (b) Pongamia pods powder.

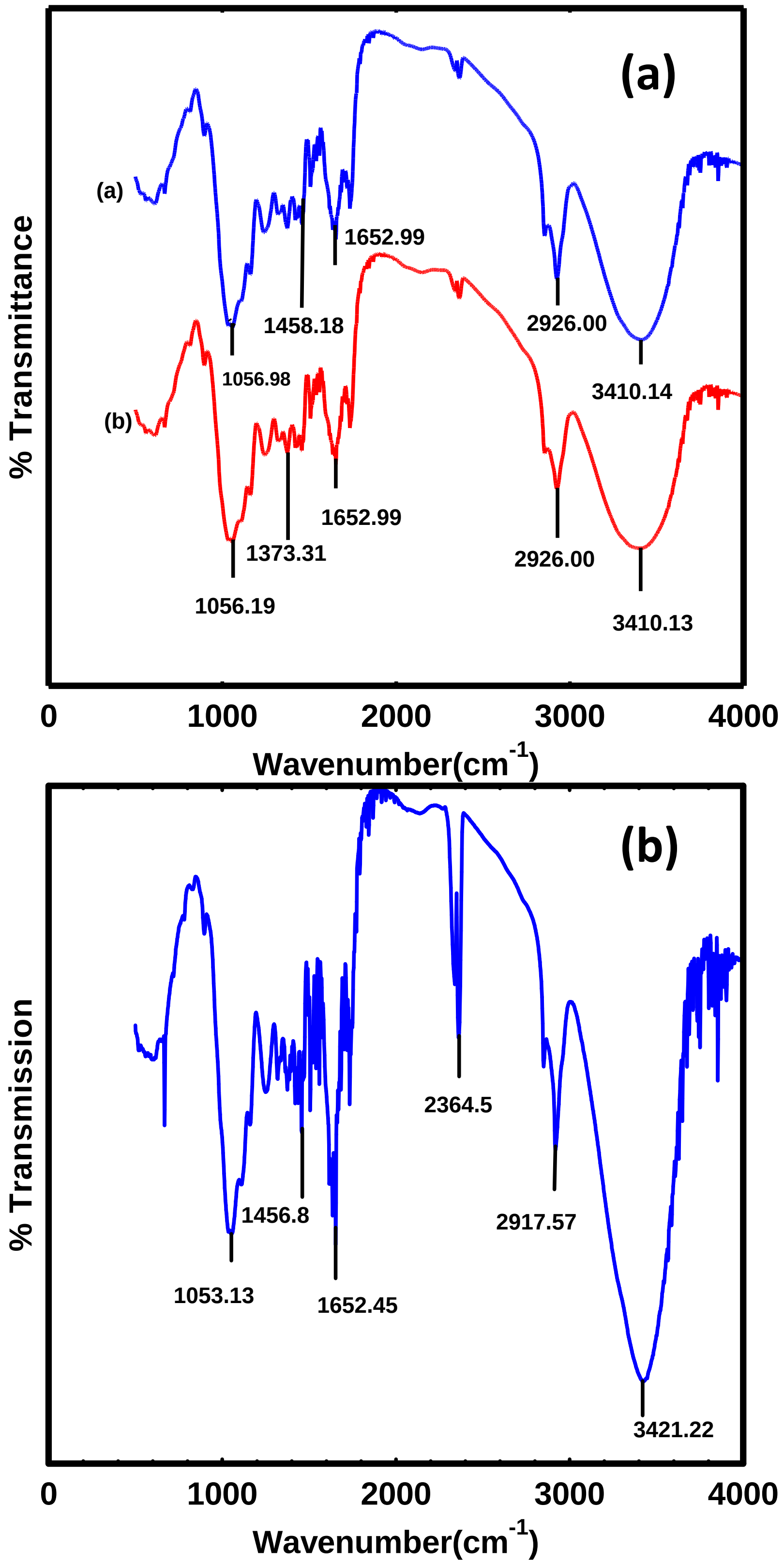

Figure 3.2 FTIR spectra of (a) Nirmali seeds powder before and after chromium biosorption (b) neat Pongamia pods powder.

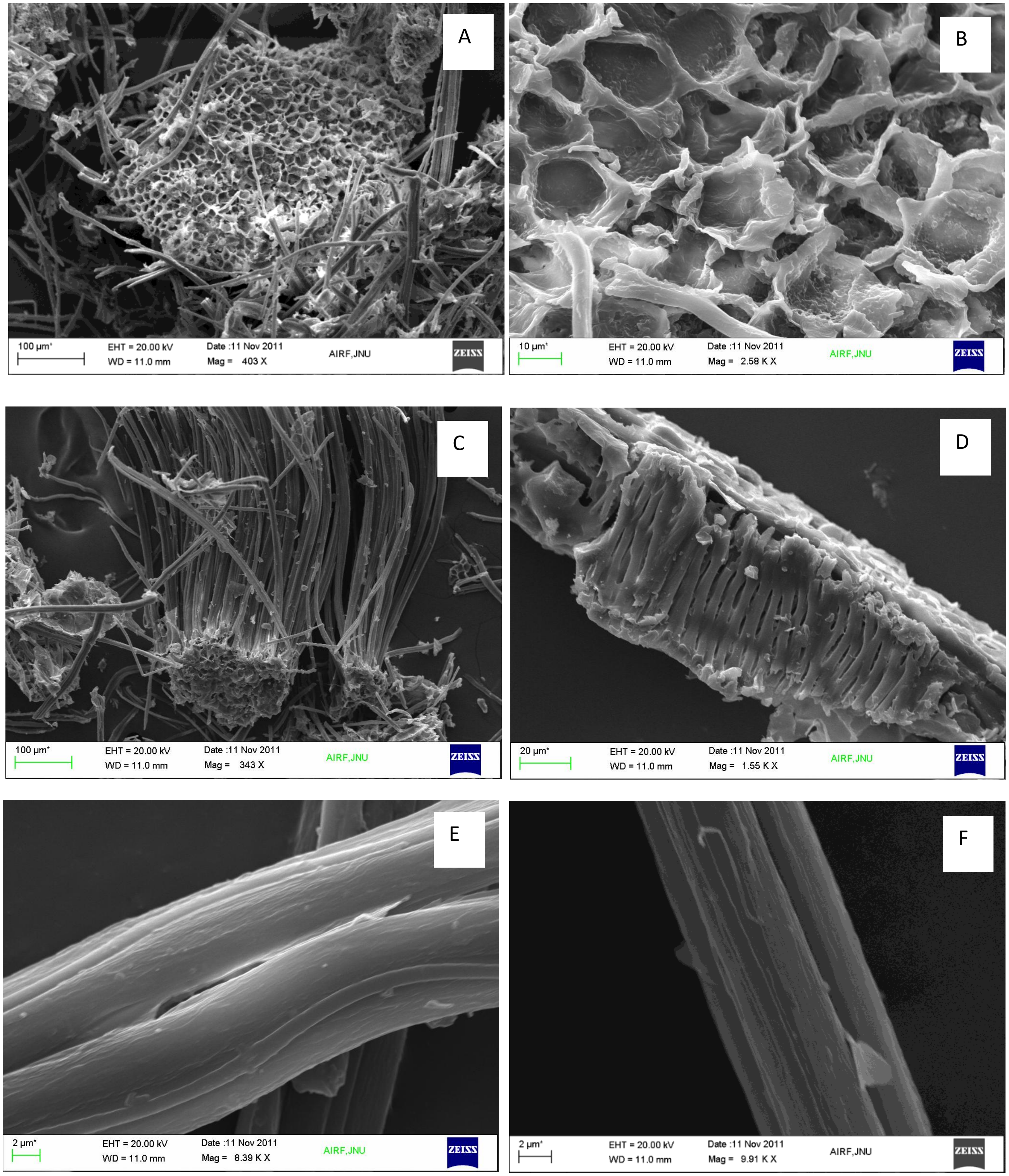

Figure 3.3 SEM micrographs of Nirmali seeds powder at different magnifications (A) 403X (B) 2.58KX (C) 343X (D) 1.55KX (E) 8.39KX and (F) 9.91KX.

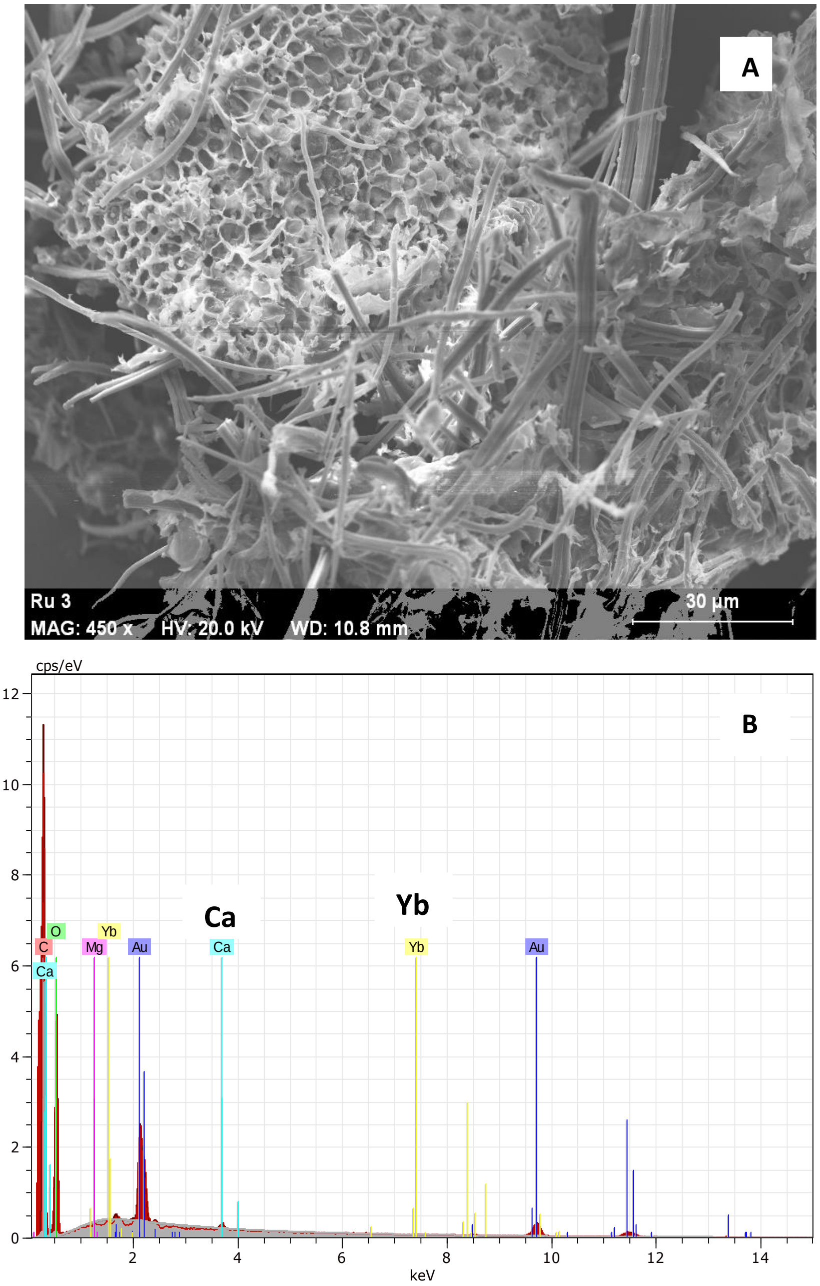

Figure 3.4 (A, B) EDX spectra of Nirmali seeds powder.

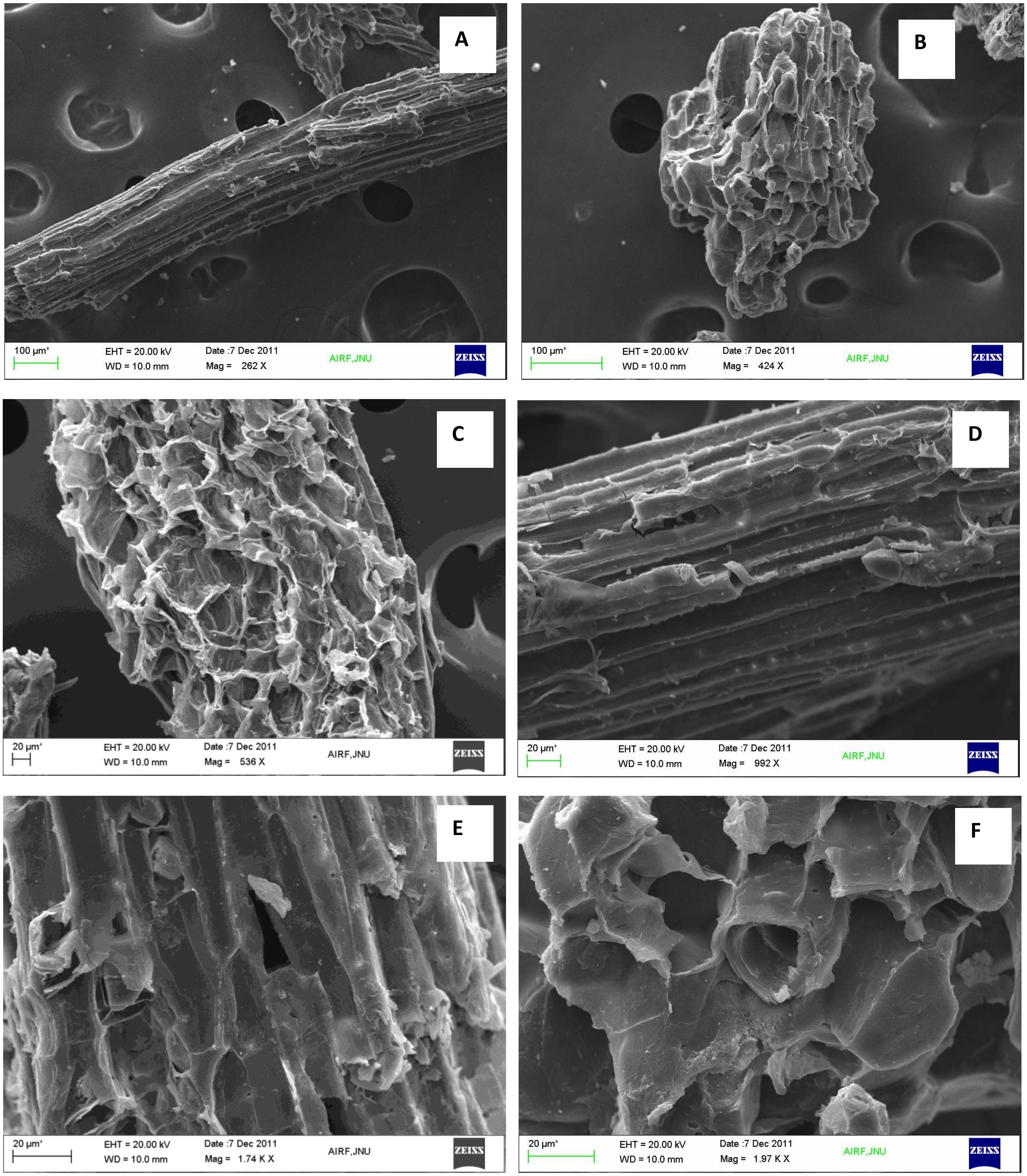

Figure 3.5 SEM micrographs of Pongamia pods powder at different magnifications (A) 262X (B) 424X (C) 536X (D) 992X (E) 1.74KX and (F) 1.97KX.

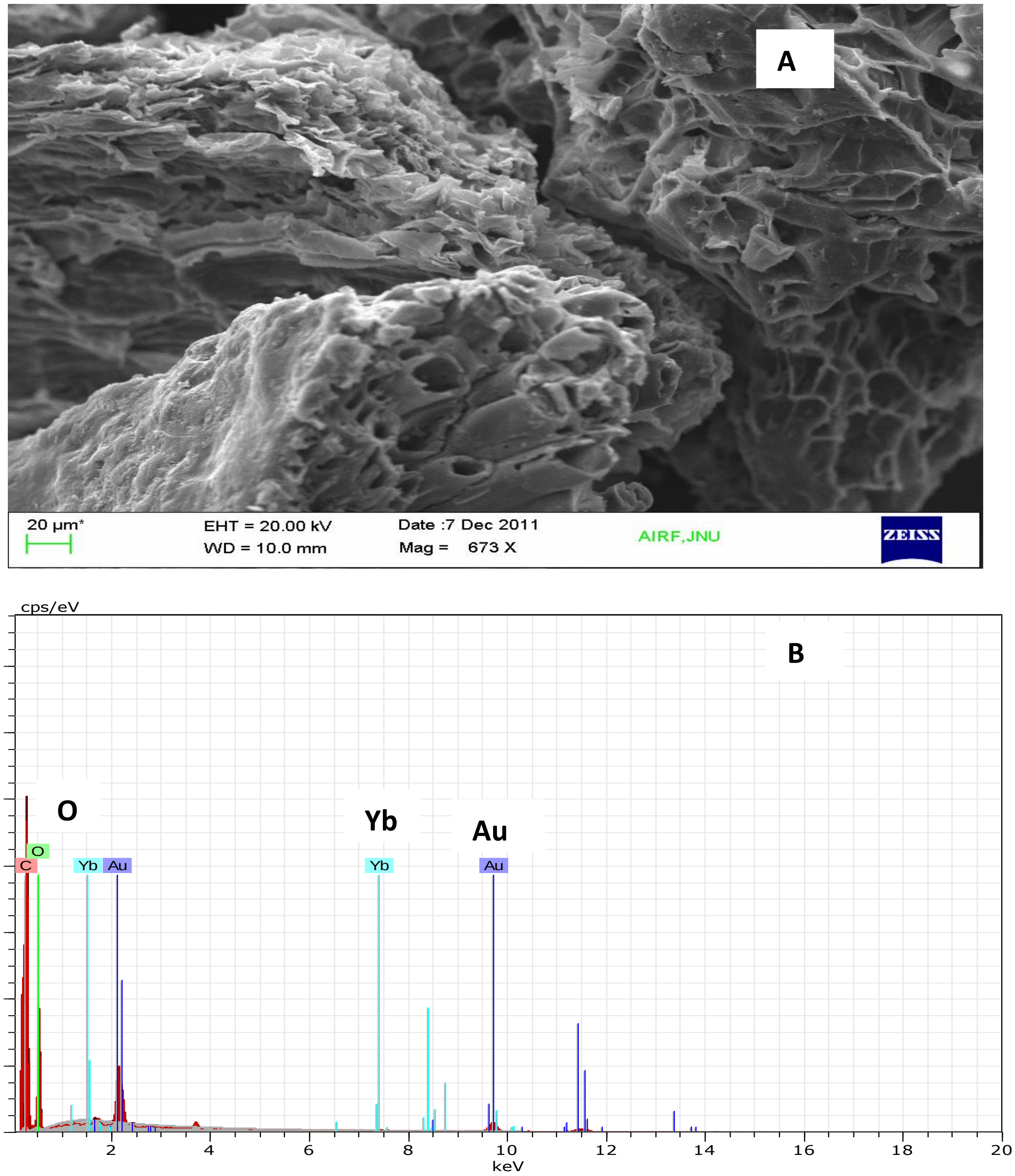

Figure 3.6 (A, B) SEM/EDX spectra of Pongamia pods powder.

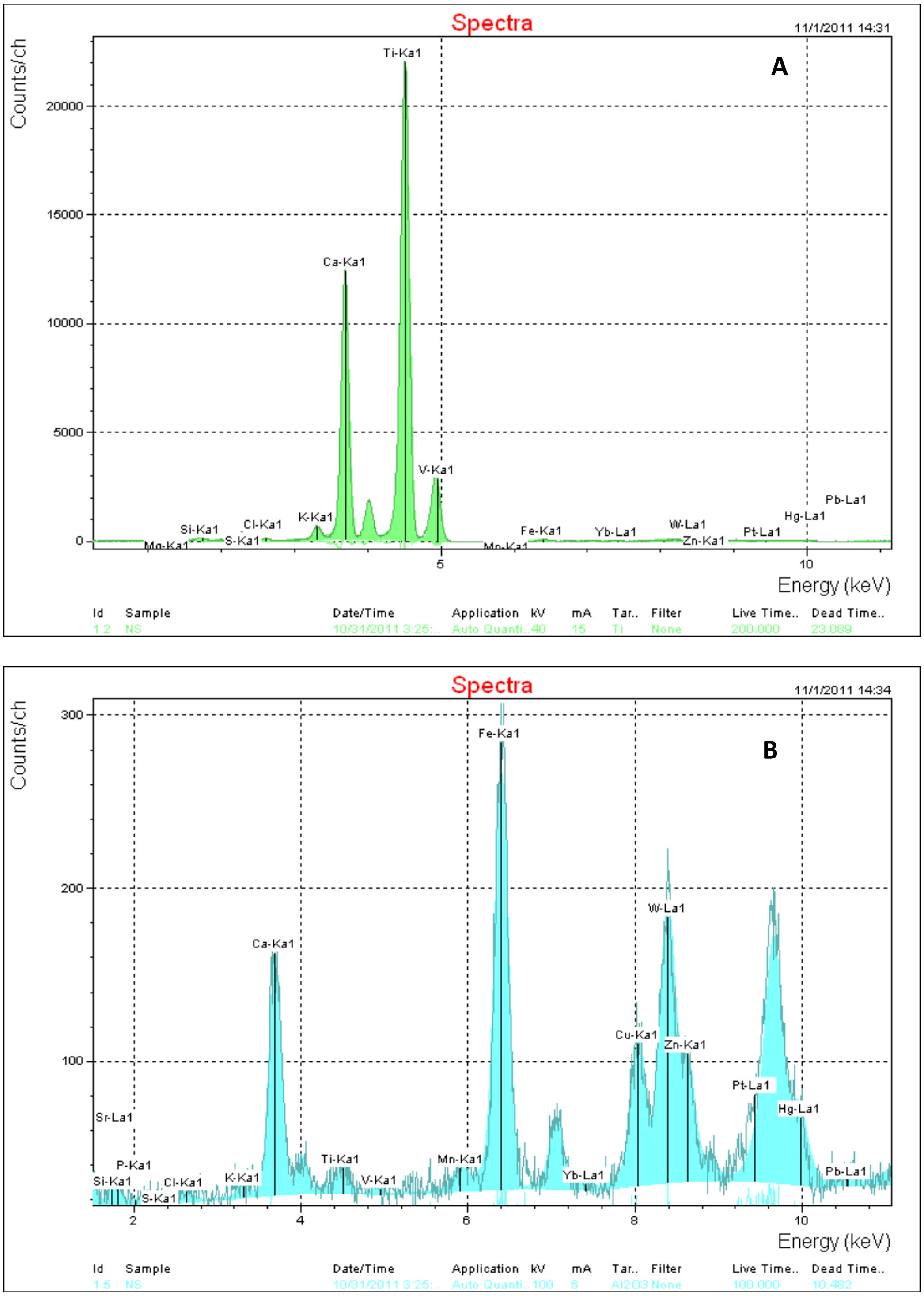

Figure 3.7 (A, B) EDXRF spectra of Nirmali seeds powder.

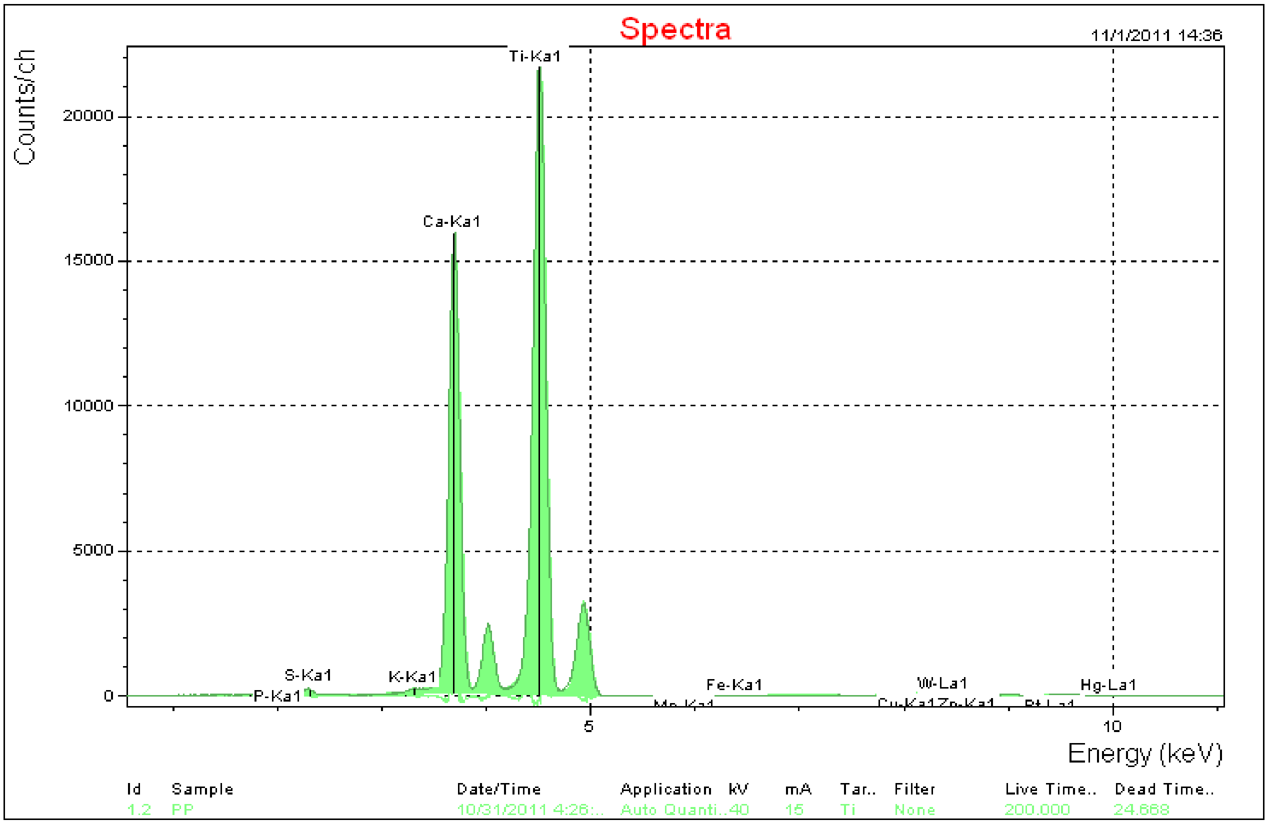

Figure 3.8 EDXRF spectrum of Pongamia pods powder.

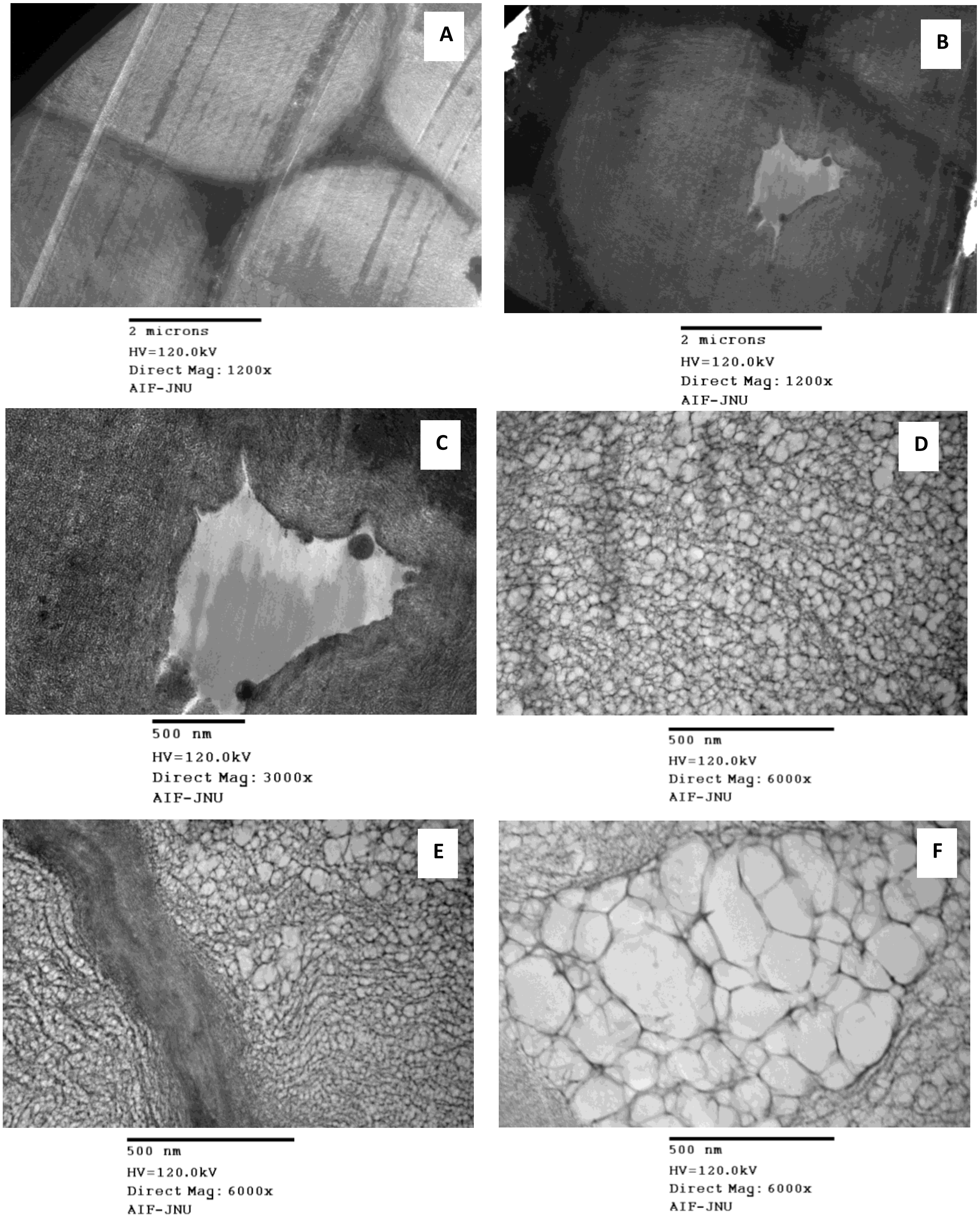

Figure 3.9 TEM of Nirmali seeds powder at different magnifications (A) 1200X (B) 1200 (C) 3000X (D) 6000X and 9 (F) 6000X.

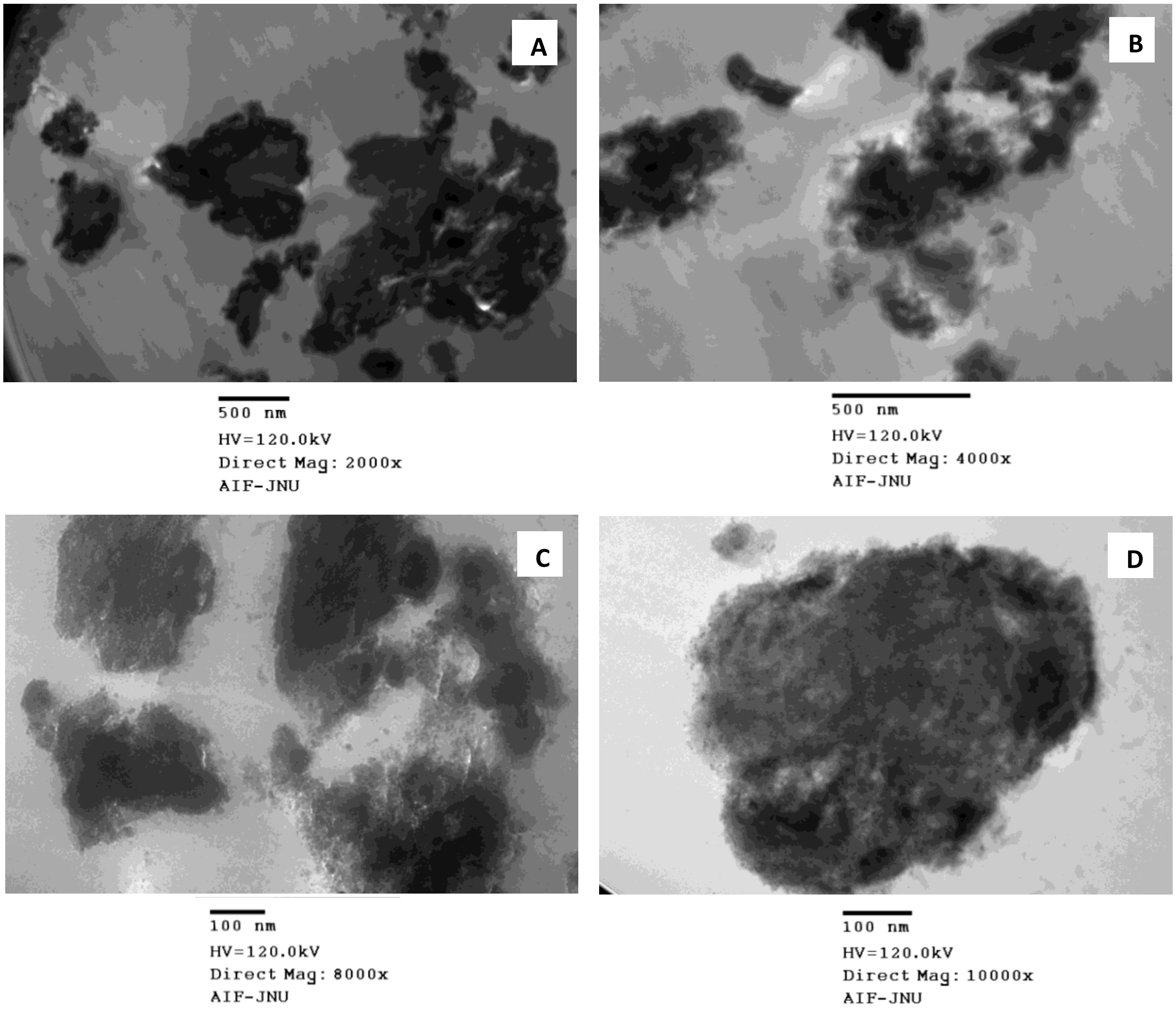

Figure 3.10 TEM images of Pongamia pods powder at different magnifications (A) 2000X (B) 4000X (C) 8000X and (D) 10000 X.

CHAPTER-IV

RESULTS AND DISCUSSIONS (II)

4.1. Sorption studies

4.1.1. Effect of pH on metal ion binding

The change in adsorption of lead and chromium in a pH range of 2.0-10.0 on Nirmali seed powder and Pongamia pods powder has been studied. The dependence of the amount of lead and chromium adsorbed on two biosorbents vis-à-vis pH is shown in Figure 4.1(a,b). The effect of pH on chromium adsorption was studied at an initial concentration of 10 mg/L and 25 °C. The optimum pH for the chromium removal is 4.0 [Figure 4.1(a)]. The equilibrium pH was also determined. There is an increase in the solution pH after complete adsorption of chromium. Similar results were also reported in literature on Mangroove leaves (Elangovan et al., 2008). The effect of pH on the adsorption of chromium is attributed to interactions between ions in solution and complexes formed at the adsorbent surfaces. Chromium exists as different species at different pH (Mohan et al., 2005). At pH 4.0, chromium exists as $Cr_2O_7^{2-}$. It is clear from pH_{PZC} (Nirmali seeds powder = 4.4 and Pongamia seeds powder = 6.0) values that below this pH, surface of biosorbents is positively charged and this helps in binding of chromate ions. The decrease in chromium adsorption at higher pH values may be due to the decrease in net positive charge at the surfaces. Thus, all the sorption and kinetic studies has been conducted at pH 4.0.

The optimum pH for lead removal on Nirmali seeds powder and Pongamia seeds powder is 4.5. At pH 2.0, the removal is insignificant (57 and 48% on Nirmali seeds powder and Pongamia seeds powder respectively). As pH increases, the removal of lead also increases. After pH 4.5, no significant change in lead adsorption took place [Figure 4.1(b)]. As pH is further increased beyond 6.0, onset of metal hydrolysis and precipitation took place (Bhattacharyya and Sharma, 2004). Thus, pH studies were restricted in the range of 2.0-6.0 to correlate metal ions removal with adsorption.

The low adsorption in acidic medium ($pH \leq 2.0$) is attributed to the fact that the surface of biosorbent are positively charged in this pH range. Due to the competition between H_3O^+ ions and metal ions for the available sites on the biosorbents, the lead adsorption is insignificant (Jayaram et al., 2009). Thus, all the subsequent studies on lead remediation using biosorbents were conducted at pH 4.5. Similar results were obtained by Pejic et al., (2009) where lead remediation was carried out on pH 4.5.

4.2 Kinetic studies and modeling

Successful applications of adsorption processes required the development of low cost, non toxic and locally available biosorbents of known kinetic parameters and sorption characteristics (Mohan et al., 2007). The knowledge of optimum conditions would help in designing a better adsorption process. In view of this, the effects of various parameters including the effect of contact time, amount of adsorbent, particle size of adsorbent, concentration of adsorbate, and temperature were examined and discussed in the subsequent paragraphs.

At a desired temperature, predetermined amount of adsorbent was added to beaker containing 50 ml of lead or chromium solutions in a water bath shaker. The solution was agitated and at predetermined intervals, adsorbate was separated and analyzed for lead and chromium uptake by AAS.

4.2.1. Effect of contact time

In simple preliminary sorption kinetic studies, different times of contacts are studied for the sorption equilibrium to be achieved or untill there is no more change in the sorption. Thus, the effect of contact time on the rate of chromium and lead removal on developed biosorbents was studied (figures 4.2 and 4.3). It is clear from the figure that removal is very fast in the beginning and typically 0 to 40.68% chromium and 0 to 90% lead on Nirmali seeds powder; 0 to 11.9% chromium and 0 to 96% lead on Pongamia pods powder were removed in the first hour of contact.

The initial rapid sorption of chromium by Nirmali seeds powder and Pongamia pods powder is followed by a very slow approach leads to equilibrium. It is also clear that ~72 hrs can be considered as the time required to complete the adsorption on both the adsorbents. The lead adsorption by Nirmali seeds powder and Pongamia pods powder was rapid as compared to chromium adsorption. Equilibrium was reached within 3 hrs of contact time for Nirmali seeds powder and 1 hr for Pongamia pods powder.

4.2.2. Effect of adsorbent dose

The effect of amount of Nirmali seeds powder and Pongamia pods powder on the rate of lead and chromium uptake is shown in figures 4.2 and 4.3. There is a substantial increase in the chromium adsorption on increasing the dose of Nirmali seeds powder and Pongamia pods powder from 2 g/L to 4 g/L. On further increase in the dose to 10 g/L, removal of chromium also increases in the same proportion. Therefore, 10 g/L has been decided as an optimum dose to carry out all the batch sorption and kinetic studies. Furthermore, the half life i.e. the time taken to reduce the concentration to 50% of its total adsorption (t_{50}) also decreases [t_{50} at 2 g/L (4 hrs); t_{50} at 4 g/L (5 hrs), t_{50} at 10 g/L (4 hrs)]

Similar trends were obtained for lead removal on Nirmali seeds powder. On doubling the dose from 5 g/L to 10 g/L, the removal also becomes double i.e. 68% to 89%. On introducing another 5 g/L, the adsorption does not increase in the same ratio. The increase in adsorption is only 4%. Thus, keeping this in view, the amount of Nirmali seeds powder taken in all subsequent studies is 10 g/L. Furthermore, the half life i.e. t_{50} is insignificant (t_{50} <30 minutes at 5, 10, and 20 g/L) at different dosage.

Studies were also conducted to determine the optimum dose of Pongamia pods powder for chromium and lead removal (figures 4.2 and 4.3).

Percent chromium adsorption increases with increase in adsorbent (Pongamia pods powder) dose from 2 to 5 g/L (33 to 59%) and 5 to 10 g/L (59 to 77%). On further addition of 10 g/L, the chromium removed also increases (77 to 94%).

Keeping this in view and handling problems of large adsorbent dose, 10 g/L was selected as an optimum dose to carry out all the subsequent kinetics and sorption studies. Furthermore, the i.e. t_{50} also decreases with increase in the adsorbent dose and found to be (24 hrs, 24 hrs, 18 hrs, and 10 hrs at 2, 5, 10, and 20 g/L doses respectively).

Similar results were obtained for lead removal on Pongamia pods powder [Figure 4.3(b)]. With increase in dose 5 g/L to 10 g/L, the adsorption of lead becomes double. On introducing additional 10 g/L, the adsorption does not increase in the same proportion. Thus, an optimum dose of 10 g/L of Pongamia pods powder was used to carry out all the subsequent studies. . Furthermore, the half life i.e. t_{50} (t_{50} <30 minutes at 5, 10, and 20 g/L) at is found to be independent of adsorbent dose.

4.2.3. Effect of temperature

The sorption studies for both biosorbents (Nirmali seeds powder and Pognamia pods powder) were carried out at 25, 35, and 45 °C for chromium metal ion. The adsorption increases with increase in temperature. This shows that the process is endothermic in nature. This is also confirmed by the fact that the time required for 50% completion of adsorption decreases with rise in temperature.

4.2.3. Effect of intial metal concentration

The adsorption of chromium by Nirmali seeds powder and Pognamia pods powder at different concentrations of metal with time is shown in Figure 4.4. The adsorption increases with increase in chromium concentration. For a purely adsorptive reaction, the rate varies directly with the adsorbate concentration. The amount of lead and chromium removed in the first hour of contact increases as the concentration of metal ion increases. Furthermore, the half life (t_{50}) is found to be independent of concentration (Figures 4.4 and 4.5). The half life values are (t_{50} is <30 minutes at 100, 200 and 500 mg/L) for lead –Nirmali system and (t_{50} is 5hrs for 10, 40, and 80 mg/L) for chromium-Nirmali system. The kinetic models were fitted to concentration data. The kinetic data are given in Table 4.3.

The simple pseudo-first order rate equation as suggested by Lagergren (Mohan et al., 2011) and pseudo-second order kinetic model were applied to the biosorbents. The fitting of data at different adsorbate concentration, adsorbent dose, and temperature are shown in figures 4.7-4.16.

All the parameters together with the regression coefficients as calculated using first and second order rate equations are given in Tables 4.3-4.5. It is clear from Tables 4.3-4.5 and figures 4.7-4.16, the R^2 value as obtained from second-order rate equation are slightly better versus first-order rate equation. The correlation coefficients for most of the linear plots are superior (in most cases >0.98). It is also clear from tables 4.3-4.5 that theoretical and experimental q_e values have an excellent agreement.

Thus, pseudo-second order model assumes that the rate limiting step is a chemical adsorption of lead and chromium on biosorbents.

4.3. Isotherm and modeling

The Freundlich isotherm model is one of the earliest empirical equation used to explain the sorption equilibrium data. This model is very frequently and popularly used in the description of adsorption of organics from aqueous streams on activated charcoal (D. D. DO, Adsorption analysis: Equilibria and Kinetics, Imperial College Press; 1998).

Various parameters of the Freundlich equation can be estimated by plotting log (C_e) versus log (q_e) as given by equation (8) in Material and Method section.

The Freundlich equation can be obtained by assuming that surface is heterogeneous due to the fact that the adsorption energy is distributed and the surface topography is patchwise i.e. having the same adsorption energy are grouped together into one path (DO, 1998).

On the other hand, the Langmiur model is based on a kinetic principle i.e. the rate of adsorption is equal to the rate of desorption from the adsorbent surface (DO, 1998).Various parameters of the Langmuir equation can be estimated by plotting C_e/q_e versus C_e or $1/C_e$ versus $1/q_e$ as given by the equation (9) in Material and Method section.

The sorption equilibrium isotherms for chromium metal uptake on Nirmali seeds powder and Pongamia pods powder are shown in figures 4.17-4.20. Sorption data have been evaluated by Langmuir. Sorption data have been evaluated by Langmuir and Freundlich adsorption isotherm models. Data is better fitted by Langmuir isotherm model than Freundlich model. Isotherm data is shown in Table 4.1.It is clear from the Table 4.1, the adsorption capacity increases with increase in temperature, thereby, indicating the process to be endothermic in nature.The maximum adsorption capacities (Q^0) of Nirmali seeds and Pongamia pods powder 5.65 and 5.56 mg/g respectively at 45 °C.

The lead uptake on Nirmali seeds powder and Pongamia pods powder at different temperatures (10 mg/L to 1000 mg/L) have also been evaluated using the Langmuir and Freundlich adsorption isotherms. It is inferred that the data is better fitted to Langmuir model.

The removal of lead by Nirmali seeds powder and Pongamia pods powder decreases with increase in temperature, thereby, indicating the process to be exothermic in nature. The lead removal decreases fro 23.81 mg/g to 23.25 mg/g when temperature increases from 25° to 45 °C. On the other hand, the lead adsorption decreases from 16.95 mg/g to 14.085 mg/g when temperature increases from 25° to 45 °C. It is clear from Table 4.2, the decrease in case of Nirmali seeds powder is very small. Similar trend was obtained for the Freundlich adsorption capacity “K_F” as reported in tables 4.1 and 4.2 for chromium and lead respectively.

4.4. Application of biosorbents to treat surface water samples

Real water/wastewater systems contain a complex mixture of ions and sorption efficacy is affected by competition of these ions for the sorption sites. The efficacy of biosorbents (Nirmali seeds powder and Pongamia pods powder) in real water systems was investigated by collecting groundwater from Mathura, Uttar Pradesh, India. An additional ~5.0 mg/L of chromium and lead solutions was spiked into this water sample. Nirmali seeds powder and Pongamia pods powder were then utilized to remediate chromium and lead from this groundwater under optimum conditions previously obtained from batch sorption studies. The pH was adjusted to 4.0 and 4.5 for chromium and lead respectively, before applying the biosorbents. A predetermined amount of biosorbents (10 g/L) was added to each sample. After equilibrating 48 hours, the samples were filtered and the metal concentrations were measured by AAS.

Nirmali seeds powder remediate >99% lead and 95% chromium from water. Pongamia pods powder removed >99% lead and 97% chromium. Thus the presence of solids and other interfering ions do not interfere in the sorption process. Therefore, these biosorbents can be applied to remediate chromium and lead from contaminated surface/groundwater.

CHAPTER-V

CONCLUSIONS

Table 4.1 Freundlich and Langmuir isotherm parameters for chromium removal on Nirmali seeds powder and Pongamia pods powder at different temperatures.

Isotherm parameters	Nirmali seeds powder			Pongamia pods powder		
	25 °C	**35 °C**	**45 °C**	**25 °C**	**35 °C**	**45 °C**
Freundlich						
K_F (mg/g)	0.558	1.282	1.374	0.627	0.793	0.906
1/n	2.155	3.497	2.710	1.927	2.101	1.972
R^2	0.980	0.652	0.678	0.990	0.961	0.917
Langmuir						
Q^0 (mg/g)	3.922	4.739	5.650	4.926	4.785	5.556
b	1.952	6.732	12.150	2.982	4.362	6.460
R^2	0.947	0.982	0.988	0.952	0.965	0.962

Table 4.2 Freundlich and Langmuir isotherm parameters for lead removal on Nirmali seeds powder and Pongamia pods powder at different temperatures.

Isotherm parameters	Nirmali seeds powder			Pongamia pods powder		
	25 °C	**35 °C**	**45 °C**	**25 °C**	**35 °C**	**45 °C**
Freundlich						
K_F (mg/g)	4.074	5.728	4.634	3.076	3.639	3.083
1/n	2.899	3.425	2.976	3.279	3.759	3.367
R^2	0.678	0.879	0.768	0.733	0.894	0.774
Langmuir						
Q^0 (mg/g)	23.810	23.810	23.256	16.949	14.925	14.085
b	0.085	0.112	0.221	0.052	0.096	0.124
R^2	0.990	0.985	0.999	0.973	0.993	0.994

Table 4.3 First order and pseudo-second order rate constants and comparative evaluation of q_e as calculated experimentally and by using first and second-order rate equations at different chromium and lead concentrations.

Conc. (mg/L)		First order rate constant, k_1 (h^{-1})	R^2	First order rate constant, k_1 (h^{-1})	R^2	Second order rate constant, k_2 ($g\ mg^{-1}\ h^{-1}$)	R^2	Second order rate constant, k_2 ($g\ mg^{-1}\ h^{-1}$)	R^2	q_e experimental (mg/g)		q_e, calculated using first-order kinetic model (mg/g)		q_e , calculated using second-order kinetic model (mg/g)	
Nirmali seeds	Pongamia pods	Nirmali seeds		Pongamia pods		Nirmali seeds		Pongamia pods		Nirmali seeds	Pongamia pods	Nirmali seeds	Pongamia pods	Nirmali seeds	Pongamia pods
Chromium															
10	10	3.178	0.940	1.243	0.984	0.27	0.995	0.031	0.99	0.955	9.549	0.553	7.816	0.99	9.615
40	40	1.382	0.997	0.967	0.974	0.33	0.988	0.006	1	2.072	38.23	33.189	2.618	2.21	38.461
80	80	3.869	0.940	1.105	0.974	7.63	0.411	0.002	1	2.572	77.97	2.512	1.285	2.46	83.33
Lead															
100	100	10.364	0.764	-	0.005	1.30	1	76.92	0.999	9.240	9.634	0.547	0.360	9.26	9.80
200	200	11.331	0.932	0.313	0.18	0.38	0.999	32.26	0.999	15.89	11.118	0.578	1.321	16.13	11.24
500	500	6.080	0.446	0.234	0.011	0.21	0.999	333.33	0.999	20.465	13.83	0.514	0.668	20.83	13.89

Table 4.4 First-order and pseudo-second-order rate constants and comparative evaluation of q_e as calculated experimentally and by using first and second order rate equations at different adsorbent dose.

Dose (g/L)		First order rate constant, k_1 (h^{-1})	R^2	First order rate constant, k_1 (h^{-1})	R^2	second order rate constant, k_2 (g mg^{-1} h^{-1})	R^2	second order rate constant, k_2 (g mg^{-1} h^{-1})	R^2	q_e experimental (mg/g)		q_e calculated using first-order kinetic model (mg/g)		q_e calculated using second-order kinetic model (mg/g)	
Nirmali seeds	Pongamia pods	Nirmali seeds		Pongamia pods		Nirmali seeds		Pongamia pods		Nirmali seeds	Pongamia pods	Nirmali seeds	Pongamia pods	Nirmali seeds	Pongamia pods
Chromium															
2	2	3.040	0.977	1.520	0.964	0.568	0.984	4.08	0.995	2.726	6.527	1.840	1.603	2.82	6.49
4	5	2.764	0.9	1.382	0.981	0.349	0.986	13.89	0.999	1.485	9.016	0.873	8.318	1.52	9.01
10	10	3.178	0.935	1.244	0.979	0.252	0.994	27.78	0.999	0.955	9.549	0.545	7.852	0.99	9.62
-	20	-	-	1.244	0.978	-	-	62.50	1	-	9.737	-	7.727	-	9.80
Lead															
5	5	3.178	0.943	-	-	500	0.999	-	0.999	46.280	8.533	1.866	-	47.619	8.55
10	10	1.244	0.974	-	-	0	0.99	-	0.999	45.870	4.609	1.644	-	47.619	4.63
20	20	1.658	0.986	-	-	0	0.99	-	1	45.99	2.397	1.069	-	47.619	2.39

Table 4.5 First-order and pseudo-second-order rate constants and comparative evaluation of q_e as calculated experimentally and by using first- and second-order rate equations at different temperature.

Temperature (°C)		First order rate constant, k_1 (h^{-1})	R^2	First order rate constant, k_1 (h^{-1})	R^2	second order rate constant, k_2 (g mg^{-1} h^{-1})	R^2	second order rate constant, k_2 (g mg^{-1} h^{-1})	R^2	q_e experimental (mg/g)		q_e calculated using first-order kinetic model (mg/g)		q_e calculated using second-order kinetic model (mg/g)	
Nirmali seeds	**Pongamia pods**	**Nirmali seeds**		**Pongamia pods**		**Nirmali seeds**		**Pongamia pods**		**Nirmali seeds**	**Pongamia pods**	**Nirmali seeds**	**Pongamia pods**	**Nirmali seeds**	**Pongamia pods**
Chromium															
25	25	1.520	0.997	2.349	0.989	0.19	0.986	0.08	0.891	1.526	1.635	44.361	54.2	1.65	1.72
35	35	2.764	0.916	2.073	0.986	0.42	0.996	0.14	0.985	1.871	1.883	1.205	1.629	1.95	2.13
45	45	1.382	0.992	0.967	0.983	0.60	0.998	0.24	0.995	1.982	1.983	36.058	46.132	2.06	2.16

Table 4.6 Chromium remediation from contaminated ground water sample using Nirmali seeds powder and Pongamia pods powder (adsorbent dose: 10 g/L; equilibrium time: 48 hour; pH: 4.0; temperature: 25 °C; particle size: 30-50 mesh; volume of the water sample taken: 50 ml)

Parameters	Values (initial pH 8.44 which is adjusted to pH 4)	Values after treatment with Nirmali seeds powder	Values after treatment with Pongamia pods powder
pH	4	4.31	4.76
Na^+ (mg/L)	189	188.8	177
K^+ (mg/L)	20.5	28.4	30.3
Li^+ (mg/L)	4.6	4.4	4.5
Ca^{2+} (mg/L)	19.5	20.4	20.1
Ba^{2+} (mg/L)	21.4	25.8	25.2
Chromium (mg/L)	5	0.173	0.251

Table 4.7 Lead remediation from contaminated ground water sample using Nirmali seeds powder and Pongamia pods powder (adsorbent dose: 10 g/L; equilibrium time: 48 hour; pH: 4.5; temperature: 25 °C; particle size: 30-50 mesh; volume of the water sample taken: 50 ml)

Parameters	Values (initial pH 8.44 which is adjusted to pH 4.5)	Values after treatment with Nirmali seeds powder	Values after treatment with Pongamia pods powder
pH	4.5	4.30	4.84
Na^+ (mg/L)	189	174	177
K^+ (mg/L)	20.5	21.6	24.3
Li^+ (mg/L)	4.6	4.5	4.3
Ca^{2+} (mg/L)	19.5	20.6	19.3
Ba^{2+} (mg/L)	21.4	20.4	20.6
Lead (mg/L)	5	0.022	0.024

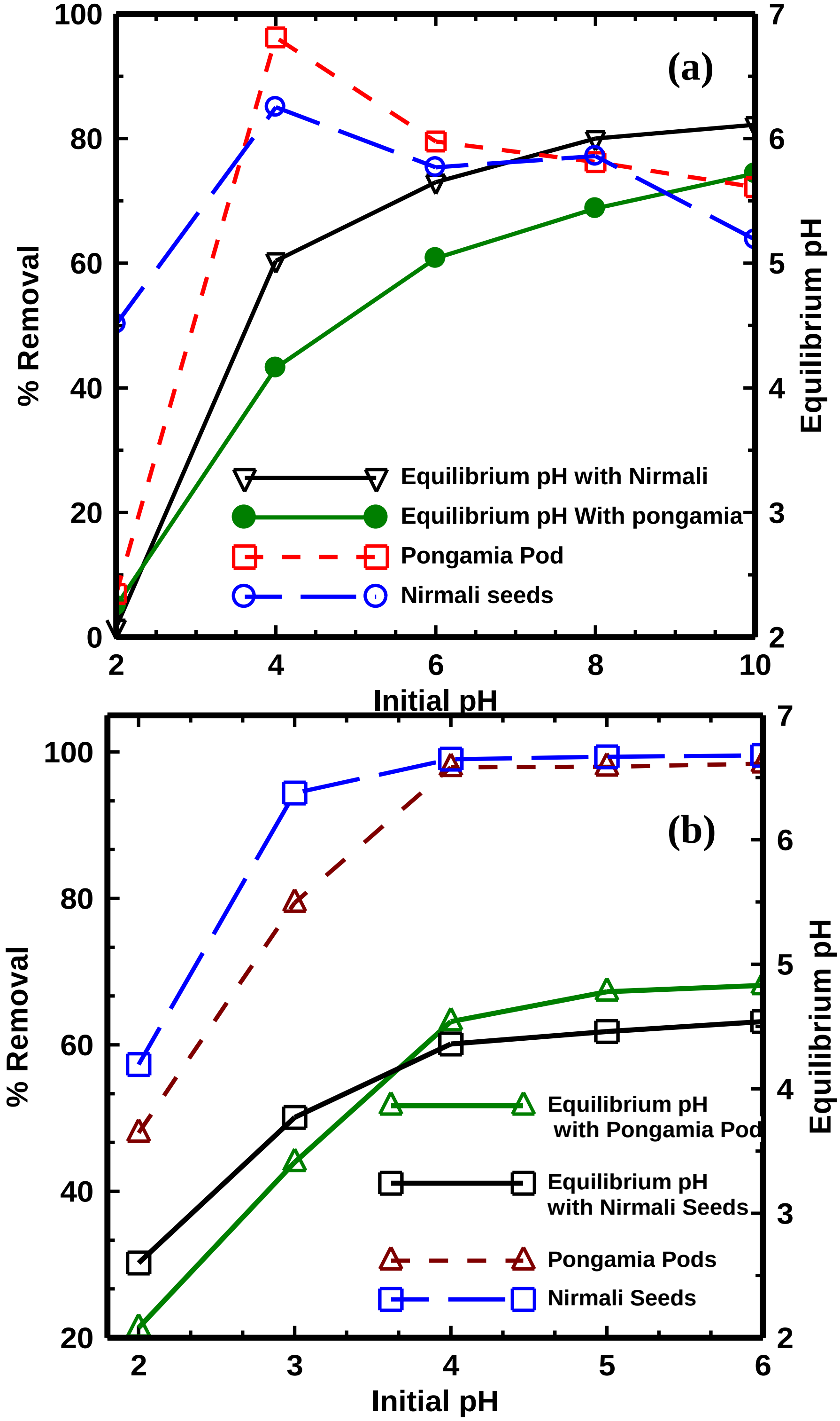

Figure. 4.1. Effect of pH on (a) chromium removal using Nirmali seeds powder and Pongamia pods powder [initial concentration of ~10 mg/L, adsorbent dose of 10 g/L, particle size 30-50 B.S.S mesh and at 25 °C] (b) lead removal using Nirmali seeds powder and Pongamia pods powder [initial concentration of ~ 40 mg/L, adsorbent dose of 10 g/L, particle size 30-50 B.S.S mesh and at 25 °C].

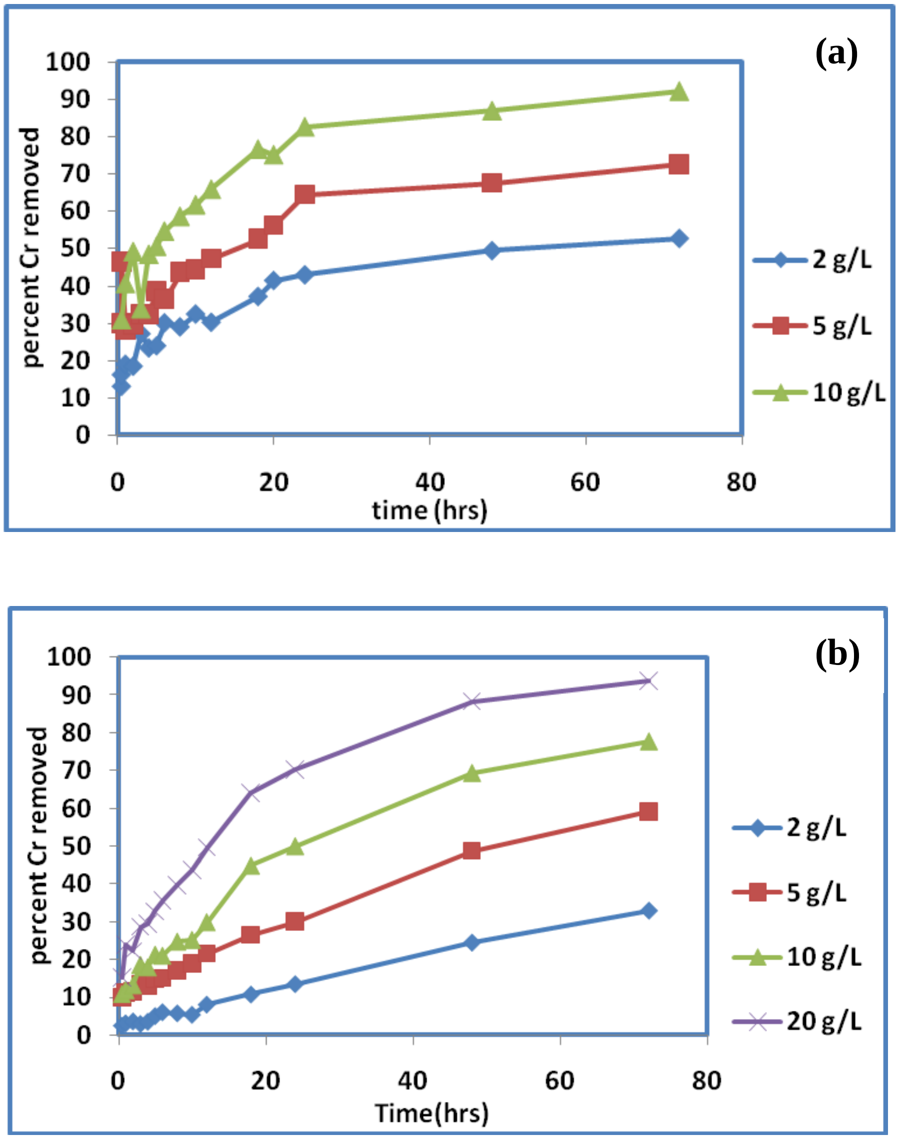

Figure 4.2. Effect of contact time on the uptake of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbent dose [pH 4.0, adsorbate concentration 10 mg/L, temperature 25 °C].

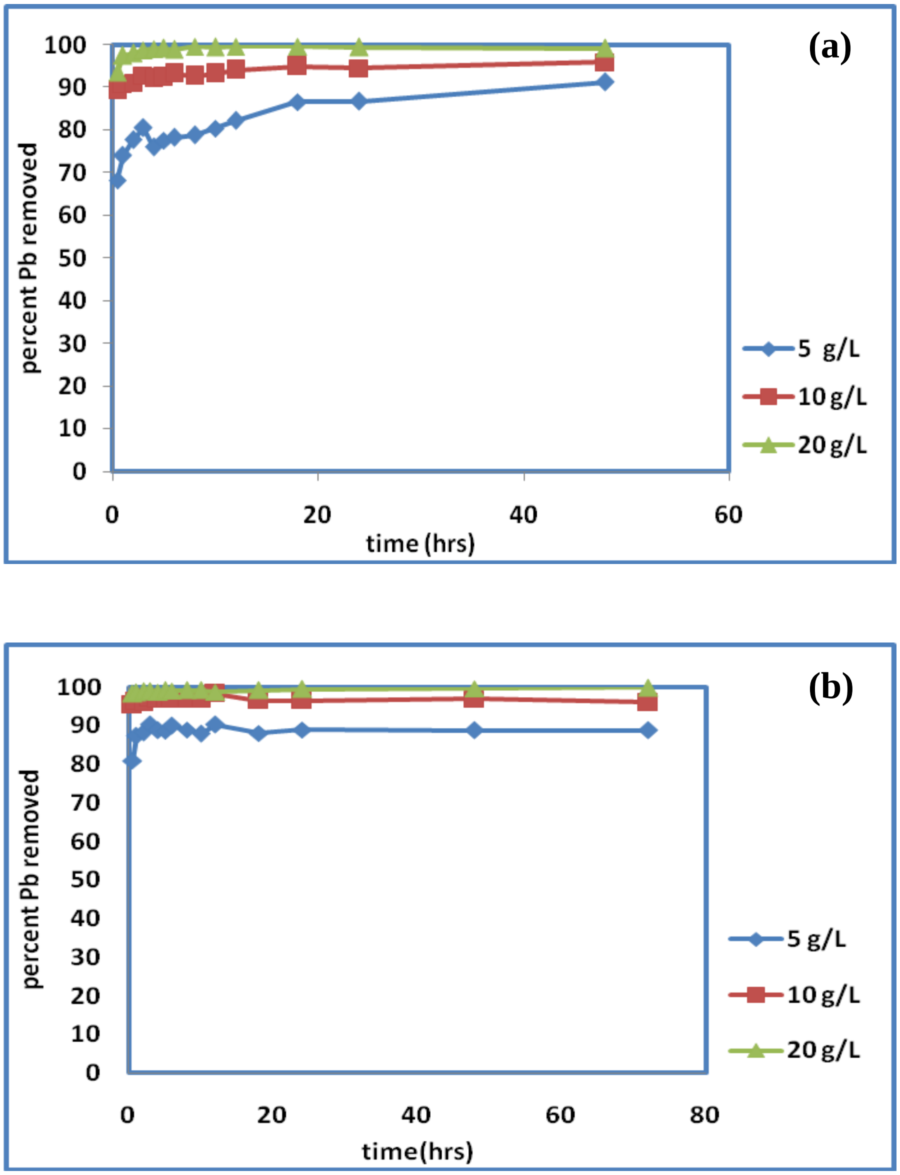

Figure 4.3. Effect of contact time on the uptake of Pb by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbent dose [pH 4.5, adsorbate concentration 10 mg/L, temperature 25 °C].

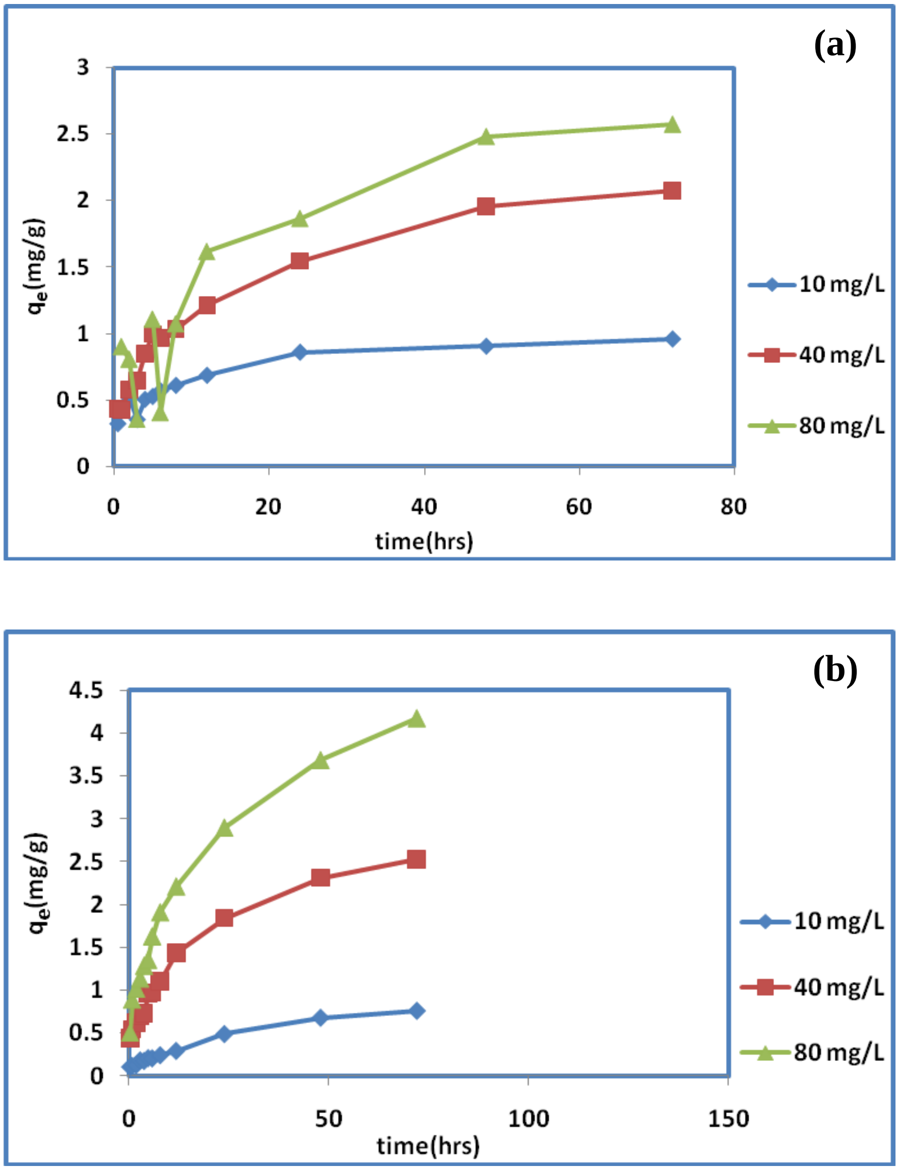

Figure 4.4. Effect of contact time on the uptake of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentrations [pH 4.0, adsorbent dose 10 g/L, temperature 25 °C].

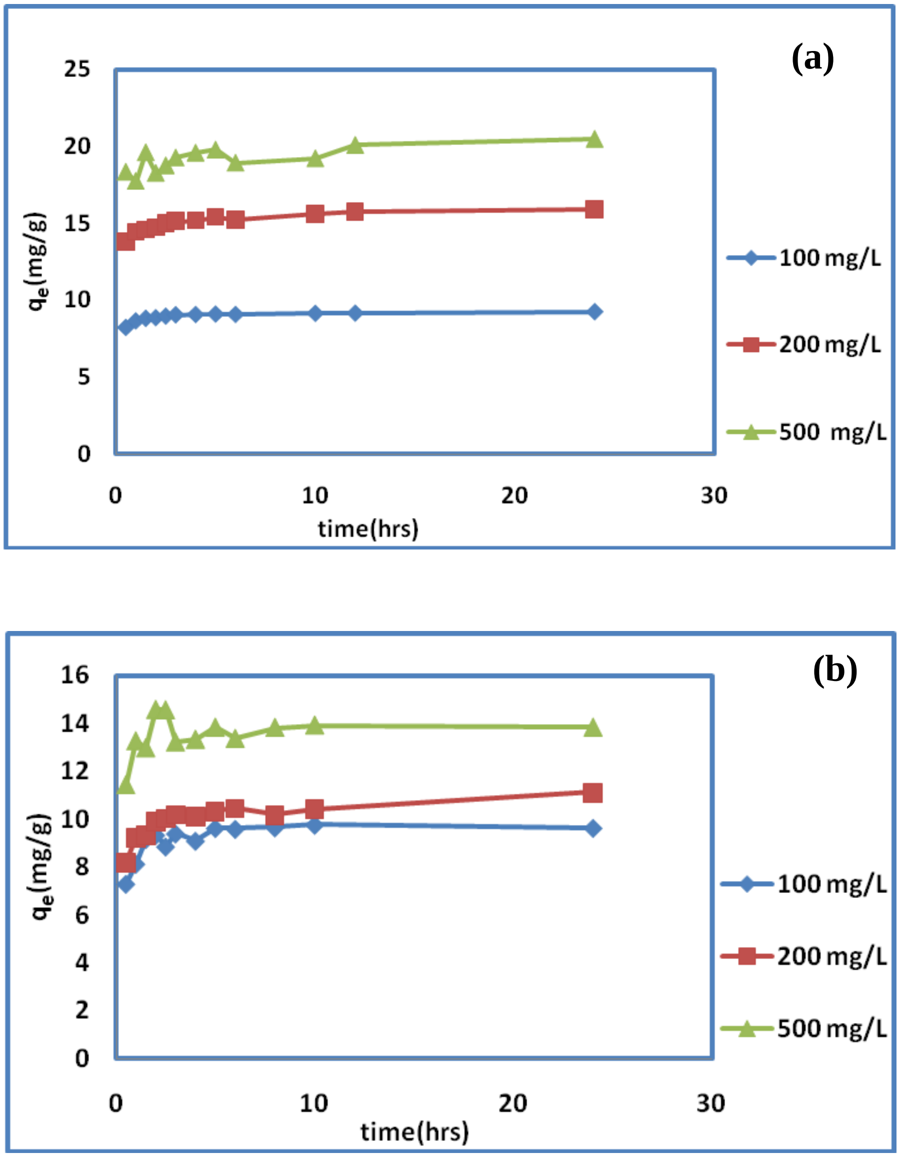

Figure 4.5. Effect of contact time on the uptake of lead by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentrations [pH 4.5, adsorbent dose 10 g/L, temperature 25 °C].

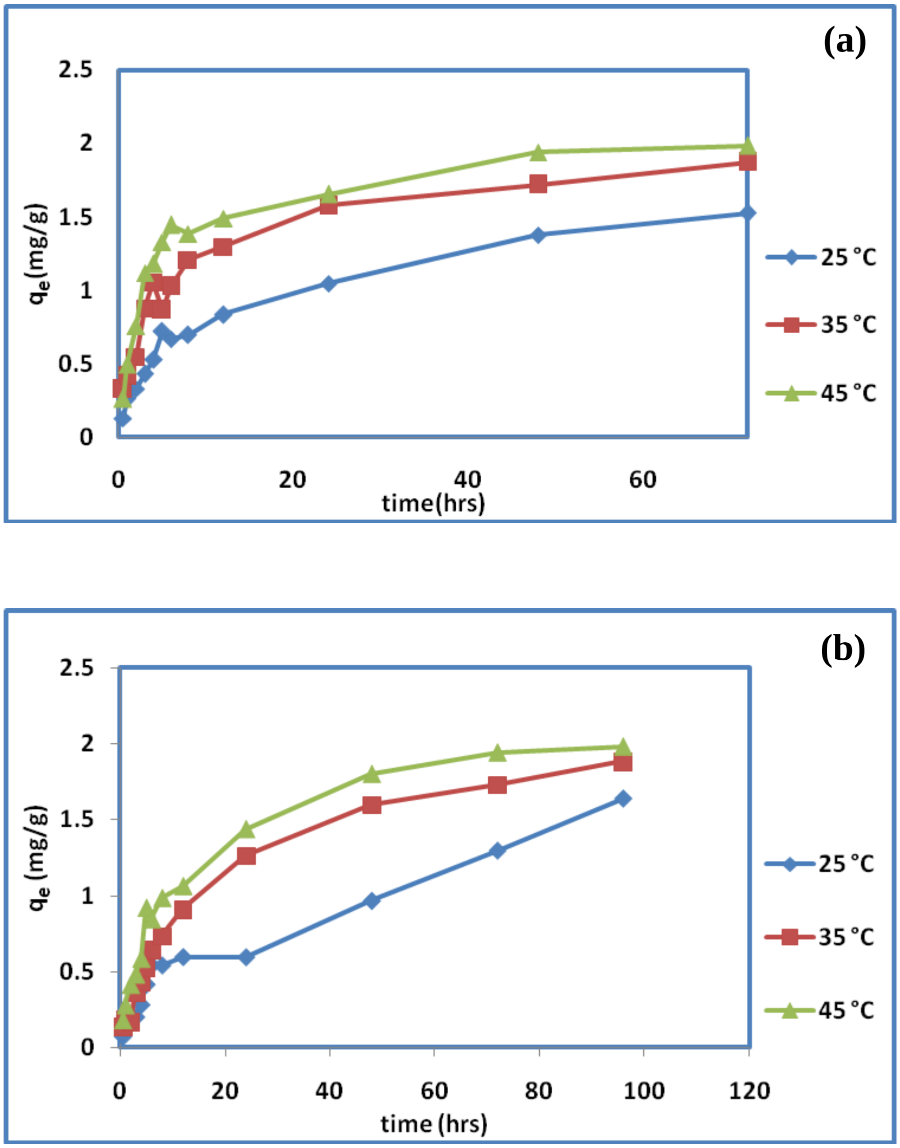

Figure 4.6. Effect of contact time on the uptake of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different temperature [pH 4.0, adsorbent dose 10 g/L, adsorbate concentration 20 mg/L].

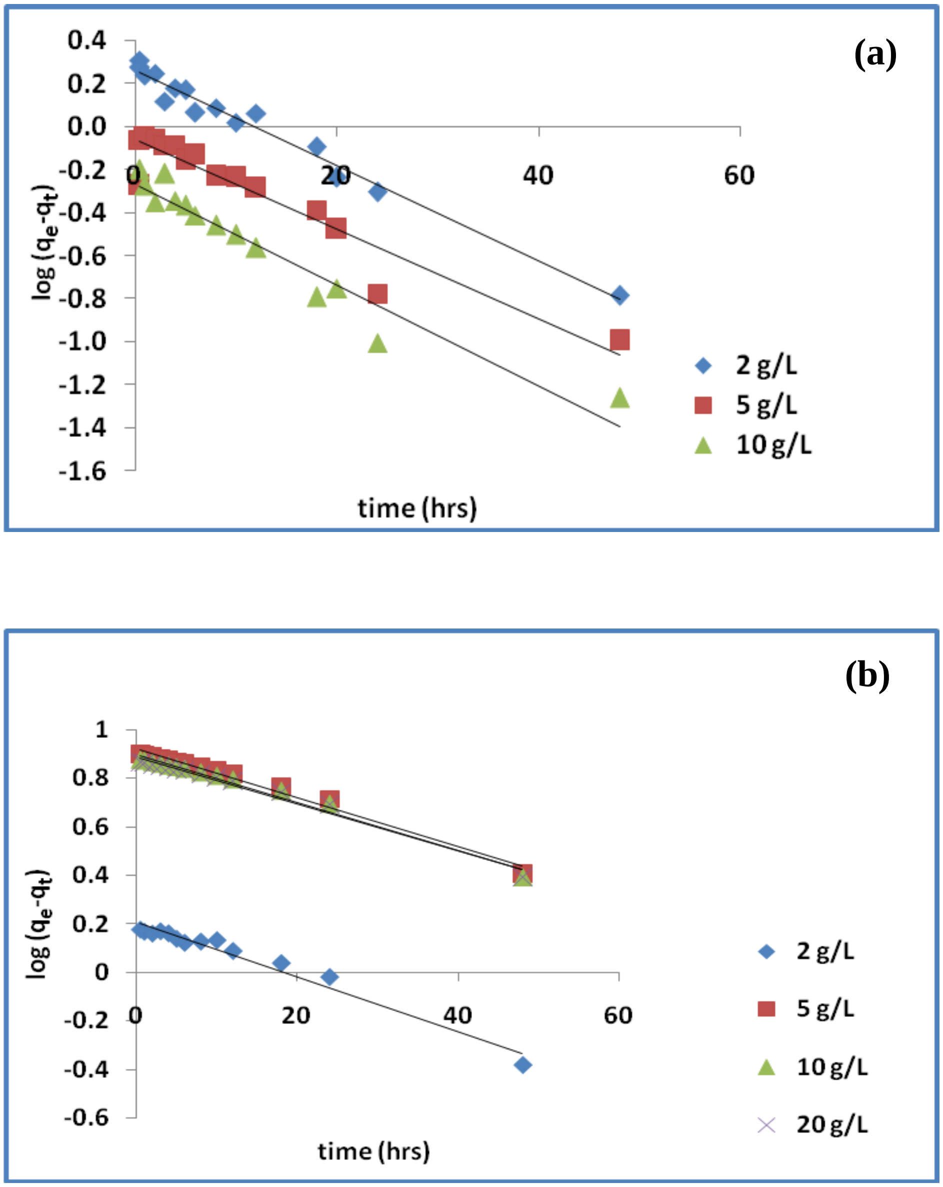

Figure 4.7. Pseudo-first order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbent dose [pH 4.0, adsorbate concentration 10 mg/L, temperature 25 °C].

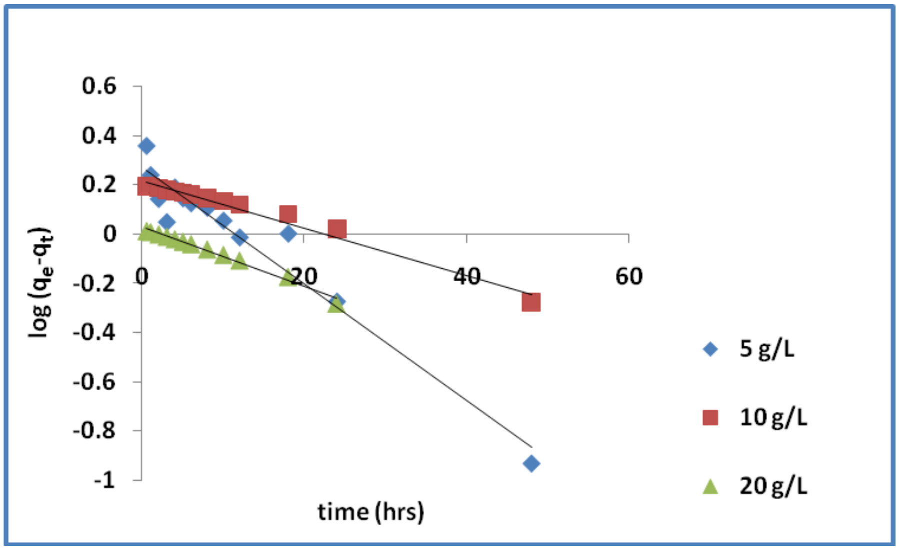

Figure 4.8. Pseudo-first order kinetic plots for the adsorption of lead by Nirmali seeds powder at different adsorbent dose [pH 4.5, adsorbate concentration 10 mg/L, temperature 25 °C].

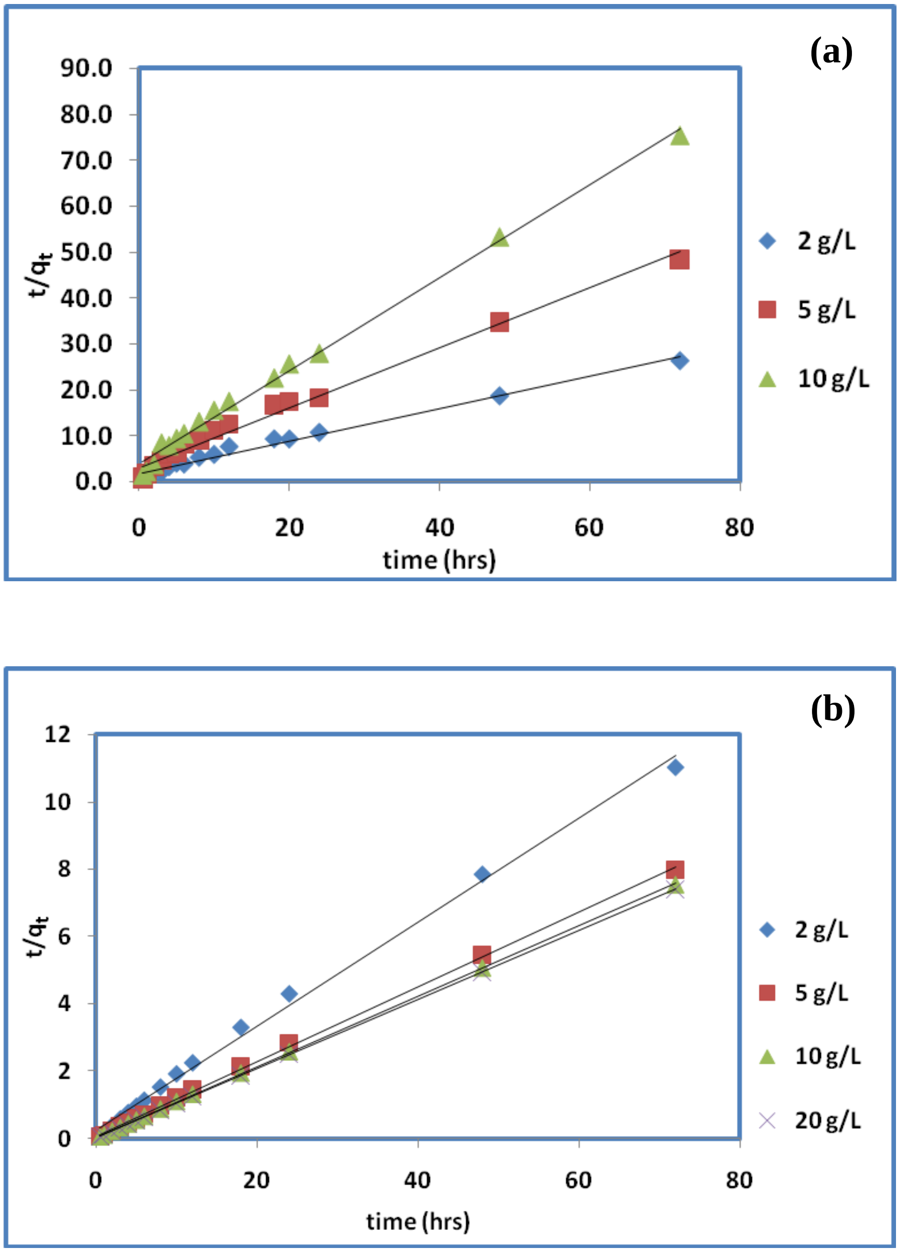

Figure 4.9. Pseudo-second order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbent dose [pH 4.0, adsorbate concentration 10 mg/L, temperature 25 °C].

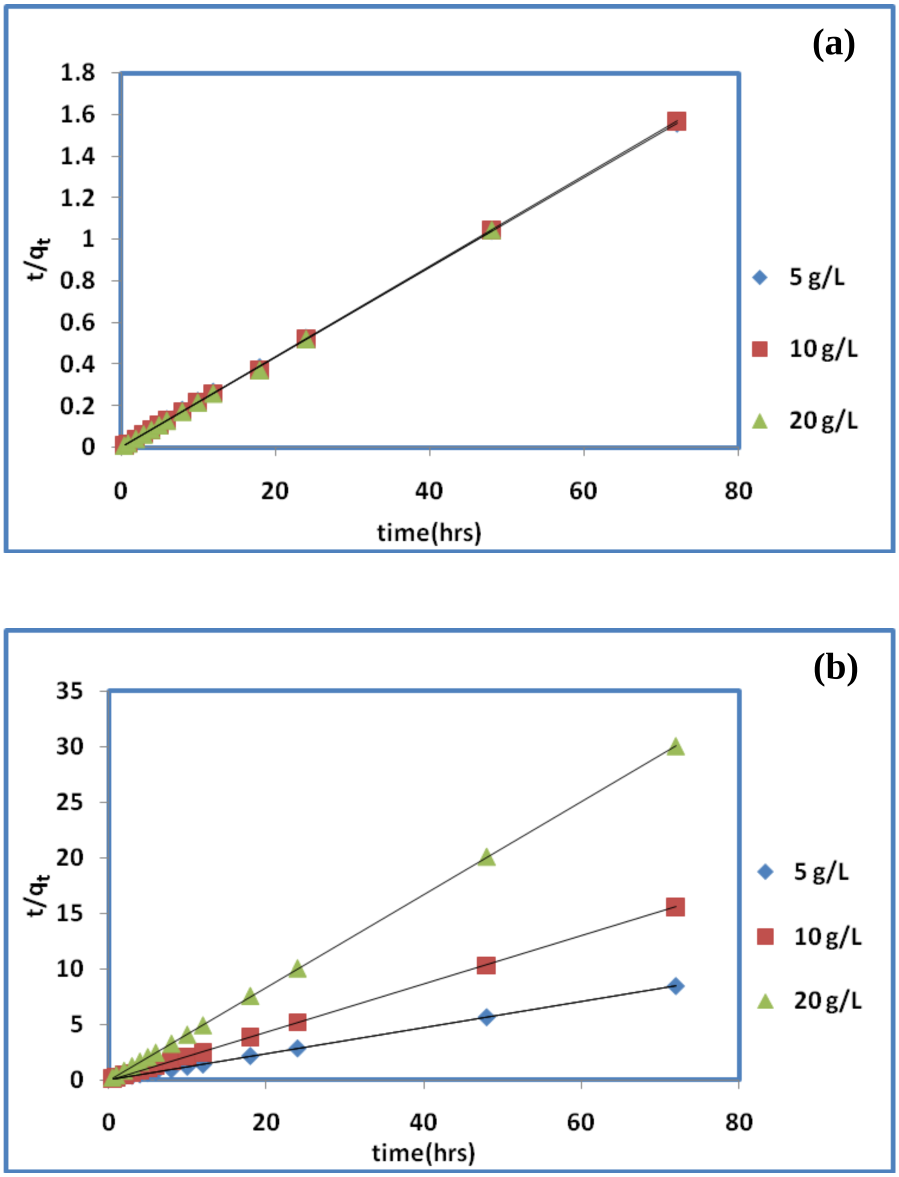

Figure 4.10. Pseudo-second order kinetic plots for the adsorption of lead by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbent dose [pH 4.5, adsorbate concentration 10 mg/L, temperature 25 °C].

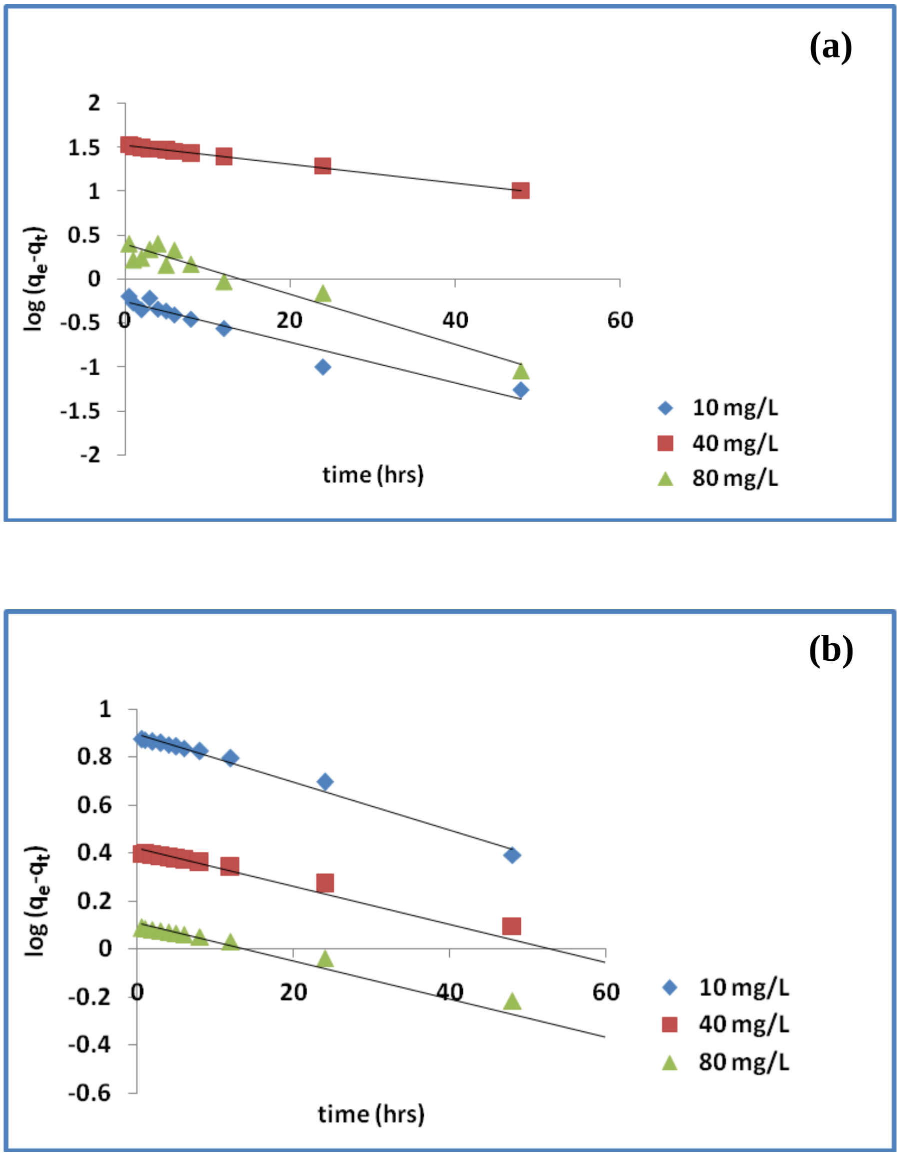

Figure 4.11. Pseudo-first order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentration [pH 4.0, temperature 25 °C, adsorbent dose 10 g/L].

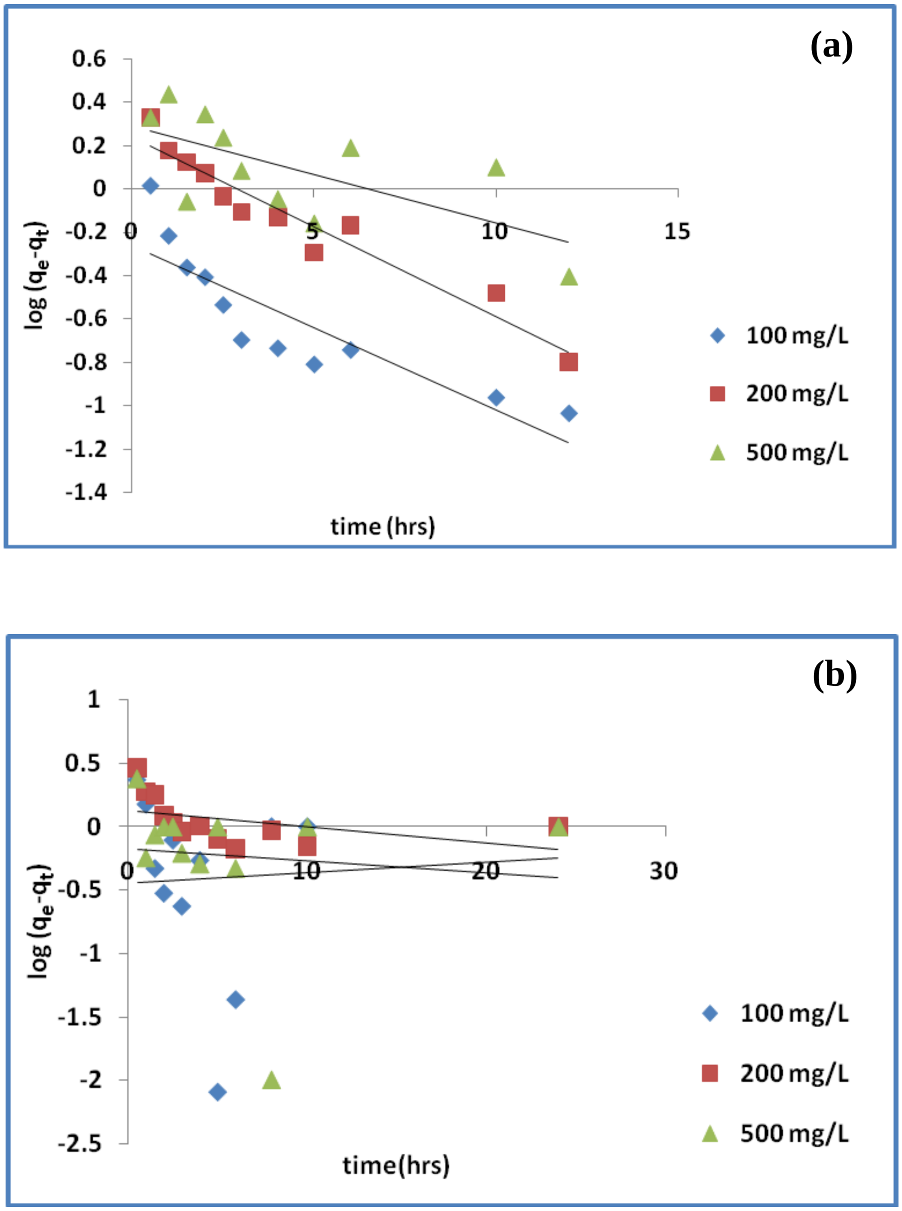

Figure 4.12. Pseudo-first order kinetic plots for the adsorption of lead by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentrations [pH 4.5, temperature 25 °C, adsorbent dose 10 g/L].

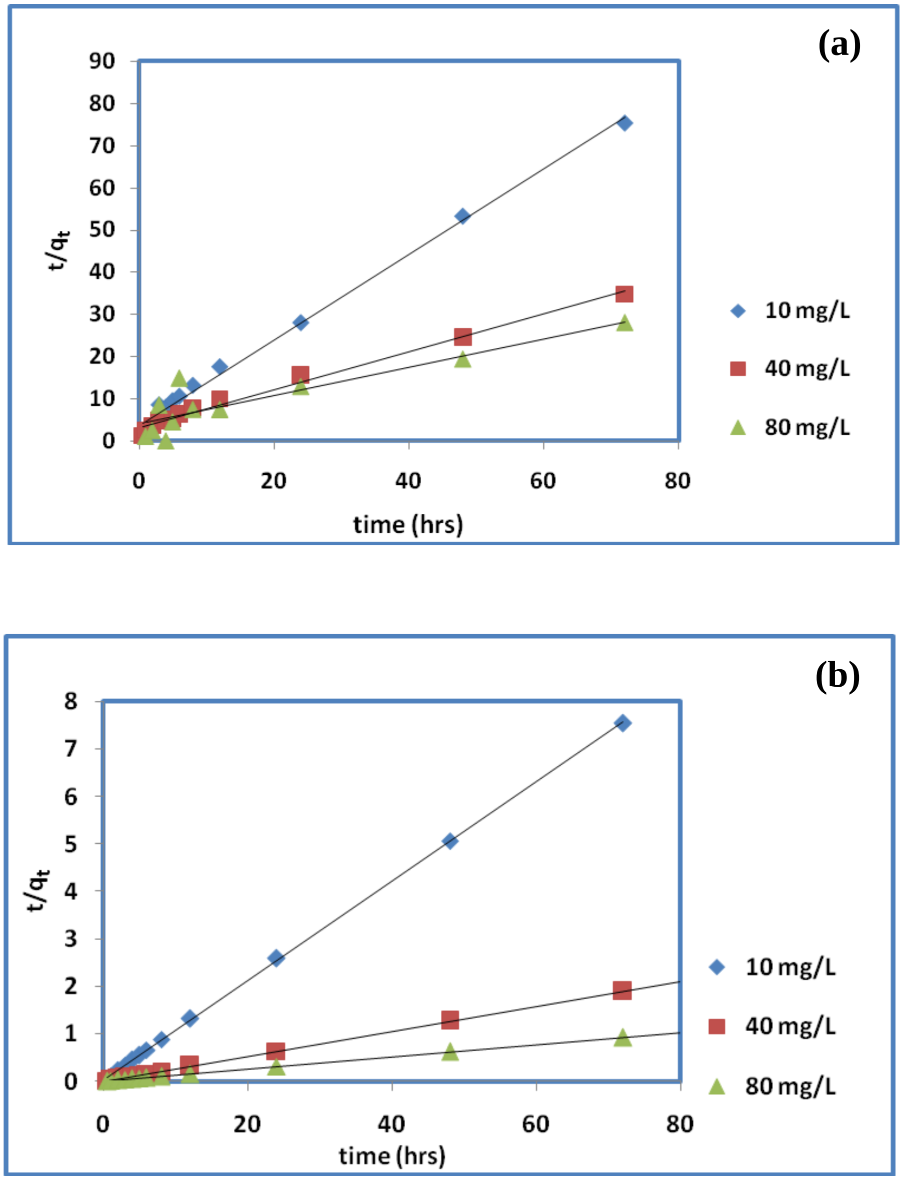

Figure 4.13. Pseudo-second order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentration [pH 4.0, adsorbent dose 10 g/L, temperature 25 °C].

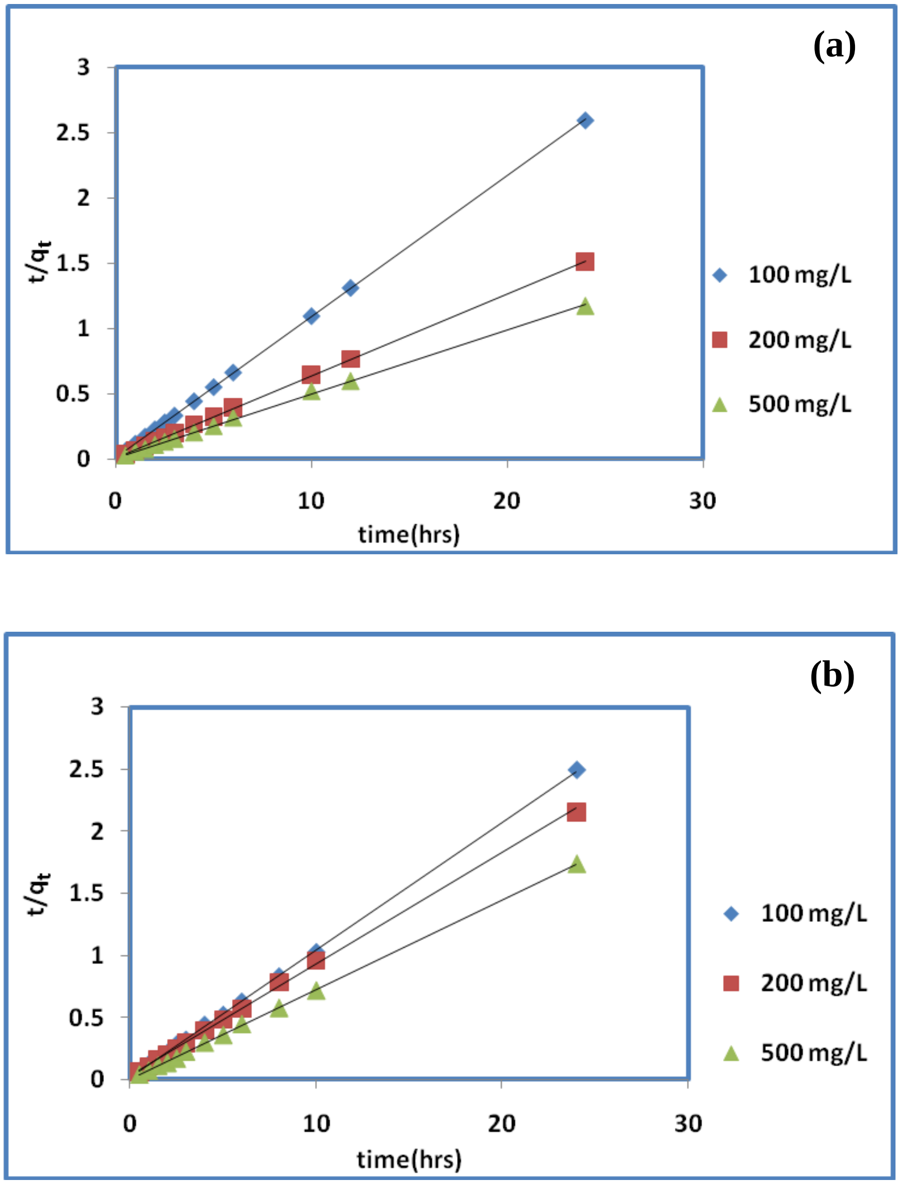

Figure 4.14. Pseudo-second order kinetic plots for the adsorption of lead by (a) Nirmali seeds powder (b) Pongamia pods powder at different adsorbate concentration [pH 4.5, adsorbent dose 10 g/L, temperature 25 °C].

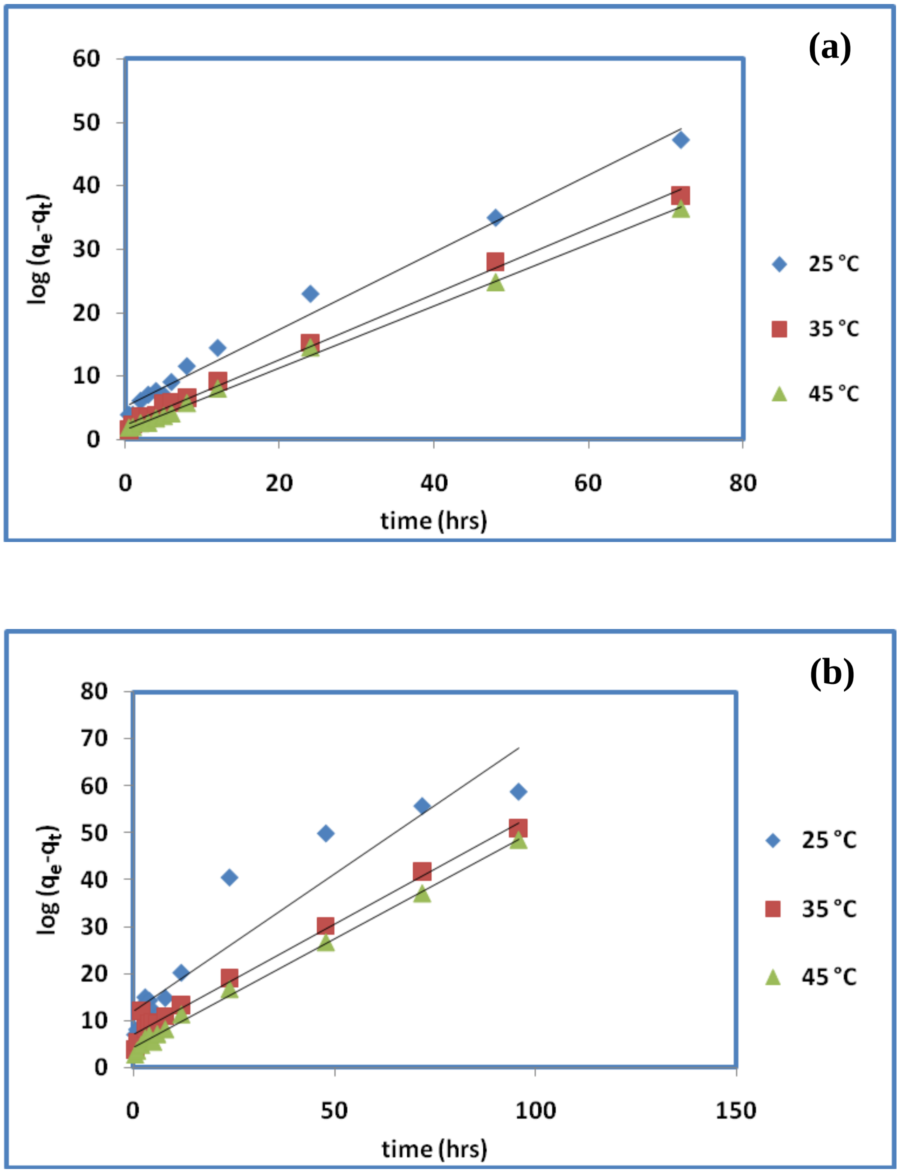

Figure 4.15. Pseudo-first order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder (b) Pongamia pods powder at different temperatures [pH 4.0, adsorbent dose 10 g/L, adsorbate concentration 20 mg/L].

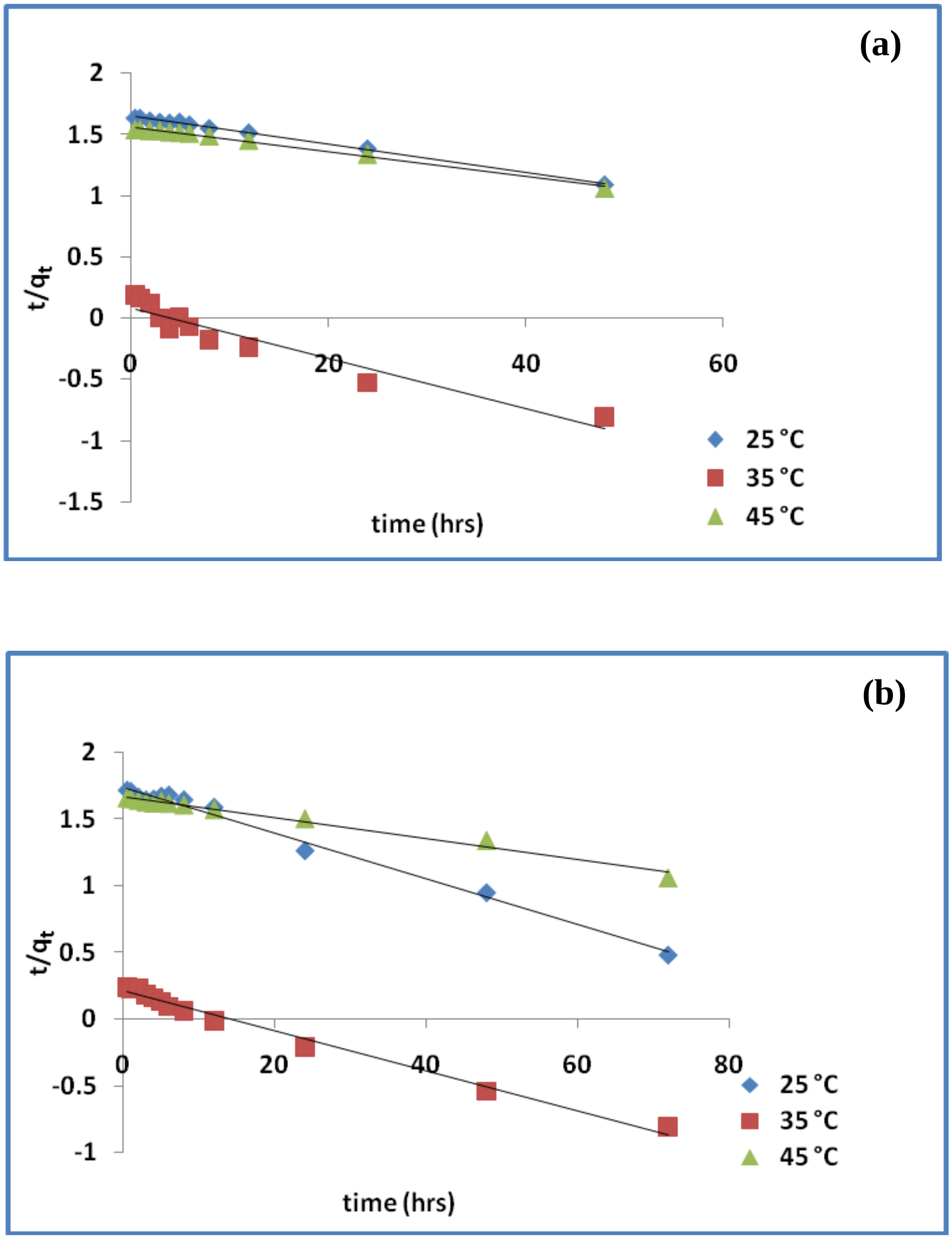

Figure 4.16. Pseudo-second order kinetic plots for the adsorption of chromium by (a) Nirmali seeds powder powder (b) Pongamia pods powder at different temperatures [pH 4.0, adsorbent dose 10 g/L, adsorbate concentration 20 mg/L].

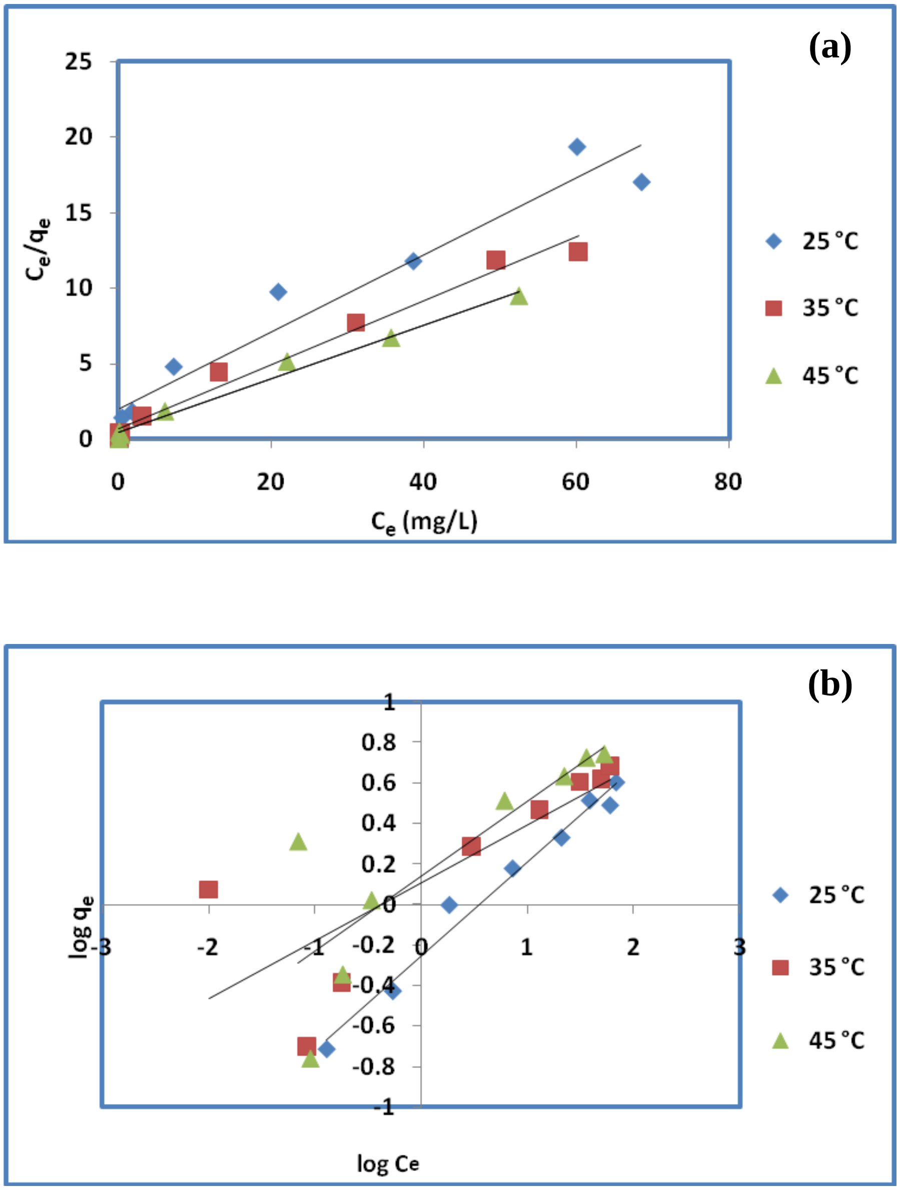

Figure 4.17. Sorption isotherm of chromium by Nirmali seeds powder at different temperature (pH 4.0, adsorbent dose 10 g/L) solid lines represent the data fitted by (a) Langmuir (b) Freundlich isotherms.

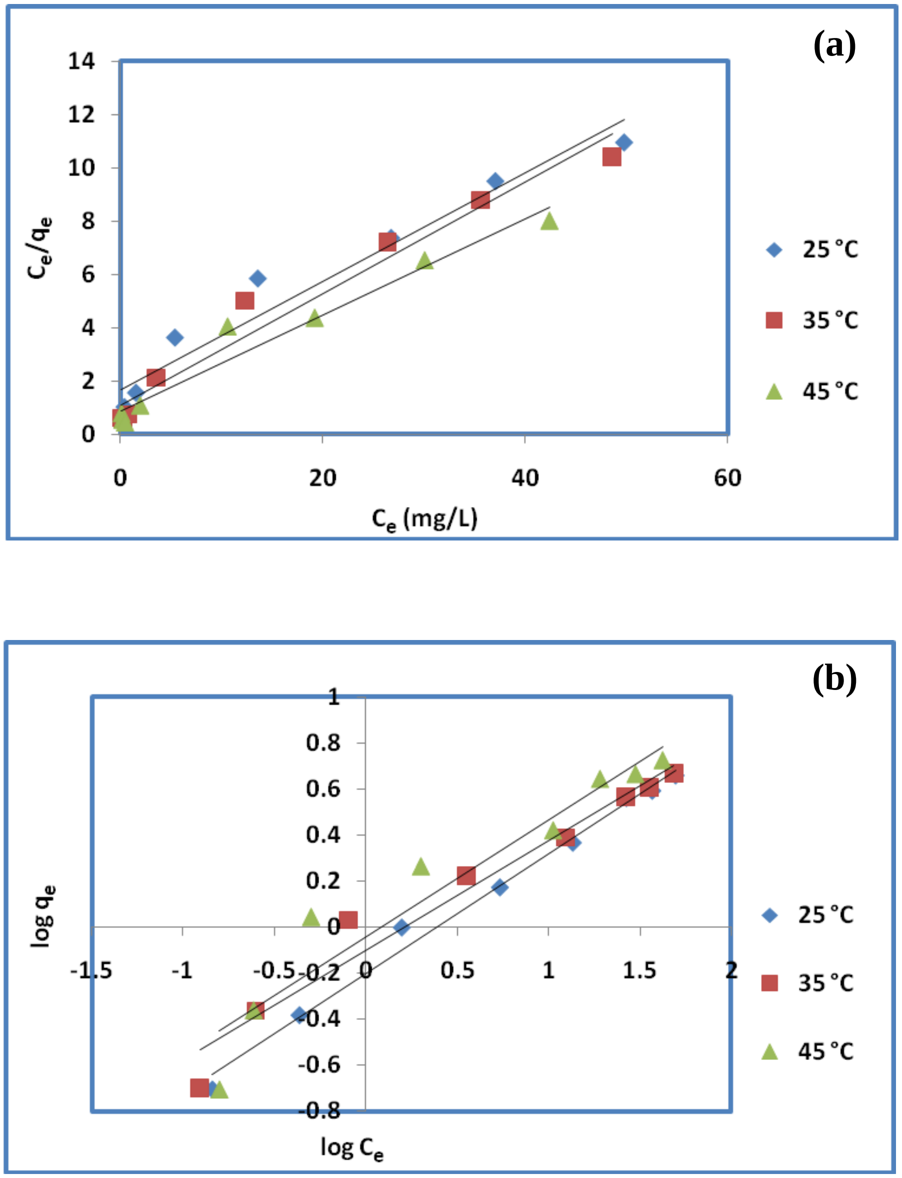

Figure 4.18. Sorption isotherm of chromium by Pongamia pods powder at different temperature [pH 4.0, adsorbent dose 10 g/L]. Solid lines represent the data fitted by (a) Langmuir (b) Freundlich isotherms.

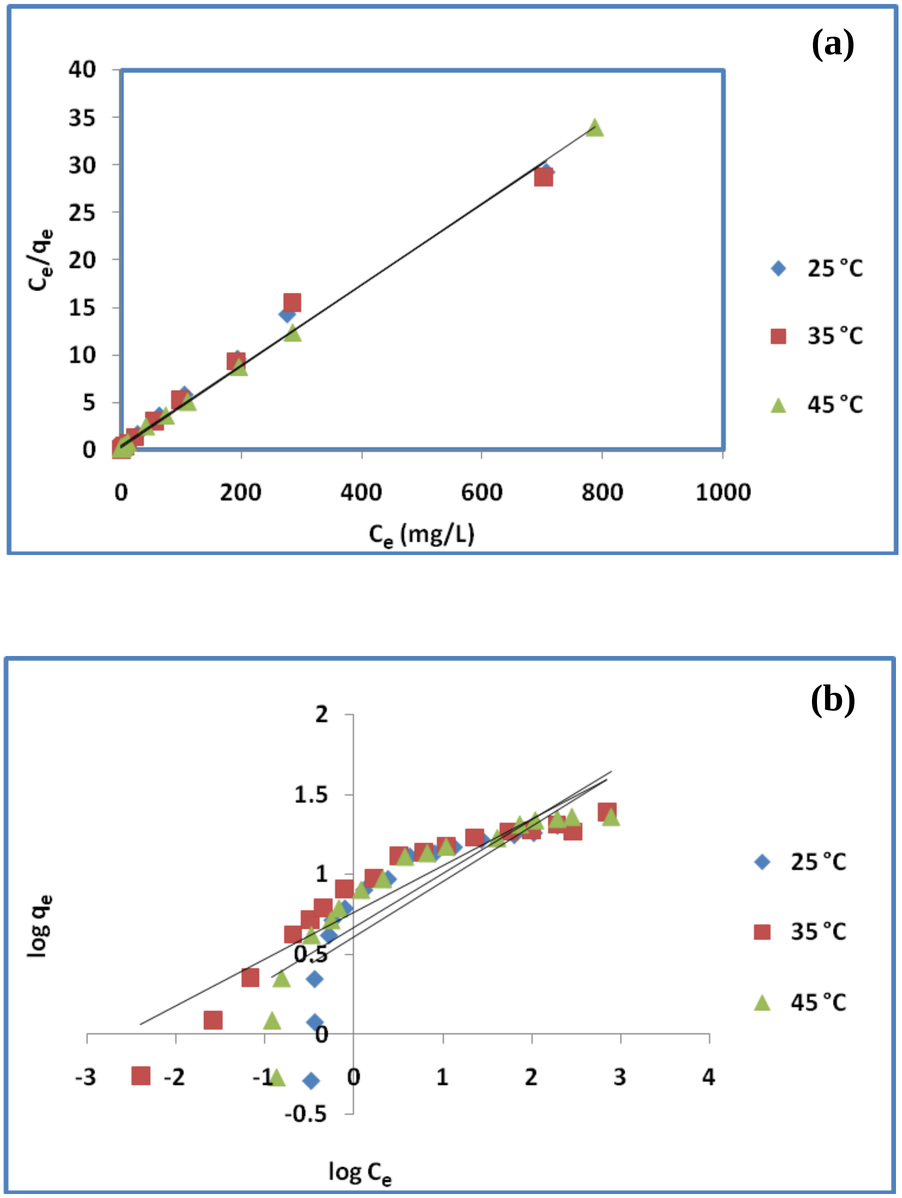

Figure 4.19. Sorption isotherm of lead by Nirmali Seeds powder at different temperature [pH 4.5, adsorbent dose 10 g/L]. Solid lines represent the data fitted by (a) Langmuir (b) Freundlich isotherms.

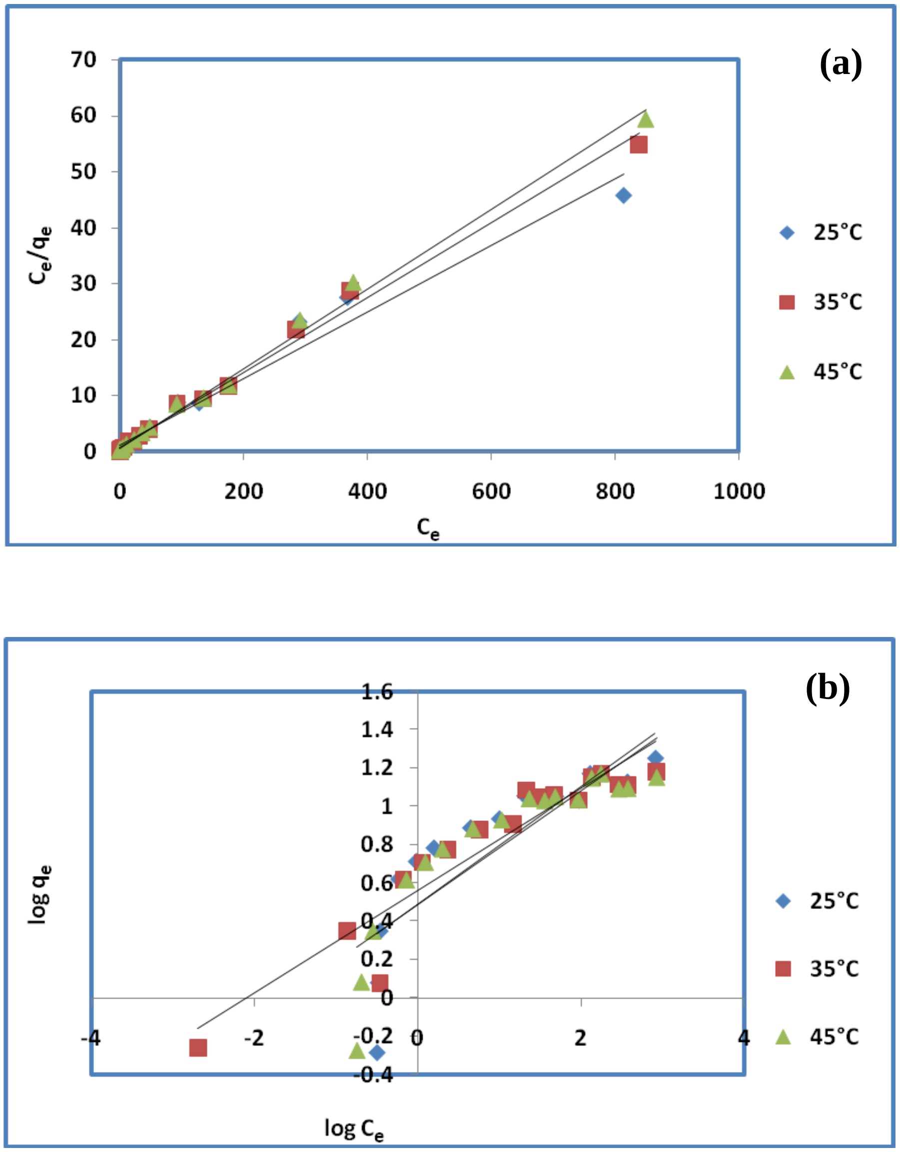

Figure 4.20. Sorption isotherm of lead by Pongamia pods powder at different temperature [pH 4.5, adsorbent dose 10 g/L]. Solid lines represent the data fitted by (a) Langmuir (b) Freundlich isotherms.

Conclusions

In the present study, Nirmali seeds powder and Pongamia pods powder were used as low cost biosorbents. The biosorbents were characterized for BET surface area, CHNS analyses and pH_{PZC}. Surface morphology was identified by SEM and TEM. Organic functional groups present in the samples were identified through FT-IR spectroscopy.

The biosorbents (Nirmali seeds powder and Pongamia pods powder) were used to remediate chromium and lead from aqueous solution, using batch sorption and kinetic studies. Equilibrium and sorption dynamics for both biosorbents were performed at optimized pHs. Sorption data were modelled using Freundlich and Langmuir isotherm models. On the basis of the present study following conclusions were made

- Based on the pH studies, maximum chromium adsorption for Nirmali seeds powder and Pongania pods powder occured at 4.5.
- Kinetic studies for chromium and lead removal was performed at different adsorbent doses, adsorbate concentrations and temperatures. Kinetic data were modelled using pseudo-first order and pseudo-second order kinetic models.
- Kinetic data of chromium and lead were better described by a pseudo-second order model.
- Chromium adsorption by Nirmali seeds powder and Pongamia pods powder is endothermic in nature.
- Lead adsorption has very insignificant effects of temperature on biosorbents (Nirmali seeds powder and Pongamia pods powder).
- Sorption of chromium on Nirmali seeds powder followed the Langmuir model.
- Both Langmuir and Freundlich models were followed in case of chromium removal on Pongamia pods powder.
- Isotherm data for Nirmali seeds powder for lead removal followed only Langmuir model.

- These biosorbents were utilized to remove chromium and lead from spiked groundwater (collected from Mathura district, Uttar Pradesh, India) successfully.
- These biosorbents can efficiently remove chromium and lead but, its efficiency can be increased with some physical and chemical treatments.
- These biosorbents could be applied to remediate lead and chromium from industrial effluents (at its optimum pH = 4.0 to 4.5).
- Biosorbents (Nirmali seeds powder and Pongamia pods powder) are effective to remediate lead and chromium, low cost and locally available. Thus, these can be utilised for heavy metals removal from water and wastewater.

REFERENCES

Agarwal, G.S., Bhuptawat, H.K., Chaudhari, S., 2006. Biosorption of aqueous chromium (VI) by *Tamarindus indica* seeds. Bioresource technology 97(7), 949-56.

Ahluwalia, S.S., Goyal, D., 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresource Technology 98, 2243-2257.

Akar, S.T., Özcan, A.S., Akar, T., Özcan, A., Kaynak, Z., 2009. Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. Desalination 249(2), 757-761.

Aksu, Z., Balibek, E., 2007. Chromium (VI) biosorption by dried Rhizopus arrhizus, Effect of salt (NaCl) concentration on equilibrium and kinetic parameters. Journal of Hazardous Materials 145, 210-220.

Al Ahmad., 2011. Electrocoagulation in Wastewater Treatment. Water 3495-525.

Allouche, F.N., Mameri, N., Guibal, E., 2011. Pb (II) biosorption on posidonia oceanica biomass. Chemical Engineering journal 168, 1174-1184.

Amina, C., Lhadi, L.K., Younsi, A., Murdy, J., 2004. Environmental impact of an urban landfill on a coastal aquifer. Journal of African Earth Sciences 39(3–5), 509–516.

Annual Report 2008 – 2009. Central Pollution Control Board, Ministry of Enviroment & Forests, Government of India.

Anonymous. World Water Day., 2010. Retrieved from www.worldwaterday2010. info, UnitedNations.

Anwar, F., 2003. Assessment and analysis of industrial liquid waste and sludge disposal at unlined landfill sites in arid climate, Waste Management 23(9), 817–824.

Aravindhan, R., Madhan, B., Rao, J.R., 2004. Bioaccumulation of chromium fromtan-nery wastewater: an approach for chrome recovery and reuse. Journal of EnvironmentalScience and Technology 38, 300–306.

Basfar, A.A., Rehim, A.F., 2002. Disinfection of wastewater froma Riyadh wastewater treatment plant with ionizing radiation. Journal of Radiation Physics and Chemistry 65, 527.

Bhattacharya, K.G., Sharma, A., 2004. Absorption of Pb (II) from aqueous solution by Azadirachta indica (Neem) leaf powder. Journal of Hazardous Materials 29, 1.

BIS, Specifications for Drinking Water, ISO:10500:1991, Bureau of Indian Standards, New Delhi, 1991.

Blazquez, G., Martin-Lara, M.A., Tenoria, G., Calero, M., 2010. Batch sorption of lead (II) from aqueous solution by olive tree pruning waste: Equilibrium, kinetics and thermodynamic study. Chemical Engineering Journal 168(1), 170-177.

Bromley-Challenor, K.C.A., Knapp, J.S., Zhang, Z., Gray, N.C.C., Hetheridge,M.J., Evans, M.R., 2000. Decolorizationof an azo dye by unacclimated activated sludge under anaerobic conditions. Journal of Water Research 34, 4410.

Bruggen, B.V., Vandecasteele, C., Gestel, T.M., Doyenb,W., Leysen,R.A., 2003. Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production. Journal of Environmental Progress 22, 46-56.

Butler, E., Hung, Y.T., Yeh,R.Y.L., Ahmad, M. S. A., 2011. Electrocoagulation in Wastewater Treatment. Journal of Water research 3, 495-525.

Cabatingan, L.K., Agapay, R.C., Rakels, J.L.L., 2001. Potential of biosorption for the recovery of chromate in industrial wastewaters. Journal of Industrial and Engineering Chemistry Research 40, 2302–2309.

Chakraarty, S., Mohanty, A., Sudha, T.N., Upadhyay, A.K., Konar, J., Sircar, J.K., Madhukar, A., 2010. Removal of Pb (II) ions from aqueous solution by adsorption using bael leaves (Aegle marmelos). Journal of Hazardous Materials 173, 502-509.

Ceribasi, I.H., Yetis, U., 2001. Biosorption of Ni (II) and Pb (II) by Phanerochaete chrysosporium from a binary metal system – kinetics. Water Research 27, 15–20.

Charles, F.H., Swartz,C.H., Badruzzaman, A.B.M., Nicole,K.B., Yu,W., Ali, A., Jay, J., Beckie, R., Niedan, V., Brabander, D., 2005. Groundwater arsenic contamination on the Ganges Delta: biogeochemistry, hydrology, human perturbations and human suffering on a large scale, Comptes Rendus Geoscience 337(1/2), 285–296.

Chen, G.Q., Zeng, G.M., Tu, X., Niu, C.G., Huang, G.H., Jiang, W., 2006. Application of a by-product of Lentinus edodes to thebioremediation of chromate contaminated water. Journal of Hazardous Material 135, 249–255.

Choi, S.B., Yun, Y.S., 2004. Lead biosorption by waste biomass of Corynebacterium glutamicum generated from lysine fermentation process. Biotechnol Letters 26, 331–336.

Davis, T.A., Volesky, B., Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Research 37, 4311–4330.

Davis, T.A., Volesky, B., Vieira, R.H.S.F., 2000. Sargassum sea weed as biosorbent for heavy metals, Water Research 34(17), 4270-4278.

Deng, L., Zhang, Y., Qin, J., Wang, X., Zhu, X., 2009. Biosorption of Cr (VI) from aqueous solutions by nonliving green algae Cladophora albida. Journal of Minerals Engineering 22(4), 372-377.

Dubinin, M.M., 1975. Physical adsorption of gases and vapors in micropore, in: J.F. Danielli, M.D. Rosenberg, D.A. Cadenhead (Eds.), Progress in Surface and Membrane Science, Academic Press, New York and London, pp. 1–70.

Dubinin, M.M., Plavnik, G.M., 1968. Microporous structures of carbonaceous adsorbents, Carbon 6, 183–192.

Dupont, L., Guillon, E., 2003. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. Environmental Science Technology 37, 4235–4241.

Elangovan, R., Philip, L., Chandraraj, K., 2008. Biosorption of chromium species byaquatic weeds: kinetics and mechanism studies. Journal of hazardous materials 152(1).

Ertugay, N., Bayhan, Y.K., 2008. Biosorption of Cr (VI) from aqueous solutions by biomass of Agaricus bisporus. Journal of hazardous materials 154(1-3), 432-9.

Farooq, U., Kozinski, J.A., Misbahul Ain Khan., Makshoof A., 2010. Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature. Bioresource Technology 101, 5043–5053.

Gardea, T., Hejazi, M., Tiemann, K.J., Parsons., 2002. Use of Hop (Humuluslupulus) agricultural by-products for the reduction of aqueous lead (II) environmental health hazards. Journal of Hazardous Material 91, 95–112.

Ghosh, A., 2007. Current knowledge of on the distribution of arsenic in ground water in five state of India. Journal of Environmental Science, Health part A, 42, 1-12.

Ghosh, A., Bhattacharya, P.K., 2006. Hexavalent chromium ion removal through micellar enhanced ultrafiltration, Chemical Engineering Journal 119, 45–53.

Giri, A.K., Patel, R.K., Mahapatra, S.S., 2011. Artificial neural network (ANN) approach for modelling of arsenic (III) biosorption from aqueous solution by living cells of Bacillus cereus biomass. Chemical Engineering Journal 178, 15-25.

Granados-Correa, F., Serrano-Gómez, J., 2009. CrO_4^{2-} ions adsorption by Fe-modified pozzolane. Sp. Journal of Science Technology 44, 924–936.

Ground water quality in shallow aquifer of India, Central Ground Water Board, Ministry of Water Resources, Government of India, Faridabad 2010.

Gupta, S.K., Gupta, R.C., Gupta, A.B., Seth, A.K., Bassin, J.K., Alka, G., 2000. Recurrent acute respiratory tract infections in areas with high nitrate concentration in drinking water. Environment and Health perspectives 108, 363-366.

Gupta, V.K., Gupta, M., Sharma, S., 2011. Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste.Journal of Water Research 35, 1125–1134.

Gupta, V.K., Shrivastava, A.K., Jain, N., 2001. Biosorption of chromium (VI) from aqueous solution by green algae spirogyra species. Water Researh 35, 4079.

Han, X., Wong, Y.S., Wong, M.H., Tam, N.F.Y., 2007.Biosorption and bioreduction of Cr (VI) by a microalgal isolate, Chlorella miniata. Journal of hazardous materials 146, (1-2).

Hanafiah, M.A.K., Ibrahim, S.C., Yahya, M.Z.A., 2006. Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (Imperatacylindrica) leaf powder. Journal of Applied Sciences Research 2, 1169–1174.

Hanafiah, M.A.K., Ngah, W.S.W., Zakaria, H., Ibrahim, S.C., 2007. Batch study of liquid-phase adsorption of lead ions using Lalang (Imperata cylindrica) leaf powder. Journal of Biological Sciences 7, 222–230.

Hanif, M.A., Nadeem, R., Zafar, M.N., Akhtar, K., Bhatti, H.N., 2007. Nickel (II) biosorption by Casia fistula biomass. Journal of Hazardous Materials B139, 345–355.

Hinrichsen, D., Tacio, H., 2002. The coming freshwater crisis is already here. The linkages between population and water. Washington, DC: Woodrow Wilson International Center for Scholars. Retrieved fromhttp://www.wilsoncenter.org/topics/pubs/popwawa2.pdf.

Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption process. Process Biochemistry 34, 451-465.

Hsu, M.J., Selvaraj, K., Agoramoorthy, G., 2006. Taiwan's industrial heavy metal pollution threatens terrestrial biota. Environmental Pollution 143, 327-334
.

Idris, A., Hassan, N., Ismail, N.S.M., Misran, E., Yusof, N.M., Ngomsik, A.O.F., Bee, A., 2010. Photocatalytic magnetic separable beads for chromium (VI) reduction. Journal of Water Research 44, 1683–1688.

Jagtap, S., Yenkie, M.K., Labhsetwar, N., Rayalu, S., 2011. Fluoride in Drinking Water and Defluoridation of Water, chemical reviews.

Jalali, R., Ghafourian, H., Asef, Y., Davarpanah, S.J., Sepehr, S., 2002. Removal and recovery of lead using nonliving biomass of marine algae. Journal of Hazardous Materials 92, 253.

Jayaram, K., Murthy, I.Y.L.N., Lalhruaitluanga, H., Prasad, M.N.V., 2009. Biosorption of lead from aqueous solution by seed powder of Strychnos potatorum L. Journal of Colloids and surfaces. B, Biointerfaces 71(2), 248-54.

Johns, M.M., Marshall, W.E., Toles, C.A., 1998. Agricultural byproductsas granular activated carbons for adsorbing dissolved metals andorganics. Journal of Chemical Technology and Biotechnology 71 , 131–140.

Kapoor, A., Viraraghavan, T., 1995. Fungal biosorption — an alternative treatment option for heavy metal bearing wastewaters: a review. Bioresource Technology 53 , 195–206.

Katarzyna, C., 2010. Biosorption and bioaccumulation–the prospects for practical applications. Environment International 36, 299–307.

Karapinar, N., 2003. Magnetic separation of ferrihydrite from wastewater by magnetic seeding and high-gradient magnetic separation. Journal of Mineral Processing 71, 45.

Kass, A., Yechieli Gavrieli, Y., Vengosh, A., Starinsky, A., 2005. The impact of freshwater and wastewater irrigation on the chemistry of shallow ground-water: a case study from the Israeli Coastal aquifer, Journal of Hydrology 300(1–4), 314–331.

Kato, S., Kojima, T., 2011. Studies on Adsorption of Cr (VI) onto Strychnos potatorum Seed from Aqueous Solution. Environmental Progress and Sustainable Energy.

Katarzyna, C., 2010. Biosorption and bioaccumulation–the prospects for practical applications. Environment International 36, 299–307.

King, P., Rakesh, N., Beenalahari, S., Kumar, P.Y., Prasad, V.S.R.K., 2007. Removal of lead from aqueous solution using Syzygium cumini L.: equilibrium and kinetic studies. Journal of hazardous materials 142(1-2), 340-7.

Kobya, M., 2004. Adsorption, kinetic and equilibrium studies of Cr (VI) by hazelnut shell activated carbon adsorption. Journal of Science Technology 22, 51–64.

Kojeg, A., Pavko, A., 2001. Laboratory experiments of lead biosorption by self immobilized Rhizopus nigricans pellets in the batch stirred reactor and the packed bed column. Journal of Chemical Biochemical Engineering 15, 75-79.

Krishen, P., 2006. Trees of Delhi (a field guide).

Krishnani, K.K., Meng, X., Christodoulatos, C., Boddu, V.M., 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. Journal of hazardous materials 153(3), 1222-34.

Kurniawan, A., Sisnandy, V.O.A., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S., 2011. Performance of durian shell waste as high capacity biosorbent for Cr (VI) removal from synthetic wastewater. Ecological Engineering 37(6), 940-947.

Kurniawan, T.A., Chan G.Y.S., Lo, W.H., Babel, S., 2009. Comparison of low-cost adsorbents for treating wastewater laden with heavy metals. Journal of Science Total Environment 366, 409–426.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H., Babel, S., 2006. Comparison of low-cost adsorbents for treating wastewater laden with heavy metals. Science Of The Total Environment 366, 409–426.

Lagergren, S., 1898. Kungliga svenska psalka de miens handlingar. 24, 1.

Lakatos, J., Brown, S.D., Snape, C.E., 2002. Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams, Fuel 81, 691–698.

Lakshmipathiraj, P., Umamaheswari, S., Bhaskar Raju,G., Prabhakar, S., CarolingG., Kato S., Kojima T., 2011. Studies on Adsorption of Cr (VI) onto Strychnos potatorum Seed from Aqueous Solution. Journal of Environmental Progress & Sustainable Energy vol-00 No-00.

LaPara, T.M., Konopka, A., Nakatsu, C.H., Alleman, J.E., 2000. Thermophilic aerobic wastewater treatment in continuous-flow bioreactors. Journal ofEnvironmental Engineering ASCE, 126, 739.

Larison, J.R., Likens, E., Fitzpatrick, J.W., Crock, J.G., 2000. Cadmium toxicity among wildlife in the Colorado rocky mountains. Nature 406, 181-183.

Lawal, O.S., Sanni, A.R., Ajayi, I.A., Rabiu, O.O., 2010. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead (II) ions onto the seed husk of Calophyllum inophyllum. Journal of Hazardous Materials 177, 829-835.

Li, L., Ekström, E.C., Goessler, W., Lönnerdal, B., Nermell, B., Yunus, M., 2008. Nutritional status has marginal influence on the metabolism of inorganic arsenic in pregnant Bangladeshi women. Environmental Health Perspective, 116, 315–321.

Lima, E.C., Royer, B., Vaghetti, J.C.P., Simon, N.M., da Cunha, B.M., Pavan, F.A., Benvenutti, E.V., 2008. Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution kinetics and equilibrium study. Journal of hazardous materials 155(3), 536-50.

Lin, C-C, Lai Y-T. 2006. Adsorption and recovery of lead (II) from aqueous solutions by immobilized Pseudomonas aeruginosa PU21 beads. Journal of Hazardous Material 137, 99–105.

Liu, A., Ming, J., Ankumah, R.O., 2005. Nitrate contamination in private wells in rural Alabama, United States, Science of the Total Environment 346(1–3), 112–120.

Liu, Y., Chang, X., Chang, Y., Guo, S. M., 2006. Biosorption and Preconcentration of lead and cadmium on waste Chinese herb Pang Da Hai. Journal of Hazardous Materials B135, 389- 394.

Liu, H., Dong, Y., Wang, H., Liu, Y., 2010. Adsorption behavior of ammonium by a bioadsorbent – Boston ivy leaf powder. Journal of Environmental Sciences, 22(10), 1513-1518.

Liu, T., Zhao, L., Sun, D., Tan, X., 2010. Entrapment of nanoscale zero-valent iron in chitosan beads for hexavalent chromium removal from wastewater. Journal of Hazardous Materials 184, 724–730.

Low, K.S., Lee, C.K., Liew, S.C., 2000. Sorption of cadmium and lead from aqueous solutions by spent grain. Process Biochemistry 36, 59–64.

Lu, W-B., Shi, J-J., Wang, C-H., Chang, J-S., 2006. Biosorption of lead, copper and cadmium by an indigenous isolate Enterobacter sp. J1 possessing high heavy-metal resistance. Journal of Hazardous Material 134, 80–86.

Mata, Y.N., Blázquez, M.L., Ballester, A., González, F., Muñoz, J. A., 2009. Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics. Chemical Engineering Journal 150(2-3), 289-301.

Meenakshi., Maheshwari, R.C., 2006. Fluoride in drinking water and its removal. Journal of hazardous materials 137(1), 456-463.

Mehta, Ã, L., 2006. Whose scarcity ? Whose property ? The case of water in western India 24, 654-663. (doi:10.1016/j.landusepol.2006.05.009).

Mehta, L., 2007. Whose scarcity? Whose property? The case of water in western India. Land Use Policy 24, 654-663.

Mesas, L.M., Navarretea, E.R., Carrillo, F., palet, C., 2011. Bioseparation of Pb (II) and Cd (II) from aqueous solution using cork waste biomass. Modeling and optimization of the parameters of the biosorption step, Chemical Engineering Journal 174,9– 17.

Mittal, A., Mittal, J., Kurup, L., 2006. Adsorption isotherms, kinetics and column operations for the removal of hazardousdye, tartrazine fromaqueous solutions using waste materials-bottom ash and de-oiled soya, as adsorbents. Journal on Hazardous Material 136, 567–578.

Mohan, D., Pittman, C.U., 2006. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water 137, 762-811.

Mohan, D., Sarswat, A., Singh, V.K., Alexandre-franco, M., Pittman C.U., 2011. Development of magnetic activated carbon from almond shells for trinitrophenol removal from water. Chemical Engineering Journal 172, 1111-1125.

Mohan, D., Singh, K.P., Singh, V.K., 2005. Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. Industrial and Engineering Chemistry Research 44, 1027-1042.

Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yanceyd, B., Mohammad J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science 310, 57–73.

Mohan, D., Singh, K.P., Singh, V.K., 2006. Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth Journal of Hazardous Material B135, 280-295.

Mohanty, K., Jha, M., Meikap, B.C., Biswas, M.N., 2006. Biosorption of Cr (VI) from aqueous solutions by Eichhorniacrassipes. Chemical Engineering Journal 117(1), 71-77.

Monitoring of Indian National Aquatic Resources, Series: MINARS/ /2010-11, Central pollution control board, Ministry of Environment & forests.

Moore, J.W., Ramamoorthy, S., 1984. Heavy metals in natural waters, Springer-Verlag, New York, 28-57, 77-99.

Moussavi, G., Barikbin, B., 2006. Biosorption of chromium (VI) from industrial wastewater onto pistachio hull waste biomass. Journal of Chemical Engineering 162(3), 893-900.

Muhammad, I.T., Afzal, S., Hussain, I., 2004. Pesticides in shallow groundwater of Bahawalnagar, Muzafargarh, D.G. Khan and Rajan Pur districts of Punjab, Pakistan, Environment International 30(4), 471–479.

Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal contaminated soils and groundwater: an evaluation. Engineering Geology 60 (1–4), 193–200.

Murphy, V., Hughes, H., McLoughlin, P., 2008, Comparative study of chromium biosorption by red, green and brown seaweed biomass, Chemosphere 70, 1128–1134.

Niu, C.G., Huang, G.H., Jiang, W., 2006. Application of a by-product of Lentinus edodes to thebioremediationof chromate contaminated water. Journal of Hazardous Material 135, 249–255.

Nourbakhsh, M., Sag, Y., Ozer, D., Aksu, Z., Katsal, T., 1994. Calgar, Process Biochem 29,1

O’Connell, D.W., Birkinshaw, C., O’Dwyer, T.F., 2008. Heavy Metal Adsorbents prepared from the modification of Cellulose: A Review. Journal of Bioresource Technology 99, 6709-6724.

Oren,O., Yechieli, Y., Bohlke, J.K., Dody, A., 2004. Contamination of groundwaterunder cultivated fields in an arid environment, Central Arava Valley, Israel,Journal of Hydrology 290(3/4), 312–328.

Ozer, A., 2006. Removal of Pb (II) ions from aqueous solutions by sulfuric acid-treated wheat bran. Journal of Hazardous Material B141, 753–76.

Park, D., Yun, Y.-S., Lee, D.S., Lim, S.-R., Park, J.M., 2006. Column study on Cr(VI)-reduction using the brown seaweed *Ecklonia* biomass. Journal of Hazardous Materials 137, 1377.

Park, D., Yun, Y.-S., Park, J.M., 2005. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. Chemosphere 60, 1356.

Park, D., Yun, Y.-S., Park, J.M., 2005. Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics Process Biochemistry 40, 2559.

Park, D., Yun, Y.S., Park, J.M., 2008. XAS and XPS studies on chromium-binding groups of biomaterial during Cr (VI) biosorption. Journal of Colloid and Interface Science 317, 54-61.

Patel, K.S., Shrivas, K., Hoffmann, P., Jakubowski, N., 2006. A survey of lead pollution in Chhattisgarh State, central India. Environmental geochemistry and health 28(1-2), 11-17.

Pavan, F.A., Mazzocato, A.C., Jacques, R.A., Dias, S.L.P., 2008. Ponkan peel: A potential biosorbent for removal of Pb (II) ions from aqueous solution. Biochemical Engineering Journal 40, 357-362.

Pehlivan, E., Altun, T., 2008. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. Journal of hazardous materials 155(1-2), 378-84.

Pejic, B. M., Vukcevic, M. M., Pajic-Lijakovic, I. D., Lausevic, M. D., Kostic, M.M., 2011. Mathematical modeling of heavy metal ions (Cd^{2+}, $Zn^{2+}$and Pb^{2+}) biosorption by chemically modified short hemp fibers. Chemical Engineering Journal 172(1), 354-360.

Pillay, K., Cukrowska, E.M., Coville, N.J., 2009. Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. Journal of hazardous materials 166(2-3), 1067-75.

Priya, J.A., Rao, P.S., Vijaya, Y., Reddy, A.S., Krishnaiah, A., 2007. Biosorption of chromium (VI), nickel (II) and copper (II) ions from aqueous solutions using Pithophora algae. Journal of Toxicological and Environmental Chemistry 893,421-442.

Puranik, P.R., Paknikar, K.M., 1997. Biosorption of lead and zinc from solutions using *Streptoverticillium cinnamoneum* waste biomass. Journal of Biotechnoly 55, 113–24.

Radovic, L.R., Moreno, C.C., Rivera, U.J., 2000. Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), Chemistry and Physics of Carbon, vol. 27, Marcel Dekker, Inc; New York.

Rahman, I.A., Ismail, J., Osman, H., 1997. Effect of nitric acid digestion on organic materials and silica in rice husk. Journal of Material Chemistry 7, 1505– 1509.

Rao, G.V.R.S., Murty, K.S., 2003. Colour removal from paper mill effluent using flyash and Niirmali seeds. Indian Journal of Environmental Protection 23(4), 379-382.

Rao, N.S., 2006. Nitrate pollution and its distribution in the groundwater of Srikakulam district, Andhra Pradesh, India. Environmental Geology 51(4), 631-645.

Rathi, A.K.A., 2002. Promotion of cleaner production for industrial pollution abatement in Gujarat (India). Journal of Cleaner Production 11(5), 583-590

Ravikumar., Dutta, P.K., 1996. Are textile finishing the environment? Indian Journal of Environmental Protection 16(7), 499-501.

Razmovski, R., Šćiban, M., 2008. Biosorption of Cr (VI) and Cu (II) by waste tea fungal biomass. Journal of Ecological Engineering 34(2), 179-186.

Reddy, H.K., Harinath, Y., Seshaiah, K., Reddy, A.V.R., 2010. Biosorption of Pb (II) from aqueous solutions using chemically modified Moringa oleifera tree leaves. Chemical Engineering Journal 162, 626-634.

Rela, P.R., Sampa, M.H.O., Duarte, C.L., Costa, F.E., Sciani, V., 2000. Development of an up-flow irradiation device for electron beam wastewater treatment. Journal of Radiation Physics and Chemistry 57, 657.

Riahi, K., Thayer, B.B., Mammou, A.B., Ammar, A.B., Jaafoura, M.H., 2009. Biosorption characteristics of phosphates from aqueous solution onto Phoenix dactylifera L. date palm fibers. Journal of Hazardous Materials 170, 511-519.

Riaz, M., Nadeem, R., Hanif, M.A., Ansari, T.M., Rehman, K., 2009. Pb (II) biosorption from hazardous aqueous streams using Gossypium hirsutum (cotton) waste biomass. Journal of Hazardous Materials 161, 88-94.

Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. Water Research 42, 4215-4232.

Robinson, T., Mc.Mullan, G., Marchant, R., Nigam, P., 2001. Remediationof dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresources Technology 77, 247–255.

Rukah, A., Alsokhny, K., 2004. Geochemical assessment of groundwater contamination with special emphasis on fluoride concentration, North Jordan, Chemie der Erde-Geochemistry 64 (2), 171–181.

Sağ, Y., Kutsal, T., 2001. Recent trends in the bio-sorption of heavy metals: a review. Journal of Biotechnology and Bioprocess Engineering 6, 376-385.

Saha, B., Orvig, C., 2010.Biosorbentsfor hexavalent chromium elimination from industrial and municipal effluents. Journal of Coordination Chemistry Reviews 254(23-24), 2959-2972.

Saif, M.M.S., Kumar, N.S., Prasad, M.N.V., 2012. Binding of cadmium to Strychnos potatorum seed proteins in aqueous solution: Adsorption kinetics and relevance to water purification. Colloids and surface B: biointerfaces 94, 73-79.

Sari, A., Mendil, D., Tuzen, M., Soylak, M., 2008. Biosorption of Cd (II) and Cr (III) from aqueous solution by moss (Hylocomium splendens) biomass: Equilibrium, kinetic and thermodynamic studies. Chemical Engineering Journal 144(1), 1-9.

Sarin, V., Pant, K.K., 2006. Removal of chromium from industrial waste by using eucalyptus bark. Journal of Bioresource technology 97(1),15-20.

Sawalha, M.F., Peralta-Videa, J.R., Romero-González, J., Gardea-Torresdey, J. L., 2006. Biosorption of Cd (II), Cr (III), and Cr (VI) by saltbush (Atriplex canescens) biomass: thermodynamic and isotherm studies. Journal of colloid and interface science 300(1), 100-104.

Say, D.A., Yakup A.M., 2001.Biosorption of cadmium (II), lead (II) and copper (II) with the filamentous fungus Phanerochaetechryosporium. Bioresource Technology 76, 67-70.

Sciban, M., Klasnja, M., Skrbic, B., 2006. Modified hardwood sawdust asadsorbentof heavy metal ions from water. Wood Science and Technology 40, 217–227.

Sharma, S., Malik, A., Satya, S., 2009. Application of response surface methodology (RSM) for optimization of nutrient supplementation for Cr (VI) removal by Aspergillus lentulus AML05, Journal of Hazardous Materials 164, 1198–1204.

Sharma, Y.C., Singh, B., Agrawal, A., Weng, C.H., 2008. Removal of chromium by riverbed sand from water and wastewater: Effect of important parameters .Journal of Hazardous Material 151, 789.

Sharma, Y.C., Singh, B., Agrawal, A.,Weng, C.H., 2011. Journal of Hazardous Material 151, 789-793**.**

Sheng, P.X., Ting, Y.P., Chen, J.P., Hong, L., 2004. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. Journal of colloid and interface science 275(1), 131-41.

Shukla, S.R., Pai, R.S., 2005. Adsorption of Cu (II), Ni (II) and Zn (II) on modified jute fibres. Bioresource Technology 96, 1430–1438.

Singh, K.K., Hasan, H.S., Talat, M., Singh, V.K., Gangwar, S.K., 2009. Removal of Cr (VI) from aqueous solutions using wheat bran. Journal ofChemical Engineering 151, 113–121.

Singh, K.K., Talat, S.H., 2006. Remoal of lead from aqueous solution by agricultural waste maize bran. Bioresource Technology 97, 2124-2130.

Singh, V., Sharma, A.K., Kumari, P., Tiwari, S., 2008. Efficient Chromium (VI) Adsorption by Cassia marginata Seed Gum Functionalized with Poly(methylmethacrylate) Using Microwave Irradiation. Journal of Industrial Engineering Chemistry Research 47,5267–5276.

Singh, V., Tiwari, S., Sharma, A.K., Sanghi, R., 2007. Removal of lead from aqueous solutions using Cassia grandis seed gum-graft-poly(methylmethacrylate). Journal of colloid and interface science 316, 224-232.

Singha, B., Das, S.K., 2011. Biosorption of Cr (VI) ions from aqueous solutions: Kinetics, equilibrium, thermodynamics and desorption studies. Colloids and Surfaces B: Journal of Biointerfaces 84, 221-232.

Sun, P., Liu, Z.-T., Liu, Z.-W., 2009. Chemically Modified Chicken Feather as Sorbent for Removing Toxic Chromium(VI) Ions. Industrial and Engineering Chemistry Research 48, 6882.

Suryavanshi, U., Shukla, S.R., 2010. Adsorption of Pb^{2+} by Alkali-Treated Citrus limetta Peels, Industrial and Engineering Chemistry Research 49, 11682–11688

Susheela, A.K., 1999. Fluorosis management programme in India, Current Sciences 77(10), 1250–1256.

Suthar, S., Bishnoi, P., Singh, S., Mutiyar, P.K., Nema, A.K., Patil, N.S., 2009. Nitrate contamination in groundwater of some rural areas of Rajasthan , India. Journal of Hazardous Materials 171, 189-199.

Suthar, S., Nema, A.K., Chabukdhara, M., Gupta, S.K., 2009. Assessment of metals in water and sediments of Hindon River , India : Impact of industrial and urban discharges 171, 1088-1095.

Suzuki, Y., Maezawa, A., Uchida, S., 2000. Utilization of ultrasonic energyin a photocatalytic oxidation process for treating waste water containing surfactants. Journal of Applied Physics 39, 2958.

Thirunavukkarasu, E., Palanivelu, K., 2007. Biosorption of Cr (VI) from plating effluent using marine algal mass. Indian Journal of Biotechnology 6, 359-3646.

Tokar, E.J., Qu, W., Waalkesm, M.P., 2011. Arsenic, stem cells, and the developmental basis of adult cancer. Toxicological Science, 120, S192–S203.

Tsuruta, T., 2004. Biosorptionand recycling of gold using various microorganisms. Journal of General and Applied Microbiology 50, 221-228.

Tunali, S., Çabuk, A., Akar, T., 2006. Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. Chemical Engineering Journal 115, 203–11.

Upatham, E.S., Boonyapookana, B., Kruatrachue, M., 2002. Biosorption of Cadmium and Chromium in Duckweed Wolffia globosa Biosorption of Cadmium and Chromium in Duckweed Wolffia globosa, International Journal of Phytoremediation 4(2), 73-86.

Uslu, G., Tanyol, M,. 2006. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto Pseudomonas putida: effect of temperature. Journal of Hazardous Materials 135, 87–93.

Valeria, M., Nurchi., Villaescusa, I., 2008. Agricultural biomasses as sorbents of some trace metals ,Coordination Chemistry Reviews 252, 1178–1188.

Varma, A.J., Deshpande, S.V., Kennedy, J.F., 2004. Metal complexation by chitosan and its derivatives: a review. Carbohydrate Polymer 55(1), 77-93

Vieira, M.G.A., Oisiovici, R.M., Gimenes, M.L., Silva, M.G.C., 2008. Biosorption of chromium (VI) using a Sargassum sp. packed-bed column. Bioresource Technology 99, 3094–3099 .

Vijayaraghavan, K., Yeoung, Y.S., 2008. Bacterial biosorbentsand biosorption. Journal of biotechnology advances 26, 266–291.

Vijayaraghavan, K., Yun, Y.S., 2008. Biosorption of C.I. Reactive Black 5 from aqueous
Volesky, B., 2001. Detoxification of metal-bearing effluents: Biosorptionfor the next century. Journal of Hydrometallurgy 59, 203–216.

Volesky, B., Schiewer, S., 2000. Biosorption, metals. Encyclopedia of Biopress technology (fermentation, Biocatalyst and Bioseparation); P. 433-453.

Volesky, B., 2007. Biosorption and me. Water Research 41(18), 4017–4029

Volesky, B., 2003. Biosorption process simulation tools. Hydrometallurgy 71, 179-190.

Waalkes, M.P., Liu, J., Diwan, B.A., 2007. Transplacental arsenic carcinogenesis in mice. Toxicology Applied Pharmacology 222, 271–280.

Wang, J.L., Chen, C., 2006. Biosorption of heavy metals by Saccharomyces cerevisiae: A review. Biotechnology Advance 24, 427–451.

Wase, J., Forster, C., 1997. Biosorbents for metal ions. London, UK: CRC Press, p.165–82.

Wei, B.G., Jiang, F.Q., Li, X.M., Mu, S.Y., 2010. Heavy metal induced ecological risk in the city of Urumqi, NW China. Environmental Monitoring and Assessment 160, 33-45.

Weyer, P.J., Cerhan, J.R., Kross, B.C., Hallberg, G.R., Kantamneni, J., Breuer, G., 2001. Municipal drinking water nitrate level and cancer risk in older women: the Iowa Women's Health Study. Epidemiology 11, 327–38.

WHO, Guidelines for Drinking Water, Vol. 2, Recommendations, World Health Organization, Geneva, 1996.

Witek-Krowiak, A., Szafran, R.G., Modelski, S., 2011. Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent.Desalination 265(1-3), 126-134.

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., 2003. Removal of Cu and Pb by tartaric acid modifiedrice husk from aqueous solutions. Journal of Chemosphere 50, 23–28.

Xu, X., Gao, B., Zhao, Y., Chen, S., Tan, X., Yue, Q., Lin, J., 2012. Nitrate removal from aqueous solution by Arundo donax L. reed based anion exchange resin. Journal of hazardous materials 203-204(3), 86-92.

Yin, C.Y., 2010. Emerging usage of plant-based coagulantsfor water and wastewater treatment. Process Bio-chemistry 45, 1437–1444.

Yuan, P., Liu, D., Fan, M., Yang, D., Zhu, R., Ge F., Zhu, J., 2010. Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by thediatomite-supported/unsupported magnetite nanoparticles. Journal of Hazardous Materials 173, 614–621.

Yun, Y.S., Park, D., Park, J.M., Volesky, B., 2001. Biosorption of Trivalent Chromium on the Brown Seaweed Biomass. Journal of Environmental Science & Technology 35(21), 4353-4358.

Zainal, I.G., 2010. Biosorption of Cr (VI) from Aqueous Solution Using New Adsorbent: Equilibrium and Thermodynamic Study,E-Journal of Chemistry . Available at http://www.e-journals.net 2010, 7(S1), S488-S494.

Zhou, M., Liu, Y., Zeng, G., Li, X., Xu, W., Fan, T., 2007. Kinetic and equilibrium studies of Cr (VI) biosorption by dead Bacillus licheniformis biomass. World Journal of Microbiology and Biotechnology 23, 43–8.

Ziagova, M., Dimitriadis, G., Aslanidou, D., Papaioannou, X., Tzannetaki, E.L.,Liakopoulou-Kyriakides, M., 2007. Comparative study of Cd (II) and Cr (VI) biosorption on Staphylococcus xylosus and Pseudomonas sp. in single and binary mixtures. Bioresource Technology 98, 2859–65.

Zouboulis, A.I., Lazaridis, N.K., Grohmann, A., 2002. Toxic metals removal from waste waters by upflow filtration with floating filter medium. I. The case of zinc. Journal of Science and Technology 37, 403.

Zvinowanda, C.M., Okonkwo, J.O., Shabalala, P.N., Agyei, N.M., 2009. A novel adsorbent for heavy metal remediation in aqueous environments, International Journal of Environmental Science & Technology 6(3), 425-434.