

Nano sized carbonized waste biomass for heavy metal ion remediation

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Utilization of agricultural waste material with approach to enhance the heavy metal remediation properties by carbonizing the biomass at nano size particles has been explored in present investigation from aqueous solutions. In this study the lignocellulosic, nitrogenous agricultural waste biomass *Delbergia sissoo* pods (DSP) has been tried for sequestering of Cd (II), Pb (II) and Ni (II) metal ions from aqueous solutions. Batch experiments were performed for removal of targeted metal ions keeping in consideration the preliminary affecting parameters such as effect of adsorption dose, pH, initial metal ion concentration, stirring speed and contact time. The sorption studies were analyzed by using, Freundlich isotherm and Langmuir isotherm models. The kinetics of the process was evaluated by pseudo pseudo-first order and pseudo second order kinetic models. Studies reveal that the equilibrium was achieved with in 30 min of the contact time at optimized parameters. Analytical studies of biosorbent were done by means of FT-IR, SEM and XRD. Desorption experiments were carried out using HCl solution with a view to regenerate the spent adsorbent and to recover the adsorbed metal ions.

Keywords: nitrogenous waste materials, carbon, heavy metal ions, kinetic studies, *Delbergia sisso* pods.

INTRODUCTION

Metals exist naturally in the earth's crust, and their contents in the environment can vary between different regions resulting in spatial variations of background concentrations. The distribution of metals in the environment is governed by the properties of the metal and influences of environmental factors¹. Of the all 92 naturally occurring elements, approximately 30 metals and metalloids are potentially toxic to humans, Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi. Heavy metals is the generic term for metallic elements having an atomic weight higher than 40.04 (the atomic mass of Ca)². Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease control agents applied to plants, air pollution fallout, and a number of others². Although some individuals are primarily exposed to these contaminants in the workplace, for most people the main route of exposure to these toxic elements is through the diet (food and water). The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human. Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration, it is well-known that chronic exposure to heavy metals and metalloids at relatively low levels can cause adverse effects^{3, 4, 5, 6, 7}. Therefore, there has been increasing concern, mainly in the developed world, about exposures, intakes and absorption of heavy metals by humans. Populations are increasingly demanding a cleaner environment in general, and reductions in the amounts of contaminants reaching people as a result of increasing human activities. A practical implication of this trend, in the developed countries, has been the imposition of new and more restrictive regulations^{8, 9}. Thus considering the importance of the threat bioremediation by means of waste agricultural materials has

gained the momentum due to their potential efficacy and cost suitability^{10, 11, 12}. Agricultural waste materials being low operating cost, availability in abundance, effective in dilute solutions, generates minimum secondary waste, completes with in a short time period, unique chemical composition and more efficiency seem to be a viable option for heavy metal ion remediation. Biosorption is a process in which physico-chemical interaction between the charged surface groups of biosorbents and ions in solution takes place by the process of complexation, ion exchange, microprecipitation, chelation and chemisorptions etc¹¹. Several investigations have been undertaken for the removal of heavy metal ions from wastewater using different low-cost agricultural waste materials such as *Arachis hypogea*, *Acacia saligna*^{12, 13}, cassia fistula biomass¹⁴, sugarcane bagasse¹⁵, waste tea leaves¹⁶, Wheat straw¹⁷, black gram husk¹⁷ and saw dust of oak and black locust¹⁸. These agricultural wastes mainly consist of lignin, cellulose, hemi-cellulose, carbohydrates and some proteins that make them effective adsorbent for heavy metal ions. Biomaterials when used in natural form may lead to release of soluble organic materials and further, as they lack mechanical strength and have a wide size distribution, leads to the problems in the operations of reactors by blocking flow lines and clogging filters, while separation of biomass and effluent can be difficult and expensive. As the adsorption capacity of an adsorbent mainly depend upon its pore size, chemical composition (influencing its interaction with polar and non-polar adsorbates) and active sites which determine the type of chemical reactions with other molecules, commercial activated carbon emerged as a potential sequestering agent due to fast and effective results but the cost factor somewhere suppressed its utilization at the large scale. Thus use of local, natural, and cheap materials that are available in large quantities or certain waste from agricultural operations for treatment of water and wastewater containing heavy metals in developing countries is an area that is gaining interest. There are many studies in the literature relating to the preparation of carbon from various agricultural wastes materials such

as sugar beet pulp, Sugarcane baggasse, fertilizer waste and olive waste cakes etc. and their application for the removal of lead, cadmium, zinc, copper, and nickel from water and wastewater¹⁹⁻²⁵. Thus the objective of present study is to investigate the binding of metal ions by selected agricultural waste material in carbonized form from aqueous solutions and to study the effect of various factors affecting the efficiency of the process.

METHOD AND MATERIAL

Preparation of Adsorbent

The selected biosorbent *Delbergia sisso* pods (DSP) were collected from Sangrur region of India. Hot water treatment was given to them for one hour to remove the soluble organic components and dust, was dried at 120°C in hot air oven for 24 h, grounded and sieved (150 MICs). The carbonized form of biomass was prepared by heating the powder of biomass in a muffle furnace at 800°C for two hours. To explore the number and positions of the functional groups available for the binding of metal ions on to the biomaterials, FT-IR spectra and XRD studies of native and metal loaded biomass and SEM studies were done to reveal the surface morphological characters of the biosorbent.

Preparation of Adsorbate

A stock solution of Ni (II), Cd (II) and Pb (II) were prepared (1000 mg/L) by dissolving desired amount of nickel nitrate, cadmium nitrate and lead nitrate in 1 L of de-ionized water. The stock solution was diluted with de-ionized millipore water to obtain the desired concentration range of metal ion solutions. The concentration in the test solutions was determined spectro photometrically using Double Array UVVIS Spectrophotometer, (Agilent 8453) at a wavelength corresponding to the maximum absorbance for particular metal ion for Ni (II), Cd (II) and Pb (II). pH of the solutions were adjusted using 0.1 m mol/L HCl or NaOH using Orion 420A pH meter. All the used chemicals were of Analytical grade. The experiments were performed in duplicates and after the simulated experiments; studies were also carried out on real industrial effluents. Composition of the industrial wastewater is given in Table 1.

Table 1. Characterization of Industrial effluent

Parameters	Amount in Effluent
pH	4.33
Temperature	22.8°C
Electric Conductivity	65.5mS
Salinity	43.4%
Total Solids	76000 mg/l
Total dissolved solids	63000 mg/l
BOD	290 mg/l
COD	312.6 mg/l
Sulphide	1.35 mg/l
TKN	210.14 mg/l
Cr (Total)	1500 mg/l
Cr (VI)	BDL
Ca	152 mg/l
Cu	0.1 mg/l
Cd	0.012 mg/l
Ni	1.152 mg/l
Pb	15.26 mg/l
Zn	0.793 mg/l

Adsorption Experiments

Adsorption experiments were carried out by using 100 ml of metal solution of varying concentration (5–500 mg/l) at varying initial pH (2–7) with different stirring speed (50–300), contact time (5–120 min) having varying adsorbent dose (50–1000 mg) in 250 ml Erlenmeyer flask at room temperature. Samples were separated by centrifugation at 4000 rpm for 10 min. The residual metal ion concentration was determined as mentioned in APHA, 1995²⁶. The removal percentage (R%), defined as the ratio of difference in metal concentration before and after adsorption ($C_i - C_e$) to the initial concentration of metal in the aqueous solution (C_i), was calculated using equation (1)

$$R\% = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

RESULTS AND DISCUSSION

In terms of their structure, *Dalbergia sissoo* pods (DSP) can be regarded as a ligno-cellulosic agricultural waste material containing high amount of proteins and crude fibers. The pods are extremely rich in the nitrogenous substances containing various functional moieties for sequestering of heavy metal ions. The mechanism of metal ion removal by ligno-cellulosic biomass is attributed to anionic adsorption or by reduction of metals by ligno-cellulosic biomass. The contributing functional groups such as N-H (amines) phenolic methoxyl and hydroxyl groups of lignin are responsible for metal ion reduction when tried in natural form and the oxidation of these functional groups gives rise to the formation of carbonyl and carboxyl groups of ligno-cellulosic material. But in carbonized form surface complexes were dominating as no major changes were observed in the peaks relating the amines and methoxyl groups. FT-IR analysis of adsorbents in carbon form before and after sorption of metal ions was performed to determine the vibrational frequency changes in the functional groups of the adsorbents. The spectra of adsorbent were measured in the range of 500–4000 cm^{-1} wave number (Fig. 1 a, b, c, d). XRD studies reveal the regular pore spacing and pore size of the particles and the size of particles lies in the nano scale (Fig. 2 a, b, c, d). Further SEM images reveal the surface morphology of the biosorbent giving information regarding the surface texture and porosity of the DSPC. The images explores that the particles have a very narrow size distribution, with large availability of surface areas as sites for the metal ion adsorption (Fig. 3 a, b, c, d).

Effect of pH

pH is an essential controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and the ionic form of the metal ion in solution. Adsorption studies were carried out in the pH range of 1 to 7, keeping all the parameters constant (Ni concentration – 50 mg L^{-1} , stirring speed – 150 rpm, contact time – 30 min, adsorbent dose – 0.5 g L^{-1} for DSPC at room temperature. The pH of the metal solution was adjusted after adding the adsorbent. The maximum adsorptions of Ni (II), Cd (II) and Pb (II) was 95%, 95%

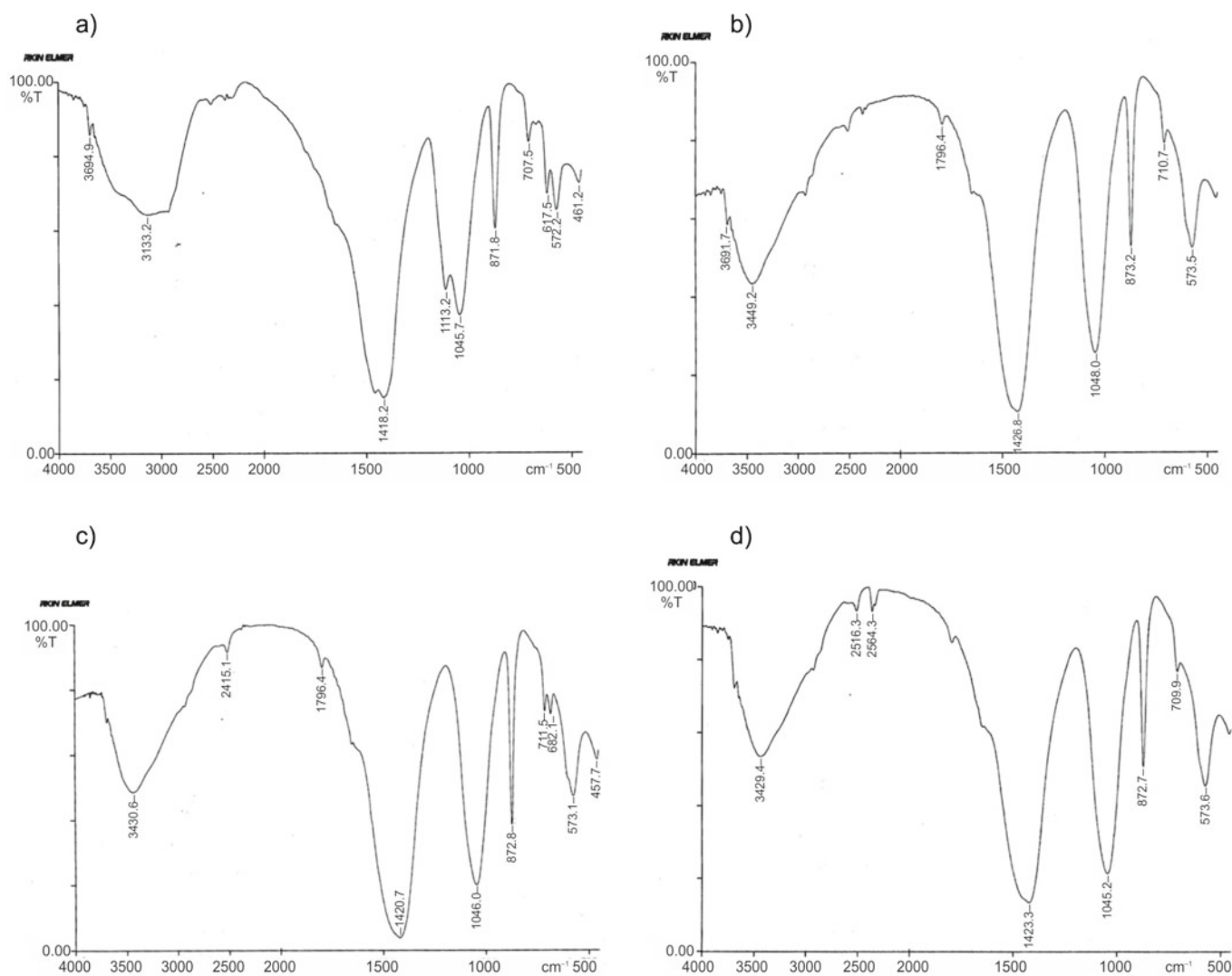


Figure 1. a) FT-IR spectra of native DSPC; b) FT-IR spectra of Cd (II) loaded DSPC; c) FT-IR spectra of Pb (II) loaded DSPC; d) FT-IR spectra of Ni (II) loaded DSPC

and 98% respectively at pH 6 for Ni (II) and at pH 5 for Cd (II) and Pb (II). It was observed that when the pH increased from 1.0 to 6.0, the adsorption efficiency was increased remarkably resulting in to maximum removal efficiency of 95% for Ni (II) and Cd (II) and 98% for Pb (II) therefore, it was taken as the optimized pH value for further adsorption experiments (Fig. 4). It was observed that there was no significant enhancement in the removal efficiency of the biosorbent increasing pH further and after pH 7 precipitation of the solution was observed. On the basis of simulated studies, real industrial effluent containing metal ions was taken from the electroplating industry, and studies were performed to determine the feasibility of the process on the real effluents. The removal efficiency was found to be near 100% for all the metal ions for selected biosorbent in carbonized form. The pH dependence of metal adsorption is largely related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry of the solution. At lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the sorbent. As pH increases from the acidic range to the neutral range, Ni (II), Cd (II) and Pb (II) are present predominantly as Ni^{2+} , Cd^{2+} and Pb^{2+} . Moreover, due to the presence of vacant hydroxyl (-OH-) and carbonyl (C=O) groups, the formation of coordination complexes with the metal ion

also occur. At low pH values, the H_3O^+ ions compete with the metal ions for the binding sites of the DSPC, leaving the metal ions in solution. As the pH increases, the concentration of H_3O^+ ions decreases and the sites on the DSPC surface become available for the metallic ions in the solution. Our results were found to be consistent with other studies that demonstrated that the removal of these metal ions decreases with a decrease in pH to 1.0 as shown by Mahajan et. al. 2012 and Garg et. al. 2008.

Effect of Adsorbent Dose

The adsorption of metal ions was studied at different adsorbent doses (50 to 500 mg) for with DSPC for selected metal ions, keeping metal ion concentration (50 mg L^{-1}), stirring speed (150 rpm), pH (5 for Cd (II) and Pb (II) and 6 for (Ni (II)), room temperature and contact time (30 min) constant. It was observed from the kinetics study that most of the metal ion removal by DSPC was achieved in 30 min, so these experiments were conducted at 30 min of contact time. There was a constant increase in the adsorption of metal ions with an increase in the adsorbent dose. The increase in the adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Fig. 5). Similar trends have

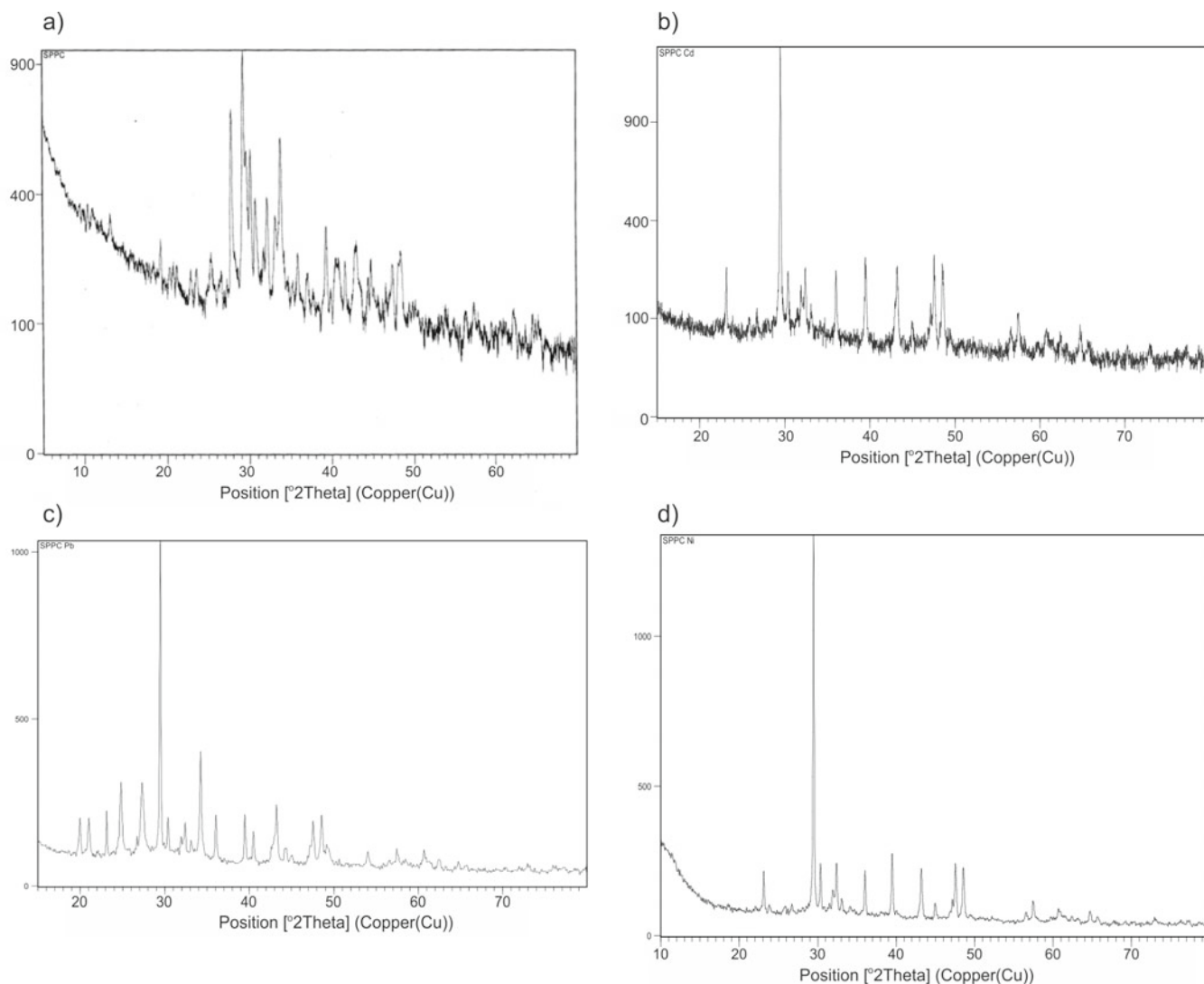


Figure 2. a) XRD pattern of native DSPC; b) XRD pattern of Cd (II) loaded DSPC; c) XRD pattern of Pb (II) loaded DSPC; d) XRD pattern of Ni (II) loaded DSPC

been found by Das et. al., 2007 and Mahajan and Sud, 2012 and 2011^{27, 28, 29}.

Effect of Contact Time/ Kinetics Studies

Kinetics studies play a key role in finding the equilibrium during a reaction. Studies on carbonized form of adsorbent were conducted by varying the contact time from 5 to 60 min at a fixed metal ion concentration (50 mg L^{-1}), stirring speed (150 rpm), room temperature and pH (5 and 6). Maximum metal ions were sequestered from the solution in 30 min by DSPC. The Ni (II) and Cd (II) removal was 95 and 98% for Pb (II) in 30 min of contact time, respectively (Fig. 6). The results shown are in trend as shown by various researchers^{12, 13, 30, 31}.

Effect of Initial Concentration

The initial concentration of the industrial solution is a major parameter. Considering the possible concentration of heavy metals that can be discharged, a wide range of metal ion concentrations has been selected from 5 ppm to 500 ppm. The adsorption of metal ions with DSPC was studied by varying the initial concentration (5, 10, 25, 50, 75, 100, 250 and 500 mg L^{-1}) and keeping the adsorbent dose (500 mg L^{-1}), stirring speed (150 rpm), pH (5 and 6) and contact time of 30 minutes constant (Fig. 7). The purpose of using a higher concentration

of metal ions was to study the maximum adsorption capacity of the adsorbent²⁷. The experimental results showed that metal ion adsorption decreased with an increase in initial metal ion concentration. However, the actual amount of metal adsorbed per unit mass of the adsorbent increased with an increase in the initial concentration in the test solution.

Adsorption Isotherms

The experimental results obtained for the adsorption of metals on DSPC at a constant room temperature ($25 \pm 1^\circ\text{C}$) under predefined conditions of pH, adsorbent dose, and stirring speed obeyed the Freundlich adsorption isotherm. The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and the concentration of the metal ion in solution at equilibrium (C_e)¹².

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Where K_f (L g^{-1}) is an indicator of adsorption capacity and n (dimensionless) indicates the effect of the concentration on the adsorption capacity and represents the adsorption intensity (dimensionless). The plot of $\log(x/m)$ versus $\log(C_e)$ for various initial concentrations was linear, indicating the applicability of the classical

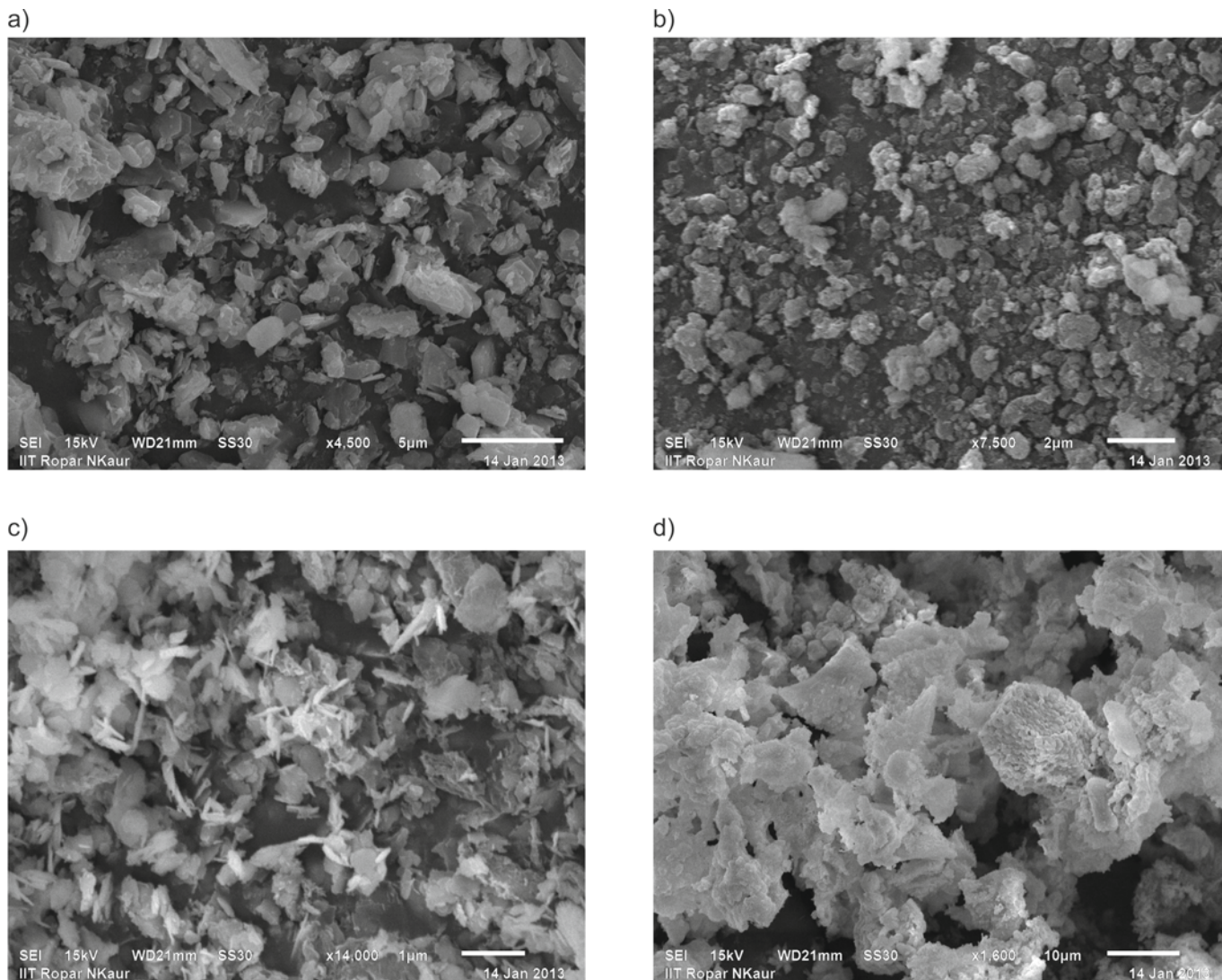


Figure 3. a) SEM of native DSPC; b) SEM of Cd (II) loaded DSPC; c) SEM of Pb (II) loaded DSPC; d) SEM of Ni (II) loaded DSPC

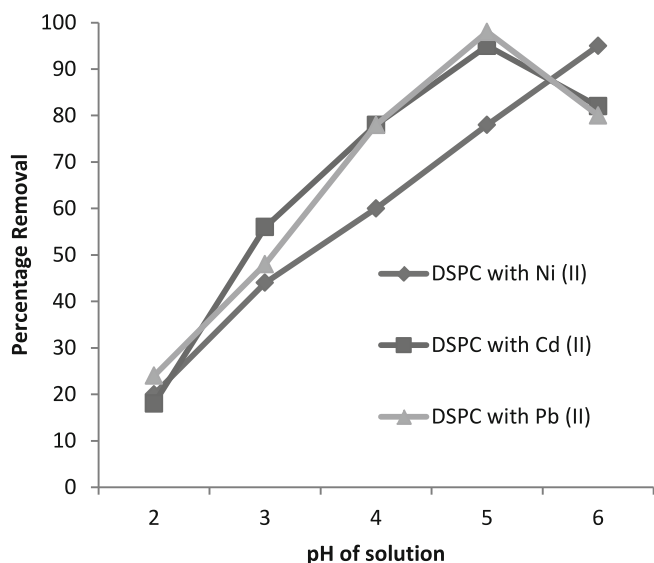


Figure 4. Effect of pH on removal efficiency of heavy metal ions (Ni (II), Cd (II) and Pb (II))

adsorption isotherm to the DSPC-Ni (II), DSPC- Cd (II) and DSPC- Pb (II) systems.

The Langmuir isotherm is applicable for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies

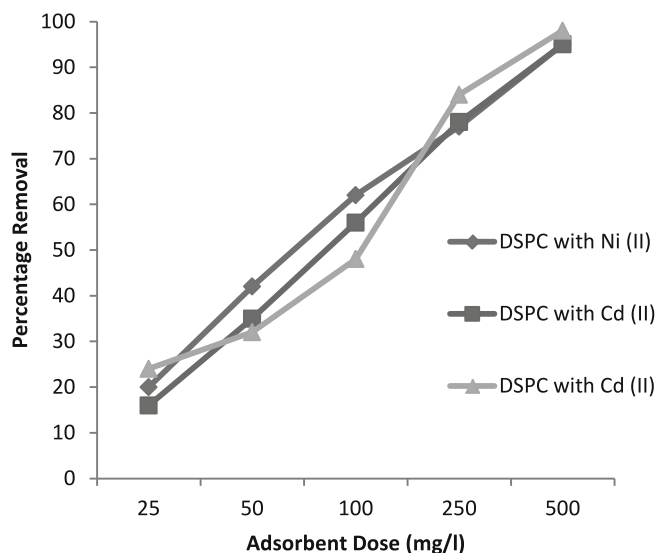


Figure 5. Effect of adsorbent dose mg L⁻¹ on removal efficiency of heavy metal ions (Ni (II), Cd (II) and Pb (II))

of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

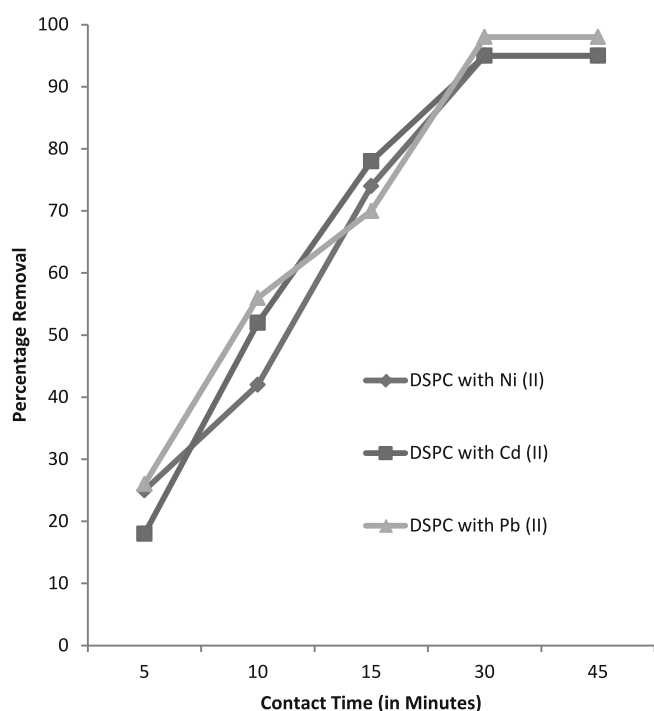


Figure 6. Effect of contact time (min) on removal efficiency of heavy metal ions (Ni (II), Cd (II) and Pb (II))

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed at equilibrium time (mg g^{-1}), Q_0 is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg g^{-1}), and b is a constant related to the affinity of binding sites with the metal ions (L mg^{-1})^{32,33}. The plots of $C_e/(x/m)$ versus C_e are linear, which shows that the adsorption of metal ions follows the Langmuir isotherm model. The correlation coefficient (R^2) values were very high for selected Adsorbent, which indicates that the data fit reasonably well to the Langmuir isotherm in the present adsorption studies. The value of the slope was found to be less than unity, implying that significant adsorption took place at a low metal ion concentration (Table 2).

ADSORPTION KINETICS

Pseudo 1st & 2nd order equations

For evaluating the adsorption kinetics of heavy metals the pseudo-first order equation of Lagergren has been used to test experimental data.

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

where Q_e (mg/g) and Q_t (mg/g) are the amount adsorbed of heavy metal ions at equilibrium and at time t , respectively, and K_1 (min^{-1}) is the rate constant of pseudo 1st order adsorption. The model was found inapplicable when this equation is fitted to the data of the selected agricultural waste biosorbent for the removal of heavy metal ions with R^2 value very low.

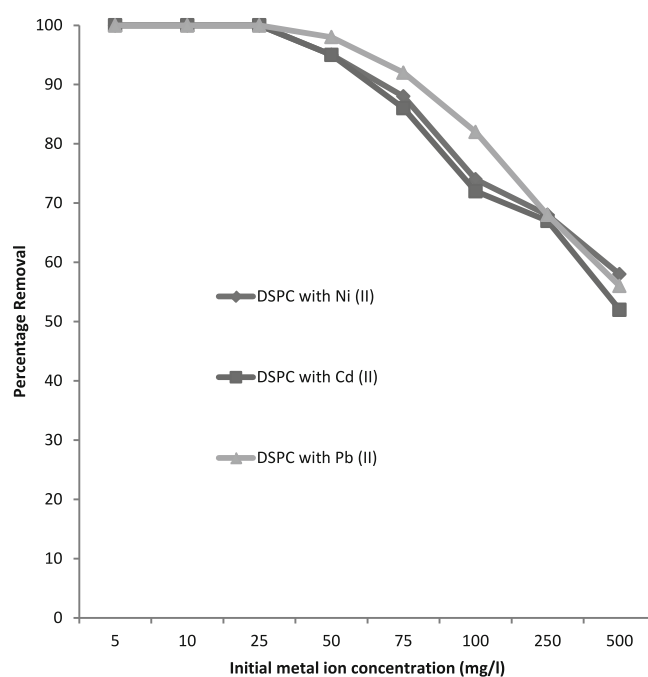


Figure 7. Effect of initial metal ion concentration mg L^{-1} on removal efficiency of heavy metal ions (Ni (II), Cd (II) and Pb (II))

The pseudo 2nd order kinetic model is linearly expressed as³⁴:

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \quad (5)$$

Where K_2 (g/mg min) is the pseudo 2nd order rate constant, which can be calculated from the intercept of the straight line obtained from plotting t/Q_t vs. t . Also, the initial sorption rate can be calculated using the relation³⁵:

$$K_o = K_2 Q_e^2 \quad (6)$$

The perfect fit of the experimental data of DSPC indicates the applicability of model for the adsorption of heavy metal ions on the DSPC.

Real Industrial Effluent Treatment

Results grafted from the previous optimization experiments were used to conduct the experiments with real industrial effluents of electroplating industry. It has been found that percentage removal efficiency was good when the biosorbent was used for treatment of real industrial effluents. For single metal simulated solutions the removal efficiency of DSPC for Ni (II) and Cd(II) has been found 95%, and 98% for Pb (II) respectively and the removal efficiency of DSPC has been found to be nearly 100% for Ni(II), Cd(II) and Pb (II) for selected real industrial effluents. Enhanced removal efficiency is due to the reason that as simulated solutions concentration is 50 ppm and the concentration of metal ions in real industrial effluent is very less therefore better removal efficiency has been found in latter.

Table 2. Freundlich and Langmuir models regression constants for different adsorbent

Adsorbent	Freundlich isotherm			Langmuir isotherm		
	K_f (1 g^{-1})	N	R^2	Q_0 (mg g^{-1})	B (1 mg^{-1})	R^2
DSPC with Ni (II)	0.82	3.15	0.9421	0.62	0.030	0.9812
DSPC with Cd (II)	0.88	3.37	0.9805	0.67	0.0312	0.9914
DSPC with Pb (II)	0.87	3.35	0.9867	0.66	0.0311	0.9923

Desorption Efficiency and Reusability

The reusability of the biosorbent is one of the key factors in assessing of its potential for commercial applications. Two different potential desorption agents (1 M HCl and 1 M HNO₃) were used to desorb the selected metal ions from the biosorbent. The desorption efficiency of Ni (II) was found to be 93% using 1 M HCl and 1 M HNO₃ respectively. Similarly Cd (II) desorption was found to be 96% and 95% for Pb (II) respectively. Therefore, 1 M HCl solution was selected as desorption agent. The greater and faster desorption resulted due to surface binding of metal ions. The reusability of the biosorbent was also tested up to 5 consecutive sorption-desorption cycles. The results showed that the biosorbent offers potential ability to be used repeatedly in metal ion sequestering process.

CONCLUSION

The present study concluded that the DSPC has potentially higher adsorption efficiency for Ni (II), Cd (II) and Pb (II) under studied experimental conditions on simulated as well as for real industrial effluents. The metal ion removal was highly dependent on pH, initial concentration and adsorbent dose. DSPC is found to be very effective and explores the promising platform for the sequestering of heavy metal ions as it outweighs the various shortcomings that are being encountered during the experimental process with biomass in its natural form. Further reusability of the biosorbent enhance its possibility to be utilized again and desorption studies makes the whole process environment friendly as the metal ions are not entering in the environment in the form of solid sludge and contaminating the aquatic systems. *Delbergia sisso* pods are one of the readily available agricultural wastes in India, especially in Punjab as the tree is declared as 'State tree' and its cultivation comes under agro-forestry and social forestry programmes. So it can be used by small scale industries having low concentrations of heavy metal ions in wastewater using batched or stirred-tank flow reactors in carbonized form.

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