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Bioremoval of Nickel and lead using bitter gourd (*Momordica charantia*) seeds

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ABSTRACT: In the present research work biomaterial obtained from *Momordica charantia* (Bitter gourd) seeds powder is used as a low cost and eco-friendly biosorbent in the effective removal of Nickel and Lead from aqueous samples. The research is a bench scale experimental type and analyses have performed by using different amounts of adsorbent in solutions with different concentrations of each metal. Biosorption of metals is dependent on the initial pH of the working solutions, initial metal ion concentration, contact time and dosage of the sorbent material. Results indicate the removal efficiency is good for both nickel and lead. At pH 5 the removal per cent of lead is 90 and at pH 6 the removal percent for nickel is 88. Equilibrium time attained at 120 minutes and maximum removal percentage of both lead and nickel at 125 mg of the adsorbent material.

KEYWORDS: Nickel, lead, Adsorption, Bitter Gourd and aqueous samples

I INTRODUCTION

Water pollution by heavy metal contamination due to rapid industrialization and other development activities has been a major global concern. It is well known that the industrial effluents are loaded with heavy metals and direct disposal of such effluent without treatment in an aquatic receiving body lead to adverse effect on aquatic life. The toxic nature of heavy metal has resulted in the enforcement of stringent laws for maximum allowable limits in the water bodies. Heavy metals such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Cu^{2+}etc. are prior toxic pollutants in industrial wastewater, which become common groundwater contaminants and tend to accumulate in organisms including human being, causing numerous diseases and disorders [1,2]. Heavy metal contamination may cause changes in the physicochemical composition of the water and finally become unsuitable for human consumption [3].

Nickel is a well known heavy metal pollutant and extensively used in electroplating, manufacturing of steel, electronic devices, ceramics and colored glasses [4]. Exposure to nickel may cause noxious effects such as carcinogen and damage to skin, lungs, nervous system and mucous [5]. Trace amounts of nickel is beneficial to humans and other organisms as an activator of some enzyme system, but if it is beyond the scope of normal levels, different types of diseases occur such as lung cancer, renal edema, skin dermatitis and gastrointestinal disorder. For this reason, the Water Sanitation and Hygiene (WSH) under World Health Organization (WHO) established the toxic limits of permissible concentrations of nickel at a level of Ni (II) and insoluble compounds of 1.0 mg/m^3, soluble compounds of 0.1mg/m^3, nickel carbonyl of 0.05-0.12 mg/m^3, and nickel sulphide of 1.0 mg/m^3. Nickel causes more hypersensitivity than any other metal and research conducted by the asthma and allergy centers indicated that 14.2% of the population suffers from nickel hypersensitivity [6].

Lead is also one of the common and most toxic pollutants discharged into the natural waters from various industrial activities. There are various industries pertaining to discharge of lead such as pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials and explosive manufacturing, ceramic, glass, oil, metal, phosphate fertilizer, electronic, wood production, combustion of fossil fuel, forest fires, mining activities, sewage wastewater, automotive, coating, painting, storage batteries, aeronautical, alloy and steel industries. Lead has been implicated as being responsible for intellectual disabilities in children and causes about1,43,000 deaths annually in developing countries [7,8]. Young children are more vulnerable to lead exposure because it affects the development of brain and nervous system [7, 9]. It also causes kidney damage and high blood pressure in adults and can lead to miscarriage, low birth

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weight, stillbirth and premature birth in pregnant women [7–10]. Ingestion of lead contaminated water has been implicated as a major route of lead toxicity [8–10].

There are various conventional treatment techniques available for the removal of heavy metals from wastewater like chemical precipitation, ion exchange, reverse osmosis, electro dialysis, electrochemical treatment, membrane separation process. Among these methods, adsorption has been found to be one of most popular process for the removal of lead and nickel from wastewater due to its low initial cost and sludge free environment. Increasing demand for eco-friendly techniques promotes the interest to natural and bio-degradable adsorbents. Amir Hossein Mahvi et al used tea waste as an adsorbent for heavy metal removal from industrial waste waters particularly lead, cadmium and nickel [11]. Ofomaja AE et.al used Coconut copra meal which is a by-product of coconut production and is characterized by functional groups such as alcohols, hydroxyls, carboxylic acids, etc. on its surface. It is effectively used as a biosorbent for the removal cadmium [12]. Ahalya N et.al used the husk of Bengal gram (*Cicer arietinum Linn*.) to remove Cr (VI) from aqueous solutions through biosorption [13]. Innocent OBOH et al used neem leaves as biosorbent material for the removal of copper, lead, nickel and zinc [14]. Various natural products have been effectively used as biosorbents for the removal of heavy metals in the literature. Some of them have summed up in Table 1.

Table 1 Natural products used as biosorbents for removal of heavy metals from aqueous solutions

Biosorbent (natural product)	**Metals**	**Adsorption capacity (mg/g)/ Efficiency (%)**
Black tea leaves	Cr (VI)	364 mg /g
Cocoa shells	Pb, Cr, Cd, Cu, Fe, Zn, Co, Mn, Ni, Al	Pb 95, Cr 53,Cd 81,Cu 70,Fe45,Zn 64,CO 57,Mn 53,Ni 50,Al 15%
Coconut copra meal	Cd	1.70 mg/g
Coconut shell carbon	Zn	90%
Coffee beans	Cu (II), Zn (II), Pb(II), Fe (III) and Cd (II)	5.98 -10^{-2} mmol /g
Crab shell	Cu and Co	243.9 mg/g and 322.6 mg /g
Egg shell	Cr (III)	160 mg/g
Husk of Bengal gram	Cr (VI)	99%
Husk of Black gram	Pb, Cd, Zn,Cu,Ni	49.97, 39.99, 33.81,25.73,19.56 (mg/g)
Papaya wood	Cu, Cd, Zn	97.8, 94.9, 66.8 (%)
Sugarbeet pulp	Cu(II)	28.5mg /g
Sunflower stem	Cr(III)	85%
Waste fruit residues	Hg (II), Pb (II), Cd (II), Cu (II), ZN (II).Ni (II)	Hg 85, Pb 90, Cd 86,Cu 96, Zn 87, Ni 85(%)
Wheat shell	Cr(VI)	364 mg /g

In this work, Bitter gourd (*Momordica charantia*) seeds powder has been used as biosorbent. *Momordica charantia* or Bitter Melon, also known as balsam pear or Karela, is a Tropical vegetable, is a common food in Indian cusine and has been used extensively in folk medicine as a remedy for diabetes. The Latin name Momordica means “to bite” (referring to the jagged edges of the leaf, which appear as if they have been bitten). In Ayurveda, the fruit is considered as tonic, stomachic, stimulant, emetic, antibilous, laxative and alterative. Bitter melon has been used in various Asian traditional medicine systems for a long time. Like most bitter-tasting foods, bitter melon stimulates digestion. To study the adsorption of nickel and lead ions, batch experiments were performed using bitter gourd seeds powder as biosorbent. The characterization of the adsorbent was carried out using FTIR. The effects of various process parameters like pH, adsorbent dose, contact time and initial metal concentration on the removal of nickel and lead from wastewater have been investigated and optimized.

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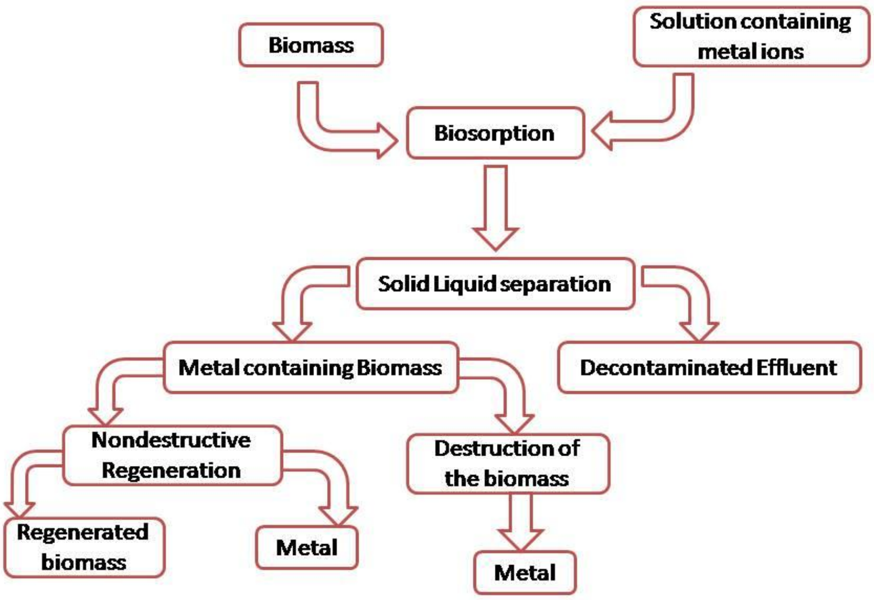

Fig 2. Main steps involved in Biosorption Process [18]

II MATERIAL AND METHODS

A. Preparation of Biosorbent

The Bitter gourd (*Momordica charantia*) seeds were collected from fruits purchased from local market in Tirupati, Andhra Pradesh, India. The seeds were washed in 0.1N HCl solution and sundried for three days. Then the seeds were dried in hot air oven at 90°C and pulverized into powder, this powder was subjected to sieve analysis in sieve shaker, to get 150µm retained powder. This powder was washed several times with distilled water to remove soluble, coloring matter and then it was sun dried and stored in air tight containers for further studies.

Fig 1a) Bitter gourd Fruits

Fig 1 b) Bitter gourd seeds

Fig 1 c) Bitter gourd seeds powder

B. Glassware and Apparatus used

All glass wares used in the present study were of Borosil. The instruments used were Flame Atomic Absorption Spectrophotometer Model 6300, Shimadzu (Japan), Digital pH Meter, Elico (India), Digital Electronic Balance Shimadzu AUX 320 and Fourier Transformed Infra-red Spectrophotometer Nicolet IR-200 (USA).

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C. Reagents and standards

4.47g of Nickel sulphate was weighed and transferred to a 1000 ml standard flask. Distilled water was added to the standard flask to dissolve the salt and is further added up to the mark to obtain a 1000 mg/L of Nickel stock solution. The pH of the aqueous solution is varied by adding the required amounts of 1N HCl and 1N NaOH. Different concentrations of metal solutions were prepared by dissolving required amount of stock solution. Standard lead (II) solution 1000 mg/L, was prepared by weighing 1.60 g of Pb (NO3)2 dissolving in double distilled water to give a volume of 1000 mL

D. Batch adsorption studies

The affinity of biomass to adsorb heavy metals like nickel and lead were studied in batch experiments. In all the sets of experiments, fixed volume of metal solution in 50 mL was stirred with the prepared biosorbent dose (50 – 200 mg) for the period of two hours. Different conditions of pH (3-8), initial concentrations (1 – 6 µg / mL) and contact time (30 – 150 minutes) were evaluated during the study. In order to regulate pH of the medium, 0.1 N of HCl and NaOH was used. The solutions were separated from the biomass by filtration through whatmann 40 filter paper. The initial and final concentrations of the metal ions in the solution were measured using Flame Atomic Absorption Spectroscopy.

Metal ion removal (%) = $[(C_0 - C_e)/C_0] \times 100$Where C_0: Initial metal ion concentration of test solution, mg/L, C_e : Final equilibrium concentration of test solution mg/L

III RESULTS AND DISCUSSION

A. FT-IR (Fourier Transform Infrared) spectral analysis

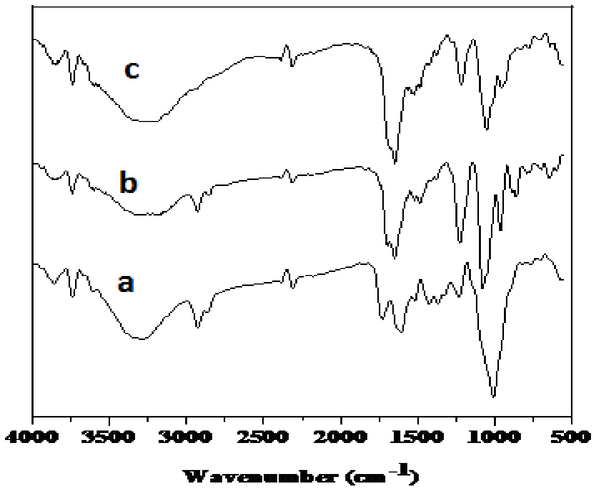

Fig 3. FTIR spectra of a) Bitter Gourd (BG) seeds powder b) Nickel loaded BG c) Lead loaded BG

FTIR spectroscopy was used to identify and show the functional groups present on the surface of the bitter gourd seeds powder. Both bitter gourd seeds powder and metal loaded bitter gourd seeds powder were analyzed by using FTIR spectra and the results are shown in Fig. 2. Bitter gourd seeds powder exhibited a number of adsorption peaks indicating the complex nature of the material examined. The broad absorptions between 3000 and 3500 cm−1 confirm the existence of carboxylic O–H groups and free COOH's of Bitter Gourd seeds powder. The doublet peaks appeared in all the spectra at wave number 2902 cm−1 and 2931 cm−1, respectively, due to the asymmetric and symmetric stretch of aliphatic chains (–CH). The peak around 1,612 cm−1 is due to the C=C stretching that can be attributed to the aromatic C-C bond, and the peak at 1,018 cm−1 can also be associated with either C-O symmetric or asymmetric stretching vibration (-C-O-C- ring). The absorption band at 1743 cm−1 is attributed to C=O of carboxylic group. The

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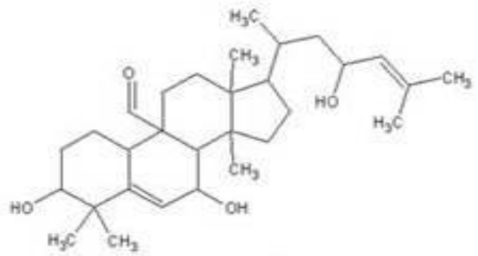
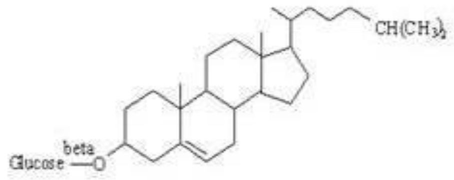
comparative study of FT-IR spectra of Bitter gourd seeds powder (Figure 2a) and metal loaded Bitter gourd seeds powder (Figure 2b & 2c) revealed that the Bitter Gourd seeds powder has functional groups such as alcoholic, ketonic, and carboxylic groups. These groups might be involved in complexation reactions with nickel and lead, could be viewed as a natural ion-exchange material that primarily contains weak acidic and basic groups on the surface [15]



Momordicin



Charantin

Momordica Charantia fruits consists glycosides, saponins, alkaloids, reducing sugars, resins, phenolic constituents, fixed oil and free acids. Chemical constituents like Alkaloids, charantin, charine, cryptoxanthin, cucurbitins, cucurbitacins, cucurbitanes, cycloartenols, diosgenin, elaeostearic acids, erythrodiol, galacturonic acids, gentisic acid, goyaglycosides, goyasaponins, guanylate cyclase inhibitors, gypsogenin, hydroxytryptamines, karounidiols, lanosterol, lauric acid, linoleic acid, linolenic acid, momorcharasides, momorcharins, momordenol, momordicilin, momordicins, momordicinin, momordicosides, momordin, momordolo, multiflorenol, myristic acid, nerolidol, oleanolic acid, oleic acid, oxalic acid, pentadecans, peptides, petroselinic acid, polypeptides, proteins, ribosome-inactivating proteins, rosmarinic acid, rubixanthin, spinasterol, steroidal glycosides, stigmasta-diols, stigmasterol, taraxerol, trehalose, trypsin inhibitors, uracil, vacine, v-insulin, verbascoside, vicine, zeatin, zeatin riboside, zeaxanthin, zeinoxanthin Amino acids-aspartic acid, serine, glutamic acid, thscinne, alanine, g-amino butyric acid and pipecolic acid, ascorbigen, b-sitosterol-d-glucoside, citrulline, elasterol, flavochrome, lutein, lycopene, pipecolic acid are also present in fruits of Momordica *Charantia.* The fruit pulp has soluble pectin but no free pectic acid. Past Research has found that the leaves are nutritious sources of calcium, magnesium, potassium, phosphorus and iron; both the edible fruit and the leaves are great sources of the B vitamins. As the seeds are within the fruits and these functional groups and phyto chemical constituents may have shown significant effect on the adsorption of nickel and lead from aqueous solutions [16].

B. Effect of pH

The pH of the solution affects the surface charge of the adsorbents and it is one of most important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals. The pH value of the solution is an important controlling parameter in the adsorption process. The effect of pH on adsorption of metal ions on to the adsorbent material was conducted in the pH range of 3.0 – 8.0. Adsorption of nickel (II) and lead (II) by Bitter gourd **(***Momordica charantia*) seeds powder was found to be maxium of 88 per cent for Ni (II) and 90 per cent for lead at pH 6 and pH 5. Increase in metal removal with increase in pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes.

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Table 1: Effect of pH on the removal of Nickel and Lead

Ni(II)		pb(II)	
pH	% Removal	pH	% Removal
3	62	3	66
4	68	4	70
5	82	5	90
6	88	6	85
7	76	7	79
8	71	8	76

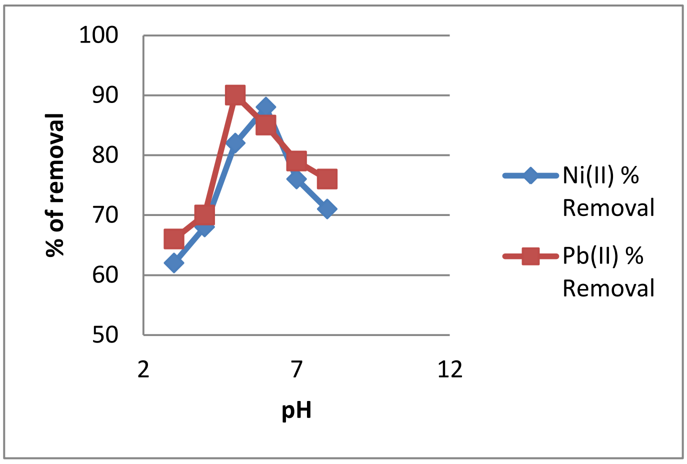

Figure 4: Effect of pH on adsorption of Ni ((II) and Pb (II)

C. Effect of adsorbent dose

Adsorption efficiency of Ni (II) and pb (II) was studied by varying the amount of adsorbent dosage from 50 to 125 mg by keeping other parameters (pH, and contact time) constant**.** Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites [17,19,20] this may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. The maximum per cent removal of Ni (II) and pb (II) was about 92 per cent and 95 per cent at the dosage of 100 mg. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent

Table 2: Effect of Adsorbent Doasge on the removal of Nickel and Lead

Dosage of Biosorbent in mg	Nickel	Lead
	Per cent Removal	Per Cent Removal
50	73	74
75	81	88

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100	92	95
125	93	94

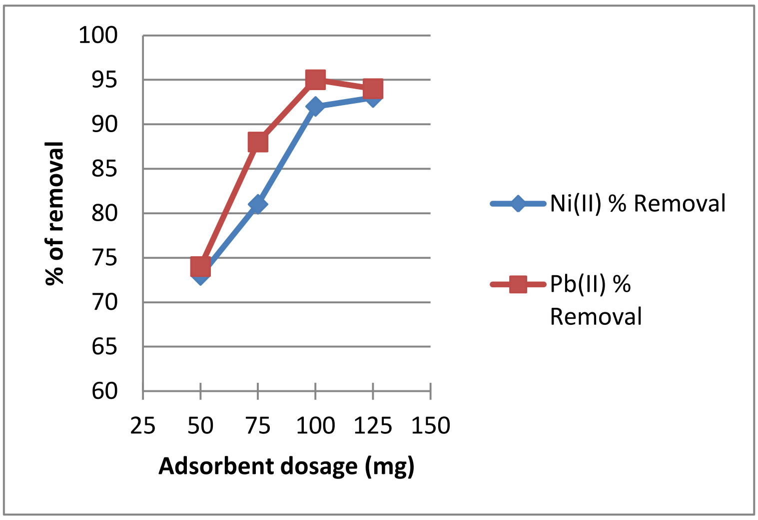

Figure 5: Effect of adsorbent dosage on the removal of Ni ((II) and Pb (II)

D. Effect of contact time

Metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent and pH of solution were kept constant. The results indicated that removal of nickel was increased from 44 to 93 per cent with the contact time variation from 30 to 120 minutes and removal of lead was increased from 45 to 90 per cent with the contact time variation from 30 to 120 minutes, Thus the results illustrated that the optimum contact time for maximum removal of nickel (93%) is 120 minutes and for lead (95%) is 90 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system.

Table 3: Effect of contact time on the removal of Nickel and Lead

Contact time in (Min)	Nickel	Lead
	Per cent Removal	Per cent Removal
30	44	45
60	75	77
90	90	95
120	93	90

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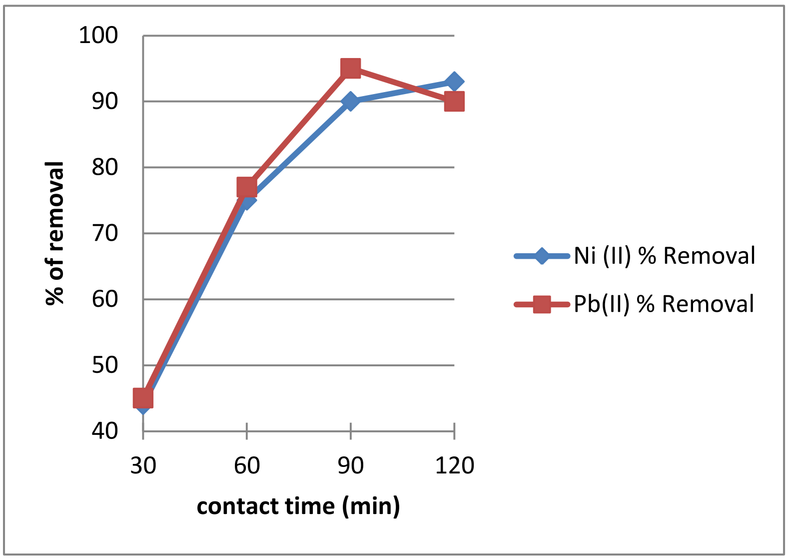

Figure 6: Effect of contact time on adsorption of Nickel and Lead

E. Effect of initial metal ion concentration

The effect of initial metal ion concentration on adsorption rate was studied in the range (1-6 mg/L) at constant pH, and contact time. It was observed that the percentage removal decreased with increasing in initial nickel and lead concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of nickel and lead to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial nickel and lead concentration. Therefore it was evident from the results that nickel and lead adsorption was dependent on the initial metal concentration.

Table: 4: Effect of Initial Metal ion concentration on adsorption of Nickel and Lead

Nickel		Lead	
Initial concentration	**Removal**	**Initial concentration**	**% Removal**
1	76	1	74
2	78	2	76
3	79	3	87
4	89	4	85
5	53	5	57
6	42	6	45

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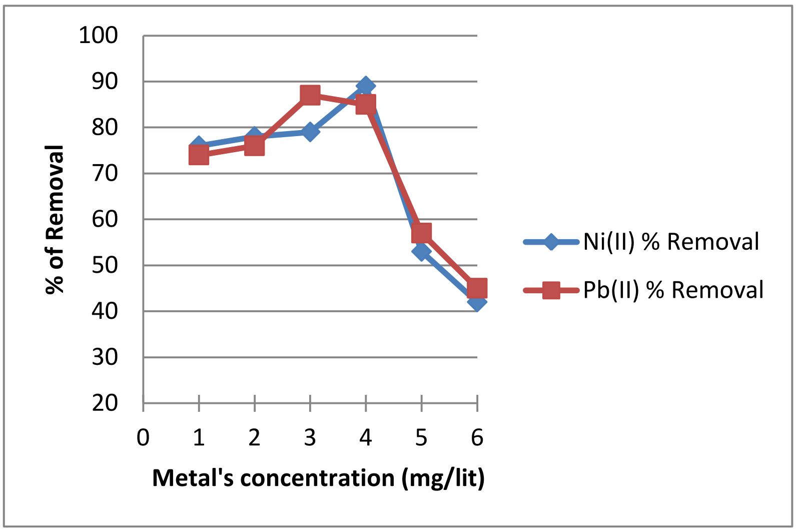

Figure 7: Effect of Metal ion concentration on adsorption of Ni ((II) and pb (II)

F. Equilibrium studies on nickel and lead

Removal percentage for Nickel is 93 and for lead is 95 at a contact time of 120 minutes and 90 minutes. Hence, 120 and 90 minutes equilibrium time for nickel and lead was considered in all the sets of the experiments. 93 per cent of nickel was removed by using 125 mg of prepared adsorbent per liter. 100 mg of prepared biosorbent is sufficed for the removal of 95 per cent lead in the aqueous solutions. The adsorption ability of Bitter gourd (*Momordica Charantia*) seeds powder has been investigated and found effective for the removal of Nickel (II) and lead from aqueous solutions.

IV CONCLUSION

The present research work examined the usage of Bitter Gourd *(Momordica charantia)* seeds powder as an inexpensive sorbent for the sorption and removal of nickel and lead from aqueous solutions. Usage of biosorbent for metal sorption bears a lot of advantages compared to classical methods such as chemical precipitation, membrane filtering, chemical oxidation or reduction, etc. From the present investigation it may be concluded that the low-cost natural adsorbent prepared from *Momordica charantia* seeds powder acts as an excellent adsorbent and can efficiently remove nickel and lead ions present in the aqueous solutions. The present work also explores a new cheaper, economical and selective adsorbent as an alternative to costly adsorbents for the reduction of lead and nickel from aqueous solutions

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