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Removal of Nickel, Cadmium and Lead from Aqueous Solutions using Combination of Sapodilla (*Manilkara zapota*) and Custard Apple (*Annona squamosa*) Seeds Powder

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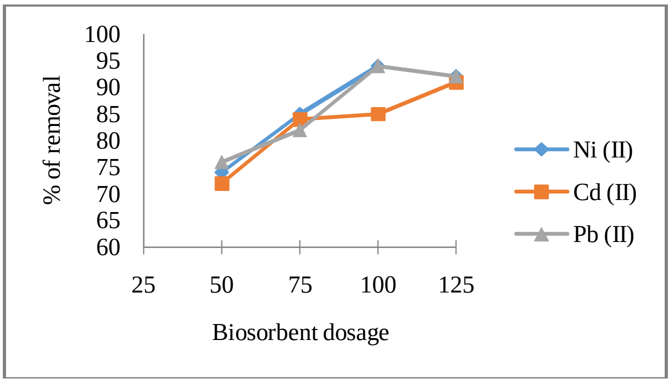
ABSTRACT

Heavy metals present in wastewater are recognized as long-term hazardous contaminants because of their non-biodegradable behavior, high toxicity, accumulation and retention in human body and carcinogenic properties. In the present investigation, combination of sapodilla (Manilkara zapota) seeds and custard apple (Annona squamosa) seeds have been identified as potentially low cost and efficient bio-sorbent material for the removal of toxic heavy metals (nickel, cadmium and lead) from aqueous solutions. The influence of pH, contact time, metal concentration, adsorbent dosage on the selectivity and sensitivity of the removal process was investigated. The results showed the removal efficiencies: (90 per cent for nickel at pH 6, 95 per cent for cadmium at pH 5 and 92 per cent for lead at pH 6. The removal efficiencies by differing contact time (96 per cent for nickel at contact time of 90 min, 95 per cent for cadmium and 94 % for lead at a contact time of 120 min). The removal efficiencies by varying adsorbent dosage: (94 % for nickel and, 94 % for lead at a 100 mg of adsorbent dosage and 91 % for cadmium, at 125 mg of adsorbent dosage). The removal efficiencies at various initial metal ion concentrations: (89 % for nickel at 4 µg mL^{-1}*, 84 % for cadmium and 89 % for lead at 4 µg mL*$^{-1}$*).*

Graphical Abstract



Effect of adsorption dosage on adsorption of Ni ((II), Cd (II) and Pb (II).

Keywords: Nickel, Cadmium, Lead, Sapodilla, Custard Apple.

INTRODUCTION

In the aqueous media the presence of pollutants particularly from the hazardous heavy metals and metalloids, is of an important environmental and social concern. Many of the elements are stable and are bio-accumulative, therefore assessment of their safe limits is very difficult in the ecosystem. Few metals, such as Iron (Fe), Zinc (Zn), Copper (Cu), Cobalt (Co), Chromium (Cr), Manganese (Mn) and Nickel (Ni), are required for biological metabolism in trace amounts; however, their higher dose may cause toxic effects. Other metals such as Lead (Pb), Mercury (Hg), Cadmium (Cd) and Arsenic (As) are not suitable for biological functions and are positively highly toxic to the life forms [1, 20].

Nickel occurs naturally in soils and volcanic rocks. Nickel and its salts are used in several industrial applications such as electroplating, automobile and aircraft parts, batteries, coins, spark plugs, cosmetics, stainless steel, and are used extensively in the production of nickel–cadmium batteries on an industrial scale. It enters into the water bodies naturally by weathering of rocks and soils and through the leaching of the minerals [2]. The water soluble salts of nickel are the major problems of contamination in aquatic systems [3]. Paint formulation and enameling industries discharges nickel containing effluents to the nearby bodies of water [4]. Nickel is also found in cigarettes, as a volatile compound commonly known as nickel carbonyl. Nickel plays an essential role in the synthesis of red blood cells; however, it becomes toxic when taken in higher doses. Trace amounts of nickel do not damage biological cells, but exposure to a high dose for a longer time may damage cells, decrease body weight and damage the liver and heart. Nickel poisoning may cause reduction in cell growth, cancer and nervous system damage [5].

Cadmium is used widely in electroplating industries, solders, batteries, television sets, ceramics, photography, insecticides, electronics, metal-finishing industries and metallurgical activities. It can be introduced into the environment by metal-ore refining, cadmium containing pigments, alloys and electronic compounds, cadmium containing phosphate fertilizers, detergents and refined petroleum products. Rechargeable batteries with nickel–cadmium compounds are also sources of cadmium [2, 3]. Cadmium exposure causes renal dysfunction, bone degeneration, liver and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium [2]. Lead has environmental importance due to its well known toxicity [7]. The current annual worldwide production of Pb(II) is approximately 5.4 million tons and continues to rise. In the manufacturing of batteries (automobile batteries in particular), sixty percent of Pb(II) is used, while the remainder is used in the production of pigments, glazes, solder, plastics, cable sheathing, ammunition, weights, gasoline additive, and a variety of other products. Such industries continue to pose a significant risk to workers, as well as surrounding communities [8]. Pb(II) can be introduced into environment as liquid wastes from different industries. In water, Pb (II) tends to accumulate in aquatic organisms through the food chain and by direct uptake [8]. Assimilation in the human body of relatively small amounts of Pb(II) over a long period of time can Lead to malfunctioning of certain organs and chronic toxicity [9]. It can damage practically all tissues, particularly the kidneys and the immune system. Intense exposure to high Pb(II) levels (from 100 to 200 g day^{-1}) causes encephalopathy with the following symptoms: vertigo, insomnia, migraine, irritability, and even convulsions, seizures, and coma [10, 11]. Because of the demand for water to feed the growing population and the needs for industrial processing, the separation and purification of generated wastewater by adsorption phenomena is gaining major relevance. Adsorption over biomass-derived biosorbents has provided the capability to treat wastewater on a large scale. Several low-cost biosorbents have been synthesized and successfully applied to remove toxic metals and metalloids from wastewater.

Heavy metal removal has become a burning issue in the industrialized as well as in the developing world where industrial use and discharging of heavy metal is gradually increasing. The adverse and toxic effect of heavy metal on aquatic life and the environment is well established. Humans are not free from this pollution because the toxic metals are entering into the human body through the complex and diverse food chain [12]. In these circumstances sustainable heavy metals removal is a serious research concern among researchers and technologists [13]. The commonly used methods for removing metal ions from aqueous streams include physical and chemical methods used separately or inclusively based on need. The available methods are chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. Most physical and chemical methods of heavy metal sequestration from aqueous solutions have exhibited low efficiency, operational sensitivity and consequently high cost, thus necessitating the need for alternative low-cost sorbents for heavy metal uptake [14, 15]. Biosorption, which is a biological-based extraction technique, has proven to be a highly cost-effective and simple method for the removal of heavy metals from aqueous solutions [16].

MATERIALS AND METHODS

Preparation of adsorbent material: The sapodilla (*Manilkara zapota)* seeds were collected from local fruit market (Figure 1). The seeds were washed in 0.1N HCl solution. It was sundried for 3 days. Then the seeds were dried in hot air oven for 90°C and pulverized into powder, this powder was subjected to sieve analysis in sieve shaker, to get 150 μm 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. Custard apple *(Annona squamosa)* seeds were obtained from local seed supplier (Figure 2). The seeds which were sorted out as waste such as shrunken, unfit for germinating were selected for the present research work.

Figure 1. Sapodilla fruit (*Manilkara zapota)* seed materials.

Figure 2. Custard apple fruit *(Annona squamosa)* seed materials.

Apparatus: All the glassware used in the present study was of Borosil. The instruments and apparatus used throughout the experiment are listed in the table 1.

Table 1. List of instrument used during experimentation

S. No.	Instrument	Make
1	Flame Atomic Absorption Spectrophotometer	Model 6300, Shimadzu (Japan)
2	Digital pH Meter	Elico (India)
3	Digital Electronic Balance	Shimadzu AUX 320
4	FT-IR	Nicolet IR-200 (USA)

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^{-1} 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 cadmium (II) solution (1000 µg mL^{-1}), was prepared by weighing 1.7911 g of $CdCl_2$ (Merck) and standard lead (II) solution 1000 µg mL^{-1}), was prepared by weighing 1.60 g of $Pb(NO_3)_2$ (Merck) dissolving in double distilled water to give a volume of 1000 mL. Standard lead (II) solution 1000 µg mL^{-1}), was prepared by weighing 1.60 g of Pb $(NO_3)_2$ dissolving in double distilled water to give a volume of 1000 mL.

Batch Adsorption Studies: The affinity of biomass to adsorb heavy metals like Cd(II), Pb(II) and Ni(II) were studied in batch experiments. In all sets of experiments, fixed volume of metal solution in 50 mL was stirred with desired biosorbent dose (50-200 mg) for the period of two hours. Different conditions of pH (3-8), initial concentrations (1-6 µg mL^{-1}) and contact time (30-150 min) 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.

$$\text{Metal ion removal (\%)} = [(C_0 - C_e)/C_0] \times 100$$

Where C_0: Initial metal ion concentration of test solution, mg L^{-1}, C_e : Final equilibrium concentration of test solution mg L^{-1}.

RESULTS AND DISCUSSION

FTIR (Fourier transform infrared) Spectroscopy: FT-IR analysis was used to identify the characteristic functional groups on the surface of biosorbent and the spectra of biosorbent is shown in figure 3. From figure 3a and 3b that different functional groups on sapodilla and custard apple seeds powder are responsible for biosorption of lead, cadmium and nickel. A change in peak position at 3390 cm^{-1} in the spectrum of the cadmium, lead and nickel loaded sapodilla and custard apple seeds powder indicates the binding of these metals with hydroxyl groups. Further, shift in the peak at 1621 cm^{-1} of sapodilla and custard apple seed powder on nickel, cadmium and lead biosorption indicating the binding of metal ions to carbonyl groups also. From these findings, it is presumed that these metals adsorbed mainly to the active groups such as hydroxyl groups (–OH) and carbonyl groups (C=O).

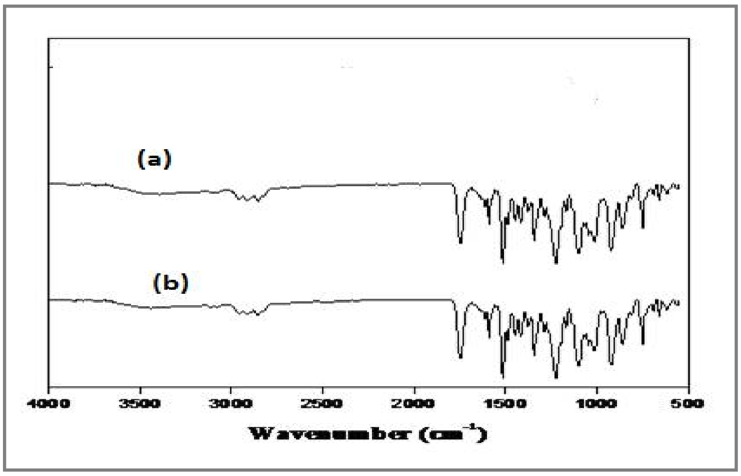


Figure 3. FTIR spectra of a) sapodilla and custard apple b) metal loaded sapodilla and custard apple.

Effect of pH: In adsorption process hydrogen ion concentration is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solution. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites, and affects the degree of ionization of the adsorbate during the reaction [17]. The results of table 2 indicated that Ni(II), Cd(II) and Pd(II) removal was increased to maximum and then decreased with pH variation from 5 to 8. The maximum percent removal of Ni(II),Cd(II) and Pb(II) was 90% , 95% and 92% at pH 5 and pH 6. The per cent removal of metal ions with the increase in pH can be explained on the basis of the 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 (Figure 4).

Table 2. Effect of pH in the removal of Ni(II), Cd(II) and Pb(II)

pH	Ni (II)	Cd (II)	Pb (II)
	% of Removal	% of Removal	% of Removal
3	63	65	63
4	69	68	70
5	80	95	84
6	90	83	92
7	74	72	73
8	69	70	70

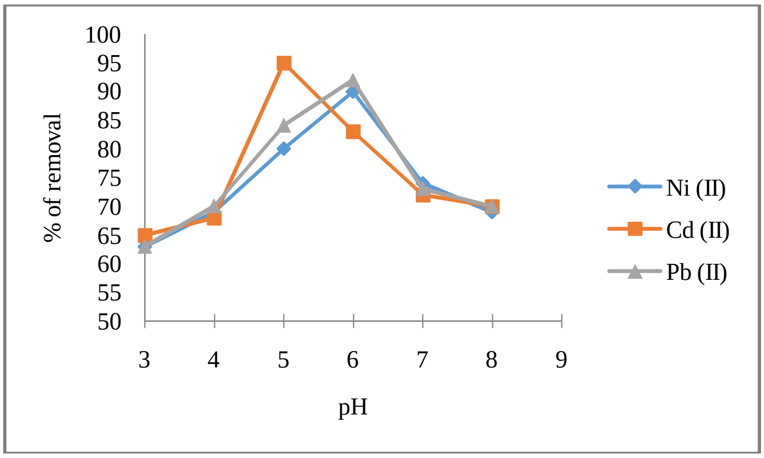


Figure 4. Effect of pH on adsorption of Ni(II), Cd(II) and Pb(II).

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 of table 3 indicated that Ni(II), Cd(II) and Pb(II) removal was increased with the contact time variation from 30 to 120 min. Thus the results illustrated that the optimum contact time for maximum removal of Ni(II) 96% with contact time of 90 min. and removal of Cd(II), Pb(II) was 96% and 94% with contact time of 120 min (Figure 5). This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system [18].

Table 3. Effect of Contact time on the removal of Ni (II),Cd (II) and Pb (II)

Contact time	Ni(II)	Cd(II)	Pb(II)
	% of Removal	% of Removal	% of Removal
30	48	49	51
60	78	77	79
90	96	90	93
120	95	96	94

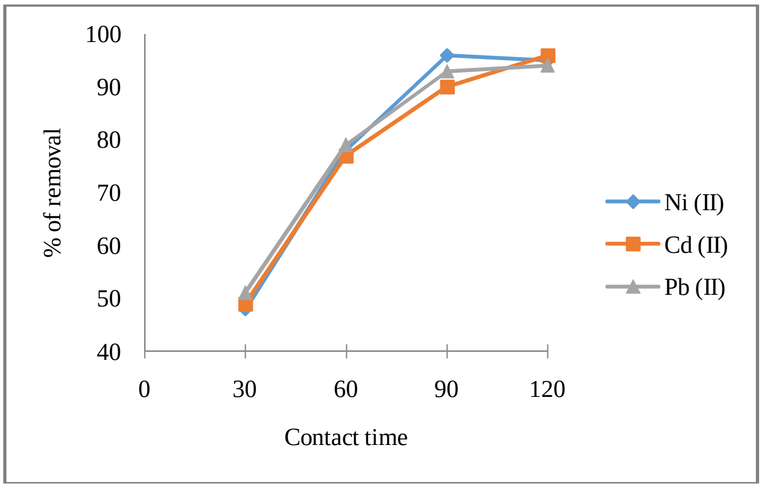


Figure 5. Effect of contact time on adsorption of Ni (II), Cd ((II) and Pb (II).

Effect of adsorbent dosage: The results for adsorptive removal of nickel, cadmium and lead with respect to adsorbent dosage are shown in table 4. Adsorption efficiency of nickel, cadmium and lead was studied by varying the amount of adsorbent dosage from 50 to 200 mg keeping other parameters (pH, and contact time) constant. The removal efficiency of the nickel, cadmium and lead has improved on increasing adsorbent dose. 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 percent removal of nickel 94% with 100 mg of biosorbent dosage, and cadmium 91% at the dosage of 125 mg. and lead 94% at the dosage of 100 mg (Figure 6). The results suggests 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 [19].

Table 4. Effect of adsorbent dosage on the removal of Ni (II),Cd (II) and Pb (II)

Biosorbent dosage	Ni (II)	Cd (II)	Pb (II)
	% of Removal	% of Removal	% of Removal
50	74	72	76
75	85	84	82
100	94	85	94
125	92	91	92

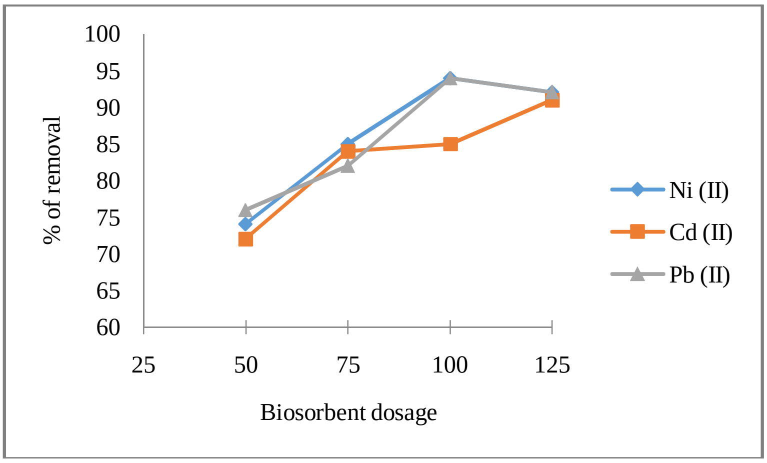


Figure 6. Effect of adsorption dosage on adsorption of Ni ((II), Cd (II) and Pb (II).

Effect of initial metal ion concentration: The effect of initial metal ions concentration on the adsorption rate was studied in the range (1-6 mg L^{-1}) at constant pH, and constant contact time. It was observed from the results of table 5 that the percentage of removal decreased with increasing in initial nickel, cadmium and lead concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of nickel, cadmium 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, cadmium and lead. Therefore it was evident from the results that nickel, cadmium and lead adsorption was dependent on the initial metal ions concentration [20].

Table 5. Effect of initial metal ion concentration on the removal of Ni ((II), Cd (II) and Pb (II)

Initial metal ion concentration mg^{-L}	Ni(II)	Cd(II)	Pb(II)
	% of Removal	% of Removal	% of Removal
1	74	72	74
2	76	77	75
3	80	82	80
4	89	83	88
5	82	84	89
6	52	54	55

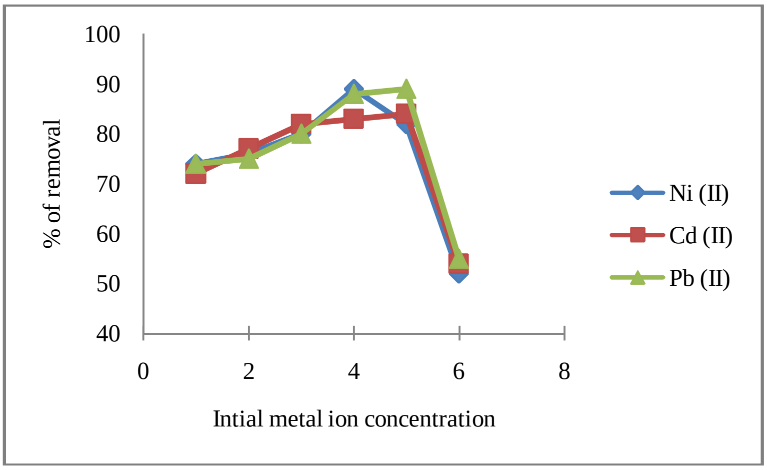


Figure 7. Effect of initial metal on concentration on adsorption of Ni ((II), Cd (II) and Pb (II).

Equilibrium studies of nickel, cadmium and lead: Maximum removal of Ni((II), Cd(II) and Pb(II**)** was 96 %, 96 % and 94% obtained at 90 minutes for nickel and 120 minutes for cadmium and lead. Hence, 90 min and 120 min equilibrium time was considered in all the experiments. Removal of Ni((II), Cd(II) and Pb(II**)** from the liquid media was 94 %, 91 % and 92 % respectively at 100 mg and 125 mg L^{-1} of adsorbent dosage. Removal of Ni(II), Cd(II) and Pb(II**)** was 90%, 95% and 92% at pH 6, pH 5 and pH 6 respectively. Combination of sapodilla (*Manilkara zapota*) seeds and custard apple (*Annona squamosa*) seeds in present investigation has immense potential of Ni(II), Cd(II) and Pb(II**)** removal from wastewater.

APPLICATION

The low cost and eco-friendly biosorbent derived from the combination of sapodilla (*Manilkara zapota*) seeds and custard apple (*Annona squamosa*) seeds are inexpensive and acts as an excellent material for the removal of nickel, cadmium and lead from aqueous solutions.

CONCLUSION

The results obtained from the present study, it is evident that the combination of sapodilla (*Manilkara zapota*) seeds and custard apple *(Annona squamosa)* seeds act as a good adsorbent for the removal of Ni(II), Cd(II) and Pb(II**)** ions. Batch experiments showed that the adsorption Ni(II), Cd(II) and Pb(II**)** ions are dependent on pH, adsorbent dosage, contact time, and initial metal ion concentration. Thus this study provide cost effective adsorbent materials for removing Ni(II), Cd(II) and Pb(II) ions from contaminated waste water or effluents.

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