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Biosorption of Nickel in Aqueous Solution Using Tamarind Shell and Carrot Peel

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Abstract

*Heavy metals are being discharged into the water bodies as a result of the various industrial activities. For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important for us to inform ourselves about the heavy metals and to take protective measures against excessive exposures. There is a need to remove these particles to prevent the accumulation of these particles in the ecosystems, thereby causing dietary problems. In this comparative study, we are measuring the ability of tamarind shell and carrot peel to remove the Nickel particles in water by the process of adsorption. The tamarind shell and the carrot peel were collected, dried, powdered and sieved. The sieved material was then washed with acid, alkali and distilled water. This was made to react with the solution containing Nickel and the amount of reduction of Ni was measured in the intervals of 2 hours till it reaches equilibrium. The physical parameters like Temperature, pH, Initial concentration, Biomass loading were varied. The experiments were designed using Minitab **v.**16 software. In Our study, the highest amount of removal of Nickel was observed for Tamarind shell treated with HCl, carrot peel treated with NaOH and carrot peel treated with distilled water. For Tamarind shell bisosorbent treated with HCl, the highest removal of Nickel is obtained at pH 4, with initial concentration 125ppm and biomass loading 7.75g/100 ml at 40 ^{0} C. For carrot peel biosorbent treated with NaOH had the highest Nickel removal rate was obtained at pH 4, with initial concentration 162.5ppm and biomass loading 7.75g/100ml at 35 ^{0}C.*

Keywords- *Heavy metals, Nickel, Tamarind shell, Carrot peel, Temperature, pH, Initial Concentration, Biomass loading.*

I. INTRODUCTION

All manuscripts must be in English. These 'Heavy metals' are chemical elements with specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 40 C (390F). Some well-known toxic metallic elements are arsenic 5.7, cadmium 8.65, iron 7.9, lead 11.34 and mercury 13.55 [1]. Heavy metals are common in our environment and good for health in small amounts, but large amounts of any may cause acute or chronic toxicity. Heavy metals toxicity can result in damaged or reduced mental and nervous function, lower energy levels, damage to lungs, kidney, liver and other vital organs [2], may even cause cancer [3]. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. These may enter into human body through food, water, air or absorption through skin [4] [5]. Nickel is naturally occurring element that can exist in various mineral forms. Natural nickel is mixture of five stable isotopes. Although it can exist in several different oxidation states, the prevalent oxidation state under environmental condition is its +2 valence state [i.e. Ni (II)], valences (-1, +1, +3 and +4) are also encountered, though less frequently. The effluents produced during electroplating, metallurgy, electronics and metal cleaning industries often contain high concentration of Ni (II) ions. Ni (II) for potable water is 0.01 mg/l and for industrial discharge water is 2mg/l.

Biosorption is the ability of certain biomaterials to bind and concentrate heavy metal from even dilute aqueous solutions, offers a technically feasible and economically attractive, alternative to the conventional technologies for the removal of heavy metal from the contaminated effluents. It is eco-friendly and cost effective new technologies are required for the removal of the heavy metals from these waste streams by appropriate treatment before releasing into water bodies [6]. Recently, agro wastes have been shown to be promising in this regard [7] [8]. The wastes from agriculture were used as adsorbents because these wastes are the dead cells in which biosorption are easily controlled. The agricultural wastes used in nickel biosorption were orange peel [7], wastes from tea factories [9], bagasse fly ash [10], fruit fresh biomass and chemically treated leached biomass [11], protonated rice bran [12], coir pith and modified coir pith [13], agricultural waste biomass [14], acacia leucocephala bark [15], sugar cane residue and bagasse [16], potato peel waste [17], pomace of olive oil [18], barley straw [19], coconut-based biosorbents [20], Moringa oleifera bark [21], cashew nut shell [22].

II. MATERIALS AND METHODS

2.1. Preparation of biosorbent

Natural adsorbents like tamarind shell and carrot peel are used for comparative studies for removal of metals.

A. Tamarind shell

Tamarind shells were collected and completely sun dried, powdered using domestic mixer. The powder was sieved using 80mesh sieve to fractionate the particles. The fraction retained on mesh was collected and stored in air tight bottles to avoid contamination.

B. Carrot peel

Carrot peels were collected from hotels and other eateries. The biomass was completely dried under the sun and powdered using domestic mixer. The powder was sieved using 80mesh sieve to fractionate the particles. The fraction retained on mesh was collected and stored in air tight bottles to avoid contamination.

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2.2. Pre-treatment of the biosorbent

A. Tamarind shell

The pre-treatment of tamarind shells was carried out to increase the metal uptake efficiency. 250g of the tamarind shells was treated with 500 ml 1N HCL and 1N NaOH for 4hrs separately. It was washed thoroughly using double distilled water and filtered using whatman filter paper. The filtrate was dried in the oven for 4hrs at 60^0 C. Thus the pre-treated tamarind fruit shells T_{HCl} and T_{NaOH} are used as a first and second biosorbent. The third biosorbent was $T_{DW.}$ It was prepared using the stored tamarind shells powder. It was treated with double distilled water and filtered using whatman filter paper. The filtrate was dried in the oven for 4hrs at 60^0 C.

B. Carrot peel

The pre-treatment of carrot peels were carried out to increase the metal uptake efficiency. 250 g of the tamarind shells was treated with 500 ml 1N HCL and 1N NaOH for 4hrs separately. It was washed thoroughly using double distilled water and filtered using whatman filter paper. The filtrate was dried in the oven for 4hrs at 60^0 C. Thus the pre-treated carrot peel C_{HCl} and C_{NaOH} are used as a fourth and fifth biosorbent. The last biosorbent was $C_{DW.}$ It was prepared using the stored carrot peel powder. It was treated with double distilled water and filtered using whatman filter paper. The filtrate was dried in the oven for 4hrs at 60^0 C.

2.3. Preparation of Adsorbate

Metal ion solution of Nickel (II) was prepared by dissolving Nickel Sulphate ($NiSO_4$) in double distilled water. The pH of the solution was adjusted to the required value using dilute hydrochloric acid and NaOH before mixing biomass. Dimethylglyoxime (DMG) forms a red coloured complex when treated with an alkaline solution of nickel in presence of an oxidising agent such as bromine. The red complex of Ni-DMG contains nickel in higher oxidation state (probably (III) and also (IV)). The complex absorbs at about 445 nm. The intensity of colour varies with time and hence it is necessary to measure the absorbance after a fixed time within 10 minutes of mixing.

A. Preparation of stock Nickel solution

1000 ppm of stock Nickel solution was prepared by dissolving 4.479 g of Nickel Sulphate in one litre of double distilled water.

B. Preparation of standard Nickel solution

50 ppm of standard Nickel solution was prepared by diluting 5ml of stock solution to 100ml in a volumetric flask using double distilled water. Similarly different concentration solutions were prepared.

C. Preparation of Dimethylglyoxime (DMG) solution

DMG solution was prepared by dissolving 0.1 g of dimethylglyoxime in 10ml volumetric flask using 95% ethyl alcohol.

2.4. Analysis of Nickel

1ml of standard solution containing known concentration of nickel was pipetted out into a 100ml volumetric flask, 25ml of 1N hydrochloric acid and 5ml of bromine water were added to the above solution. The flask was cooled with cold running tap water and then 10 ml of concentrated ammonium hydroxide was added. 20ml of ethyl alcohol was added immediately to the above solution. The solution was mixed well and made up to the mark in the 100ml volumetric flask with double distilled water. After full colour development for 10 min, 2µl of this solution was used in an absorption cell and the concentration are measured at 445nm using a Nanodrop photo spectrophotometer. A reagent blank was simultaneously prepared in the same way without the metal solution and is used as a reference. Trials were repeated for different concentrations. The calibration chart was prepared as shown in Fig.1.

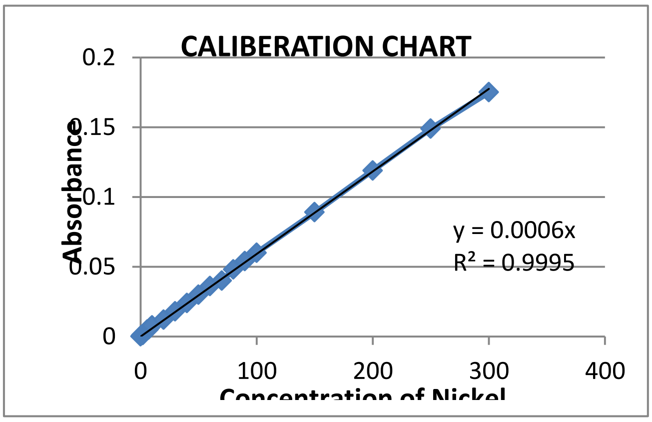

Fig.1. Caliberation chart

III. RESULTS AND DISCUSSION

Biosorption of heavy metals using tamarind shell and carrot peel was studied by evaluating the specific surface properties of the biosorbent and the physicochemical parameters of the metal solutions such as pH, initial metal ion concentration, biomass loading and temperature. The results of all the 31 experiments conducted for each biosorbent i.e., for tamarind shell treated with HCl – T_{HCl}, tamarind shell treated with NaOH – T_{NaOH}, tamarind shell treated with distilled water T_{DW}, Carrot peel treated with HCl – C_{HCl}, Carrot peel treated with NaOH – C_{NaOH} and carrot peel treated with distilled water – C_{DW} were tabulated as shown below in tables. The results of the percentage removal after 24hrs of these biosorbents were tabulated in the same table. The effect of different parameters on the removal of Nickel by the adsorbents was studied. The run order for which the highest percentage removal was obtained was considered to study the effect of individual parameters on the percentage removal of the biosorbents. Design of experiment is defined as the systematic procedure carried out under controlled conditions in order to discover an unknown effect, to test or establish a hypothesis, or to illustrate a known effect. The parameters initial metal ion concentration, pH, temperature and biosorbent dosage were chosen as independent variables and the output response,

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removal efficiency of Cr metal .A 2^4 full-factorial experimental designs, with seven replicates at the center point and thus a total of 31 experiments were employed in this study. The center point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property. Each independent variable had 5levels which were -2, –1, 0, +1 and +2. A total 31 different combinations (including seven replicates of centre point each sighed the coded value 0) were chose in random order according to a CCD configuration for four factors [23].

Table - 1
Percentage Nickel ion removal by different pre-treated Tamarind shell

Sl. No	pH	Temperature (^{0}C)	Initial Concentration (ppm)	Adsorbent Dosage (g/100ml)	% Nickel Removal		
					HCL treated	NaOH treated	Distilled water treated
1	4.0	40	125.0	5.50	61	70	54
2	4.0	40	125.0	5.50	25	52	32
3	7.0	40	125.0	5.50	57	58	42
4	5.5	45	87.5	3.25	70	74	80
5	4.0	40	125.0	5.50	62	66	50
6	2.5	45	162.5	3.25	93	86	75
7	4.0	40	50.0	5.50	80	82	73
8	2.5	35	87.5	3.25	45	66	84
9	4.0	35	125.0	5.50	75	69	**92**
10	2.5	45	87.5	7.75	83	85	83
11	5.5	35	87.5	3.25	79	77	76
12	4.0	40	125.0	10.00	83	75	58
13	4.0	40	125.0	5.50	76	94	66
14	5.5	35	162.5	7.75	89	86	75
15	2.5	45	162.5	7.75	85	76	78
16	5.5	45	162.5	3.25	79	81	88
17	5.5	35	162.5	3.25	74	85	90
18	2.5	40	125.0	7.75	77	**96**	76
19	1.0	40	125.0	5.50	76	68	69
20	4.0	40	200.0	5.50	82	82	74
21	4.0	40	125.0	1.00	68	89	88
22	2.5	35	162.5	3.25	68	72	82
23	4.0	50	125.0	5.50	45	78	64
24	2.5	35	87.5	7.75	74	73	66
25	4.0	30	125.0	5.50	92	88	85
26	4.0	40	125.0	5.50	81	72	82
27	4.0	40	125.0	7.75	**98**	68	78
28	5.5	45	162.5	5.50	35	89	91
29	5.5	35	87.5	7.75	76	78	83
30	5.5	45	87.5	7.75	80	66	72
31	2.5	45	87.5	3.25	93	85	75

Percentage removal of Nickel by the adsorbents was calculated by below formula

$$\textbf{Nickel Removal (\%)} = \{(N_{initial} - N_{final})/N_{initial}\} * 100$$

Where

$N_{Initial}$ – Initial Nickel Concentration in ppm
N_{Final} – Final Nickel Concentration in ppm

Table - 2

Percentage Nickel ion removal by different pre-treated Carrot peel

Sl. No	pH	Temperature (^{0}C)	Initial Concentration (ppm)	Adsorbent Dosage (g/100ml)	% Nickel Removal		
					HCL treated	NaOH treated	Distilled water treated
1	4.0	40	125.0	5.50	20	32	15
2	4.0	40	125.0	5.50	45	76	89
3	7.0	40	125.0	5.50	48	63	53
4	5.5	45	87.5	3.25	70	78	89
5	4.0	40	125.0	5.50	59	74	79
6	2.5	45	162.5	3.25	65	30	81
7	4.0	40	50.0	5.50	69	84	80
8	2.5	35	87.5	3.25	57	86	74
9	4.0	40	125.0	5.50	81	15	30
10	2.5	45	87.5	7.75	78	35	45
11	5.5	35	87.5	3.25	82	69	69
12	4.0	40	125.0	10.00	85	72	74
13	4.0	40	125.0	5.50	70	88	83
14	5.5	35	162.5	7.75	78	69	96
15	2.5	45	162.5	7.75	81	74	54
16	5.5	45	162.5	3.25	93	88	83
17	4.0	35	162.5	7.75	78	**98**	69
18	2.5	35	162.5	7.75	84	83	76
19	1.0	40	162.5	5.50	86	80	**98**
20	4.0	40	200.0	5.50	74	86	66
21	4.0	40	125.0	1.00	84	90	46
22	2.5	35	162.5	3.25	82	73	88
23	4.0	50	125.0	5.50	90	83	74
24	2.5	40	87.5	5.50	**94**	78	61
25	4.0	30	125.0	7.75	68	80	68
26	4.0	40	125.0	5.50	84	86	78
27	4.0	40	125.0	7.75	60	82	82
28	5.5	45	162.5	5.50	72	72	63
29	5.5	35	87.5	7.75	82	80	82
30	5.5	45	87.5	7.75	80	82	89
31	2.5	45	87.5	3.25	88	76	92

Table - 3
Optimized results for different Biosorbents

Biosorbents	pH	Temperature (^{0}C)	Initial Concentration (ppm)	Biomass Loading (g/100ml)	% nickel removal
Tamarind shell treated with HCl - T_{HCl}	4.0	40	125.0	7.75	98
Tamarind shell treated with NaOH - T_{NaOH}	2.5	40	125	7.75	96
Tamarind shell treated with Distilled Water - T_{DW}	4.0	35	125	5.5	92
Carrot peel treated with HCl- C_{HCl}	2.5	40	87.5	5.5	94
Carrot peel treated with NaOH - C_{NaOH}	4.0	35	162.5	7.75	98
Carrot peel treated with Distilled Water - C_{DW}	1.0	40	162.5	5.50	98

IV. CONCLUSION

On the whole, the tamarind shell and carrot peel work as good biosorbents in removal of nickel from a solution. In our study, the highest amount of removal of nickel was observed for tamarind shell treated with HCl, carrot peel treated with NaOH and carrot peel treated with distilled water. From the results we can conclude that for tamarind shell biosorbent treated with HCl, the highest removal of nickel is obtained at pH4, with initial concentration 125ppm and biomass 7.75g/100 ml at 40^0C. From the results, the carrot peel biosorbent treated with NaOH and the highest Nickel removal rate when compared with other biosorbents. This was obtained at pH4, with initial concentration of 162.5ppm and biomass loading at 7.75g/100ml at 35^0C. For the same metal ion different adsorbents have different removal rates. The removal rates depend on the conditions and the pre-treatment of the biosorbent. Since both the biosorbents used (i.e. Tamarind shell and carrot peel) are available in large quantity (usually as wastes), they can be used for large scale application of plant biomass for removal of heavy metals. Therefore these biosorbents are good prospects to be used as an alternative to existing commercial biosorbents. The findings of this study revealed that both tamarind shell and carrot peel dried powder are promising biosorbent for the removal of nickel from contaminated waste water.

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