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Studies on Removal of Ni (II) Ions in Aqueous Solutions with Two Natural Wastes

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Abstract: *This article reports, the removal of Ni (II) on Papayya Seed Powder (PSP) and Sweet lime Peelings Powder (SLP) as a function of pertinent variables. Adsorption kinetics data reveal the applicability Of Lagergren equation for adsorption on PSP and SLP. Experimentally measured values have been found to follow Langmuir adsorption isotherm. With these prelude studies an attempt has been made to investigate the effectiveness of low cost agro based dissipate materials in removing heavy metals. It is found that adsorption potential varies with pH, initial concentration, contact time and adsorbent dose. Out of two low cost adsorbents used in this study Papaya Seed Powder (PSP) is found to possess greater adsorption efficiency of Ni (II) ions than SLP under nearly identical experimental conditions.*

1. Introduction

Water is undoubtedly the most precious natural resource that exists on our planet. It is essential and pivotal for everything on our planet to grow and prosper. But Water pollution has become a threat not only to aquatic flora and fauna but also to human population causing health hazards. Heavy metals presence in water is considered to be most dangerous even at trace concentrations. Nickel being an important toxic metal finds its way to the water bodies through polluted water from refineries of silver metal, electroplating industries and storage battery industries (Kadirvelu, 2003). The nickel salts are known to be acutely and chronically toxic to human. Acute poisoning of Ni (II) causes headache, dizziness, nausea, and tightness of the chest, chest pain and shortness of breath, dry cough, cyanosis, and extreme weakness (Parker, 1980). At higher concentrations it is a potent carcinogen and causes cancer of lungs, nose and bone. Nickel carbonyl [$Ni(Co)_4$] has been estimated as lethal in humans at atmospheric exposure of 30 ppm for 30 min (Namasivayam and Ranganathan, 1994). The toxic nature in fish, crops and algae was also reported (David, 1977). Prenatal toxicity on female rats when exposed to nickel chloride was also reported. (Kate Smith *et al.*, 1993).

The appreciation of adsorption for the process of heavy metal removal at trace level has been constantly encouraged over other processes because of its cheapness and high quality treated effluents it produced. A huge number of low cost adsorbents have been tried by several scientists, such as coconut shell (Muthukumaran et al., 1995), bagasse (chand et al., 1994), saw dust (khaagesan et al., 1995), used waste tea leaves (Singh et al., 1993), wood barks (Ansari et al., 2000), etc.

2. Adsorbents

In the present study two adsorbents were employed to find out their utility for the removal of heavy metal ions of Ni (II) from aqueous solutions and they are papaya seeds and sweet lime peelings.

2.1. Papaya Seed Powder (PSP)

Papaya is a luscious and nutritious fruit that can easily grow widely in most areas of the tropics in most types of soil with tolerable pH level. Papaya seeds were either black or gray in color, fruit which is used for various medicinal purposes is widely irrigated in the agricultural fields. They were collected in bulk from fruit shops at Ongole, A.P. They were cleaned thoroughly with distilled water and soaked for 24 hrs and again washed with distilled water and dried in sun light. The dehydrated papaya seeds were powdered by mechanical means and are screened for particle sizes of 0.6 mm, 0.8 mm and 1.7 mm.

2.2. Sweet Lime Peelings Powder (SLP)

Sweet Lime (*Citrus limettoides* Tan. or *C. lumia* Risso et Poit), is called the *limettier* in French, *limadulce* in spanish; *mitha limbu*, *mitha nimbu* or *mitha nebu*, in India (mitha meaning sweet), *quit giddy* in Vietnam; *limun helou* or *succari* in Egypt; *laymu-helo* in Syria and Palestine. In certain areas, is referred to as "sweet lime". The origin of sweet lime is not known but it is thought to be a hybrid in Mexican-type and a sweet lemon or sweet citron. Mediterranean botanists referred it as an Indian native. In India sweet lime is grown from cuttings. Peelings of sweet lime were collected in bulk from juice shops at Ongole, A.P, and are made into small pieces, cleaned well and soaked in distilled water for 24 hours and washed with distilled water and dried under sun light and the material was pulverized using mechanical method and sieved to different particle sizes.

Particle size of 0.6 mm was used for both Papaya Seed Powder and Sweet Lime Peelings Powder characterization as its efficiency of metal up take is more.

All the chemicals used were of analytical reagent grade. Double distilled water was used in the preparation of solutions. All pH measurements were made by Elico pH meter, agitation of solutions were done in NeoLab Orbit shaker and colorimetric estimations were carried out in UV-Visible spectrophotometer (Type 118, Chemito).

3. PREPARATION OF METAL ION SOLUTION

3.1. Nickel Ammonium Sulphate Solutions

Pure Nickel ammonium sulphate was used to prepare nickel (II) solution. A stock solution of 1000 mg/l of Ni (II) was prepared by dissolving 6.7280 g of nickel ammonium sulphate in 5 ml of 1% HNO_3 solution to prevent hydrolysis and diluted with distilled water and made up to 1000 ml.

3.2. Analysis of Nickel (II) (Stewart, 1974)

Nickel (II) was estimated using a UV-Visible spectrophoto meter (Chemito) by using dimethylglyoxime (DMG). To a series of Ni (II) standard solutions containing less than 100 mg/l of Ni (II) concentration, 2 ml of 20% (W/V) solution of Sodium Tartrate, 10 ml of 4% (W/V) solution of Potassium Persulphate, 2.5 ml of 5 M sodium hydroxide solution and 15 ml solution of (1+30) Hcl were added and this mixture was mixed with 0.6 ml of 1% DMG solution. The contents were made up to 50 ml with distilled water and after 30 minutes the absorbance was measured at 465 nm against a reagent blank. A calibration graph with absorbance vs concentrations of Ni (II) solution was prepared. The amount of Ni (II) in the sample was obtained from the calibration plot.

3.3. Batch Mode Method

Entire experiments were carried out in batch mode by taking 50 ml of respective metal ion solution (simulated sample) and known amount of the adsorbent in lid conical flasks of 100 ml capacity. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker at room temperature (27^{o}c). Effects of pH, agitation time, initial metal ion concentration and amount of adsorbent were studied on the removal of metal ions. Also Control experiments were carried out without adsorbent to give correction for metal ion adsorption on the walls of the container. A very negligible adsorption of metal ion is found on the walls of the container.

4. RESULT & DISCUSSION

4.1. Effect of pH

The pH is one of the most important factor controlling the uptake of ions of metals from aqueous solutions by adsorbents.

Figure -1 shows the effect of pH in the removal of Ni (II) ions by Papaya Seed Powder and Sweet Lime Peelings Powder. Maximum percent removal of 95.96% was achieved at pH 3.0 for PSP and 92.56% were observed at pH 4.0 for SLP. At pH > 6 precipitation started in both the cases in the absence of adsorbent. So the adsorption of Ni (II) ion is reported to be highly pH dependent.

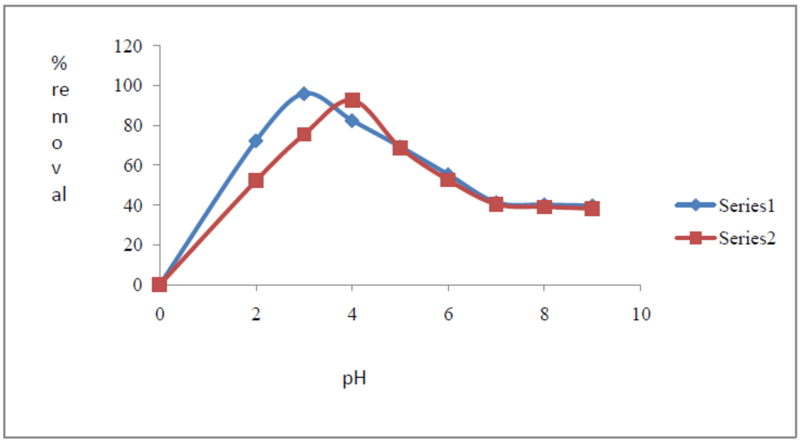

Figure1. *Effect of pH (Series1-PSP,Series 2-SLP)*

4.2. Effect of Initial Concentration and Contact Time

From Figure -2 and Table 1 & 2 we can compare the % removal of Ni (II) ions in aqueous solutions by increasing initial concentration and contact time using Papayya Seed Powder and Sweet Lime Peelings Powder at 125 mg/50 ml of adsorbent doses and 90 minutes contact time. In Figure-2, series-1, 2, 3 and series-4, 5, 6 indicates 50mg/l, 75mg/l and100mg/l initial concentrations of Papayya Seed Powder and Sweet Lime Peelings Powder respectively.PSP and SLP gave 95.96% and 92.96% removal percentage respectively for Ni(II) initial concentration of 50mg/l from which the percent removal gradually decreases with increasing concentration, because at lower initial concentrations, sufficient sites are available for adsorption of metal ions. Therefore the fractional adsorption is independent of initial concentration. However, at higher concentrations the number of metal ion is relatively higher compared to availability of adsorption sites. Hence, the % removal of metal ion depends on initial concentration. The solutions were equilibrated for 120 minutes where maximum removal and equilibrium attained at 90 minutes irrespective of initial concentration. The rate of uptake was rapid in the beginning and became slow in the later stages and reached saturation at 90 minutes. This is due to the fact that the metal ion occupied the sites in a random manner because of maximum availability of sites. As the time passed, the active sites were blocked and hence the rate was slowed. The slight difference in the percent removal of Ni (II) ions in PSP and SLP may be due to the difference in Chemical affinity on the surface of adsorbent.

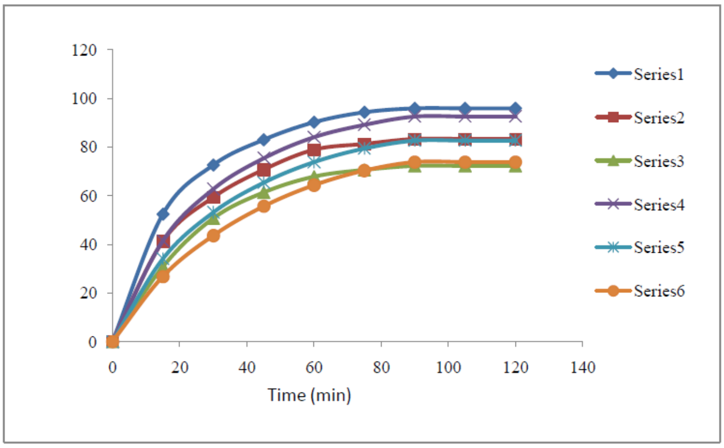

Figure2. *Effect of Initial Concentration And Contact Time (Series1,2,3-PSP & Series 4,5,6-SLP)*

Table1. *Series 1, 2, 3-PSP*

Ni(II) mg/l	Agitation time in (min)	15	30	45	60	75	90	105	120
50	%Removal	52.42	72.65	83.04	90.25	94.35	95.96	95.96	95.96
	Amount of Ni(II) adsorbed q (mg/g)	10.48	14.13	16.60	18.05	18.87	19.19	19.19	19.19
	q_e-q	8.71	5.06	2.59	1.14	0.32	-	-	-

75	%Removal	41.25	59.29	70.68	78.85	81.25	83.28	83.28	83.28
	Amount of Ni(II) adsorbed q (mg/ g)	12.37	17.78	21.20	23.65	24.37	24.98	24.98	24.98
	q_e-q	12.61	7.20	3.78	1.33	0.61	-	-	-
100	%Removal	30.80	50.71	61.36	67.87	70.64	72.28	72.28	72.28
	Amount of Ni(II) adsorbed q (mg /g)	12.32	20.28	24.54	27.14	28.25	28.91	28.91	28.91
	q_e-q	16.59	8.63	4.37	1.77	0.66	-	-	-

qe for 50 mg/L = 19.19 mg/g, 75 mg/L = 24.98 mg/g, 100 mg/L = 28.91 mg/g

Table2. *Series 4, 5, 6-SLP*

Ni(II) mg/l	**Agitation time min**	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
50	%Removal	41.44	62.70	75.40	84.08	89.16	92.56	92.56	92.56
	Amount of Ni(II) adsorbed q (mg/ g)	8.28	12.54	15.08	16.81	17.83	18.51	18.51	18.51
	q_e-q	10.22	5.97	3.43	1.70	0.68	-	-	-
75	%Removal	34.04	53.13	65.36	73.84	79.44	82.66	82.66	82.66
	Amount of Ni(II) adsorbed q (mg/ g)	10.21	15.94	19.60	22.15	23.83	24.80	24.80	24.80
	q_e-q	14.59	8.86	5.20	2.65	0.97	-	-	-
100	%Removal	26.77	43.58	55.62	64.33	70.32	73.82	73.82	73.82
	Amount of Ni(II) adsorbed q (mg /g)	10.70	17.43	22.24	25.73	28.12	29.52	29.52	29.52
	q_e-q	18.82	12.09	7.28	3.79	1.40	-	-	-

qe for 50 mg/L = 18.51 mg/g, 75 mg/L = 24.80 mg/g, 100 mg/L = 29.52mg/g

5. Effect of Adsorbent Dose

From Figure-3, in Table3 and Table4 it is observed that the adsorptive behavior of Ni (II) ions on Papaya Seed Powder and Sweet Lime Peelings Powder increased with increasing adsorbent dosage. It is observed that there is increase in % removal of Ni (II) ions with increasing dosage of PSP, i.e. from 31.18 - 100 % at 25 to 175 gm/50 ml adsorbent dosage. Also % removal with SLP increased from 28.70 - 99.07% for Ni (11) ions at 25-175 gm / 50 ml adsorbent dosage. It is apparent that there is gradual increase in percent removal with increase in adsorbent dosage in both the cases. It is attributed to the greater availability of the active sites or surface area at higher doses of the adsorbent.

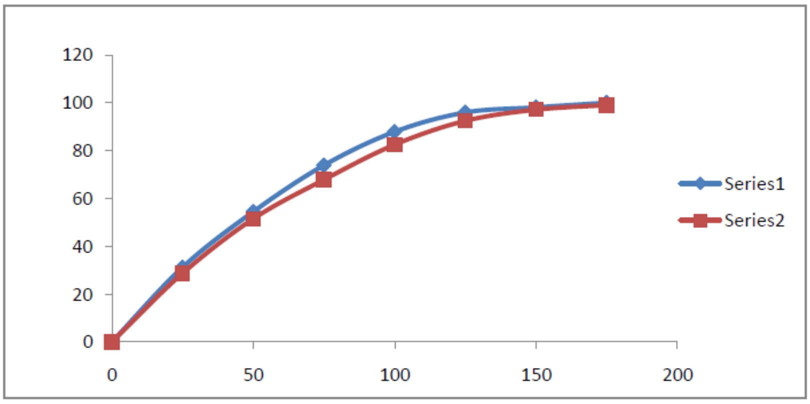

Figure3. *Effect of Adsorbent Dosage (Series1-PSP & Series2-SLP)*

Table3. *PSP Adsorbent Dose*

Adsorbent dose (g/50ml)	% Removal	Equilibrium concentration Ce (mg/l)	Amount adsorbed mg/g
25	31.18	29.89	40.22
50	54.42	22.79	27.21
75	73.82	13.09	24.60
100	89.84	5.08	22.46
125	95.92	2.04	19.18
150	98.08	0.96	16.34
175	100.00	0.00	14.28

Table4. *SLP Adsorbent Dose*

Adsorbent dose mg/50ml	% Removal	Equilibrium Concentration Ce(mg/l)	Amount adsorbed (mg/g)
25	28.70	35.64	28.72
50	51.48	24.26	25.74
75	67.84	16.08	22.61
100	82.50	8.75	20.62
125	92.48	3.76	18.49
150	97.16	1.42	16.19
175	99.04	0.48	14.14
200	100.00	0.00	12.50

(Agitation time – 90 Initial pH – 4.0,Ni (II) - 50mg / l ,Particle size 0.6mm

6. Adsorption Kinetics

Kinetics and equilibrium are the two major factors to evaluate adsorption dynamics. The mechanism involved in the metal ion removal is assumed to be basically complexation (Krishnan et al., 2002). The kinetics of metal removal can be expressed as.

$$N + M = NM \qquad (1)$$

Where M is the concentration of free metal ion in solution, N is the number of active sites present on the adsorbent. NM is the concentration of metal bound to adsorbent. Adsorption occurs only on localized sites and involves no interaction between adsorbed ions. The energy of adsorption is independent of surface coverage, maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface. The process of metal uptake on Papayya Seed Powder and Sweet Lime Peelings Powder is governed by first order and is Chemical in nature, i.e. Chemisorption. The adsorption kinetics of Ni (II) ions adsorption on Papayya Seed Powder and Sweet Lime Peelings Powder follows Lagergren equation.

$$\log\left(q_e - q\right) = \log q_e - \frac{K_{ad}}{2.303} t \qquad \textbf{2}$$

Where K_{ad} is the rate constant of adsorption (min.$^{-1}$), q and q_e is the amount of metal ions adsorbed (mg/g) at time t and equilibrium time respectively, linear plots of Log (q_e-q) vs t i.e. Figure-4 and Figure-4s show the applicability of above equation for Papayya Seed Powder and Sweet Lime Peelings Powder. The K_{ad} values of Ni (II) ion of various concentrations and adsorbent dose of 125 mg. / 50 ml. of PSP and SLP were calculated from the slope of linear plots. The K_{ad} values are comparable with recently reported values of Ni (II) ions in the literature.

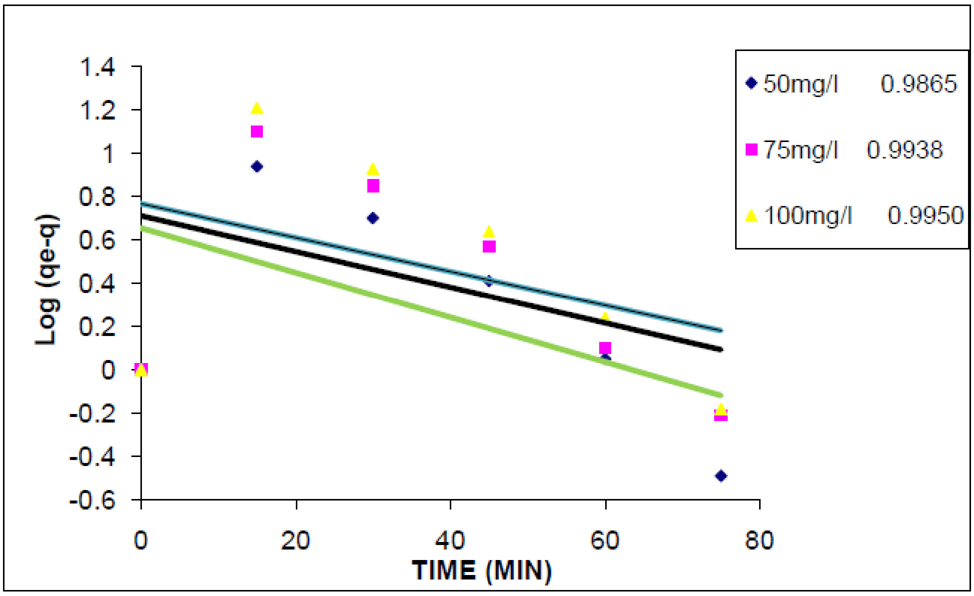

Figure4. *Lagergren Rate Constant-PSP*

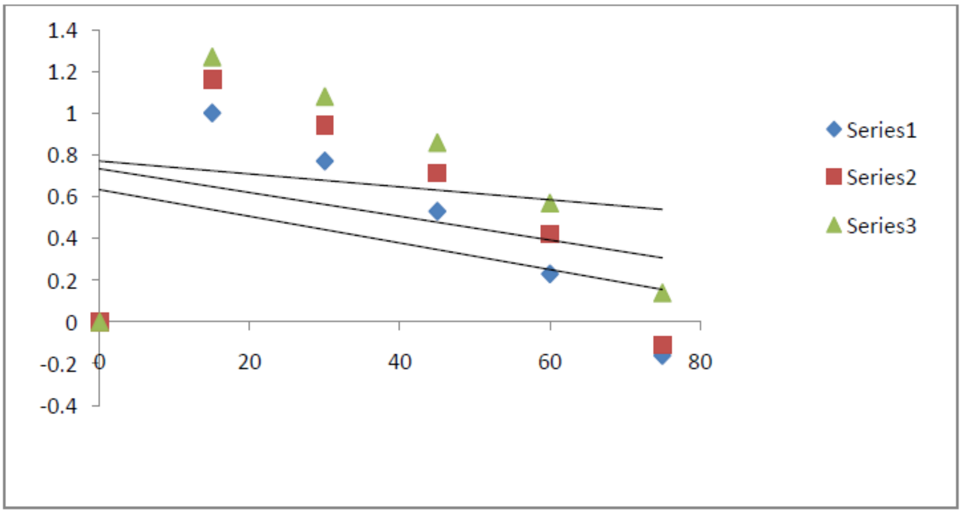

Figure4s. *Lagergren Rate Constant-SLP*

7. FREUNDLICH EQUATION

The freundlich expression is an empirical equation based on adsorption of heterogeneous surface. It is commonly represented as (Freundlich, 1939)

$$\log x/m = \log k_f + \frac{1}{n} \log Ce \qquad 3$$

Where (X/m) is the amount adsorbed (mg/l), Ce is the equilibrium concentration (mg/l) and K_f and n are Freundlich constants, where K_f indicates the adsorbent capacity and n indicates the favorability of adsorption. Linear plots of log (x/m) vs log Ce in Figure-5 and Figure-5s shows that the adsorption follows Freundlich Isotherm. In case of PSP K_f and n are 28.13 and 3.43 respectively and for SLP K_f and n are 23.92 and 2.24 respectively. If the value of n lie between 1 and 10 indicates favorable adsorption also these K_f values are comparable to literature with silk cotton hull activated carbon 39.8(Shanmugavalli.M.2006).

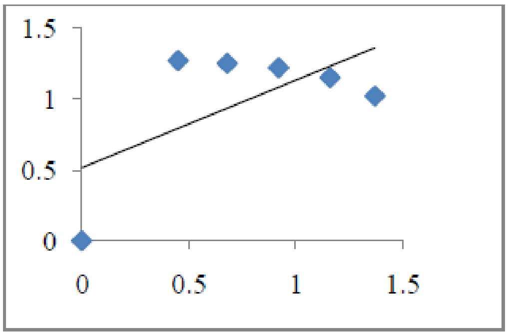

Figure5. *Freundlich Isotherm –PSP*

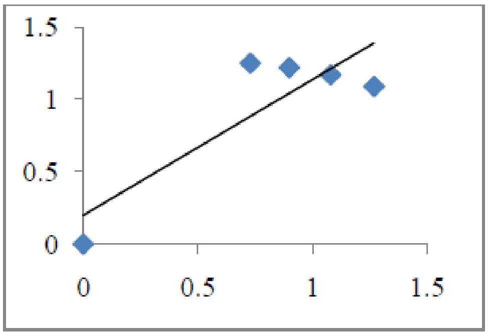

Figure5s. *Freundlich Isotherm -SLP*

8. LANGMUIR EQUATION

The most widely used isotherm for equilibrium data of dilute solutions is the Langmuir equation. It may be represented as (Langmuir, 1918)

$$\frac{Ce}{qe} = \frac{1}{Q_0 b} + \frac{Ce}{Q_0} \qquad 4$$

Where qe is the amount of Ni (II) adsorbed at equilibrium. This is applicable to homogeneous adsorption and also obeys Henry's law at low concentrations. The Linear plot of Ce/qe vs. Ce in Figure-6 and Figure-6s show that the adsorption obeys Langmuir model. Here Q_0 and b were determined from the slope and intercept of the Langmuir plot. Q_0 for Papaya Seed Powder and Sweet Lime Peelings Powder were 30.58 and 29.14 and b for Papaya Seed Powder and Sweet Lime Peelings Powder were 0.5092 and 0.4789 respectively.

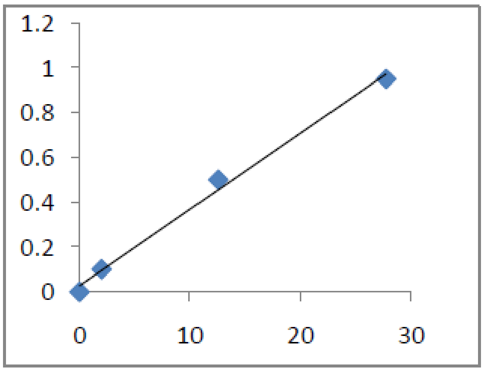

Figure6. *Langmuir Isotherm –PSP*

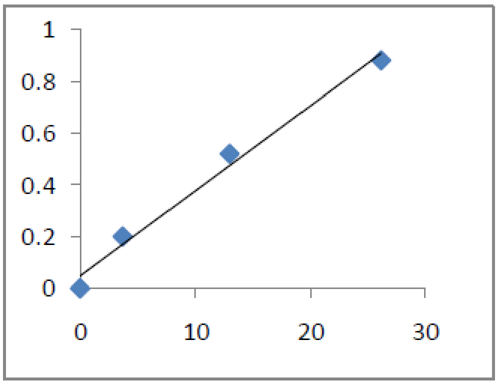

Figure6s. *Langmuir Isotherm -SLP*

On the basis of regression analysis of the experimental data on the adsorptive behavior of Ni (II) on PSP and SLP, it may be inferred that the adsorption behavior of Ni (II) is in good concurrence with Langmuir model.

This can be attributed to the formation of mono layer coverage on the surface of Papaya Seed Powder and Sweet Lime Peelings Powder with minimal interaction among molecules of substrate, immobile and localized adsorption and all sites having equal adsorption energies. The essential characteristics of Langmuir isotherm can be described by a separation factor of equilibrium constant R_L, which is given as

$$R_L = \frac{1}{1 + bc_i} \qquad 5$$

Where C_i is the initial concentration (mg/l) and b is the Langmuir constant.

The value of R_L indicates the nature of isotherm as presented in format below.

Equilibrium Parameter and Nature of Isotherm

R_L	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L values indicate the type of isotherm. The R_L values were set up between zero and one (Hall, 1966) which were also proved to subsist in Papayya Seed Powder and Sweet Lime Peelings Powder for Ni (II) ions and so they exhibit a favorable adsorption.

9. Conclusion

1. Aim of this research work is to develop inexpensive and effective heavy metal ion removal methods to compensate existing commercial and expensive methods.
2. The availability of material source is bounteous.
3. The adsorption is p^H dependent and hence maximum adsorption occurs at a p^H of 3.0 and 4.0 for PSP and SLP respectively i.e. uptake of Ni (II) is found to be maximum at lower p^H.
4. PSP showed 95.96% and SLP showed 92.56% adsorptive removal of Ni (II) under the conditions of 125mg/50ml adsorbent dose with a 90 minute contact time and a particle size of 0.6 mm.
5. The Langmuir model was found to be in good agreement with experimental data on the adsorptive behavior of Ni (II) on PSP and SLP.
6. The adsorption follows first order kinetics. Lagergren kinetic model had been applicable for PSP and SLP on Ni (II) adsorption.
7. Out of two low cost adsorbents used in this study, Papayya Seed Powder is found to exhibit greater adsorption efficiency of Ni (II) ions than Sweet Lime Peelings Powder under identical experimental conditions.

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