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Comparative Study On The Adsorption Capacity Of Snail And Perewinkle Shells For The Removalof Nickel(Ii) Ion From Aqueous Solution

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Abstract: ***This study was investigated to compare the adsorptive capacity of Snail and Perewinkle Shells (SS and PS) for the removal of Nickel (II) ion from aqueous solution. The sample was characterised for some important properties and the effects of some experimental conditions were examined using analysis of variance. FT-IR analysis was carried out to determine the functional groups of the shell.The results obtained from the characterisation of the SS and PS are pH, 6.8 and 7.12; moisture content, 24.33 and 15.69; bulk density, 1.25 a nd 1.30; porosity, 0.0249 and 0.0767; surface area, 295 and 199 m^2/g respectively. The spectra line for both SS and PS gave rise to some important compounds such as N-H, CN, OH,C=C and R-CHO. Analysis of variance (ANOVA) indicated that PS perform better than SS.***

Keywords: Adsorbent, Characterisation, FT-IR, Anova

1. Introduction

Water is the most common and widespread chemical compound in nature which is a major constituent of all living creatures. Heavy metal pollution of the environment has become a growing ecological crisis and concern and therefore the subject of many researches. These heavy metals are continuously released into the aquatic environment from natural process like volcanic activity and weathering of rocks. Industrial processes like electro plating, metal finishing, metallurgical, chemical manufacturing and mining industries have greatly enhanced the concentration of heavy metals in the water.

Ions of heavy metals like Copper, Nickel, Zinc, Cadmium, Lead, Chromium and Mercury have a significant impact on the environment. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. Out of these ions, Nickel (II) ion is the most abundant element in the Earth's crust, comprising about 3% of the composition of the earth.

It is the 5th most abundant element by weight after Iron, Oxygen, Magnesium and Silicon. It is released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material. Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources.

Nickel and nickel compounds have many industrial and commercial uses. Most Nickel is used for the production of stainless steel and other Nickel alloys with high corrosion and temperature resistance. Nickel metal and its alloys are used widely in the metallurgical, chemical and food processing industries, especially as catalysts and pigments. The nickel salts of greatest commercial importance are Nickel-Chloride, Sulphate, Nitrate, Carbonate, Hydroxide, Acetate and Oxide [1].

Nickel has been implicated as an embryotoxin and teratogen. The higher concentration of Nickel causes poisoning effects like headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness. Studies of human cell cultures have indicated that nickel is a possible carcinogen, creating a need for the cleanup of nickel pollution. So it is very essential to remove Ni from soil, industrial wastewater and effluents.

The conventional methods which are commonly used for the removal of nickel from the industrial effluents are physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies. These processes may be ineffective or expensive especially when the heavy metal ions in the contaminated media are high i.e. in order of 1- 100 mg dissolved heavy metal ions/L.

Secondly the operational problems and the high cost of treatment necessitate the research for some newer methods [2].

Adsorption is one of the more popular methods for the removal of metals ions from the aqueous solutions. Adsorption is a surface phenomenon, in which molecules of adsorbate are attracted and held to the surface of an adsorbent until equilibrium is reached between adsorbed molecules and those still freely distributed in the carrying gas or liquid. The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species.

Snails belong to the class Gastropoda and the African land snail is classified as *Achatina achatina*. The snail shell has got the same basic construction as other Mollusk shells. It consists of three layers.

The Periostracum, the outermost shell layer, is not made of $CaCO_3$, but of an organic material called Conchin, a mixture of organic compounds, mostly of proteids. Conchin not only makes the outer shell layer, but also embedded between the $CaCO_3$ crystals of deeper layers[3].

Periwinkle shell is a waste product generated from the consumption of a small greenish-blue marine snail (periwinkle), housed in a V-shaped spiral shell, found in many coastal communities within Nigeria and word-wide is a very strong, hard and brittle material. These snails called periwinkle are found in the lagoons and mudflats of the Niger Delta between Calabar in the East and Badagry in the West of Nigeria, the people in this area consume the edible part as sea food and dispose off the shell as a waste, though few people utilize the shell as coarse aggregate in concrete in areas where there are neither stones not granite for purposes such as paving of water logged areas e.t.c., but a large amount of these shells are still disposed off as waste and with disposal already constituting a problem in areas where they cannot find any use for it, and large deposits have accumulated in many places over the years[4].

With the aim of increasing rate of Nickel removal from pollution resulting from discharge of Nickel containing effluents by industries into the environment, this study was carried out to investigate the removal of Nickel (II) ion from aqueous solutions by using periwinkle and snail shells. The effects of contact time and concentration on adsorption, kinetics of sorption and adsorption models would be examined to optimize the conditions to be utilized for decontamination of effluents containing Ni (II) ion.

Many industrial wastewaters contain substances that are difficult to remove via conventional/secondary treatment, are toxic or hazardous, are volatile and cannot be transferred to the atmosphere, have the potential for creating noxious vapours or odour, or for imparting colour to the wastewater are present in very small concentrations that make their removal via other methods difficult.

Activated Carbon is one of the most commonly used adsorbents in industry, but due to its high cost, thermal disintegration of the structure during regeneration which gives rise to 10-15% losses, the persistence of a grey tinge after treatment, have induced several investigations to search for alternative low cost, non-conventional adsorbents.

Thus, this research offers low cost and readily available adsorbents that could be employed in the treatment of wastewater and the optimal conditions for maximum sorption efficiency.

2. MATERIALS AND METHODS

2.1 Sample collection and preparation

The absorbent samples used were snail shell (SS), periwinkle shell (PS) . The empty shells were obtained from waste bins in Nembe waterside Market, Port Harcourt, Rivers State, Nigeria. They were washed with tap water to remove adhered impurities, rinsed with de-ionized water and sun dried.

They were then crushed and oven dried at 100^oC for 12 hrs, ground to powdery form and screened with 80-mesh.

Each weighed sample, carbonized in a muffle furnace (model GLM 3, Japan) at a temperature of 600^oC for 2 hrs and allowed to cool to room temperature. The powders were then leached with 0.1M HCl and washed with distilled water.

Activation of the samples was carried out using ortho-phosphoric acid (H_3PO_4). During the process, each sample was placed in a crucible; 0.5M H_3PO_4 was added, mixed and heated until a paste was formed. It was then subjected to a temperature of 700^oC for 3 hrs and then cooled to room temperature. The activated samples were washed with distilled water to remove excess acid and oven-dried at 100^oC for 12 hrs. Samples were then stored in an air-tight container.

2.2 Preparation of nickel solution

A stock solution of 1000ppm was used and the test solutions of desired concentration were prepared by diluting the stock solution with distilled water. NaOH and HCl was used to adjust the pH to the required value as well.

2.3 Characterization and Adsorption studies of the Biosorbent

The proximate and ultimate analysis of SS and PS produced were characterized under the properties of pore size, pH, moisture contents, bulk density and specific gravity. Also, adsorption studies at different contact times, pH, .adsorbent dose and temperature were studied

2.4 FT-IR Analysis of the Adsorbent

Fourier Transform Infra Red Spectroscopy (FTIR) (Bulk-Scientific model 530 Infrared Spectrophotometer), was used to determine the characteristic and the functional group of the sorbents. The samples were grinded below the wavelength of incident radiation that will be passing through them and then oil often referred to as Nujul were added to smoothen the sample. IR transparent salt plates were used to hold the sample in front of the beam in order to acquire data. After each analysis the plate were cleaned with acetone before another sample were added

3. RESULTS AND DISCUSSION

3.1 FT-IR SPECTRA ANALYSIS

To investigate the functional groups of SS and PS, a FT-IR study was carried CN. The peak value of cm^{-1} shows the presence of transition metal anhydride and Hydroxyl group, H-bonded OH stretch is shown by the $3448cm^{-1}$ peak value.

Phenol/ tertiary alcohol, Alkenyl C=C and Aromatic Amine stretch were show by the peak value of the PS spectra of $1356cm^{-1}$, $1644cm^{-1}$ and $155cm^{-1}$ respectively. The hydroxyl group OH stretch was indicated at a peak value of $3211cm^{-1}$. The spectra also show the presence of Aliphatic chloro compounds.[5]

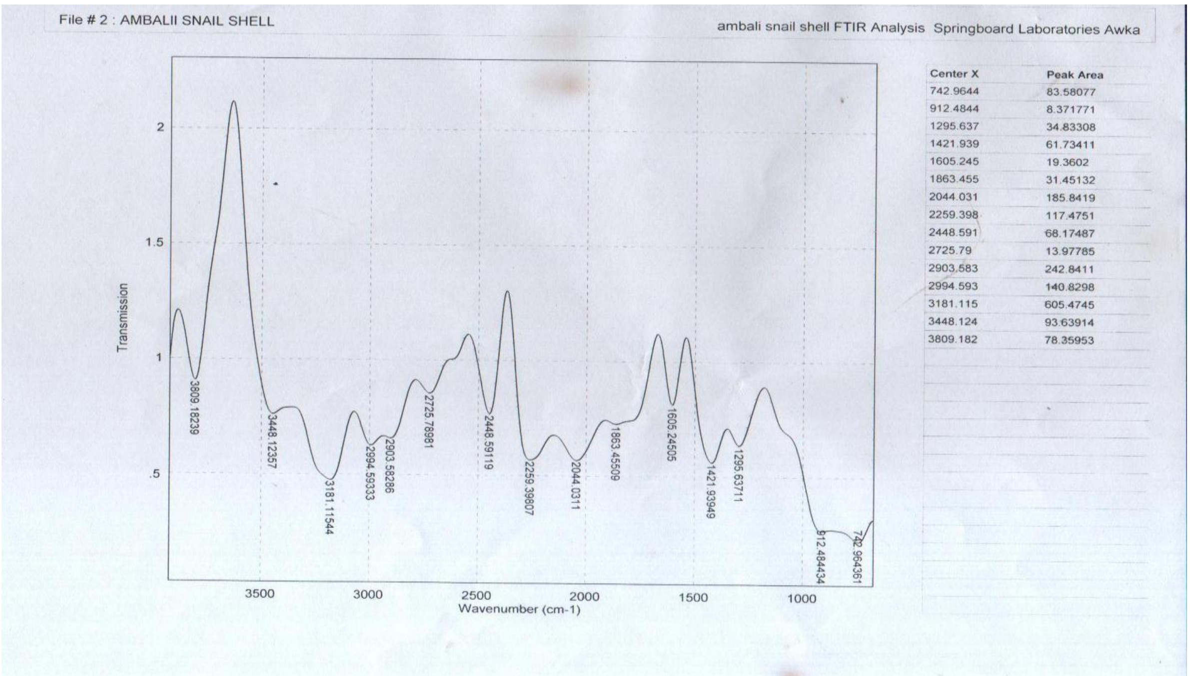


Figure 3.1 FT-IR Analysis for Snail Shell

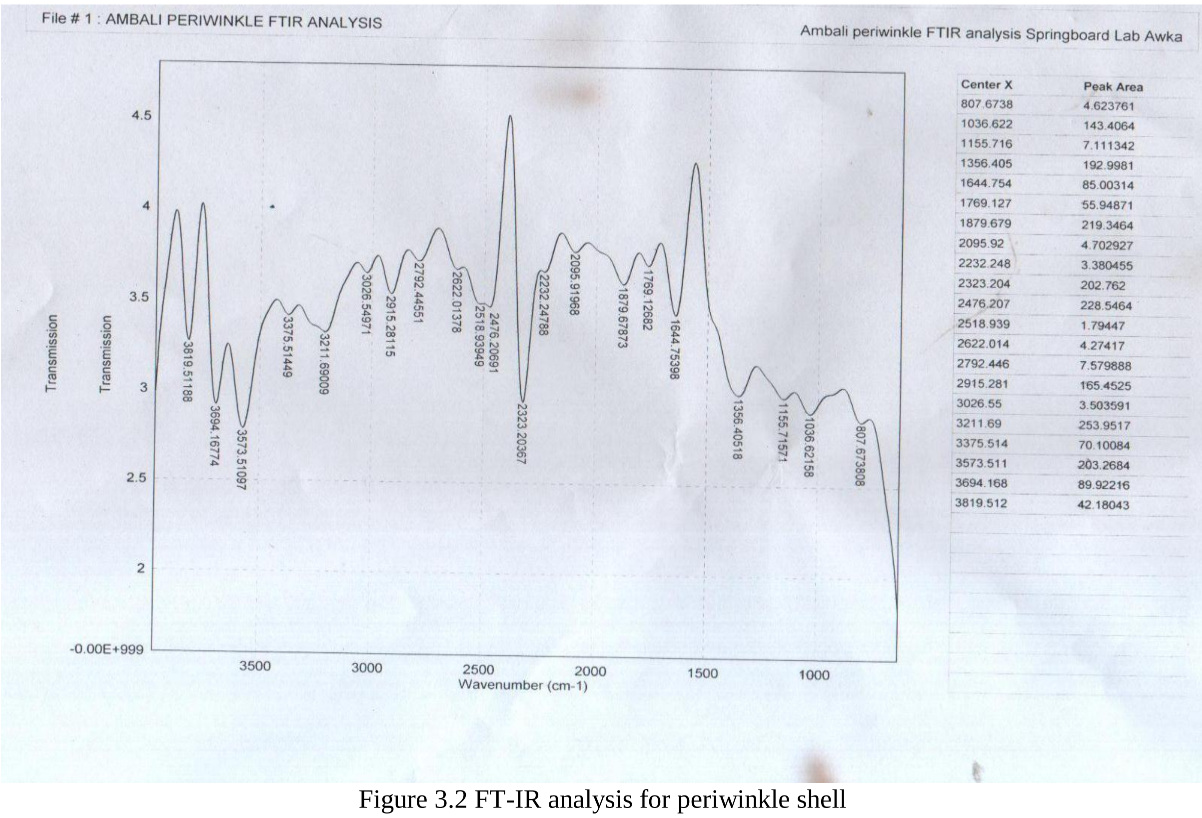


Figure 3.2 FT-IR analysis for periwinkle shell

3.2 PHYSICO-CHEMICAL CHARACTERIZATION OF SNAIL AND PERIWINKLE SHELLS

The pH, Moisture Content, Bulk Density, Surface Area and Porosity of the adsorbents was determined. The summary is shown in Table. The PS has a slightly higher pH of 7.12 compared to that of SS of 6.8. The SS moisture content is higher at a value of 24.33, while that of PS is 15.69. The SS has a higher Surface Area of 295 m^2 as against that of 199 m^2 for PS. The Surface Area is an important property of an adsorbent and the greater the Surface Area the greater the adsorption capacity as there is more sites for the adsorption [6]. The pHs of the adsorbents are close to neutrality with that of SS tilting towards acidity and PS, towards alkalinity. SS has a higher moisture content of 24.33% as against 15.69% for PS and the two has similar Bulk density.

Table 3.1: Physico-chemical Properties of adsorbents used

Parameter (Unit)	Snail Shell (SS)	Periwinkle Shell (PS)
pH	6.8	7.12
Moisture Content, %	24.33	15.69
Bulk Density	1.25	1.30
Porosity	0.0249	0.0767
Surface Area m^2/g	295	199

3.3 ANALYSIS OF VARIANCE

Analysis of Variance technique was designed to ascertain or rank the adsorbent in the order of higher selectivity for the SS and PS . The p-value was found be less than 0.05 in all the cases with the exception of effect of initial concentration and dosage on SS shell. Thus the PS gave better results than the SS[7] [8].

3.1 Effect of pH on Ni Concentration

Snail Shell (SS)			**Periwinkle Shell (PS)**	
pH	**Ni Conc. (mg/l)@50mg/l**		**pH**	**Ni Conc. (mg/l)@50mg/l**
2.00	11.00		2.00	13.00
4.00	9.50		4.00	11.10
6.00	7.20		6.00	6.50
8.00	8.50		8.00	9.00
10.00	10.00		10.00	8.10

SUMMARY OUTPUT FOR SNAIL SHELL (SS)

Regression Statistics	
Multiple R	0.326318
R Square	0.106484
Adjusted R Square	-0.19136
Standard Error	1.586611
Observations	5

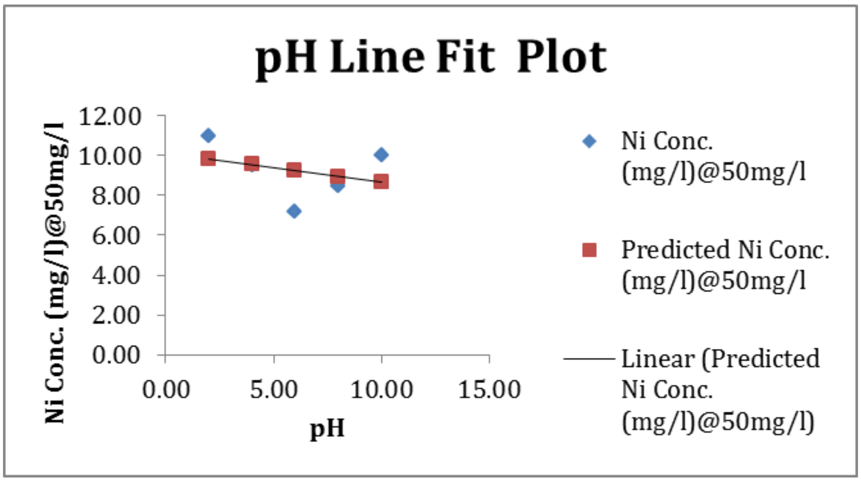
ANOVA

	Df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.9	0.9	0.357521	0.592015
Residual	3	7.552	2.517333		
Total	4	8.452			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	10.14	1.664051	6.093562	0.008877	4.844246	15.43575
pH	-0.15	0.250865	-0.59793	0.592015	-0.94836	0.648365

RESIDUAL OUTPUT

Observation	*Predicted Ni Conc. (mg/l)@50mg/l*	*Residuals*
1	9.84	1.16
2	9.54	-0.04
3	9.24	-2.04
4	8.94	-0.44
5	8.64	1.36



SUMMARY OUTPUT FOR PERIWINKLE SHELL (PS)

Regression Statistics	
Multiple R	0.737836
R Square	0.544403
Adjusted R Square	0.392537
Standard Error	1.987545
Observations	5

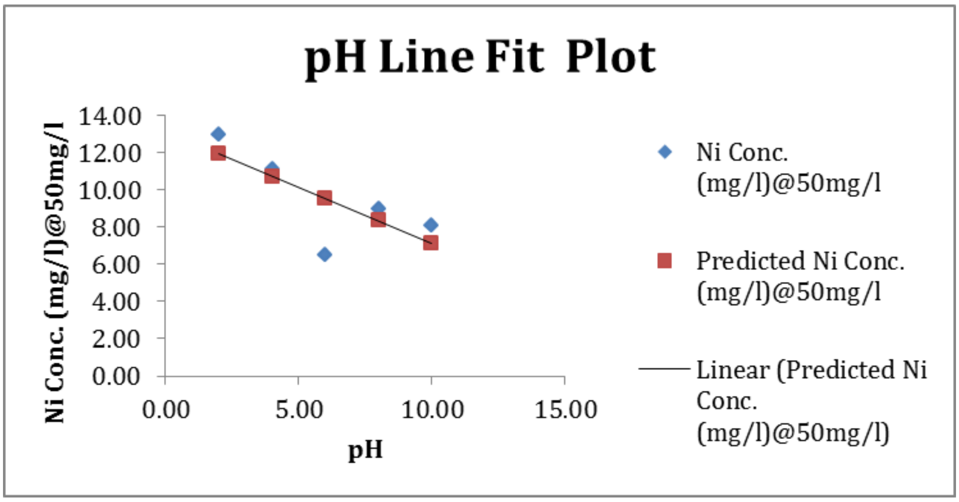
ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	14.161	14.161	3.584761	0.154643
Residual	3	11.851	3.950333		
Total	4	26.012			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	13.11	2.084554	6.289114	0.008119	6.476018	19.7439 8
pH	-0.595	0.314258	-1.89335	0.154643	-1.59511	0.40511

RESIDUAL OUTPUT

Observation	*Predicted Ni Conc. (mg/l)@50mg/l*	*Residuals*
1	11.92	1.08
2	10.73	0.37
3	9.54	-3.04
4	8.35	0.65
5	7.16	0.94



3.2 Effect of initial Concentration

Snail Shell (SS)			Periwinkle Shell (PS)	
Concentration (mg/l)	**Final Ni (mg/l) @pH = 2**		**Concentration (mg/l)**	**Final Ni (mg/l) @pH = 2**
20.00	5.10		20.00	6.30
40.00	7.00		40.00	8.10
60.00	6.50		60.00	10.00
80.00	8.50		80.00	7.50
100.00	12.00		100.00	11.80

SUMMARY OUTPUT FOR SNAIL SHELL (SS)

Regression Statistics	
Multiple R	0.918492
R Square	0.843628
Adjusted R Square	0.791504
Standard Error	1.202636
Observations	5

ANOVA

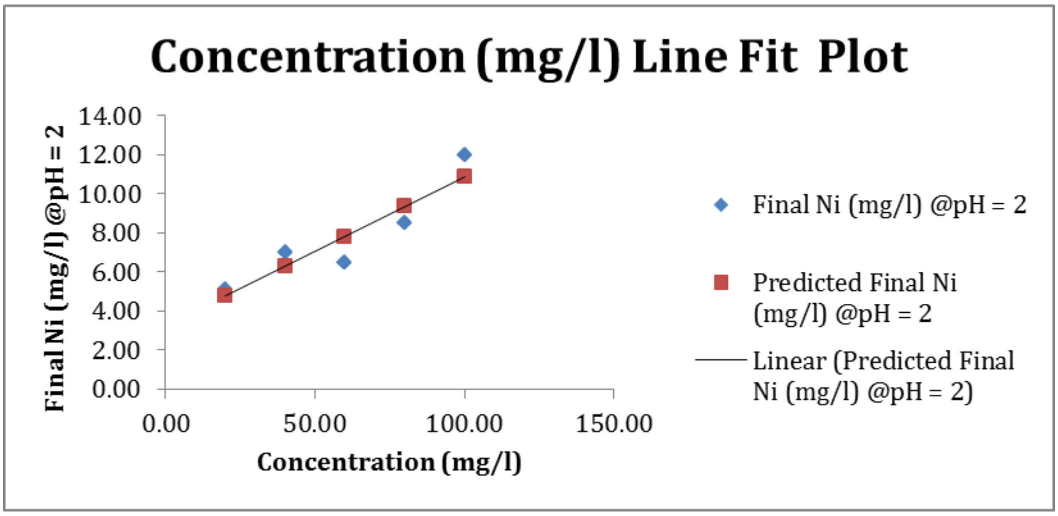
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	23.409	23.409	16.18507	0.02759
Residual	3	4.339	1.446333		
Total	4	27.748			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	3.23	1.261335	2.560778	0.083158	-0.78413	7.244132
Concentration (mg/l)	0.0765	0.019015	4.023067	0.02759	0.015985	0.137015

RESIDUAL OUTPUT

Observation	*Predicted Final Ni (mg/l) @pH = 2*	*Residuals*
1	4.76	0.34

2	6.29	0.71
3	7.82	-1.32
4	9.35	-0.85
5	10.88	1.12



SUMMARY OUTPUT FOR PERIWINKLE SHELL (PS)

Regression Statistics	
Multiple R	0.757451
R Square	0.573732
Adjusted R Square	0.431643
Standard Error	1.636663
Observations	5

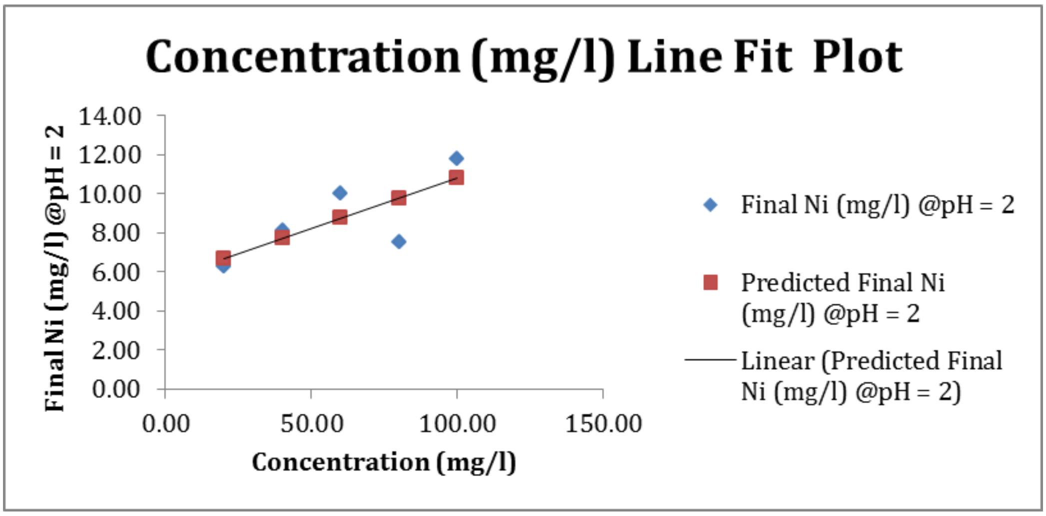
ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	10.816	10.816	4.03783	0.138059
Residual	3	8.036	2.678667		
Total	4	18.852			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	5.62	1.716547	3.274015	0.046636	0.157182	11.08282
Concentration (mg/l)	0.052	0.025878	2.009435	0.138059	-0.03036	0.134355

RESIDUAL OUTPUT

Observation	*Predicted Final Ni (mg/l) @pH = 2*	*Residuals*
1	6.66	-0.36
2	7.7	0.4
3	8.74	1.26
4	9.78	-2.28
5	10.82	0.98



3.3 Effect of contact time

Snail Shell (SS)			Periwinkle Shell (PS)	
Time (mins)	**Ni (mg/l) @pH = 2**		**Time (mins)**	**Ni (mg/l) @pH = 2**
20.00	6.70		20.00	7.10
40.00	6.10		40.00	8.00
60.00	7.00		60.00	7.80
80.00	8.00		80.00	9.50
100.00	7.50		100.00	10.00

SUMMARY OUTPUT FOR SNAIL SHELL (SS)

Regression Statistics	
Multiple R	0.758009
R Square	0.574578
Adjusted R Square	0.43277
Standard Error	0.549848
Observations	5

ANOVA

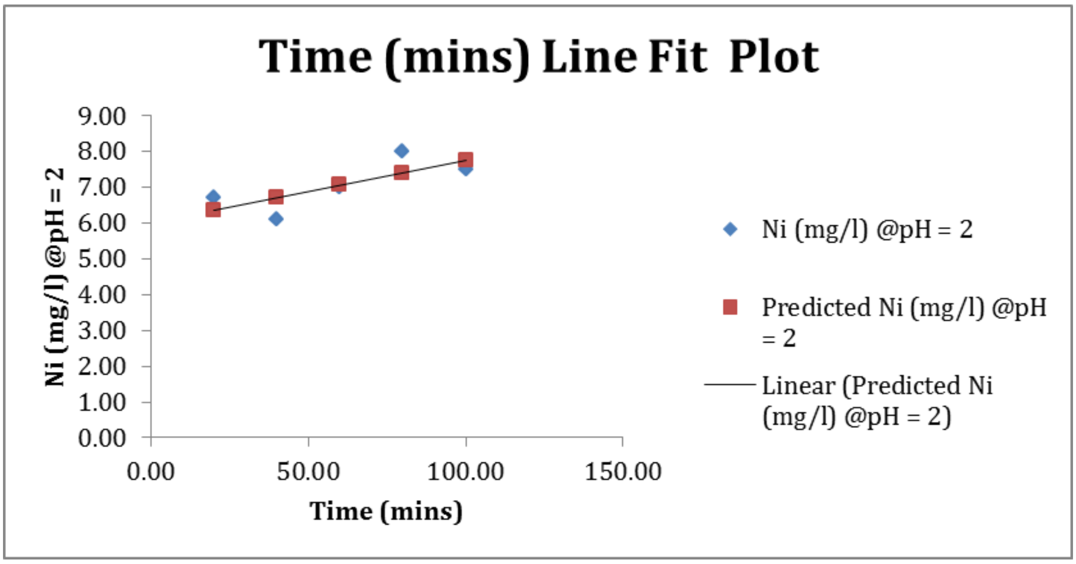
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.225	1.225	4.051819	0.137595
Residual	3	0.907	0.302333		
Total	4	2.132			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	6.01	0.576686	10.42162	0.001886	4.174728	7.845272
Time (mins)	0.0175	0.008694	2.012913	0.137595	-0.01017	0.045168

RESIDUAL OUTPUT

Observation	*Predicted Ni (mg/l) @pH = 2*	*Residuals*
1	6.36	0.34
2	6.71	-0.61

3	7.06	-0.06
4	7.41	0.59
5	7.76	-0.26



SUMMARY OUTPUT FOR PERIWINKLE SHELL (PS)

Regression Statistics	
Multiple R	0.946537
R Square	0.895931
Adjusted R Square	0.861242
Standard Error	0.454239
Observations	5

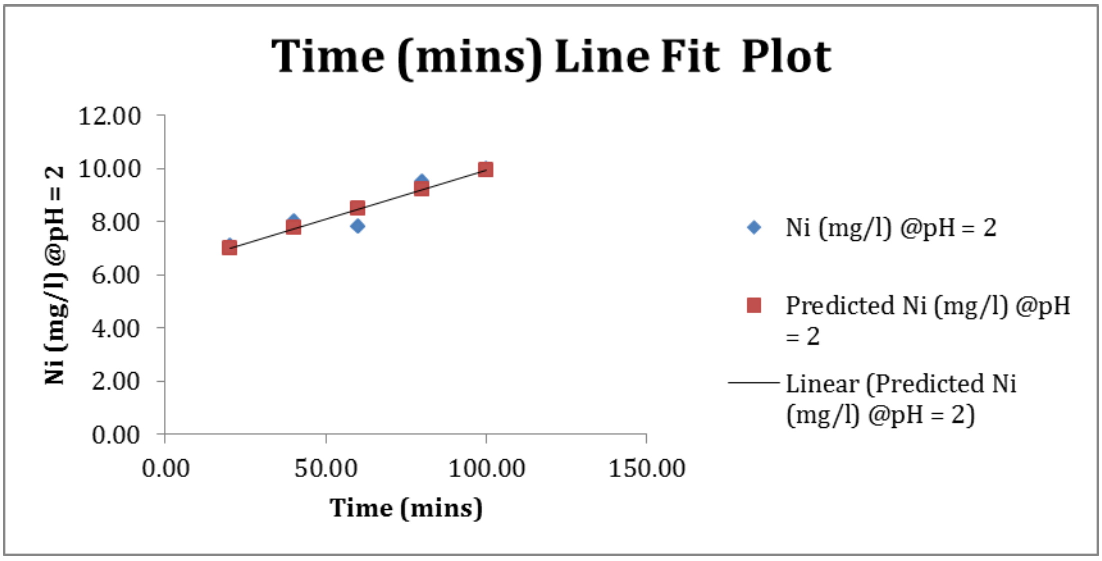
ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	5.329	5.329	25.82714	0.01472
Residual	3	0.619	0.206333		
Total	4	5.948			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	6.29	0.47641	13.20291	0.000939	4.77385	7.80615
Time (mins)	0.0365	0.007182	5.082041	0.01472	0.013643	0.059357

RESIDUAL OUTPUT

Observation	*Predicted Ni (mg/l) @pH = 2*	*Residuals*
1	7.02	0.08
2	7.75	0.25
3	8.48	-0.68
4	9.21	0.29
5	9.94	0.06



3.4 Effect of dosage

Snail Shell (SS)			Periwinkle Shell (PS)	
Dosage (g)	**Ni (mg/l) @pH = 2**		**Dosage (g)**	**Ni (mg/l) @pH = 2**
0.20	5.10		0.20	4.30
0.40	3.70		0.40	8.10
0.60	6.10		0.60	6.00
0.80	9.55		0.80	10.00
1.00	16.10		1.00	15.20

SUMMARY OUTPUT FOR SNAIL SHELL (SS)

Regression Statistics	
Multiple R	0.887546
R Square	0.787738
Adjusted R Square	0.716984
Standard Error	2.639429
Observations	5

ANOVA

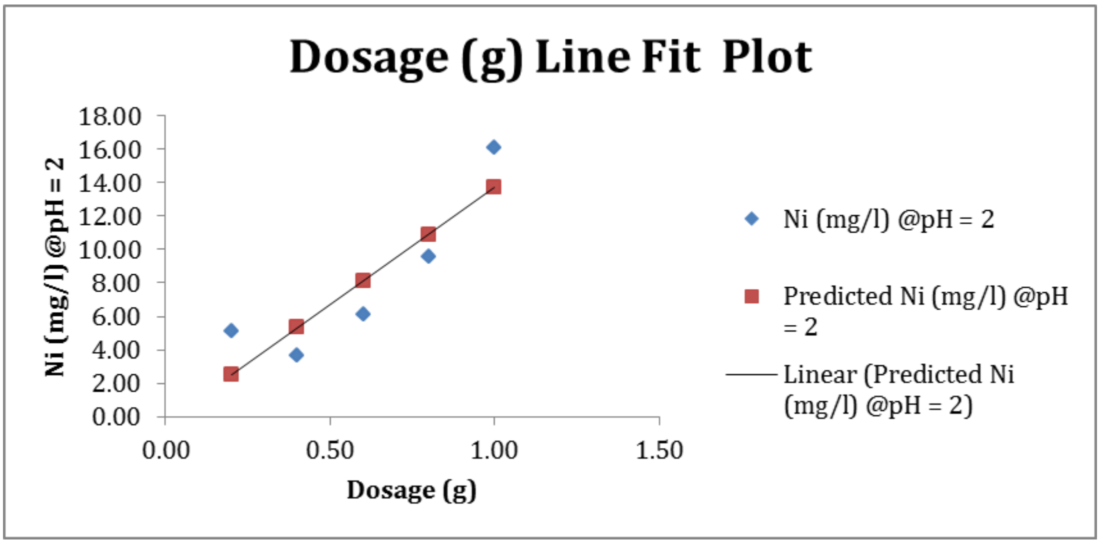
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	77.56225	77.56225	11.13347	0.044497
Residual	3	20.89975	6.966583		
Total	4	98.462			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-0.245	2.768256	-0.0885	0.935054	-9.05483	8.564826
Dosage (g)	13.925	4.173303	3.336686	0.044497	0.643687	27.20631

RESIDUAL OUTPUT

Observation	*Predicted Ni (mg/l) @pH = 2*	*Residuals*
1	2.54	2.56

2	5.325	-1.625
3	8.11	-2.01
4	10.895	-1.345
5	13.68	2.42



SUMMARY OUTPUT FOR PERIWINKLE SHELL (PS)

Regression Statistics	
Multiple R	0.889771
R Square	0.791693
Adjusted R Square	0.722257
Standard Error	2.219534
Observations	5

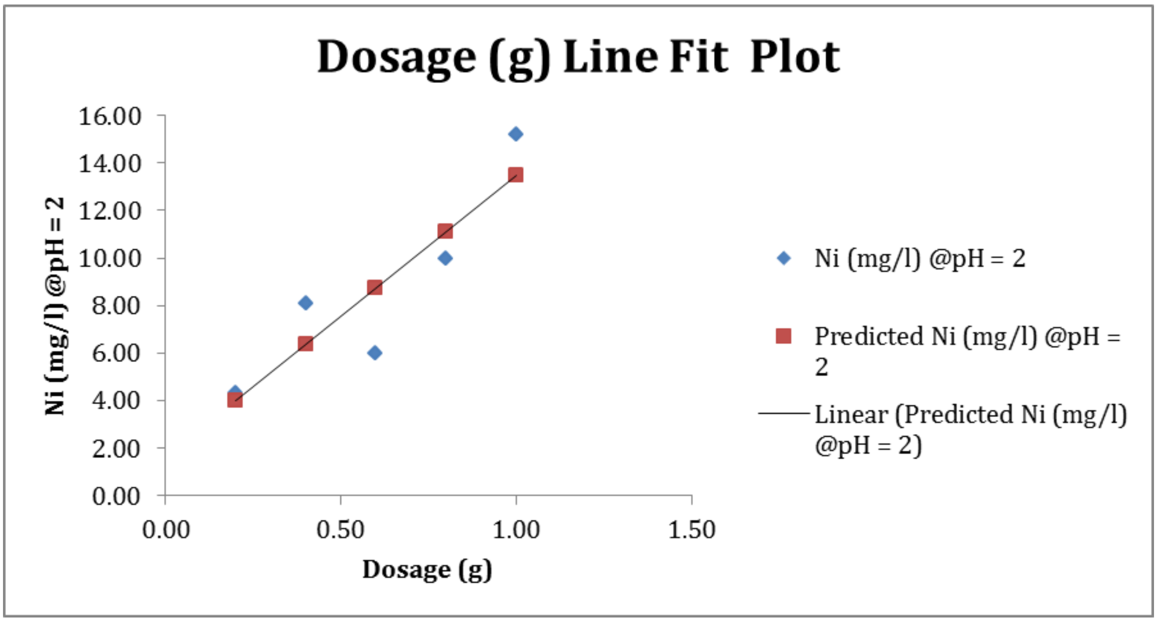
ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	56.169	56.169	11.40179	0.043198
Residual	3	14.779	4.926333		
Total	4	70.948			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1.61	2.327867	0.69162	0.538894	-5.79831	9.018313
Dosage (g)	11.85	3.509392	3.376653	0.043198	0.681548	23.01845

RESIDUAL OUTPUT

Observation	*Predicted Ni (mg/l) @pH = 2*	*Residuals*
1	3.98	0.32
2	6.35	1.75
3	8.72	-2.72
4	11.09	-1.09
5	13.46	1.74



4. CONCLUSION

It has been found that shells of snail and periwinkle are good adsorbents for the removal of Ni (II) ion from aqueous solution. From this study, the following conclusions are made:

i. Based on their relative values of adsorption capacity, available surface area and adsorption efficiencies of these shells, snail shell is a better adsorbent than periwinkle shell.

ii. Adsorption capacities of snail and periwinkle shells are affected by contact time, pH and by the initial concentration of Ni (II) ion in the solution.

Within the limit of the studied concentrations, snail and periwinkle shells are confirmed to be good adsorbents for Ni (II) ion from aqueous solution.

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