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Adsorption Studies on Removal of Nickel Ions Using Modified Groundnut Shell (*Arachishypogaea)*

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ABSTRACT:
Groundnut shells were modified through functionalization and carbonization processes to produce three distinct GS-HCL^C, GS-KOH^C and GS-TPP adsorbents for adsorption of Pb (II) ions from aqueous solution. Adsorption studies was carried out under varying conditions of pH, contact time, adsorbent dosage, metal ion concentration and temperature after the results were documented. Batch adsorption experiments revealed that the highest adsorption capacities were observed at a pH of 11 and the adsorption process was dependent upon changes in contact time for all adsorbents. Adsorption capacity was observed to increase with increase in adsorbent dosage and decrease with increase in lead ion concentration across all adsorbents during the adsorption of Nickel ions from the aqueous medium.

Keywords: *Nickel, Groundnut shell, Adsorption, Adsorbent, Adsorption capacity.*

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I. INTRODUCTION

Water is one of the most important elements necessary for the sustenance of life, hence it should be available in clean and large proportions to ensure longevity of human live. However, in developing countries especially in Nigeria, although tap water meets the common requirement of potable drinking water, it is not the most available source of drinking water especially to communities in rural and village settings. The disadvantage of this is that some industries dump their water effluent into the same river bodies without treatment [1].There are a large number of factors which cause water pollution in Nigeria ranging from water runoffs from top soil, indiscriminate dumping of solid and liquid waste into water bodies, public defecation and public bathing in water bodies [2]. Among these wastes dumped indiscriminately into various water bodies, pollution due to heavy metals are some of the most dangerous. The effects caused by heavy metal effluent into water bodies are too numerous to mention. In a study carried out [3] they observed that untreated groundwater containing some heavy metals lead to sickness and diseases such as hepatitis, Cholera dysentery and even typhoid. He observed that the groundwater pollution could have come from a wide number sources ranging from leaky underground tanks, excess application of pesticides and fertilizer on lawns and fields, spill or leak or pollutants etc.lignonocellulose materials have been discovered as effective materials for removal of heavy metals from waste water. Although groundnut shells can be used for water treatment, literature [4] still further suggests that functionalization, modification and effect of particle size can increase the effectiveness of groundnut shell as a tool for removal of heavy metal effluent from water. Carbonization reduces the particle size of lignocellulosic materials which causes micro pores to be formed in the interlayer spacing with widths in the range of 0.34 – 0.8 nm [5]. Literature also records that carbonization of lignocellulosic biomass of any source is also very efficient in the removal of heavy metal from aqueous medium [6]. In a thesis carried out byNwabanne [7]. They successfully carbonized a lignocellulosic biomass from Palmyra palmnut and activated it. The adsorbent was then used for removal of lead ions from an aqueous medium and the report on the adsorption studies carried out suggested it was an efficient engineering material for removal of lead ions.

II. MATERIALS AND METHODS

Sample Preparation:

The raw material (Groundnut shell) was obtained locally in Fruit market in Port Harcourt city, Rivers State Nigeria. Analytical grade chemicals were obtained from Campal Scientific Company in Onitsha Anambra State, Nigeria while other reagents were obtained from Soil Science Technology Laboratory Federal University of Technology Owerri. The groundnut shells (GS) was cut into small particles and then washed with distilled water numerous times to remove impurities, sand and dust. It is then sun dried for two weeks after which it was further shredded by a mill and then sieved using a sieve of 75um.

Preparation of Activated Carbon from groundnut shells using Hydrogen chloride and Zinc Chloride (GS-HCL)

150g of the 75um groundnut shell was chemically modified using acid treatment of 1M Hydrochloric acid as described in a similar process by Elkady[8] with some modifications. The acid activation processes were carried out under heating at 60°C for 2 hours with continuous stirring. The yielded chemically modified material was further chemically activated zinc chloride ($ZnCl_2$) for (6-8) hours with intermittent stirring at an interval of 2 hours for 30mins to treat the parent adsorbent materials prior to the carbonization process. The produced powder materials after chemical activation were filtered, washed several and then dried at 100℃ for 24 hours. The dried materials were burned for carbonization at a temperature of 400 ℃ for 2hours.

Preparation of Activated carbon from Groundnut shells using Potassium Hydroxide (GS-KOH)

150g of the groundnut shells with a particle size of 75um was impregnated in 500 ml of 2wt.% KOH solution for 24 hrs. after which the sample was then filtered and washed with distilled water for several times until the pH is neutral. It was then at dried at 100^oC in a Genilab Oven for 12 h before carbonization in Biotech muffle furnace. The temperature for carbonization was set at 400 with a holding time of 2 hrs. the procedure is similar to Pagketenang and Artenaseaw[9] report with some modifications.

Preparation of functionalized groundnut shells using Tripolyphosphate (GS-TPP)

The process used is similar to that as described by Mariam [10] with some minor modifications. A solution of the lignocellulosic biomass was prepared by adding 1L of 2% acetic acid which is 0.1M to a known mass (150g) of the lignocellulose. The solution was then stirred for 30 mins. at an interval of 4hrs for two days. After which a known mass (35.7 gm) of Tripolyphosphate (85% TPP) was then dissolved in 1 litre of double distilled water to prepare 0.1 M solution of TPP. The lignocellulosic particles was then prepared by adding the GS Acetic Acid solution in a drop wise manner to the TPP solution to the ratio 1:1. (GS acetic Acid: TPP v/v). After this, the phosphorylated groundnut shells were then filtered and washed several times with double distilled water.

Batch Adsorption through Filtration Studies

A standard solution containing 1000ppm (1g/l) of the Ni (II) ion metal concentration was prepared by dissolving 4.9544g of the salt Nickel (II) nitrate hexahydrate in double distilled water. Effects of each factor were determined keeping other variables constant. All experiments were carried out in triplicates and mean values as well as their standard deviation were calculated using ANOVA.

Effect of pH

50ml of solution containing 50mg/l of Ni (II) ions was measured into several polyethylene bottles with 0.25g of resin added into the bottles. The PE bottles were labelled pH 3, 5, 7, 9 and 11; the pH of the solutions were adjusted as desired using 0.1M of sodium hydroxide and 0.1M of hydrochloric acid. Solutions were thoroughly agitated using a mechanical flask shaker at 200rpm for 60minutes to reach attain equilibrium. The pH experiments were carried out at room temperature for the batch tests. At the end of the agitation period, resins were separated from the solution by filtration method using Whattman filter paper and the final concentrations of the Pb(II) and Ni(II) Ions in the solution was determined using the Atomic Adsorption Spectrophotometer.

Effect of Contact Time

The same procedure as in 3.3.1 was repeated and optimum pH value for each metal was used but at varying contact time intervals of 10mins, 30mins, 60mins, 90mins and 120mins. The experiment was carried out at room temperature.

Effect of Adsorbent Dosage

The same procedure as in 3.3.1 was used at optimum pH and contact time values but varying resin dosages; 50mg, 100mg, 150mg, 200mg and 250mg. The experiment was also carried out at room temperature.

Effect of Initial Ion Concentration

The same procedure as in 3.3.1 was used at optimum pH, agitation time and resin dosage values but at varying initial metal concentrations; 50mg/l, 100mg/l, 150mg/l, 200mg/l, and 250mg/l.

Effect of Temperature

The effect of temperature was studied at optimum pH, optimum contact time and optimum adsorbent dosage using 50ml of solution containing 50mg/l of Pb(II), and Ni(II) solution at temperatures of 20^0C, 30^0C, 40^0C, 50^0C and 60^0C.

Adsorption Capacity

The adsorption capacity that is the metal ions adsorbed onto the resin was calculated using mass balance relation as in equation 3.14 [11] .

$$q_e = \frac{(C_o - C_e)V}{M} \qquad (3.14)$$

Where: q_e(mg/g) is the adsorption capacity of the adsorbent; C_o and C_e (mg/l) are the initial and final concentration of the metal ions in solution phase, V is the volume of the aqueous solution (l) and M is the weight of the adsorbent (g)

The percentage of ions removed was calculated as thus 3.15.

$$\%\ of\ ions\ Adsorbed = \frac{(Co - Ce)}{C_o}\ x\ 100 \qquad (3.15)$$

III. RESULTS AND DISCUSSION

Effect of pH

Table 1Table of plot for effect of pH of Ni (II) ion aqueous solution on adsorbents

Effect of pH of Ni (II) ions solution on the adsorbents (C_o= 50mg)												
	GS-HCl^C				GS-KOH^C				GS-TPP			
pH	C_e	C_o-C_e	q_e	% adsorbed	C_e	C_o-C_e	q_e	% adsorbed	C_e	C_o-C_e	q_e	% adsorbed
3	39.4280	10.5720	2.1144	21.1440	0.1430	49.8570	9.9714	99.7140	25.2620	24.7380	4.9476	49.4760
5	33.4280	16.5720	3.3144	33.1440	0.1360	49.8640	9.9728	99.7280	19.6650	30.3350	6.0670	60.6700
7	32.5240	17.4760	3.4952	34.9520	0.1430	49.8570	9.9714	99.7140	14.9050	35.0950	7.0190	70.1900
9	11.3330	38.6670	7.7334	77.3340	0.1430	49.8570	9.9714	99.7140	13.7140	36.2860	7.2572	72.5720
11	2.5240	47.4760	9.4952	94.9520	0.1340	49.8660	9.9732	99.7320	0.5810	49.4190	9.8838	98.8380

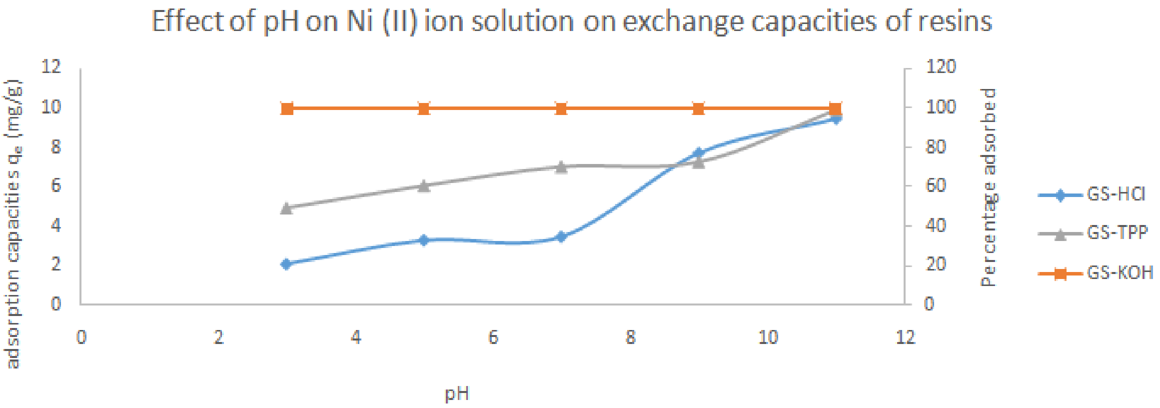

Figure 1Effect of pH on Ni (II) ion Solution

The adsorption capacity of absorbents during adsorption of Ni (II) ions is explained graphically in figure 1 above. The adsorption capacity of GS-KOH^C seems to be unaffected by changes in pH both in the acidic and alkaline region. This is especially useful as it indicates that the adsorbent will still exhibit maximum adsorption capacity irrespective of the type of region it is placed in. However, the adsorption capacities of the other two adsorbents GS-TPP and GS-HCL^C increases from the acidic to the alkaline region with maximum adsorption capacities occurring at pH respectively with maximum percentage removal at 98% and 94% respectively at pH of 11. Adsorption capacity of GS-HCL^C and GS-TPP is very poor in the acidic region. This may be attributed to the abundance of H^+ groups present in the acidic region. This effect seems more pronounced especially with the sample treated with HCL that is GS-HCL^C with percentage absorbed as low as 10.5720mg at initial concentration of 50mg at a pH of 2. All three adsorbents have high adsorption capacities in the alkaline regions especially at pH 11 which the maximum adsorption capacity.

Table 2Table of plot for effect of contact time of Ni (II) ion aqueous solution on adsorbents

Effect of Contact time of Ni (II) ions solution on the adsorbents (C_o= 50mg)												
	GS-HCl^C				GS-KOH^C				GS-TPP			
Contact Time (mins)	C_e	C_0-C_e	q_e	% adsorbed	C_e	C_0-C_e	q_e	% adsorbed	C_e	C_0-C_e	q_e	% adsorbed
10	3.3190	46.6810	9.3362	93.3620	1.0230	48.9770	9.7954	97.9540	0.6320	49.3680	9.8736	98.7360
30	3.0040	46.9960	9.3992	93.9920	0.5930	49.4070	9.8814	98.8140	0.6850	49.3150	9.8630	98.6300
60	2.8450	47.1550	9.4310	94.3100	0.2230	49.7770	9.9554	99.5540	0.6370	49.3630	9.8726	98.7260
90	1.0357	48.9643	9.7929	97.9286	0.1280	49.8720	9.9744	99.7440	0.6590	49.3410	9.8682	98.6820
120	0.1820	49.8180	9.9636	99.6360	0.1070	49.8930	9.9786	99.7860	1.0053	48.9947	9.7989	97.9894

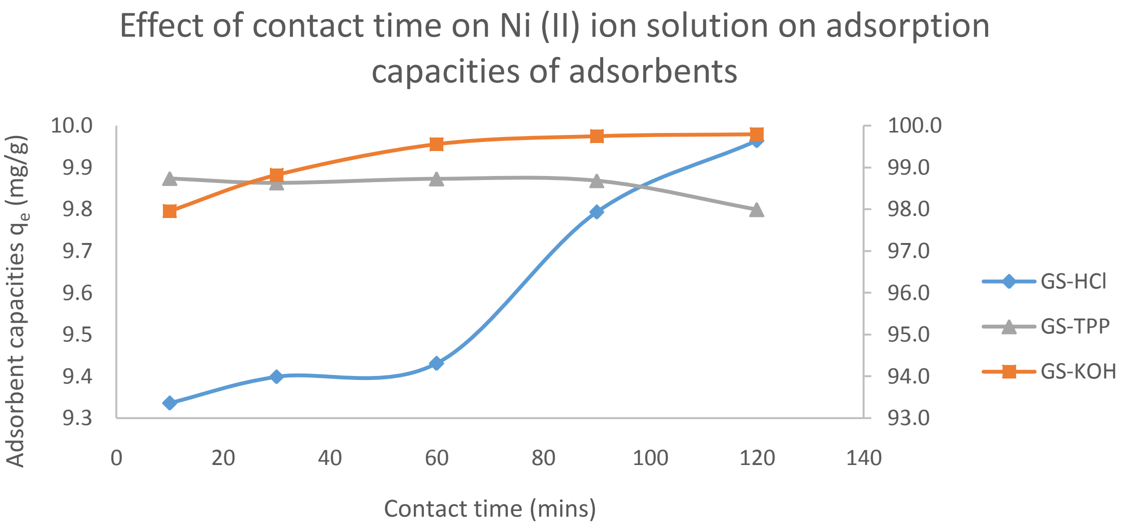

Figure 2Effect of Contact time on Ni (II) ions

The effect of adsorbate – adsorbent duration of contact was studied to determine the equilibrium time for the adsorption of Ni (II) ions. The rate of metal uptake increases with increasing duration of contact for the GS-HCL^C and GS-KOH^C adsorbents in which maximum adsorption was observed at 120mins respectively. However, the rate of metal uptake with respect to time for GS-HCL^C was sharp between 60mins and 90mins from 94.31% to 97.92% while for the GS-KOH^C adsorbent rate of metal uptake increased gradual with time up to a maximum percentage adsorption of 99.786%. The GS-TPP adsorbent had maximum adsorption at 30mins after which slight reduction in adsorption capacity and percentage removal was being observed in response to increase in time duration.

Table 3Table of plot for effect of adsorbent dosage of resins on Ni (II) ion aqueous solution

Effect of Adsorbent dosage on Ni (II) ions (C_o= 50mg)												
	GS-HCl^C				GS-KOH^C				GS-TPP			
Resin Dosage (g)	C_e	C_0-C_e	q_e	% adsorbed	C_e	C_0-C_e	q_e	% adsorbed	C_e	C_0-C_e	q_e	% adsorbed
0.05	3.8360	46.1640	46.1640	92.3280	0.9930	49.0070	49.0070	98.0140	5.7237	44.2763	44.2763	88.5526
0.10	1.8040	48.1960	24.0980	96.3920	0.5100	49.4900	24.7450	98.9800	1.9850	48.0150	24.0075	96.0300
0.15	0.9637	49.0363	16.3454	98.0726	0.2017	49.7983	16.5994	99.5966	0.6377	49.3623	16.4541	98.7246
0.20	0.6030	49.3970	12.3493	98.7940	0.0950	49.9050	12.4763	99.8100	0.8990	49.1010	12.2753	98.2020
0.25	0.1957	49.8043	9.9609	99.6086	0.0840	49.9160	9.9832	99.8320	0.6720	49.3280	9.8656	98.6560

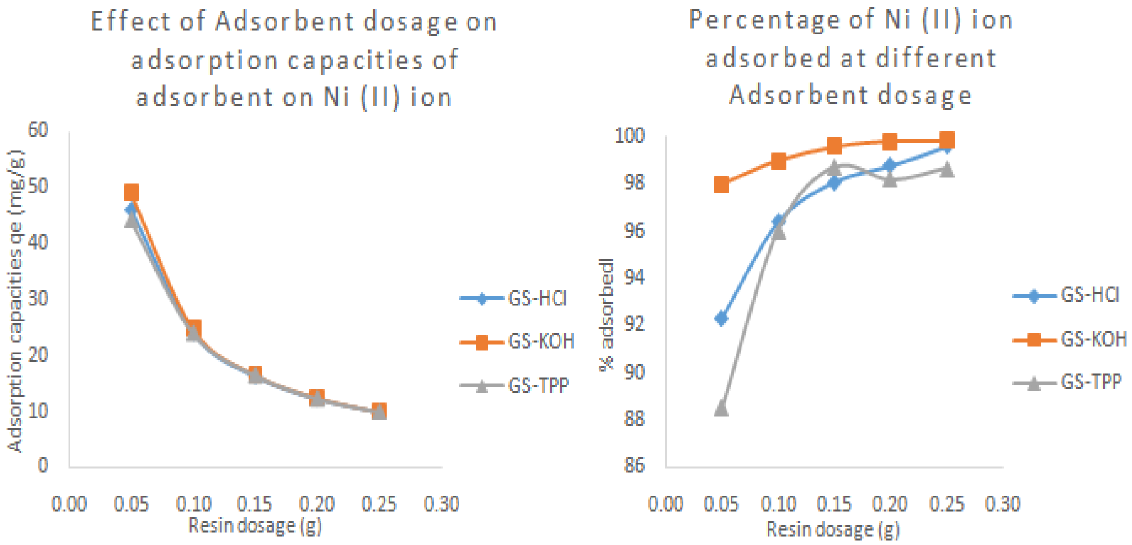

Figure 3Effect of Adsorbent Dosage on Ni (II) ions

The effect of adsorbent dosage was also carried out to know the maximum dosage of adsorbent required for the adsorption of Ni (II) ions. Increase in adsorbent dosage of GS-HCL^C, and GS-KOH^C increases the percentage adsorption of Pb^{2+} as shown in figure 3 above, this can be explained by the fact that increased amount of adsorbent provides larger surface area for the adsorption of the metal. However, during the adsorption dosage studies for GS-TPP increase in dosage increased metal ion uptake up to 0.15g after which a negligible decrease in percentage of metal ion removal was observed at 0.20g and then continued to increase. The adsorption capacity q_e was highest 46.1640mg/g, 49.0070mg/g, and 44.2763mg/g at 0.05g of adsorbent and decrease to 9.9609mg/g, 9.9832mg/g and 9.8656mg/g at 0.25g of adsorbent for GS-HCL^C, GS-KOH^C and GS-TPP respectively.

Table 4Table of plot for effect of metal ion concentration of Ni (II) ion aqueous solution on adsorbents

Effect of Metal ion concentration of Ni (II) ions on the adsorbents (m = 0.25g)												
	GS-HCl^C				GS-KOH^C				GS-TPP			
Metal ion conc.	C_e	C_0-C_e	q_e	% removal	C_e	C_0-C_e	q_e	% removal	C_e	C_0-C_e	q_e	% Removal
50	0.1865	49.8135	9.9627	99.6270	0.1059	49.8941	9.9788	99.7882	0.6560	49.3440	9.8688	98.6880
100	0.4670	99.5330	19.9066	99.5330	0.1220	99.8780	19.9756	99.8780	1.3785	98.6215	19.7243	98.6215
150	0.9950	149.0050	29.8010	99.3367	0.4560	149.5440	29.9088	99.6960	6.9960	143.0040	28.6008	95.3360
200	7.7830	192.2170	38.4434	96.1085	5.7820	194.2180	38.8436	97.1090	23.3485	176.6515	35.3303	88.3258
250	15.9865	234.0135	46.8027	93.6054	8.4568	241.5433	48.3087	96.6173	43.7785	206.2215	41.2443	82.4886

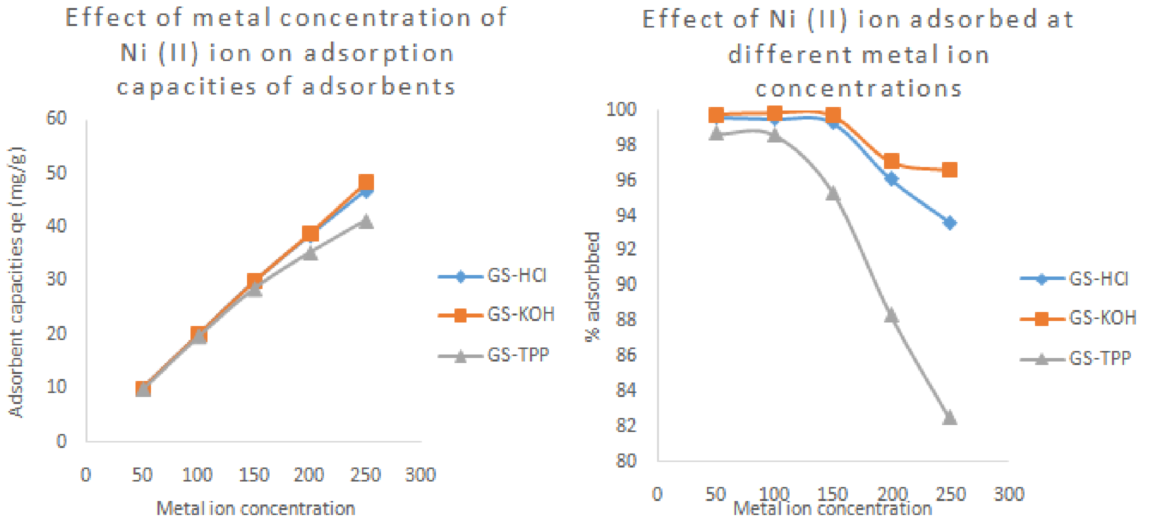

Figure 4Effect of Ni (II) ion Concentration on Adsorbents

The adsorption capacity increase with increasing concentration of Nickel ions as shown in figure 4 while the percentage of metal ion removal decreases with increase in initial metal ion concentration as illustrated in the figure above.

Table 5 Table of plot for effect of Temperature of Ni (II) ion aqueous solution on adsorbents

Effect of Temperature on the adsorption of Ni (II) ions onto the adsorbent (C_o= 50mg)												
	GS-HCl^C				GS-KOH^C				GS-TPP			
Temp.	C_e	C_o-C_e	q_e	% removal	C_e	C_o-C_e	q_e	% removal	C_e	C_o-C_e	q_e	% removal
20	0.7110	49.2890	9.8578	98.5780	0.4770	49.5230	9.9046	99.0460	1.6670	48.3330	9.6666	96.6660
30	0.2687	49.7313	9.9463	99.4626	0.3953	49.6047	9.9209	99.2094	0.7853	49.2147	9.8429	98.4294
40	0.2780	49.7220	9.9444	99.4440	0.1020	49.8980	9.9796	99.7960	0.7947	49.2053	9.8411	98.4106
50	0.3300	49.6700	9.9340	99.3400	0.1100	49.8900	9.9780	99.7800	0.8643	49.1357	9.8271	98.2714
60	0.5653	49.4347	9.8869	98.8694	0.2100	49.7900	9.9580	99.5800	0.9120	49.0880	9.8176	98.1760

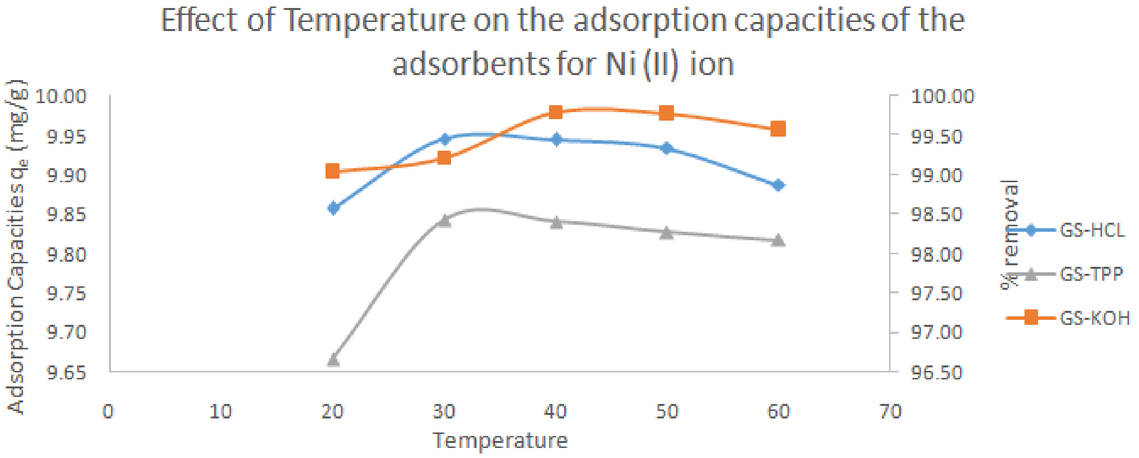

Figure 5Effect of Temperature on Adsorption of Ni (II) ions

The temperature studies were also carried out to determine its effect on the adsorption of Ni (II) ions. As can be seen from figure 5 above, temperature ranging from 20^{O}C to 60^{O}C has a negligible effect on the adsorption capacities of GS-HCL^C, GS-KOH^C and GS-TPP. A similar observation was made in the research of Alemayehu et al. [12]. This is an excellent quality for any adsorbent to possess as the percentage removal efficiencies are as it peak averaging 99% for all adsorbents. The maximum adsorption capacities are

9.9463mg/g, 9.9796mg/g and 9.8429mg/g at temperatures of 30^{O}C, 40^{O}C and 30^{O}C for GS-HCL^{C}, GS-KOH^{C} and GS-TPP respectively.

IV. CONCLUSION

This research shows that lignocellulose materials such as groundnut shells when subjected to activation and carbonization process can be used for removal of Nickel ions from water effluent. The batch adsorption results indicated the dependence of the adsorbents on changes with contact time adsorbent dosage and the Nickel ion concentration. However, the GS-KOH^{C} adsorbent was independent of changes in pH while the GS-HCL^{C} and GS-TPP adsorbent had optimum adsorption capacities in the alkaline region of pH 11. The high percentage removal of heavy metals during the batch adsorption studies suggests that the adsorbents are excellent materials for the removal of Nickel ions from aqueous mediums.

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