



## Adsorption of Pb(II) Ions from Aqueous Solution Using Functionalized and Carbonized Groundnut Shell

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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### **ABSTRACT**

Groundnut shells were modified through functionalization and carbonization processes to produce three distinct 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 adsorbents performed optimally at a pH of 11 and the adsorption process was dependent upon changes in contact time. Adsorption capacity was observed to increase with increase in adsorbent dosage and decrease with increase in lead ion concentration across all adsorbents. Highest metal ion removal was by the GS-KOH<sup>C</sup> where 239.86 mg/g of lead ion was removed from the aqueous solution followed by the GS-HCL<sup>C</sup> at 228.0750 mg/g and then the GS-TPP adsorbent was least at 179.1235 mg/g.

*Keywords: Lead; groundnut shell; adsorption; adsorbent; adsorption capacity.*

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## 1. INTRODUCTION

Indiscriminate human activities have led to the pollution and contamination of our water bodies by various sources [1]. Water can be contaminated through various actions either naturally by unprecedented activities (such as earthquakes, volcanoes, naturally stored heavy metal deposits, natural flow effluent into water bodies, acidic rainfall, etc.) or by man's action in the cause of science technological advancement or generally plain ignorance [2]. This is indeed a prevalent phenomenon especially in Nigeria where industries and individuals dump their effluent into water bodies without proper treatment. This is the most common form of heavy metal pollution in Nigeria [3]. Due to this existing problem new solutions are being targeted to develop highly effective adsorbents to completely remove heavy metals from waste water effluent. Heavy metal pollution especially by lead ions has been documented in various literatures to have a disastrous effect on the human body. These can also adversely cause oxygen deficiency, excessive growth of algae in river bodies and then lead to death of aquatic life. Water bodies filled with metal effluent for example lead can disrupt enzyme activities and distort the formation of red blood cells in human beings. Also, lead can affect nerves and brain activity even at very low concentrations in the human body. In some cases death by lead poisoning has been known to be highest cause for heavy metal poisoning in water bodies [4]. However, new and emerging technologies are being designed such as the adsorbents described in this research from effectively removing lead ions and other heavy metals from aqueous medium. Isah and Yusuf [5] work focused on the application of activated carbon primed from groundnut shell for the elimination of lead from water. The paraphernalia of temperature, contact time, and initial concentration of lead on the adsorption method were investigated. Groundnut shell activated carbon was proven to be proficient of removing lead from water with a very high efficacy under ambient settings. However, it is worthy to note that in this case there was no modification to the groundnut shells used.

## 2. MATERIALS AND METHODS

### 2.1 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 75  $\mu\text{m}$ .

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

150 g of the 75  $\mu\text{m}$  groundnut shell was chemically modified using acid treatment of 1M Hydrochloric acid as described in a similar process by Elkady [6] 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 ( $\text{ZnCl}_2$ ) for (6-8) hours with intermittent stirring at an interval of 2 hours for 30 mins 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°C for 24 hours. The dried materials were burned for carbonization at a temperature of 400°C for 2hours.

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

150 g of the groundnut shells with a particle size of 75  $\mu\text{m}$  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°C 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 Pagketang [7] report with some modifications.

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

The process used is similar to that as described by Miram [8] 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 (150 g) 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 were 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.

## 2.2 Batch Adsorption through Filtration Studies

A standard solution containing 1000 ppm (1g/l) of the Pb (II) ion metal concentration was prepared by dissolving 1.598 g of the  $Pb(NO_3)_2$  salt in double distilled water. Subsequent concentrations were obtained by serial dilution. 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:** 50 ml of solution containing 50 mg/l of Pb (II) ions was measured into several polyethylene bottles with 0.25 g of resin added into the bottles. The PE bottles were labelled pH 3, 5, 7, 9 and 11; the pH of the solutions was 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 200 rpm for 60 minutes 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 Whatman 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 10 mins, 30 mins, 60 mins, 90 mins and 120 mins. 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; 50 mg, 100 mg, 150 mg, 200 mg and 250 mg. 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; 50 mg/l, 100 mg/l, 150 mg/l, 200 mg/l, and 250 mg/l.

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

**Adsorption Capacity:** The adsorption capacity that is the metal ions adsorbed onto the resin was calculated using mass balance relation as in equation 1 [9].

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

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 equation 2.

$$\% \text{ of ions Adsorbed} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

## 3. RESULTS AND DISCUSSION

**Effect of pH:** As seen from Fig. 1, the adsorption capacity of the adsorbents is dependent of pH during the uptake of Pb (II) ions from solution. Maximum adsorption capacity of all the adsorbents occurred in the alkaline region with maximum adsorption capacities occurring at pH 11 for all adsorbents. The graphs show increase in adsorption capacity and percentage adsorbed increasing from the acidic to the alkaline region. At higher pH values increase in adsorption may be attributed to the abundance of  $OH^-$  which causes increase in diffusion of the  $Pb^{2+}$  ions. The adsorption capacity was especially low in the acidic region for GS-HCL<sup>C</sup> this may be attributed to the overabundance of  $H^+$  groups present at that pH thereby reducing the efficiency of diffusion the Pb (II) ions for adsorption unto the adsorbent.

**Effect of Contact Time:** Experiments carried out to determine the effect of contact time on the adsorption of Pb (II) ions were negligent on the carbonized samples (GS-KOH<sup>C</sup> and GS-TPP) as

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

Effect of pH of Pb (II) ions solution on the adsorbents (C <sub>o</sub> = 50 mg)												
GS-HCl <sup>c</sup>					GS-KOH <sup>c</sup>				GS-TPP			
pH	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% Adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% Adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% Adsorbed
3	38.4230	11.5770	2.3154	23.1540	11.9620	38.0380	7.6076	76.0760	17.8850	32.1150	6.4230	64.2300
5	25.1540	24.8460	4.9692	49.6920	5.1930	44.8070	8.9614	89.6140	16.0000	34.0000	6.8000	68.0000
7	10.1540	39.8460	7.9692	79.6920	2.0770	47.9230	9.5846	95.8460	12.6150	37.3850	7.4770	74.7700
9	3.8110	46.1890	9.2378	92.3780	0.4890	49.5110	9.9022	99.0220	12.2310	37.7690	7.5538	75.5380
11	0.3310	49.6690	9.9338	99.3380	0.5390	49.4610	9.8922	98.9220	11.6920	38.3080	7.6616	76.6160

Effect of pH on Pb (II) ion solution on exchange capacities of the resins.

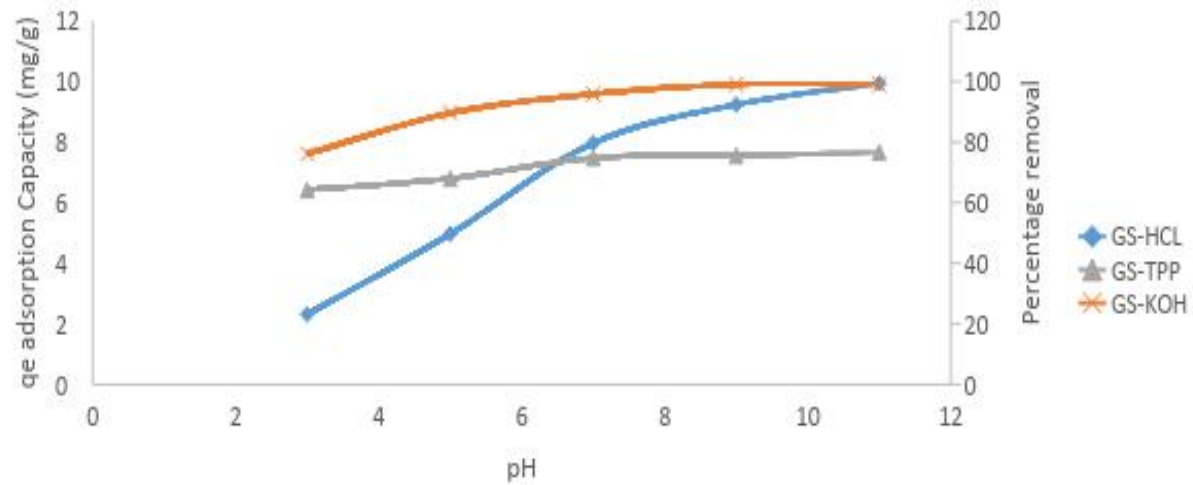


Fig. 1. Effect of pH on Pb (II) ion solution on exchange capacities of the resin

Table 2. Plot for effect of contact time of Pb (II) ion aqueous solution on adsorbents

Contact time (mins)	Effect of contact time of Pb (II) ions solution on the adsorbents (C <sub>o</sub> = 50 mg)											
	GS-HCl <sup>c</sup>				GS-KOH <sup>c</sup>				GS-TPP			
	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% adsorbed
10	1.4120	48.5880	9.7176	97.1760	0.8940	49.1060	9.8212	98.2120	10.0880	39.9120	7.9824	79.8240
30	0.7263	49.2737	9.8547	98.5474	0.5767	49.4233	9.8847	98.8466	9.1470	40.8530	8.1706	81.7060
60	0.2340	49.7660	9.9532	99.5320	0.3187	49.6813	9.9363	99.3626	11.4120	38.5880	7.7176	77.1760
90	0.2350	49.7650	9.9530	99.5300	0.2630	49.7370	9.9474	99.4740	11.1180	38.8820	7.7764	77.7640
120	0.5243	49.4757	9.8951	98.9514	0.2350	49.7650	9.9530	99.5300	12.0410	37.9590	7.5918	75.9180

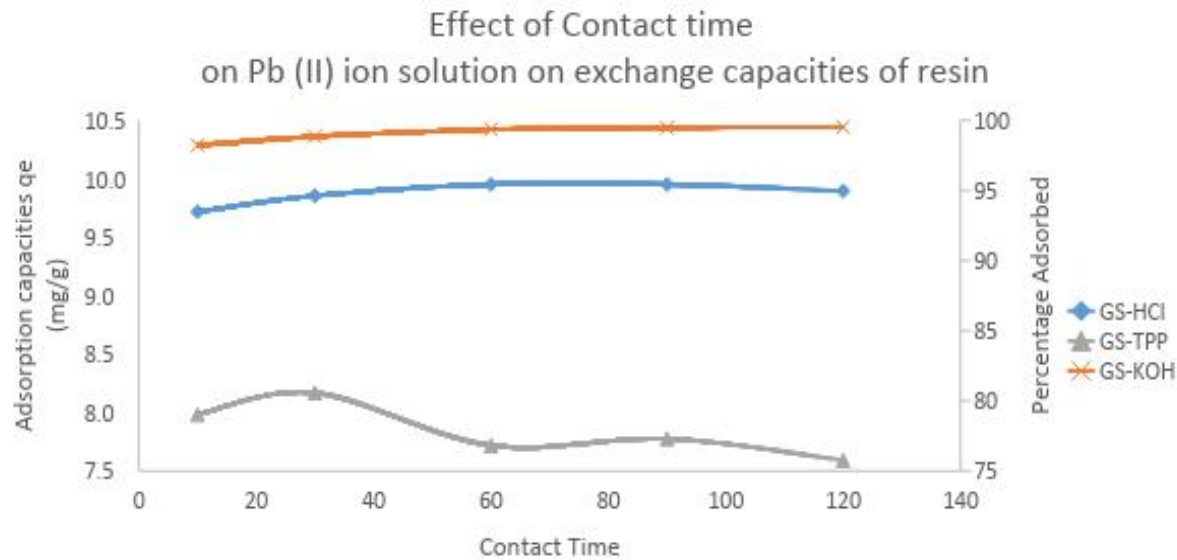
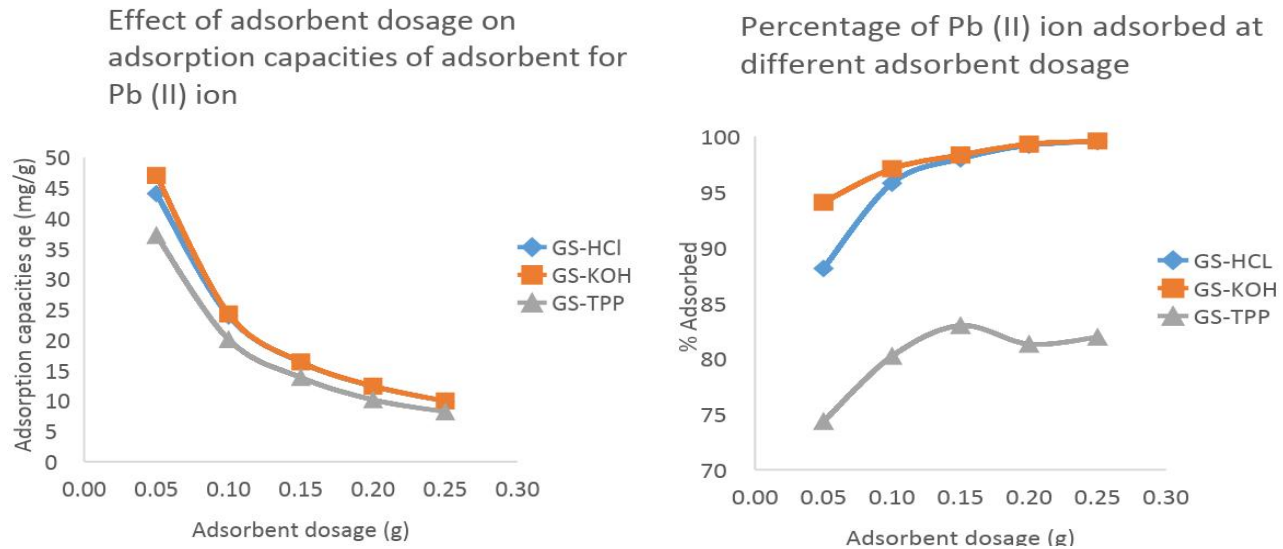


Fig. 2. Effect of contact time on Pb (II) Ion solution on exchange capacities of resin

**Table 3. Plot for effect of adsorbent dosage of resins on Pb (II) ion aqueous solution**

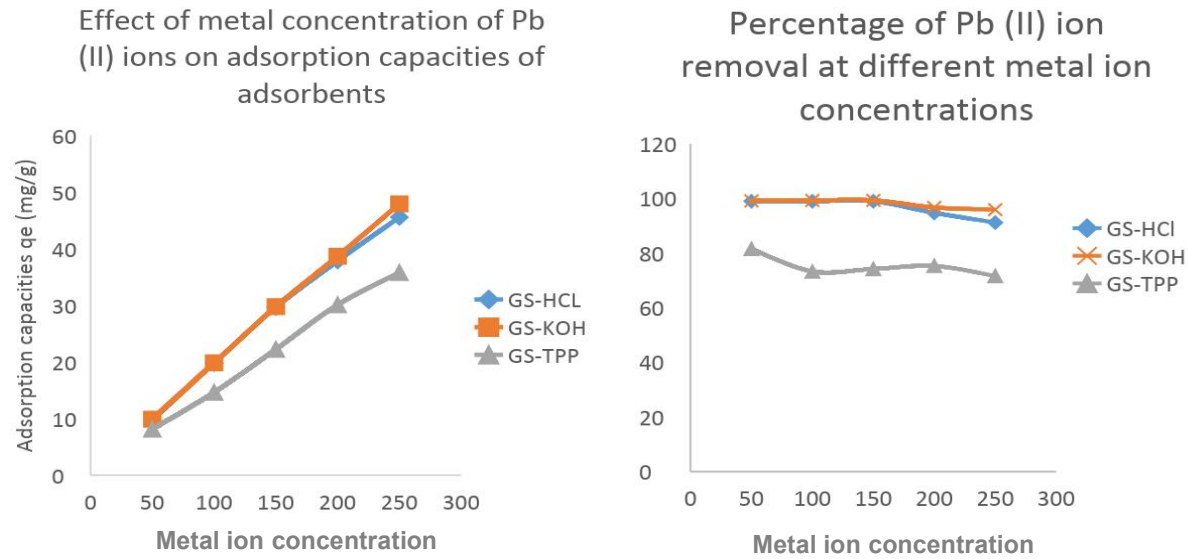
Resin dosage (g)	Effect of adsorbent dosage on Pb (II) ion ( $C_o = 50$ mg)											
	GS-HCl <sup>c</sup>				GS-KOH <sup>c</sup>				GS-TPP			
	$C_e$	$C_o - C_e$	$q_e$	% adsorbed	$C_e$	$C_o - C_e$	$q_e$	% adsorbed	$C_e$	$C_o - C_e$	$q_e$	% adsorbed
0.05	5.9437	44.0563	44.0563	88.1126	2.9680	47.0320	47.0320	94.0640	12.8283	37.1717	37.1717	74.3434
0.10	2.1030	47.8970	23.9485	95.7940	1.4550	48.5450	24.2725	97.0900	9.8947	40.1053	20.0527	80.2106
0.15	1.0083	48.9917	16.3306	97.9834	0.8347	49.1653	16.3884	98.3306	8.5140	41.4860	13.8287	82.9720
0.20	0.4000	49.6000	12.4000	99.2000	0.3457	49.6543	12.4136	99.3086	9.3513	40.6487	10.1622	81.2974
0.25	0.2340	49.7660	9.9532	99.5320	0.2067	49.7933	9.9587	99.5866	9.0360	40.9640	8.1928	81.9280



**Fig. 3. Effect of adsorbent dosage on Pb (II) ions**

**Table 4. Plot for effect of of Pb (II) ion aqueous solution on adsorbents**

Effect of metal ion concentration of Pb (II) ions on the adsorbents (m = 0.25 g)												
Metal ion conc.	GS-HCl <sup>c</sup>				GS-KOH <sup>c</sup>				GS-TPP			
	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% adsorbed	C <sub>e</sub>	C <sub>o</sub> -C <sub>e</sub>	q <sub>e</sub>	% Adsorbed
50	0.4780	49.5220	9.9044	99.0440	0.4300	49.5700	9.9140	99.1400	9.2100	40.7900	8.1580	81.5800
100	0.9970	99.0030	19.8006	99.0030	0.6756	99.3244	19.8649	99.3244	26.7000	73.3000	14.6600	73.3000
150	1.4955	148.5045	29.7009	99.0030	0.9970	149.0030	29.8006	99.3353	38.6680	111.3320	22.2664	74.2213
200	10.4680	189.5320	37.9064	94.7660	6.5100	193.4900	38.6980	96.7450	49.3670	150.6330	30.1266	75.3165
250	21.9250	228.0750	45.6150	91.2300	10.1400	239.8600	47.9720	95.9440	70.8765	179.1235	35.8247	71.6494



**Fig. 4 Effect of Pb (II) Ion concentration on adsorbents**

Table 5. Table of plot for effect of temperature of Pb (II) ion aqueous solution on adsorbents

Temp.	Effect of temperature on the adsorption of Pb (II) ions onto the adsorbent ( $C_o= 50$ mg)											
	GS-HCl <sup>c</sup>				GS-KOH <sup>c</sup>				GS-TPP			
	$C_e$	$C_o-C_e$	$q_e$	% removal	$C_e$	$C_o-C_e$	$q_e$	% removal	$C_e$	$C_o-C_e$	$q_e$	% removal
20	1.2147	48.7853	9.7571	97.5706	0.9586	49.0414	9.8083	98.0828	30.9600	19.0400	3.8080	38.0800
30	0.2597	49.7403	9.9481	99.4806	0.2283	49.7717	9.9543	99.5434	9.3740	40.6260	8.1252	81.2520
40	0.3390	49.6610	9.9322	99.3220	0.2660	49.7340	9.9468	99.4680	8.9686	41.0314	8.2063	82.0628
50	0.5773	49.4227	9.8845	98.8454	0.4170	49.5830	9.9166	99.1660	11.2460	38.7540	7.7508	77.5080
60	0.7206	49.2794	9.8559	98.5588	0.6047	49.3953	9.8791	98.7906	14.5917	35.4083	7.0817	70.8166

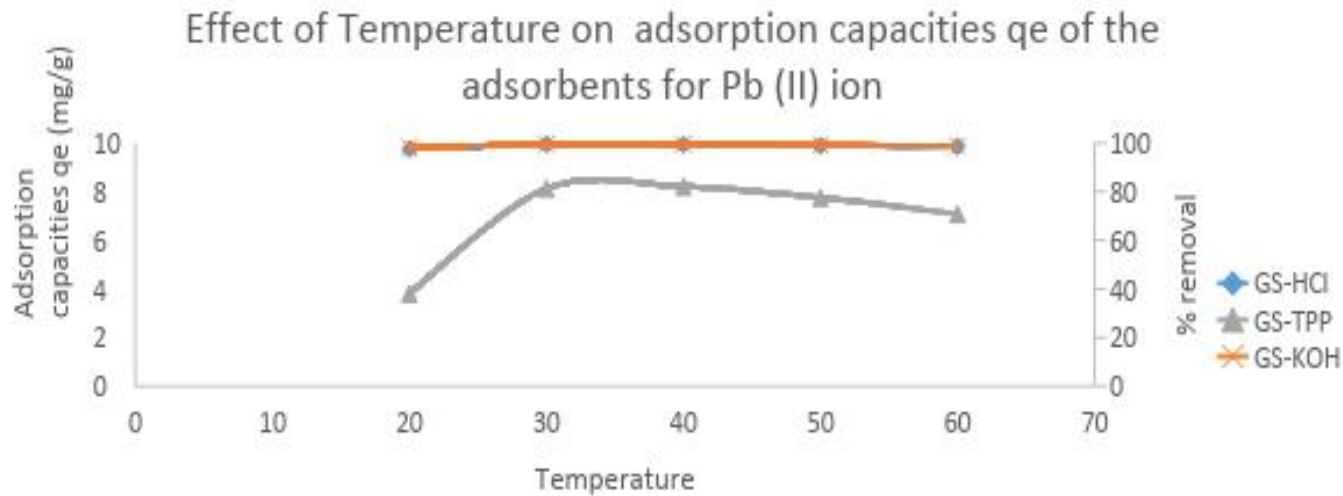


Fig. 5. Effect of temperature on adsorption of Pb (II) ions



there was little change on the adsorption capacities of the resins. This effect is attributed to the high surface area and metal ion retention capabilities of the carbonized samples [5]. However, there was noticeable effect on GS-TPP adsorbent with maximum adsorption occurring at 30 mins after which adsorption capacity and percentage removal was on the decline. It is evident from Fig. 4.14 that Pb (II) ion uptake unto the GS-TPP is rapid at the initial stage of contact time up till 30 mins after which desorption noticed may be attributed to the presence of weak electrostatic force [4].

**Effect of Adsorbent Dosage:** The effect of adsorbent dosage was carried out to know the maximum dosage of adsorbent required for the adsorption of Pb (II) ions. Increase in adsorbent dosage of GS-HCL<sup>C</sup>, and GS-KOH<sup>C</sup> increases the percentage adsorption of Pb<sup>2+</sup> as shown in Fig. 3, 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 0.15 g after which a negligible decrease in percentage of metal ion removal was observed. The adsorption capacity  $q_e$  was highest 44.0563 mg/g, 47.0320 mg/g, and 37.1717 mg/g at 0.05 g of adsorbent and decrease to 9.952 mg/g, 9.9587 mg/g and 8.1928 mg/g at 0.25 g of adsorbent for GS-HCL<sup>C</sup>, GS-KOH<sup>C</sup> and GS-TPP respectively.

**Effect of Metal Ion Concentration:** The study of varying concentration of Pb<sup>2+</sup> ion in solution show that the adsorption capacity increase with increasing concentration of lead ions as shown in figure above while the percentage of metal ion removal decreases with increase in initial metal ion concentration as illustrated in the figure above. Similar observations were made by Singh and Singh (2012) [10] on the adsorption of chromium ion using rice husk carbon.

**Effect of Temperature:** The temperature studies were carried out to determine its effect on the adsorption of Pb (II) ions. As can be seen from Fig. 5, temperature ranging from 20°C to 60°C has a negligible effect on the adsorption capacities of GS-HCL<sup>C</sup> and GS-KOH<sup>C</sup>. A similar observation was made in the research of Alemayehu et al. [11]. This is an excellent quality for any adsorbent to possess as the percentage removal efficiencies are as it peak averaging 99 % for both adsorbents. However, on the GS-TPP adsorbent temperature has a considerable effect.

The adsorption capacity and percentage metal ion removal increased sharply from 20°C to 40°C which was its optimum with adsorption capacity at 8.2063 mg/g after which steady decrease in adsorption capacity and percentage metal ion removal was observed up until final temperature of 60°C.

#### 4. CONCLUSION

This research study shows that groundnut shells through functionalization and carbonization process can be used as an excellent material for adsorption of lead from an aqueous medium. The results of the batch sorption experiments showed that the adsorbents were dependent on changes in pH, contact time, adsorbent dosage and metal ion concentration however, carbonized adsorbents GS-HCL<sup>C</sup> and GS-KOH<sup>C</sup> were independent of change in temperature while GS-TPP is temperature dependent. The high adsorption capacities and high percentage of lead ion removal indicates that the adsorbents are highly effective in removal of lead ions from contaminated water.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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