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### REMOVAL OF CHROMIUM AND NICKEL IN AQUEOUS SOLUTIONS USING GROUNDNUT SHELL POWDER AS AN ADSORBENT

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#### ABSTRACT

There is a rising genuine danger to the earth from unpredictable arrival of heavy metals into the wastewaters and soil from human modern practices. In this examination, the take-up of chromium and nickel, being among the significant toxins from our industries, by thermally and artificially activated groundnut shell powder was investigated. The impacts of various states of contact time, adsorbate dosage, mixing speed, pH and initial concentration on adsorption process were studied. The adsorbent materials were characterised by SEM, XRD and EDS. The adsorption procedure of chromium and nickel particles onto both the thermally and artificially activated groundnut shell powder is in great concurrence with the Langmuir adsorption isotherm and Freundlich adsorption isotherm.

#### INTRODUCTION

Heavy metals are of major concern nowadays as it is causing lot of ill effects on human beings as well as on the environment. "Heavy metal is defined as a metal of relatively high density or high relative atomic weight"[1]. Industrial activity, agricultural activity, improper waste disposal practices and other human activities will often alter the physical, thermal, chemical and biological quality of the ground water, surface water and soil leading to its contamination. Toxic heavy metal has become one of the major causes of concern for human kind because it is non bio-degradable, stable and tend to accumulate in plants and animals. Indiscriminate use of fertilizer, insecticide, pesticide and natural process such as weathering and erosion of crustal material increases the content of toxic metals in water and soil. The major sources of heavy metals in the surrounding environment include geological, manufacturing, agronomic, medicinal, domestic effluents, and atmospheric sources[2]. The presence of heavy metals in the earth's crust is relatively very less but are present in numerous aspects of life for example, they are used in thermometers, cars, disinfectants, ovens, plastics, solar panels, mobile phones, and computers. It is high time to protect our environment and ourselves to lead a better life. Groundnut shell contains more lignin content hence takes lot of time to degrade. Instead of dumping it can be used to treat heavy metals.

#### MATERIALS AND METHODS

##### Materials

Groundnut shells were collected from Krishna Raja Market, Bengaluru. It was then washed several times to remove all the dirt particles attached to it. They were sundried for 3 to 4 days to remove all the moisture content in it. After sun drying it was crushed with the help of mixer. It was later passed through 300micron sieve, the particles passing 300micron sieve were taken for the experimental analysis. The groundnut shell was activated both thermally and chemically.

##### Chemical Activation

A known amount of raw sample was taken in a silica crucible and was introduced into a muffle furnace at 600<sup>0</sup>C for 5 minutes after which they were poured from the crucible into ice water bath. The surplus water was removed and the carbonized sample obtained was washed with 0.1M HCL to remove the surface ash. It was further washed with distilled water to remove the residual acid. Far along it was dried in an oven for about 50 minutes at 100<sup>0</sup>C. After that, 5g of already carbonized sample was mixed with 5cm<sup>3</sup> of 1M H<sub>2</sub>SO<sub>4</sub> (activating agent). The sample was allowed to stand for 1 hour, after which it was introduced into a muffle furnace and heated for 5 minutes at



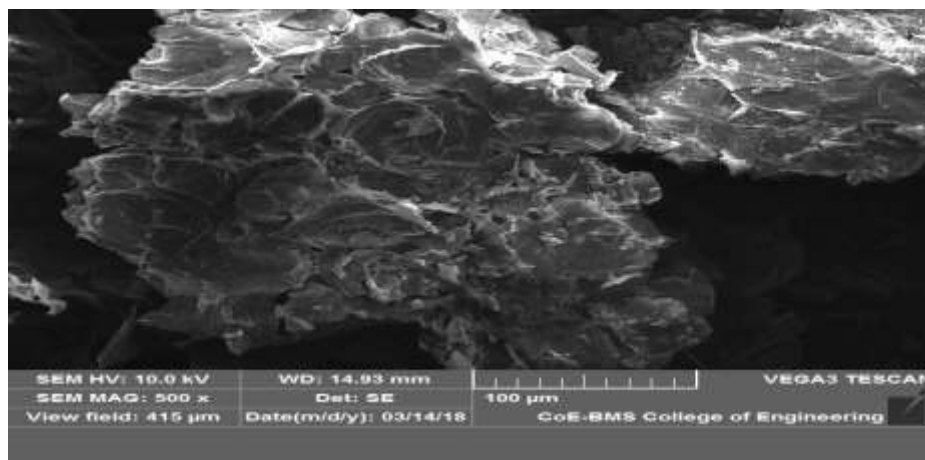
600°C. The activated sample was cooled with ice cold water, excess water was drained off and the sample dried out at room temperature [3].

### Thermal activation

A known amount of raw sample was taken in a silica crucible and was heated in the muffle furnace for 5 minutes at 600°C. The sample was then cooled with ice water bath and was dried in an oven for 50 minutes at 100°C[3].

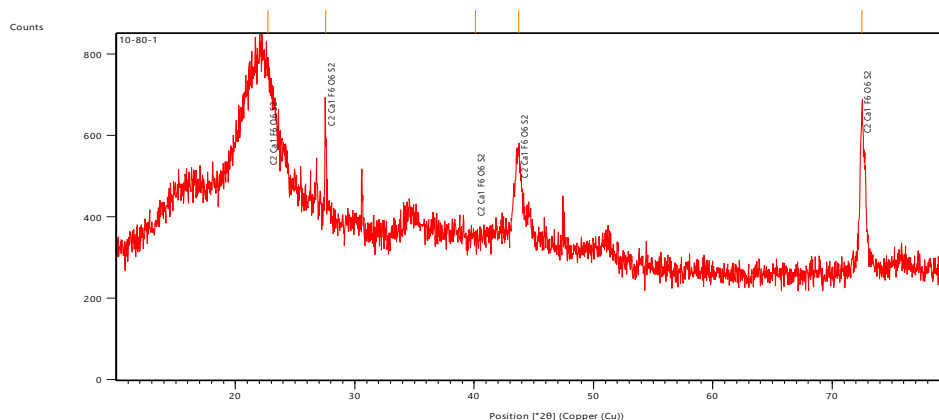
### Characterisation

Characterization of the groundnut shell powder was done using Scanning Electron Microscope(SEM), X –ray powder Diffraction (XRD), Energy Dispersive X –ray Spectroscopy (EDS).



*Figure 1: SEM image of groundnut shell powder*

The above image is obtained from SEM at a view field of 415 micro meter. It can be observed that there very less number of pores in the natural groundnut shell powder.



*Figure 2: XRD image of groundnut shell powder*

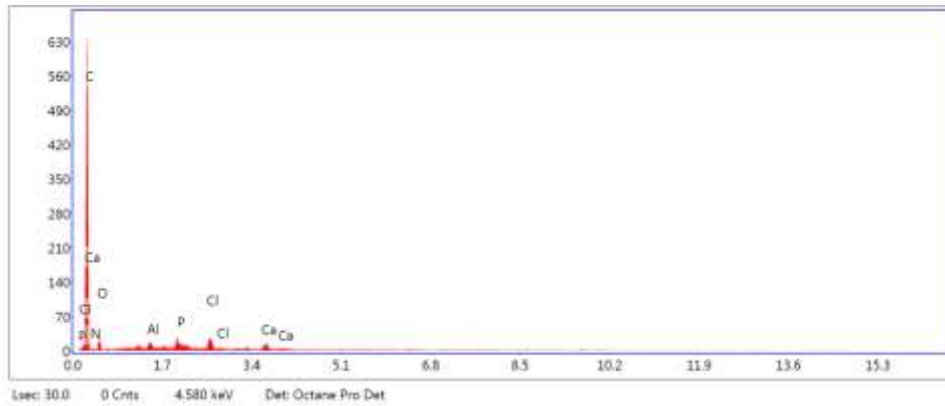
The figure 2 is obtained from XRD. It says that the natural groundnut shell powder used in the study contains compound - Calcium Bis(trifluoromethylsulfonate).





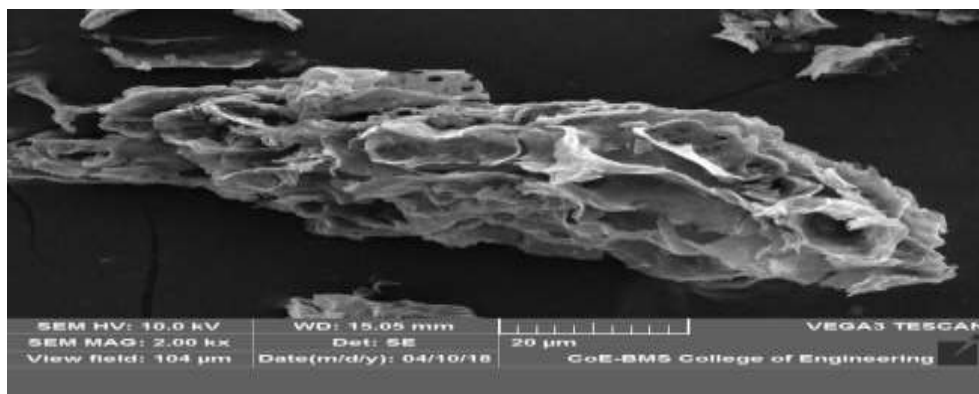
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The figure 5 is obtained from XRD. It says that the natural groundnut shell powder used in the study contains compounds viz Carbon Dioxide - Ii, Hp, Ht , Zeolite CNU-1, Calcium Carbonate – Iii



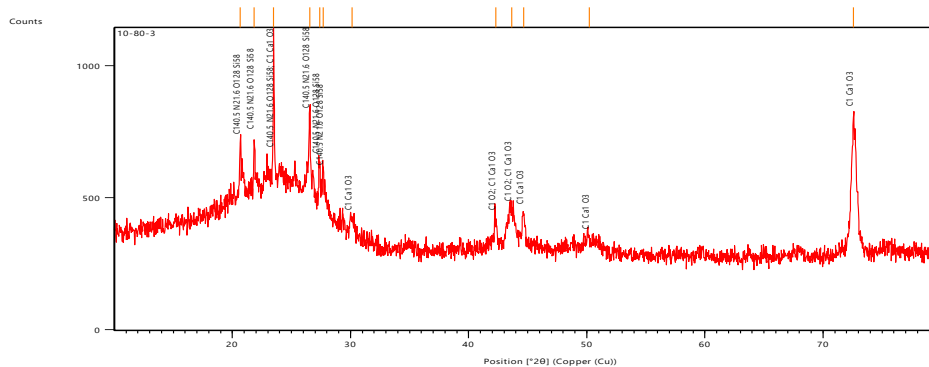
**Figure 6: EDS image of groundnut shell powder after thermal activation**

The above figure is obtained from EDS. It says that the groundnut shell powder used in the study contains elemental composition of carbon, oxygen and calcium, chlorine, phosphorous and nitrogen respectively after thermal activation.



**Figure 7: SEM image of groundnut shell powder after chemical activation**

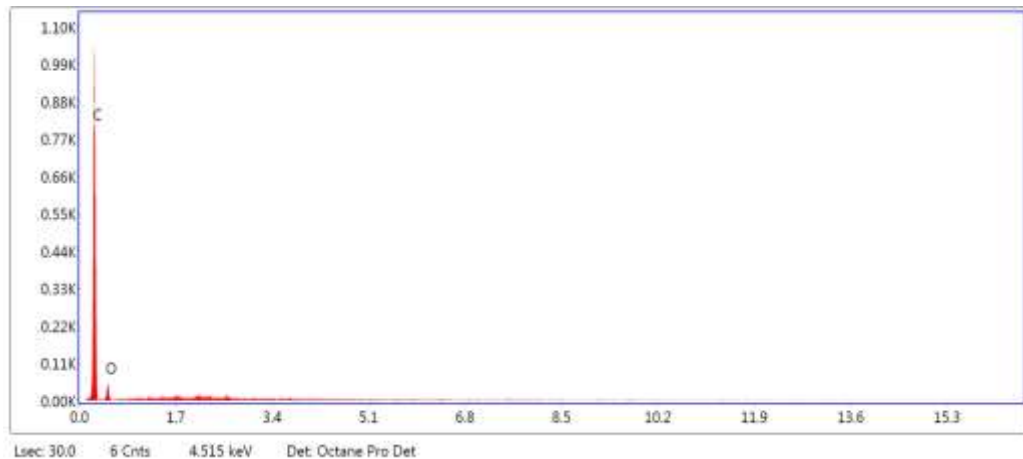
The above image is obtained from SEM at a view field of 104 micro meter. It can be observed that there are creation of large number of pores in the groundnut shell powder after chemical activation.



**Figure 8: XRD SEM image of groundnut shell powder after chemical activation**



The above figure 8 is obtained from XRD. It says that the natural groundnut shell powder used in the study contains compounds viz Defernite, Berlinite.



*Figure 9: EDS SEM image of groundnut shell powder after chemical activation*

The above figure is obtained from EDS. It says that the groundnut shell powder used in the study contains elemental composition of carbon and oxygen after chemical activation.

## PREPARATION OF SYNTHETIC SOLUTION

### *Chromium*

A stock solution of 1000mg/l of Chromium is prepared by dissolving 2.8287g of AR grade potassium dichromate in 1000ml distilled water. The solution is diluted as required to obtain standard solutions containing 10 mg/l of Chromium. The pH adjustments were carried out using Sulphuric acid(H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide(NaOH)[4].

### *Nickel*

Nickel solution was prepared by using AR Grade nickel ammonium sulphate. 6.7280 g of nickel ammonium sulphate was taken into a 1000 ml volumetric flask to this 5 ml of 1% HNO<sub>3</sub> was added to it immediately. Then the contents were made up to 1000 ml with double distilled water[5].

## RESULTS AND DISCUSSIONS

Batch adsorption experiments were carried out to find the optimum dosage, contact time, mixing speed(RPM), pH, initial concentration and the following results were obtained.

### **Effect of adsorbent dosage**

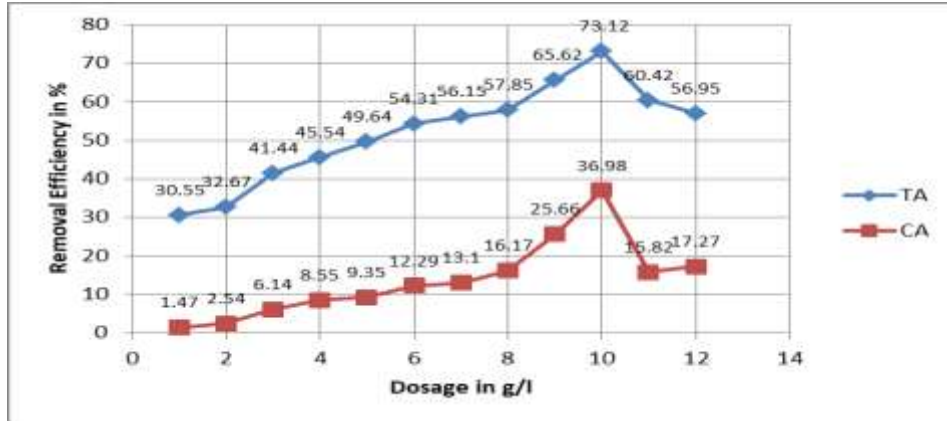


Figure 10: Effect of adsorbent dosage on chromium removal

The Effect of adsorbent dosage was studied and graph of percentage of chromium removal versus dosage was plotted as shown in the figure 10. From the above graph it can be observed that the maximum removal efficiency obtained was 73.12% and 36.98% for the dosage of 10g/l for both TA and CA respectively.

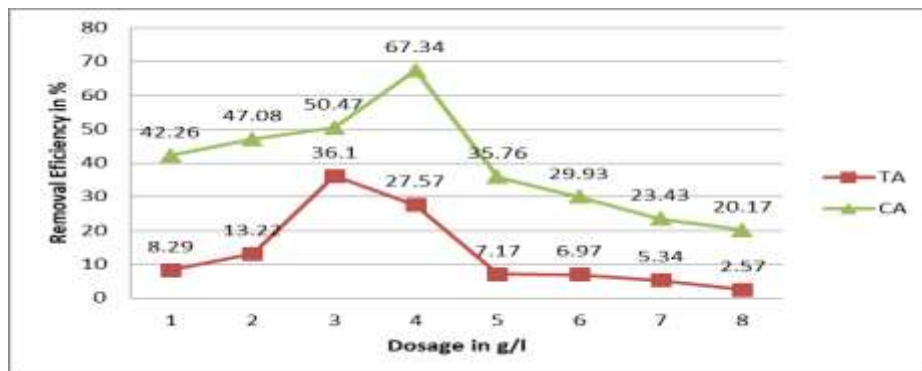


Figure 11: Effect of adsorbent dosage on nickel removal

The Effect of adsorbent dosage was studied and graph of percentage of nickel removal versus dosage was plotted as shown in the above figure. From the above graph it can be observed that the maximum removal efficiency obtained was 36.1% and 67.34% for the dosage of 3g/l and 4g/l for TA and CA respectively.

Effect of contact time

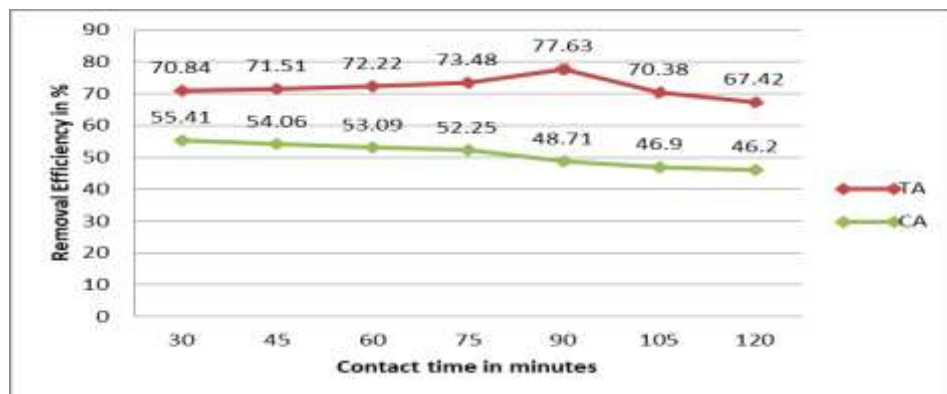


Figure 12: Effect of contact time on chromium removal



Effect of contact time was studied and graph of percentage of chromium removal versus contact time in minutes was plotted as shown in the above figure. From the above graph it can be observed that the maximum removal efficiency obtained was 77.63% and 55.41% for the contact time of 90 minutes and 30 minutes for TA and CA respectively.

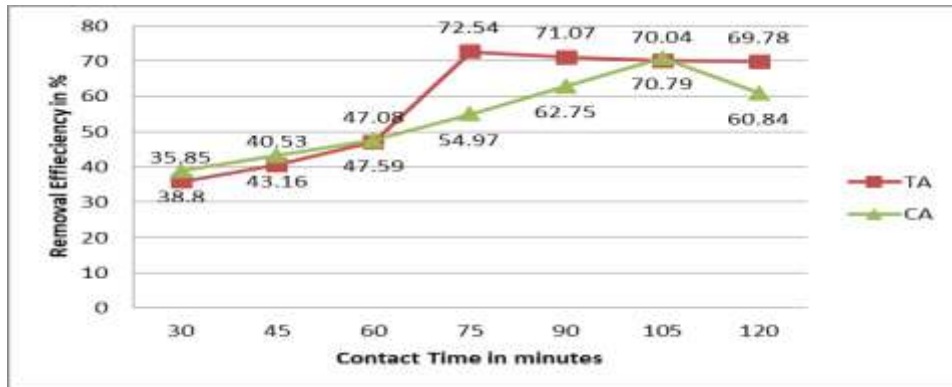


Figure 13: Effect of contact time on nickel removal

Effect of contact time was studied and graph of percentage of nickel removal versus contact time in minutes was plotted as shown in the above figure 13. From the above graph it can be observed that the maximum removal efficiency obtained was 72.54% and 70.09% for the contact time of 75 minutes and 105 minutes for TA and CA respectively.

**Effect of mixing speed**

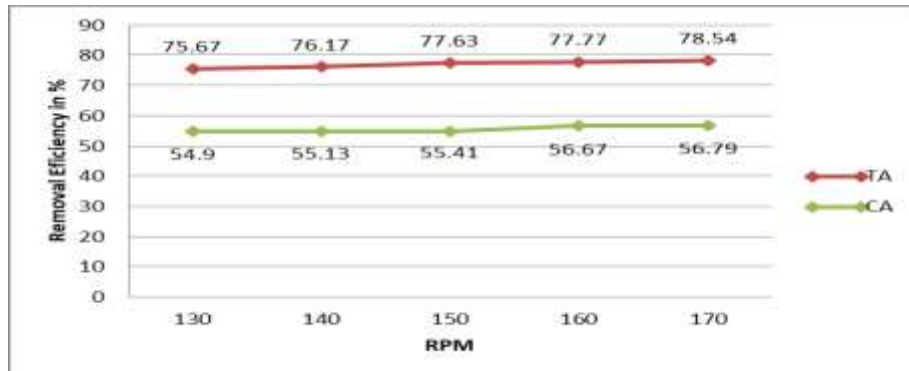


Figure 14: Effect of mixing speed on chromium removal

Effect of mixing time was studied and graph of percentage of chromium removal versus mixing speed was plotted as shown in the figure. From the above graph it can be observed that there is very slight variation in the removal efficiency.

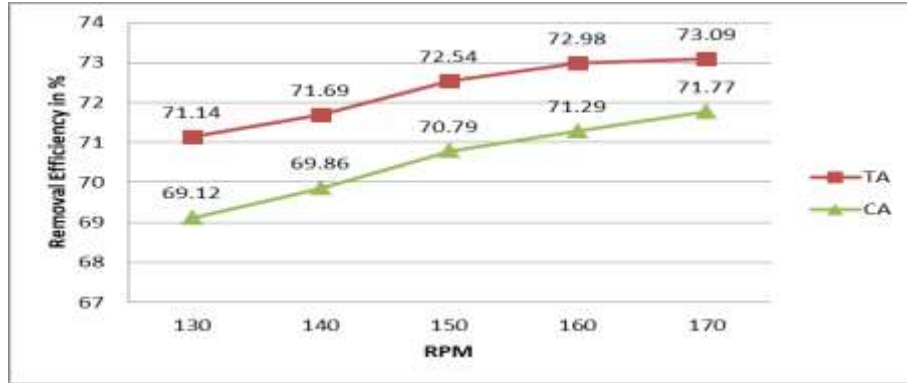


Figure 15: Effect of mixing speed on nickel removal

Effect of mixing time was studied and graph of percentage of chromium removal versus mixing speed was plotted as shown in the figure. From the above graph it can be observed that there is very minor variation in the removal efficiency.

Effect of pH

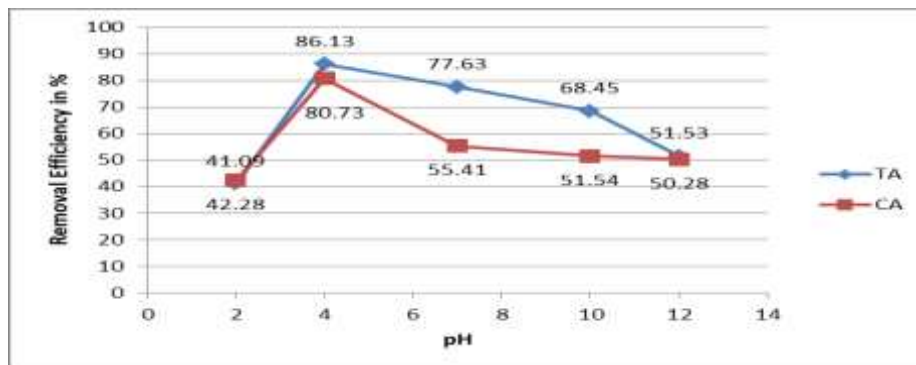


Figure 16: Effect of pH on chromium removal

Effect of pH was studied and graph of percentage of chromium removal versus pH was plotted as shown in the figure 16. From the above graph it can be observed that the maximum removal efficiency obtained was 86.13% and 80.73% for the pH of 4 for both TA and CA respectively

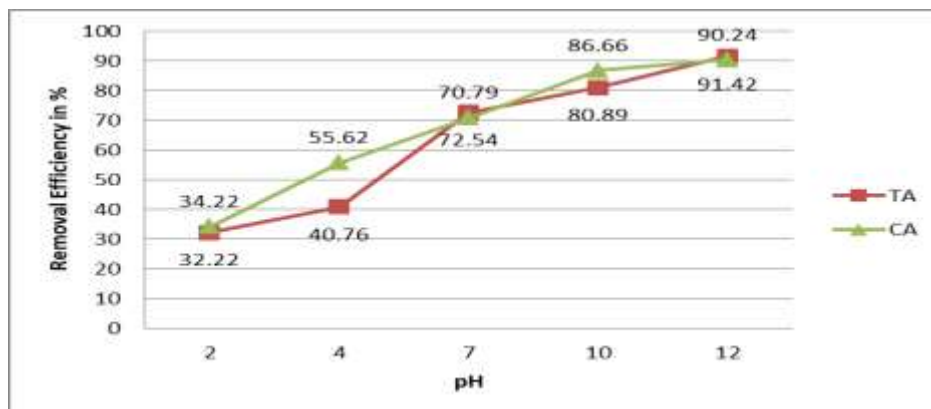


Figure 17: Effect of pH on nickel removal





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Effect of pH was studied and graph of percentage of nickel removal versus pH was plotted as shown in the above figure. From the above graph it can be observed that the maximum removal efficiency obtained was 90.24% and 91.42% for the pH of 12 for both TA and CA respectively

### Effect of initial concentration

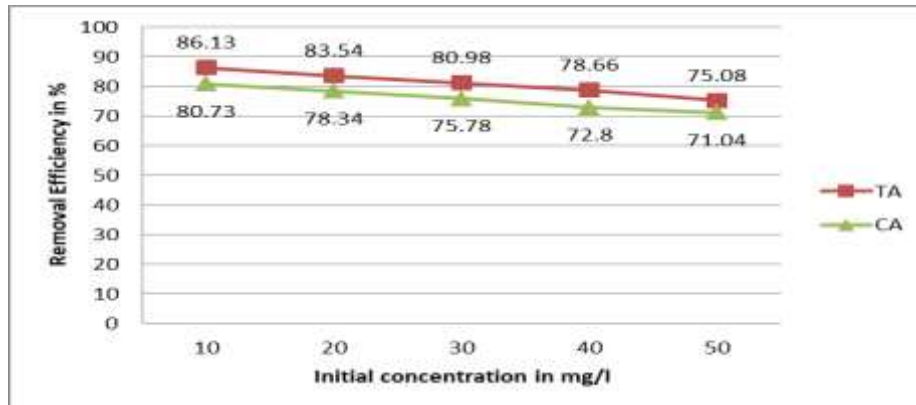


Figure 18: Effect of initial concentration on chromium removal

Effect of initial concentration was studied and graph of percentage of chromium removal versus initial concentration was plotted as shown in the above figure. From the above graph it can be observed that as the initial concentration is increasing the removal efficiency is decreasing.

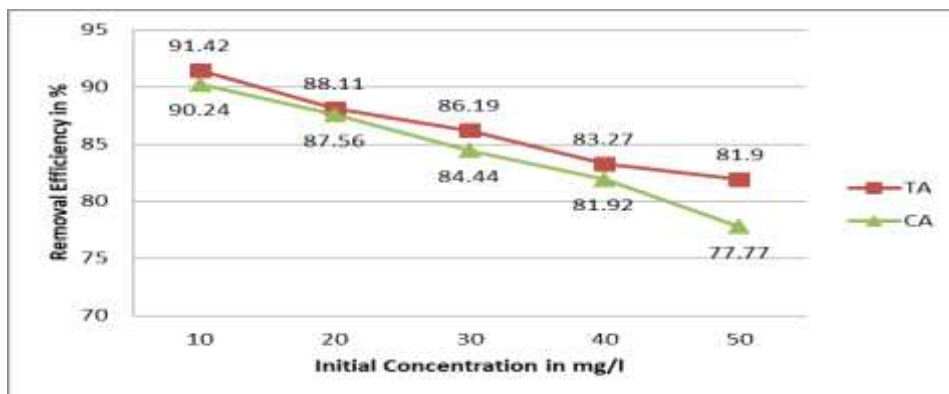


Figure 19: Effect of initial concentration on nickel removal

Effect of initial concentration was studied and graph of percentage of nickel removal versus initial concentration was plotted as shown in the figure 19. From the above graph it can be observed that as the initial concentration is increasing the removal efficiency is decreasing.

## ADSORPTION ISOTHERMS

### LANGMUIR ADSORPTION ISOTHERM

Langmuir condition was connected for adsorption harmony for both TA and CA. The Langmuir treatment depends on the assumption that greatest adsorption corresponds to an immersed monolayer of adsorbate particles on the adsorbent surface, that the vitality of adsorption is consistent, and that there is no transmigration of adsorbate in the plane of the surface.

$$C_e/q_e = C_e/S_m + 1/K_L S_m \dots \dots \dots (1)$$

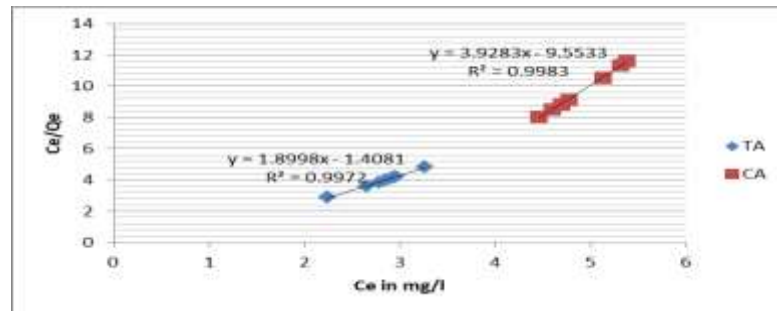


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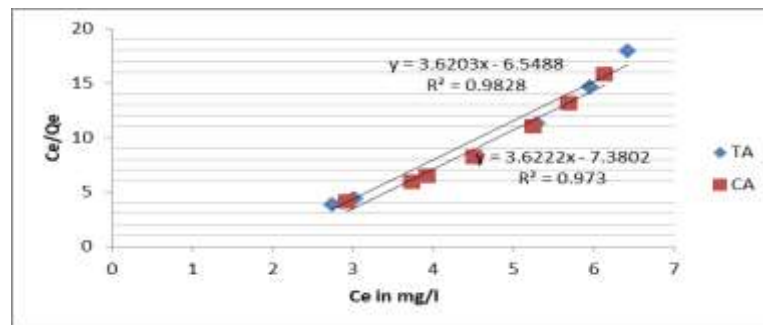
Where,  $C_e$  is the equilibrium concentration in mg/l,  $q_e$  is the amount adsorbed at equilibrium in mg/g,  $S_m$  and  $K_L$  are Langmuir constants. The linear plots of  $C_e/q_e$  vs  $C_e$  shows that the adsorption obeys Langmuir adsorption model for both TA and CA[6]. The parameters of the Langmuir adsorption isotherm are mentioned in the table below.

*Table 1 : parameters of Langmuir adsorption model.*

HEAVY METALS	GROUNDNUT SHELL POWDER	1/ $S_m$	1/ $K_L S_m$	$R^2$
CHROMIUM	TA	1.8998	1.4081	0.9972
	CA	3.9283	9.5533	0.9983
NICKEL	TA	3.6203	6.5488	0.9828
	CA	3.6222	7.3802	0.9730



*Figure 20: Langmuir Adsorption plot for Chromium removal*



*Figure 21: Langmuir Adsorption plot for Nickel removal*

### **FREUNDLICH ADSORPTION ISOTHERM**

The Freundlich condition was additionally connected for the adsorption. The Freundlich condition is fundamentally exact however is regularly valuable as a methods for information portrayal. For most of the data it harmonizes great with the Langmuir condition and exploratory information over a direct scope of adsorbate concentrations. The Freundlich isotherm is represented by the equation,

$$\log \frac{q_e}{K_F} = \frac{1}{n} \log C_e + \log K_F \quad (2)$$

where,  $C_e$  is the equilibrium concentration in mg/l,  $q_e$  is the amount adsorbed at equilibrium in mg/g,  $K_F$  is the Freundlich constant related to the adsorption capacity,  $1/n$  is related to the adsorption intensity. The linear plots of  $\log C_e$  vs  $\log q_e$  shows that the adsorption obeys Freundlich adsorption model for both TA and CA[6]. The parameters of the Freundlich adsorption isotherm are mentioned in the table below.



Table 2 : parameters of Freundlich adsorption model

HEAVY METALS	GROUNDNUT SHELL POWDER	1/n	log KF	R <sup>2</sup>
CHROMIUM	TA	2.6822	0.0611	0.9912
	CA	1.024	0.3887	0.9981
NICKEL	TA	1.2386	0.2825	0.9854
	CA	1.1857	0.3228	0.9644

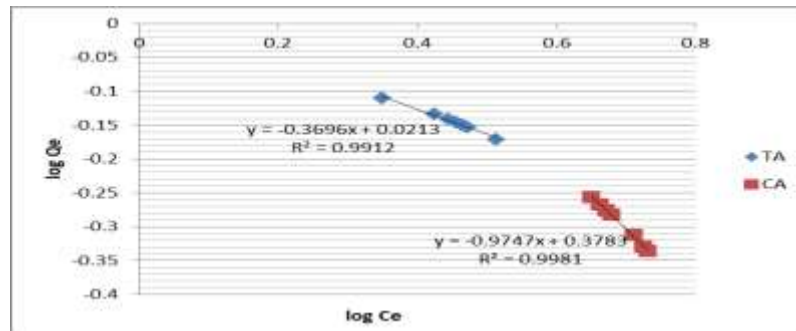


Figure 22: Freundlich Adsorption plot for Chromium removal

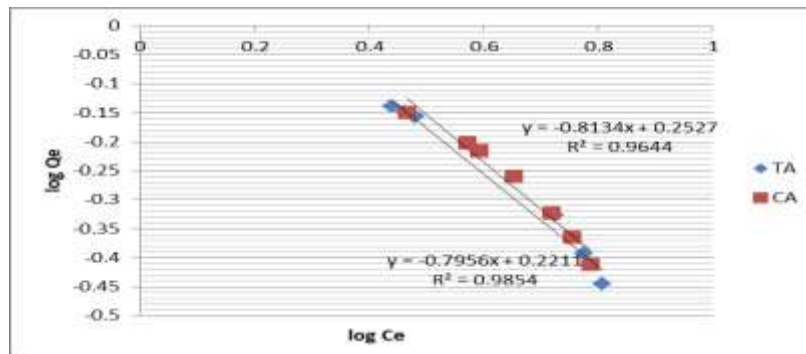


Figure 23: Freundlich Adsorption plot for Nickel removal

**CONCLUSION**

- The results of varied adsorbent dose showed that the optimum adsorbent dose were found to be 10 g/l for both thermally and chemically activated groundnut shell powder for chromium and 3 g/l and 4 g/l for thermally and chemically activated groundnut shell powder for nickel.
- The results of the optimum contact time were found to be to be 90 and 30 minutes for thermally and chemically activated groundnut shell powder for chromium and 75 and 105 minutes for thermally and chemically activated groundnut shell powder for nickel.
- The results of varied rotation speed showed that for both the metals(chromium and nickel) the removal efficiency was increasing as the rotation speed was increased for both thermally and chemically activated groundnut shell powder.
- The results of optimum pH were found to be 4 for both thermally and chemically activated groundnut shell powder for chromium and 12 for both thermally and chemically activated groundnut shell powder for nickel.
- The results of initial concentration were found to be, as the initial concentration is increased the removal efficiency was decreased for both the metals(chromium and nickel).



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- The correlation coefficients for the linear regression fits of the Langmuir plots for chromium and nickel were found to be 0.9972, 0.9828 for thermally activated groundnut shell powder and 0.9983, 0.973 for chemically activated groundnut shell powder.
- The correlation coefficients for the Freundlich plots for chromium and nickel were found to be 0.9912, 0.9854 for thermally activated groundnut shell powder and 0.9981, 0.9644 for chemically activated groundnut shell powder.

### ACKNOWLEDGEMENTS

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