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Research Article

## Sorption Ability of Modified Fruit Nut Shells in the Removal of Co (II) ions from Aqueous Solutions

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### Abstract:

The present work deals with the efficiency of modified *Terminalia catappa seed shell (TCSS)*, an agricultural waste, for the removal of Co(II) from aqueous solutions. Three methods of modifications of the sorbent material have been done and the experiments were carried out by employing batch equilibration method. The influences of variable parameters viz., particle sizes and adsorbent dosages of the sorbent material, agitation time, initial concentrations of the sorbate solutions, pH, cations, anions, co-ions and temperatures have been studied. The surface characteristic study of the modified TCSS has been supported by FT-IR, SEM and EDAX techniques. The linearity of the isothermal plots suggests that the Co(II) – TCSS system obeys Langmuir and Freundlich adsorption models.

**Keywords:** adsorption, *Terminalia catappa*, modification, characterization, parameters

### 1.0 Introduction:

Heavy metal contamination in the aqueous waste streams of many industries, such as metal plating, mining operations, tanneries etc are gaining much concern in recent times towards remedial approach. Some of the metals which are associated with these activities are cadmium, chromium, cobalt, lead, copper and mercury. Heavy metals are non biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Susan *etal.*, 1999, Netzer and Hughes, 1984, Gomez-Lahoz *etal.*, 1993). Cobalt, a natural element present in certain ores of the Earth's crust, is essential for life in trace amounts. Important natural sources of cobalt in the environment are soil, dust and sea water. It exists in the form of various salts. Pure cobalt is an odourless, steel-grey, shiny, hard metal. Every one of us is exposed to low levels of cobalt in air, water and food. Cobalt has both beneficial and harmful effects on health. The metal and its salts are used in nuclear medicine, enamels and semiconductors, grinding wheels, painting on glass and porcelain, hygrometers and electroplating, as a foam stabilizer in beer, in vitamin B12 manufacture, as a drier for lacquers, varnishes and paints, and as a catalyst for organic

chemical reactions (Rengaraj and Seung- Hyeon Moon, 2002).

Cobalt is one of the priority pollutants in aqueous waste discharges. Cobalt containing compounds are widely used in many industries such as mining, metallurgical, paints, pigments and electronics. Exposure to higher concentrations of the metal may cause paralysis, diarrhea, low blood pressure, lung irritation and bone defects. The tolerance limit in potable water has been fixed as 0.05mg/L (Neha Gupta *etal.*, 2011). Many conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, co-precipitation and adsorption have been employed for the removal of heavy metals in wastewater treatment (EduInam *etal.*, 2012). Amongst all the removal techniques, adsorption is one of the most popular and effective process for the removal of heavy metals from wastewater.

The adsorption process offers flexibility in design and operation and in many cases produces treated effluent suitable for reuse, free of colour and odour. In addition, as adsorption is a reversible process, regeneration of the adsorbent adds to the economy of the operation. Adsorption is the

process of accumulating substances that are in solution on a suitable interface. It is a surface phenomenon, which involves a mass transfer operation, in that a constituent in the liquid phase is transferred to the solid phase. Adsorbate is the substance that is removed from the liquid phase at the interface and adsorbent is the solid phase onto which the adsorbate accumulates. The adsorption process takes place in different steps (1) bulk solution transfer (2) film diffusion transfer (3) pore transport and (4) adsorption. Bulk solution transfer involves the movement of the material to be adsorbed through the bulk liquid to the boundary layer of fixed film of liquid surrounding the adsorbent. Film diffusion transport involves the transport by diffusion of the material to be adsorbed through the stagnant liquid film to the entrance of the pores of the adsorbent. Pore transport involves the transport of material to be adsorbed through the pores by a combination of molecular diffusion through the pore liquid and/or by diffusion along the surface of the adsorbent. Adsorption involves the attachment of the material to be adsorbed onto adsorbent at available adsorption sites (Ira N. Levine et al 1995).

Naturally occurring waste materials have been effectively employed in the sorption method due to their abundance, cheap, biodegradability and reusability characteristics. Therefore, they serve a better choice to commercially available activated carbons, which is highly expensive and pose greater disposable /regeneration problems after use. Some waste materials which have been reported are peat (Coupal and Spiff, 1999, Brown *etal .*, 2000, Ho *etal .*, 1996), living and death biomass (An *etal .*, 2001, Volesky and Holan, 1995, Rae and Gibb, 2003), clay and related minerals (Angove *etal .*, 1999, Chen and Lu, 2008, Hayes and Leckie, 1987). In view of abundant availability of these naturally occurring materials, a systematic study to assess the potential use of modified *Terminalia catappa* seed shell powder for the removal of Co(II) from aqueous solutions is carried out in this paper.

The adsorbent used in this study is almond tree biomass. The almond tree belongs to the family called Combretaceae (Combretum family). The botanical name of the tropical almond tree is *Terminalia catappa* L (Enemose Edith and Osakwe, 2012). So far, no reports are available for the removal of Co(II) ions using TCSS powder and thence, this paper is the first study of its kind.

## 2.0 Materials and Methods:

Fruit seed shells of *Terminalia catappa* were collected from various localities in Coimbatore, washed well with distilled water and sun dried. Then the dried seed shells were ground in a laboratory blender and sorted into different particle sizes viz., 0.71 mm, 0.42 mm, 0.30 mm, 0.21 mm and 0.18 mm using standard test sieves. The varied sizes of TCSS were treated with HCl and citric acid (CA) to modify the nature of the sorbent materials. The surface characteristics of modified adsorbents were studied using FT-IR, SEM and EDAX. Experiments were conducted to estimate the influence of varied particle sizes and dosages of the TCSS powder, prescribed agitation time intervals between the sorbent- sorbate interface, initial Co(II) concentrations, solution pH, interference of cations, anions, co-ions and effect of solution temperatures in order to establish the optimum experimental conditions for adsorption process. The stock solution of Co(II) ions were prepared from CoCl<sub>2</sub>.6H<sub>2</sub>O salt of analaR grade using Double Distilled water. Aliquots of the adsorbate solutions of varying Co(II) ions concentrations 2-14 ppm: 2ppm intervals were prepared from the stock solution (1000 mg/L). The experiments were performed in 250ml Erlenmeyer flasks for the mentioned particle sizes and dosages of TCSS powder varying between 50-200mg: 50mg interval for the Co(II) ion concentrations. The flasks with the contents were agitated at preset time intervals using mechanical shaker (setup given in fig 1). The other experimentally verified factors are the pH environments varying between 3 and 11, cationic & anionic influences of Na<sup>+</sup>, Mg<sup>+</sup>, and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> respectively, Cu<sup>2+</sup>, Cr<sup>6+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> ions as influential ions, temperature ranges from 20<sup>0</sup>C to 60<sup>0</sup>C:10<sup>0</sup>C intervals (setup given in fig 2). The filtered samples were complexed to bluish-green colour using ammonium thiocyanate (analaR grade) and the residual concentrations were analyzed at a λ<sub>max</sub> of 630 nm in UV- Visible spectrophotometer (Lab India make). The quantity of Co(II) ions adsorbed onto the adsorbent at the time of equilibrium (q<sub>e</sub>) was calculated using the following expression:

$$q_e = (C_o - C_e) V/m \text{ ----- (1)}$$

where C<sub>o</sub> and C<sub>e</sub> are the initial and equilibrium concentrations (mg/L) of Co(II) ions in solution. V is volume (L) of solution and m is weight of adsorbent (g) taken for experiment.



**Fig 1: Experimental setup for batch studies**



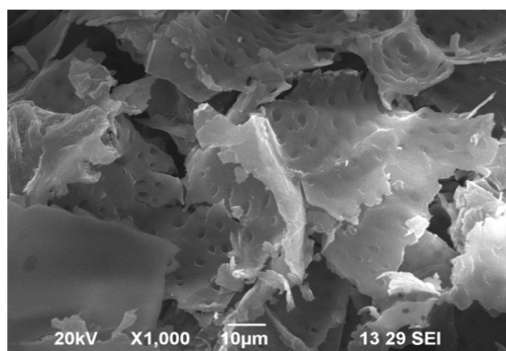
**Fig 2: Incubator Shaker for Temperature studies**

proven and accepted to be a powerful tool for the study of biomass samples (Fatemeh Kafshgari *et al.*, 2013). The inference from the spectra of SEM and EDAX supported the citric acid modification. Therefore, FTIR spectra were recorded for unloaded and loaded citric acid modified TCSS in the range of 400-4000 $\text{cm}^{-1}$  and are presented in Fig 5a and 5b respectively. It is observed that the most characteristic change had occurred in the range of 1700- 1737  $\text{cm}^{-1}$ . The band centered at 1731  $\text{cm}^{-1}$  is ascribed to the stretching vibrations of carboxyl group (C=O in carboxylic acid group) on the edges of layer planes or to the conjugated carbonyl groups (Tao and Xiaoqin *et al.*, 2008). Peaks at 1350-1200  $\text{cm}^{-1}$  band interval may be due to the vibration of C-N peptidic bond of proteins present in the seed shell moiety. The strong band observed at 1041.5  $\text{cm}^{-1}$  indicates the C-OH stretching vibrations (Stuart, 1996). Thus, it is observed that the IR-spectral analysis indicates the presence of ionizable functional groups and their ionization leaves behind vacant sites which might have been replaced by Co(II) ions.

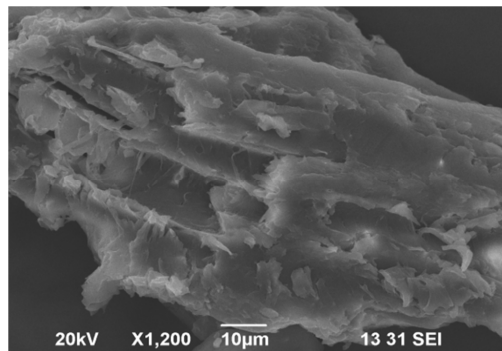
### 3.0 Results and Discussion:

#### 3.1 Adsorption mechanism of Co(II) on TCSS Powder

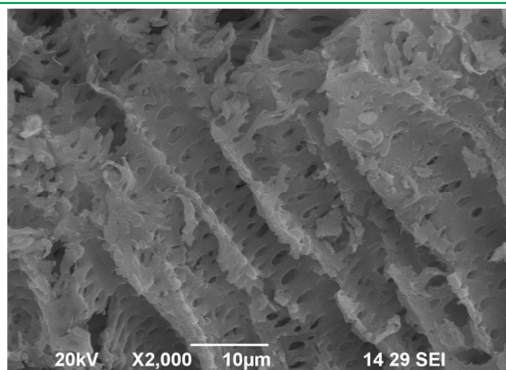
Scanning Electron Microscopy was used for characterizing the surface morphology and structure of the adsorbent material. Over the adsorption period, the morphology of the treated seed shells had undergone a remarkable physical change. The integrated and cluster arrangements for unloaded and loaded samples are presented in figures 3a, 3c and 3b, 3d respectively which clearly indicate that the metal ion had adhered to the surface of the adsorbent. This can be further confirmed by the less and smaller pores on the surface of the loaded sorbents that could have been occupied by metal ions (Cong Liu *et al.*, 2012). The EDAX spectra were recorded to analyze the elemental constitution qualitatively for the modified adsorbent. Figures 4a, 4b, 4c and 4d depict the EDAX spectra for unloaded as well as Co(II) loaded samples. The presence of cobalt peaks in figures 4b and 4d confirms the adsorption of cobalt ions by modified seed shells. Fourier Transform Infrared Spectroscopy (FTIR) has been



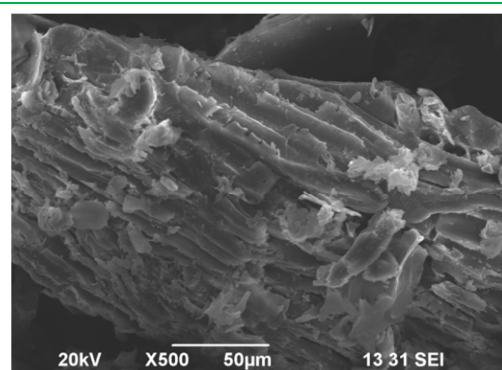
**Fig 3a: SEM of unloaded citric acid modified seed shell**



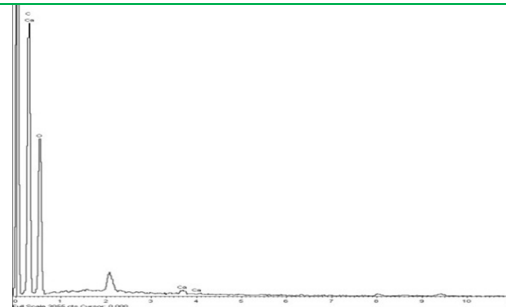
**Fig 1b: SEM of loaded citric acid modified seed shell**



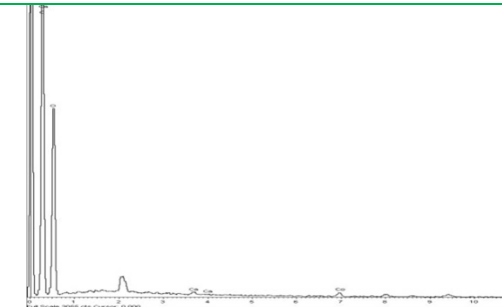
**Fig 3c: SEM of unloaded HCl modified seed shell**



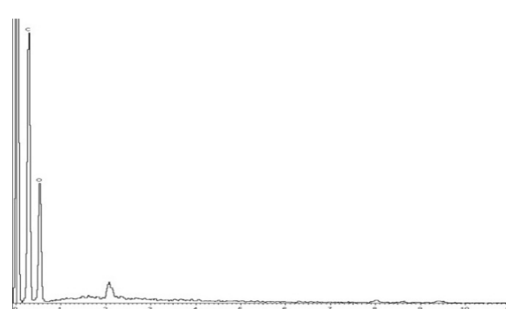
**Fig 3d: SEM of loaded HCl modified seed shell**



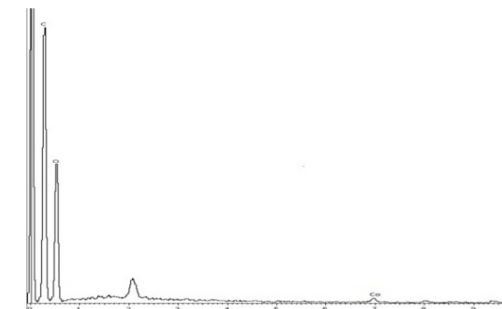
**Fig 4(a): EDAX of unloaded citric acid Modified seed shell**



**Fig 4(b): EDAX of loaded citric acid modified seed shell**



**Fig 4(c): EDAX of unloaded HCl modified seed shell**



**Fig 4(d): EDAX of loaded HCl modified seed shell**

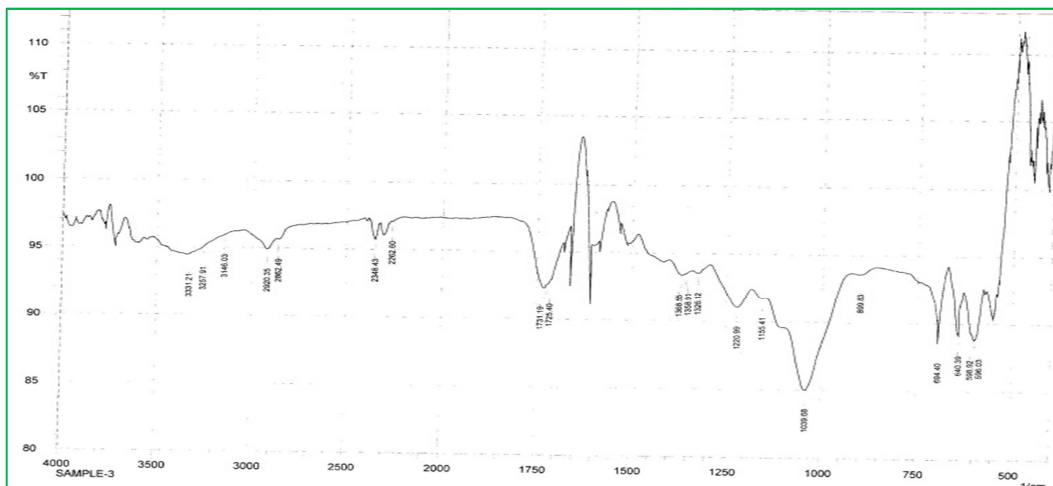


Figure 5a: IR Spectrum of unloaded citric acid modified seed shell

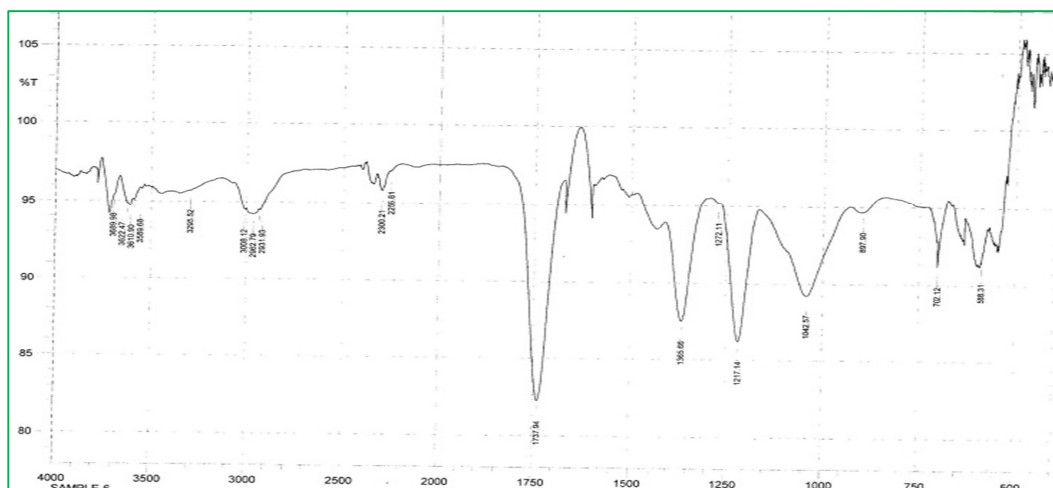


Figure 5b: IR Spectrum of loaded citric acid modified seed shell

**3.2 Effect of Agitation Time**

Batch experimental results for an initial concentration of 8ppm Co(II) ions at varying time intervals for the two modified adsorbent material are shown in fig 6. The smooth continuous steep rise in the curves represents increased uptake of Co(II) ions at preset time intervals (3-15 minutes: 3 minutes interval). After 9 minutes, a dip in the curve indicates that the systems tend towards saturation and had attained equilibrium at 9 minutes. Of the two modified adsorbent material, TCSS-CA registered higher amount adsorbed ( $q_e = 3.4$  mg/g) compared to HCl modification. Hence, the study of other variable parameters were restricted to Co(II)- TCSS-CA system only.

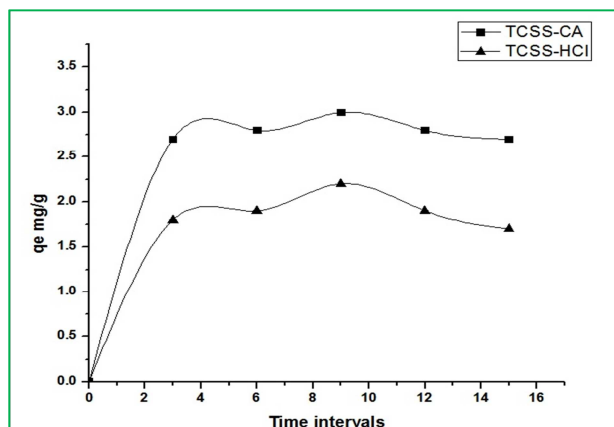


Fig 6: Effect of agitation time on the removal Co(II) by TCSS

### 3.2 Effect of Particle Size

Adsorbent particle size has a significant influence on the kinetics of sorption due to change in number of adsorption sites. The removal of the Co(II) ions at different particle sizes of TCSS-CA viz., 0.71 mm, 0.42 mm, 0.30 mm, 0.21 mm and 0.18 mm is depicted in fig 5. The uptake of Co(II) ions increased with a decrease in particle size (ie) from 0.71mm-0.18mm. Surface area of the adsorbent is an important parameter for adsorption. Smaller the particle size, greater the surface area per unit weight of the adsorbent (Montanher *et al.*, 2005). Interaction of metal ion is found to be more with the adsorbent possessing higher surface area and hence enhanced amount of Co(II) ions was adsorbed for the smaller particle size of 0.18mm ( $q_e = 3.4 \text{ mg/g}$ ) as evident from the smooth steep maximum curve obtained at 0.18 mm particle size (Fig 7). This shows the enhancement in the amount adsorbed with respect to time compared to other particle sizes employed.

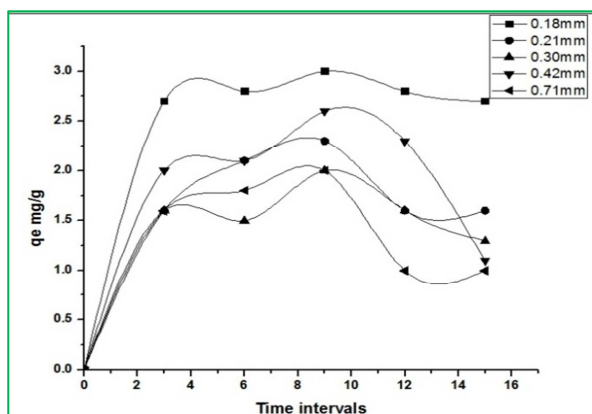


Fig 7: Effect of particle size on the removal Co(II) by TCSS-CA

### 3.3 Effect of Adsorbent Dosage

Removal of Co(II) were investigated at four different adsorbent dosages (50- 200mg:50mg) the clear sharp rise in the curve for 100mg of TCSS-CA sorbent represents the maximum sorption of Co(II) ions, the other dose curves being entangled. Decreased sorption at higher dosages (150 and 200mg) can be attributed to the fact that agglomeration of the fine size (0.18mm) had occurred. This shall be due to a decrease in available sorbent surface area per unit mass which is caused by overlapping and aggregation of adsorption sites (Hanim Awad and Paramalingam, 2011). Hence, an optimum dose of 100 mg was fixed for all experiments.

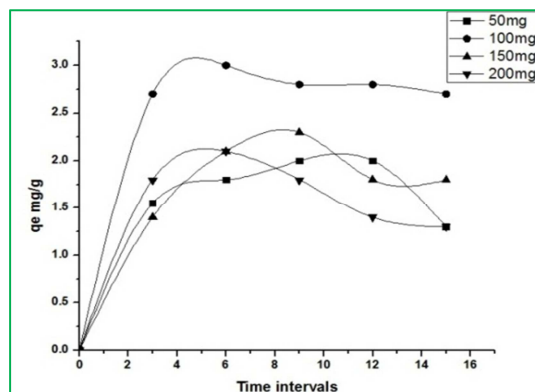


Fig 8: Effect of adsorbent dosage on the removal Co(II) by TCSS-CA

### 3.4 Effect of pH

Metal sorption is linked with pH and the effect of pH on the solution is an important controlling factor in the sorption experiment. The acidity of the medium affects the competition ability of hydrogen ions with metal ions towards the active sites on the adsorption surface. It also influences ionization of functional groups on the adsorbent surface and chemical speciation of metal ions. In order to optimize the pH for maximum removal efficiency, experiments were conducted at varying pH ranges from 3-11. The inverted parabolic curve with maximum removal of Co(II) (83.8%) at pH 7 is depicted in fig 9. There is absence of marked percentage removal of Co(II) at acidic and alkaline pH values. This can be due to the rapid changes in protonated and unprotonated forms of the surface sites of the sorbent. Also, it can be interpreted that the adsorption rate for  $\text{pH} \geq 9$  experience a decline, because of the hydroxide ion forming complexes with the Co(II) ions leading to suppression of the sorption (Ajmal *et al.*, 2000).

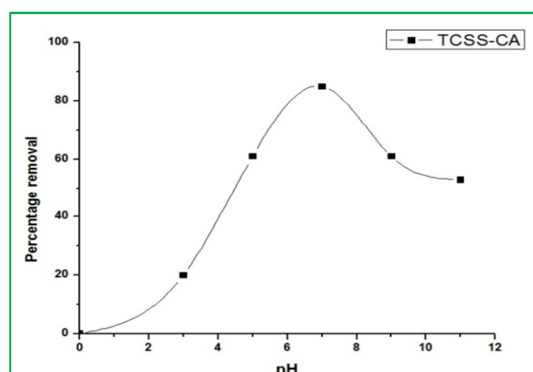


Fig 9: Effect of pH on the removal Co(II) by TCSS-CA Effect of cations and anions

Industrial wastewater discharges may contain cations and anions which may interfere in the removal of heavy metal ions. Thence, the influence

of these ions was studied and the results are depicted in fig 10. Of the cations( $Mg^{2+}$  and  $Na^+$ ), the removal of Co(II) diminished from 83% to 35% at increasing concentrations of  $Mg^{2+}$  ions against the influence of  $Na^+$  ions, where the percentage removal is least inhibited i.e., 85% to 77%. This is in agreement with other studies that showed stronger inhibitions with the ions of higher valence than that of lower ones (Emine Malkoc, 2006). Of the anions, ( $Cl^-$  and  $NO_3^-$ ), while the concentration of  $Cl^-$  increased, the removal of Co(II) ions decreased from 83% to 64% against the influence of  $NO_3^-$  ions, where the percentage removal is least inhibited (i.e.) 83% to 74%.

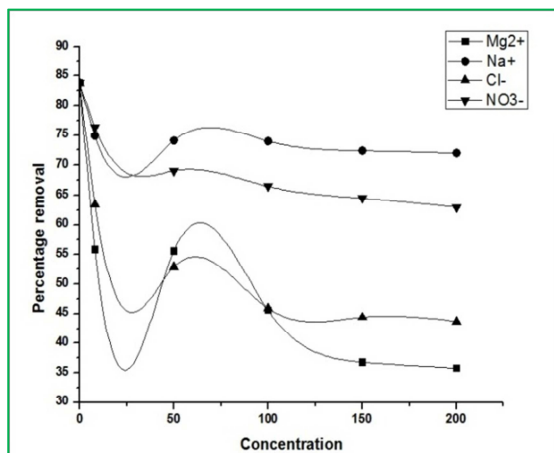


Fig 10: Effect of cations and anions on Co(II) removal by TCSS-CA

### 3.5 Effect of Co-ions

Study of the influence of co-ions on the removal of a specific metal ion becomes relevant when selective adsorption of metal ions occurs from the aqueous solutions. The study on the influence of co-ions in the removal of Co(II) ions gives an insight into the sorption capacity of TCSS-CA. The percentage removal values of 8ppm Co(II) in the presence of an equal concentration of influential ions is tabulated in table 1 and the data is plotted in fig.11. The inhibition characteristics was found to decrease in the order  $Ni^{2+} < Pb^{2+} < Cd^{2+} < Cr^{6+} < Mn^{2+} < Cu^{2+}$ . It is obvious from the figure, where the dip in the curve for Cu(II) ions suggests that the Cu(II) ions are preferentially adsorbed onto the adsorbent surface rather than Co(II) ions. The removal of Co(II) ions registered a decrease at higher environments of co-ions.

Table 1: Percentage removal of Co(II) on TCSS-CA in presence of co-ions

Adsorbent	Percentage Removal						
	Co <sup>2+</sup> in the absence of co-ions	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Mn <sup>2+</sup>	Cr <sup>6+</sup>
TCSS-CA	83	75	61	63	42	54	55

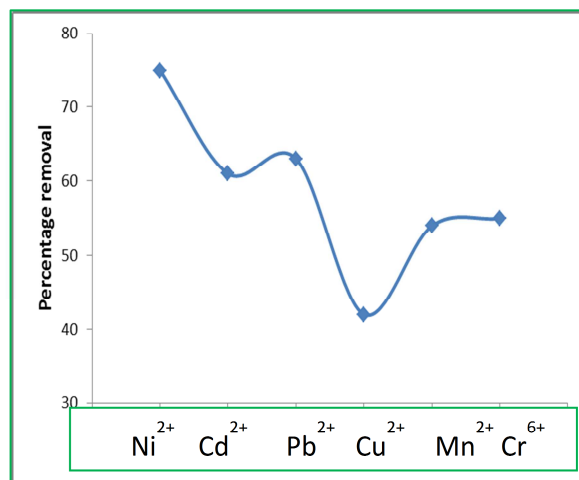


Fig 11: Effect of Co-ions on Co(II) removal by TCSS-CA

### 3.6 Effect of Temperature:

Temperature has an important effect on the process of adsorption. The percentage removal of Co(II) as a function of temperature (293K to 333K) are presented in figure 12. The smooth steep maximum increase in the curve at 303K and further decrease at high temperatures suggests that maximum percentage removal (83%) had occurred at room temperature. The decrease in percentage values with rise in temperatures may be due to the desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate molecules causing desorption (Ira N. Levine).

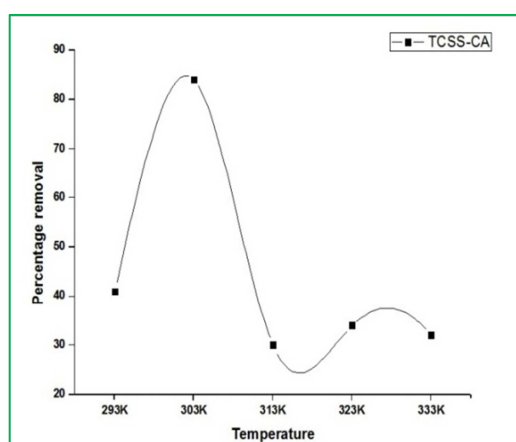


Fig 12: Effect of temperature on Co(II) removal by TCSS-CA

#### Adsorption Isotherm

The Langmuir and Freundlich equations are commonly used for describing the surface adsorption equilibrium. Based on the experimental results discussed so far, the fit in of the sorption isotherms were determined for Co(II)-TCSS-CA system at a fixed temperature (25°C) for a concentration range varying between 2 -12 mg/L. All solutions contained a fixed mass of 100mg of the adsorbent material.

#### Langmuir Isotherm

The mostly used Langmuir model assumes that

- i. Sorption occurs at specific homogeneous adsorption sites each of which can hold only one molecule.

- ii. The adsorption is limited to monolayer
- iii. All adsorption sites are energetically equivalent and there is no interaction or migration between the adsorbed ions on the surface of adsorbent

This model proposed by Langmuir suggests that the adsorption had occurred on homogeneous surface by monolayer sorption with no interactions between sorbed species. The linear form of Langmuir isotherm is given by the following equation:

$$1/q_e = 1/q_m + 1/bq_m$$

Where  $q_e$ (mg/g) is the amount adsorbed at equilibrium,  $C_e$  the equilibrium concentration (mg/L)

$b$  and  $q_m$  are Langmuir constants related to the energy and maximum adsorption capacity respectively. Langmuir plot of  $C_e / q_e$  vs  $C_e$  depicted in fig.13 shows a straight line. The Langmuir constants,  $b$  and  $q_m$  were calculated from the slope ( $1/q_{max}$ ) and intercept ( $1/q_{max} \cdot K_c$ ) respectively. The  $R^2$  value of 0.977 from the plot suggests maximum linearity and fit in of the Co(II)-TCSS-CA system on Langmuir adsorption isotherm.

#### Freundlich Isotherm

The Freundlich isotherm model has been widely used for heterogeneous surface energies. The Freundlich isotherm has a general linear form. The logarithmic form of Freundlich model is given by  $\log q_e = \log K_f + 1/n \log C_e$

Where  $q_e$ (mg/g) is the amount adsorbed at equilibrium,  $C_e$  is the equilibrium concentration of the adsorbate (mg/L).  $K_f$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Both  $K_f$  and  $1/n$  are empirical constants being indicative of sorption capacity and adsorption intensity, respectively (Hanim Awad and Paramalingam, 2011). From the slope and intercept of plots  $\log q_e$  vs  $\log C_e$  (fig 12), values of  $K_f$  and  $R^2$  were determined. From the linearity coefficient value, it is obvious that the Co(II)- TCSS-CA system has a better fit for Freundlich isothermal model rather than its Langmuir counterpart.



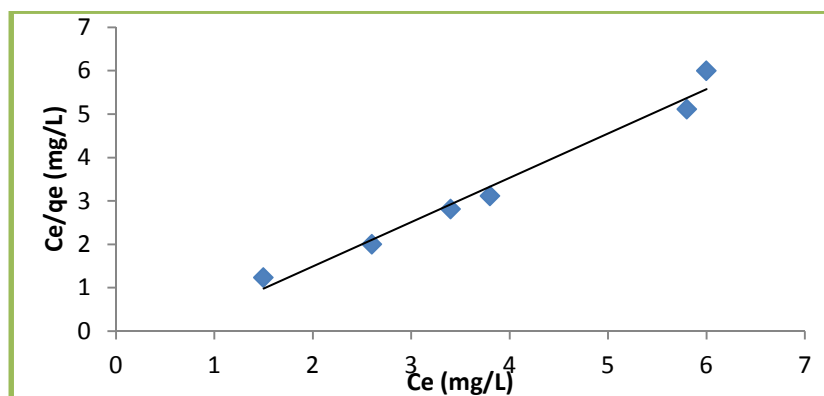


Fig 13: Langmuir Isotherm for the sorption of Co(II) by TCSS-CA

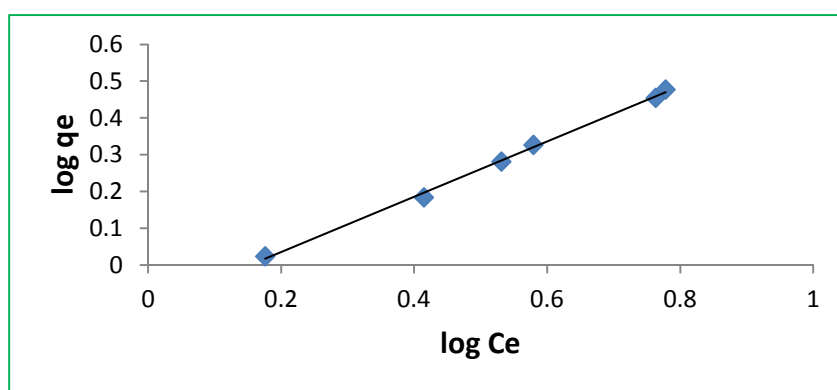


Fig 14: Freundlich Isotherm for the sorption of Co(II) by TCSS-CA

Table 2: Langmuir and Freundlich isotherm data for adsorption of Co(II) on TCSS-CA

Adsorbents	Langmuir Constants			Freundlich Constants		
	$q_m$	B	$R^2$	K	1/n	$R^2$
TCSS-CA	98.04	1.8579	0.977	1.3032	0.77	0.997

**4.0 Conclusion:**

The selected agricultural waste (*Terminalia catappa seed shell*) was modified using citric acid and HCl for the removal of Co(II) ions. Both the modification procedures employed show significant sorption capacity in the removal of Co(II). The studies on the characterization of both loaded and unloaded sorbent samples were carried out using FTIR, SEM and EDAX. The changes in the FTIR spectra confirmed the complexation of Co(II) ions with the functional groups present in the sorbent material. Also, the surface morphological change and appearance of sharp peak denoting the presence of Co(II) ions in SEM and EDAX respectively, supported the sorption capacity of the modified materials. However, the uptake capacity was greater for TCSS-CA. From the batch experiments conducted to study the influence of varying parameters, 0.18mm particle size and 100 mg dosage, 9

minutes agitation time, 8ppm initial concentration of Co(II) ions, pH 7 of the solution medium, room temperature (30°C) were fixed as the optimum conditions. The effect of cations, anions and co-ions revealed that  $Mg^{2+}$ ,  $Cl^-$  and  $Cu^{2+}$  possessed higher inhibitive nature, compared to other selected ions. A decrease in the Co(II) adsorption onto TCSS-CA was observed at higher concentrations of the studied ions. The Freundlich isothermal plot registered a better linearity fit with  $R^2$  value of 0.997 than Langmuir model in describing the adsorption behavior. Thus, the experimental results has led to the conclusion that citric acid modified *Terminalia catappa seed shell* is a promising material for Co(II) removal due to its greater adsorption capacity. Further probe of the study concentrates on the immobilization of the trapped Co(II) ions on the surface moiety of the selected sorbent material.

## 5.0 Acknowledgments:

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