Kinetic Studies for Chromium (VI) removal by using Strychnos potatorum Seed powder And Fly ash

S.Sasikala, G.Muthuraman*

Presidency College, Department of chemistry, Chennai-05, India.

Abstract:

Release of wastewater into the environment due to anthropogenic industrial or commercial activities is an emerging challenge for developing countries. The main objective of this work is to evaluate the total hardness and efficiency of chromium removal by using strychnos potatorum seed powder in treating wastewater. Hexavalent chromium is a well known highly toxic metal considered a priority pollutant. The strychnos potatorum seeds are highest percentage of chromium removal compared with chemical coagulants. The influences of contact time, adsorbent dosage, Cr (VI) Concentration, pH and temperature on adsorption were investigated. The maximum adsorption took place 2hrs at a dose of 0.250g strychnos potatorum seed powder. The percentage of adsorption increased with increasing temperature. Adsorption kinetics studies were also investigated. XRD and FT-IR spectra of strychnos potatorum before and after uptake of Cr (VI) also were recorded to explore the nature of functional groups responsible for binding of Cr (VI) onto the natural biosorbents. The surface morphological structures (SEM) were also studied.

*Corresponding Author: Tel+91-044-28544894, Fax:+91-044-28510732

E-mail Address: raman. gm@g.mail.com (G.Muthuraman)

ISSN: 2278 – 7798

I.Introduction:

Chromium is widely distributed in the environment. Increased industrialization and human activities have created impact on the environment through the disposal of Waste containing heavy metals. Discharging of industrial wastewaters containing different pollutants can lead to contamination of environment and disorder in its ecosystem. Chromium is a contaminant that is known mutagen, teratogen and carcinogen[1]. Chromium occurs in +2, +3,+6 oxidation states but Cr^{2+} is unstable and very little is known about its hydrolysis. The hydrolysis Conventional technologies for the removal of heavy metal ions from aqueous solutions such as chemical precipitation, ion exchange, membrane separation, reverse osmosis and electrochemical treatments have been reported . The permissible limit of chromium in natural water is only 0.05mg/l. Chromium is released into the environment from electroplating, anodizing, chromating, metal finishing, tannery, dyeing and fertilizer industries. Chemical coagulation is a quite effective method for treating heavy metal bearing wastewaters but may induce secondary pollution by adding coagulants, such as aluminium or iron salts or organic polyelectrolyte's to remove colloidal matter as gelatinous hydroxides [2]-[5]. Also this wastewater treatment process produces a large amount of sludge . Adsorption and coagulation methods are best methods for the removal of water pollutants. Using plant based material for adsorption and coagulation studies are the most popular and widely used method because of high adsorption efficiency and ecofriendly too[6]. The seed extracts of strychnos potatorum (Nirmali) contain the anionic polyelectrolyte. Strychnos potatorum seeds are non-toxic and effective coagulant aids useful for removing turbidity and bacteria from water. In addition that the seed extracts also contain lipids, Carbohydrates and alkaloids containing the –COOH and free –OH surface groups which enhance the extracts coagulation capability report that a mixture of polysaccharide fraction extracted from strychnos potatorum seeds contained galactomannan and galactan capable of reducing Cr(VI) from aqueous solution[7]. In all cases, the galactomannan are made up of a main chain of 1,4 linked –d-mannanopyranosyl residues bearing terminal –d-galactopyranosyl units linked at the 0-6 position of some mannose residues. Strychnos potatorum seed treated with water both Mg^{2+} and Ca^{2+} were not removed on treatment and results have indicated that those ion concentrations were raised with the added dose. Thus it may possibly increase finished water hardness. In the present study, performance of strychnos potatorum seed powder removal of Cr (VI) was studied. The parameters such as effect of adsorbent dosage, effect of pH, effect of initial chromium concentration, effect of temperature, Adsorption isotherm and kinetics were studied. These results were compared with strychnos potatorum fly ash highest removal of Cr (VI) compared with seed powder.

II. Materials and Methods:

[A]. Sample collection and Preparation

Strychnos potatorum seeds were collected from local markets. The Seeds were washed extensively in running tap water to removing dirt and other particulate matter. Subsequently the seeds were sun dried for three days and sieved through ordinary food processor. The strychnos potatorum fly ash was prepared by carbonized at low temperature 250° C in a muffle furnace. The fly ash was sieved through pest line mortar.

[B]. Preparation of adsorb ate solutions

Stock solution of Cr (VI) was prepared by dissolving required quantity of potassium dichromate in double distilled water. Experimental Cr (VI) solutions of different concentrations were prepared by diluting the stock solution with suitable volume of double distilled water.

[C]. Chemicals and instruments

All chemicals used were of analytical grade and supplied by Merck (purity >99%). All dilutions and washings were carried out using double distilled water. Muffle furnace was used to carbonize Strychnos potatorum seed. The stock solution of Cr (VI) was prepared at a concentration of 1000 mg/L from potassium dichromate using double distilled water. The pH adjustments were made using 0.1 M NaOH and 0.1M HCl. The ground water samples were collected from west mugapair Chennai.

[D]. Equilibrium experiments

Equilibrium studies at different metal ions concentrations were investigated using the batch adsorption process as described earlier. Batch adsorption studies were conducted in a set of 250 ml glass stopper Erlenmeyer flasks

ISSN: 2278 – 7798

containing appropriate dose (0.250 g) of adsorbent and 50 ml of metal ion solution. This mixture solution was agitated at a speed of 500 rpm in a thermo shaker until the equilibrium was attained. After equilibrium, supernatant was filtered and the equilibrium concentration of Cr (VI) was analyzed, respectively, using UV–Visible spectrophotometer. The percentage metal ion removal (R) was calculated using the following equations:

$$\% \, Removal\ of\ Cr(VI) = \frac{C_i - C_e}{C_i} X\ 100$$

Where C_0 and Ce are the initial and equilibrium concentrations of the metal ion solution (mg/L), V is the volume of the solution (L) and M is the mass of the adsorbent used (g). The obtained data were fitted into adsorption isotherms, Pseudo-first-order, pseudo-second-order.

III. Result and Discussion:

[A]. Adsorption isotherms

Adsorption isotherms can be generated based on numerous theoretical models. Where Langmuir and Freundlich models are the most commonly used. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions. The model takes the following form. The Langmuir isotherm model represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to describe adsorption isotherm according to Langmuir:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$

Where Ce is the equilibrium concentration of metal ion in solution (mg/L), Qe is the amount adsorbed at equilibrium on adsorbent (mg/g), qo is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Thus, a plot of Ce/qe vs. Ce should be linear if Langmuir adsorption were applicable; consequently the Langmuir constants could be calculated. The results in Fig. 1a &b shows the equilibrium adsorption isotherm of metal ions in water samples, using strychnos potatorum seed powder and fly ash sample as an adsorbent. The isotherm rises sharply in the initial stages for low Ce and qe values. This indicates that there are plenty of radial accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decreases in the curvature of the isotherm are tending to a monolayer adsorption. Considerably increasing the Ce values with slight increase in qe, is possibly due to less active sites being available at the end of the adsorption process and/or the difficulty of the edge molecules in penetrating the adsorbent, while metal ions partially covering the surface sites. In order to optimize the design of sorption system for removal metal ions from water sample, it is important to establish the most appropriate correlation for the equilibrium curve. The linear zed Langmuir plot is shown in Fig.1 a&b the Langmuir parameters were calculated and recorded in Table 1. The essential feature of Langmuir isotherm can be expressed by means of dimensionless constant referred to as the separation factor or equilibrium parameter, R_L which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_i}$$

Where C_i is the initial Cr (VI) concentration (mg L^{-1}). The value of separation factor R_L, indicates the nature of the adsorption process as given below:

R_L value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L values calculated for this study are given in Table 2. The adsorption process will be favorable if the R_L values lie between 0 and 1. The R_L values given in Table 2 very well lie in this range and hence the adsorption process is favorable. The Freundlich model was chosen to estimate the adsorption intensity of the metal ions on the carbon adsorbent surface. The Freundlich equation is presented as :

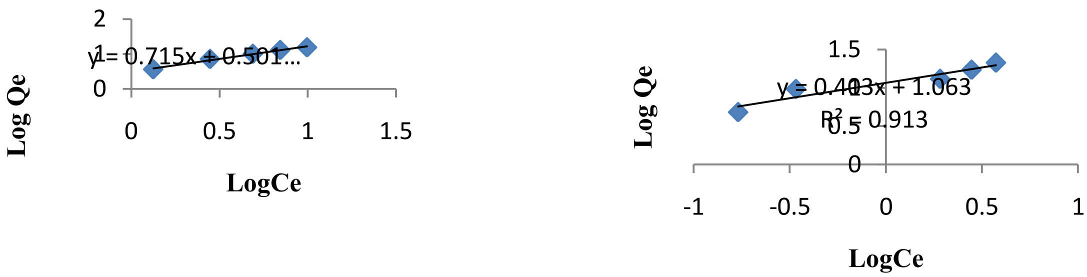
$$Q_e = K_F C_e^{\frac{1}{n}}$$

ISSN: 2278 – 7798

This expression can be linearized to give the following equation:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e$$

where Kf (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. These constants are determined from the intercept and slope. The linear plot of log qe versus log Ce is shown in Fig.2a&b r2 values are listed in Table 3. Although the correlation coefficients are greater than 95%, they do not correlate the data as well as the Langmuir isotherm, which has consistently higher correlation coefficients.



(b)

(a) (b)

Fig.1a&b. Freundlich isotherm for the adsorption of Cr (VI) on Strychnos potatorum seed powder and fly ash adsorbent.

Fig.2a&b. Langmuir isotherm for the adsorption of Cr(VI) on Strychnos potatorum seed powder and fly ash adsorbent.

Table.1Langmuir isotherm

Natural coagulants	Q_m (mg g^{-1}) (10^{-2})	K_L (L mg^{-1}) (10^{-3})	R^2
Strychnos potatorum seed powder	31.74	0.995	0.9878
Strychnos potatorum fly ash	23.04	1.319	0.9226

Table.2.

Cr (VI) concentration (mg L^{-1})	The R_L value	
	S.P.	S.P.F.A
5	0.6677	0.1316
10	0.5012	0.0704
20	0.4012	0.0481
30	0.3344	0.0365
40	0.2867	0.0294

ISSN: 2278 – 7798

Table.3.Freundlich isotherm

Natural coagulants	1/n	K_F (mg g^{-1})	R^2
Strychnos potatorum seed powder	0.886	2.404	0.997
Strychnos potatorum fly ash	0.887	2.148	0.998

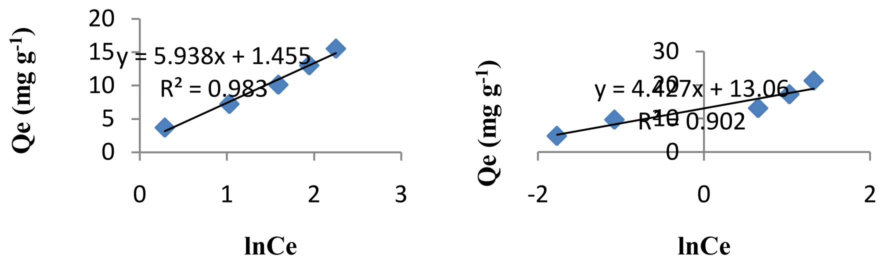
[B]. Tempkin isotherm model

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species- adsorb ate interactions. This isotherm assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbate-adsorbent interaction and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Tempkin isotherm has generally been used in the linear zed and rearranged form as following:

$$Q_e = \beta \, lnK_T + \beta \ln C_e$$

where, K_T is an equilibrium constant of binding corresponding to the maximum energy of binding (mg L^{-1}) and the β is related to the heat of adsorption.

Fig. 3a&b shows a plot of Q_e versus ln C_e, which enables the determination of the isotherm constants K_T and β. The values of K_T, β and correlation coefficient R^2 for Tempkin isotherm model are given in Table 4.



(a) (b)

Fig.3a &b. Tempkin isotherm for the adsorption of Cr (VI) on Strychnos potatorum seed powder adsorbent and fly ash.

Table.4. Tempkin isothern

Adsorbent	β	K_T (mg L^{-1})	R^2
Strychnos potatorum seed powder	5.938	0.564	0.983
Strychnos potatorum fly ash	4.427	6.797	0.902

[c] Adsorption kinetics

The kinetic study is important for the adsorption process because it describes the uptake rate of adsorb ate and controls the residual time of the whole adsorption process .Two kinetic models namely the pseudo first order and pseudo second order are selected in this study for describe the adsorption process. The pseudo first order equation is given by

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t$$

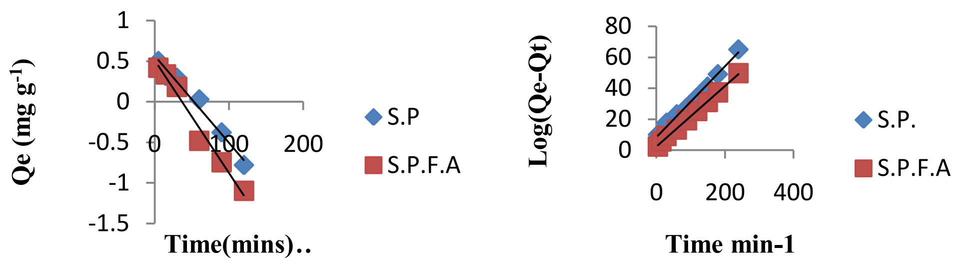
The pseudo second order model is given by

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where qt (mg/g) is the amount of Cr(VI) adsorbed on the strychnos potatorum seed powder and fly ash at the time t(min) K_1 (min^{-1}) and K_2 (g/mg min^{-1}) are the rate constants of pseudo first order and pseudo second order kinetic models respectively. The rate constants predicted uptakes and the corresponding correlation co efficient of strychnos potatorum seed powder and fly ash are shown in Table 5&6. For the pseudo first order kinetic the experimental data deviated greatly from linearity as evidenced from low values of qe and C_0. Therefore the pseudo first order model is inapplicable for this system. By contrast the co-relation coefficient and the qe.cal determined from pseudo second order kinetic model are in good agreement with the experimental results. The applicability of the pseudo second order kinetic model suggested that the adsorption Cr (VI) onto strychnos potatorum seed powder and fly ash based

ISSN: 2278 – 7798

on chemical reaction involving an exchange of electrons between adsorbent and adsorb ate. In chemisorptions the metal ions are attached to the adsorbent surface by forming a chemical bond tends to find sites that maximize their co-ordination number with the surface. The mechanism of the adsorption reaction of metals has been proposed to interpret the phenomenon is shown in Fig.4a&b.



(a) (b)

Fig.4a Lagergren first-order-kinetic model of Cr (VI) adsorption onto 1g L^{-1} adsorbent, initial Cr(VI) concentration 5mg L^{-1}, pH 5.

Fig.4b. Pseudo-second-order kinetic model for the adsorption of Cr(VI) onto1 g L^{-1} of adsorbent with initial Cr(VI) concentration of 5mg L^{-1} at pH 5.

Table.5 and 6..Pseudo first order and second order kinetics

Adsorbent	$Q_{e\,(exp)}$	$Q_{e\,(cal)}$ (mg g^{-1})	K_1x 10^{-2}	R^2
S.P.	3.665	1.96	2.46	0.978
S.P.F.A	4.43	1.76	3.20	0.980

Adsorbent	$Q_{e\,(exp)}$	$Q_{e\,(cal)}$ (mg g^{-1})	K_2x 10^{-2}	R^2
S.P.	3.665	4.35	6.548	0.991
S.P.F.A	4.83	5.09	1.8	0.998

[C]. Elovich kinetic model

Elovich model suggests that the chemisorptions, i.e. a chemical reaction, is probably the Mechanism that controls the rate of adsorption. This model can be applied with success in liquid solution and the linear form of the Elovich equation is:

$$Q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ln t$$

Where, α (mg g^{-1}) is the initial sorption rate and β (g mg^{-1}) is the desorption constant. The values of α and β can be calculated from the slope and intercept of the plot of Q_t versus ln t (Fig.5).

As can be seen from the table 7, the values of R^2 are closer to unity for pseudo second order model than pseudo first order model and Elovich model. Thus, adsorption of chromium onto adsorbent follows the pseudo second order model. Furthermore, values of $Q_{e\,(cal)}$ calculated from pseudo second order model were in good agreement with experimental values, $Q_{e\,(exp)}$ than those calculated from pseudo first order. The values of R^2 for pseudo first order and Elovich model are lower than the pseudo second order model and thus indicate that pseudo first order and Elovich model cannot be adequate to describe the kinetics of adsorption chromium metal onto Strychnos potatorum seed powder and fly ash.

ISSN: 2278 – 7798

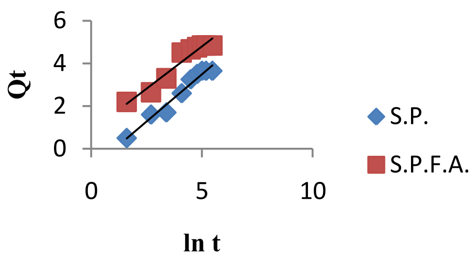


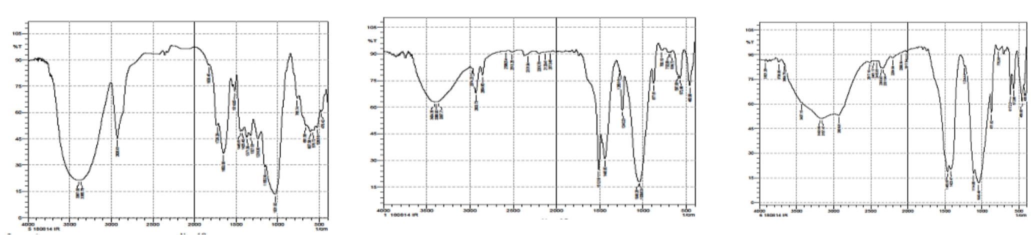
Fig.5. Elovich kinetic model for the adsorption of Cr (VI) onto 1g L^{-1} of adsorbent with initial Cr(VI) concentration 5mg L^{-1} at pH 5.

Table.7.Elovich kinetic model

Adsorbent	α	β	R^2
S.P.	2.723	1.060	0.968
S.P.F.A	2.720	1.042	0.936

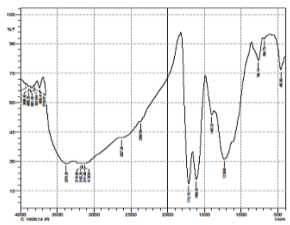
[D]. FT-IR and XRD Analysis

Fig 6 a-d shows FT-IR spectra in which spectrum (a) is for pure strychnos potatorum seed powder and spectrum (b) is for strychnos potatorum seed powder treated with 5ppm at pH 5 at 30° C.FT-IR analysis of pretreated strychnos potatorum was taken before and after Cr (VI) uptake. Table 8.listed band assignments and the typical functional group present in Strychnos potatorum seed powder and fly ash were shown in Fig 6a-d. The main functional group present on surface of Strychnos potatorum seed powder and fly ash were 1712cm^{-1}. After contact with Cr(VI) solutions the strychnos potatorum seed powder and activated carbon exhibited FTIR spectra with clear appearance of a band ranging from 1400, 3437-3739 cm^{-1} which specified carboxylic and alcohol compounds in solid samples. This could be attributed to an interaction between Cr(VI) species and N-Containing bio-ligands. After adsorption of 971 cm^{-1} ,853 cm^{-1} ,584 cm^{-1} this band indicates C=O, Cr-O-Cr adsorption between functional groups and Cr(VI). This may be attributed to the specific interaction between functional groups and Cr (VI). The XRD Patterns of Strychnos potatorum seed powder and fly ash before and after Cr (VI) removal were shown in Fig 7a-d. Therefore, before and after adsorption both strychnos potatorum seed powder and fly ash in Cr (VI) removal existed mainly as amorphous forms. The results showed that the amorphous seed sample subjected to Cr (VI) adsorption showed that the Formation of peaks. This shows that there are more vacant sites for adsorption on adsorbent surface.

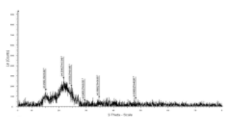


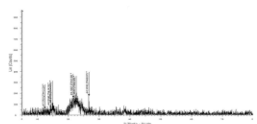
(a) **(b)** **(c)**

ISSN: 2278 – 7798

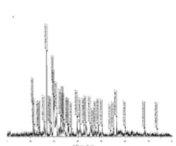


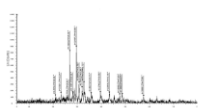
(d)





(a) (b)





©

(d)

Fig.6. FT-IR Spectra of a) Strychnos potatorum seed powder before adsorption b) Strychnos potatorum seed powder after adsorption of Cr (VI) and c) Fly ash before adsorption d) Fly ash after adsorption.

Fig.7. XRD Patterns of a) Strychnos potatorum seed powder before adsorption b) Strychnos potatorum seed powder after adsorption of Cr (VI) and c) Fly ash before adsorption d) Fly ash after adsorption.

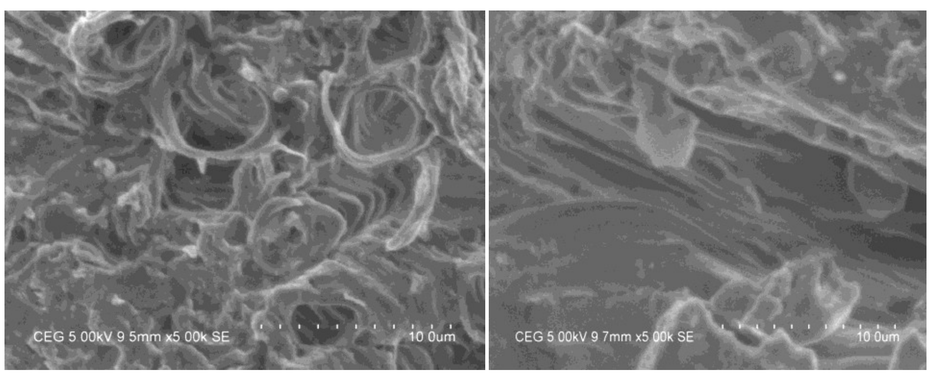
ISSN: 2278 – 7798

STable.8.FT-IR before and after adsorption

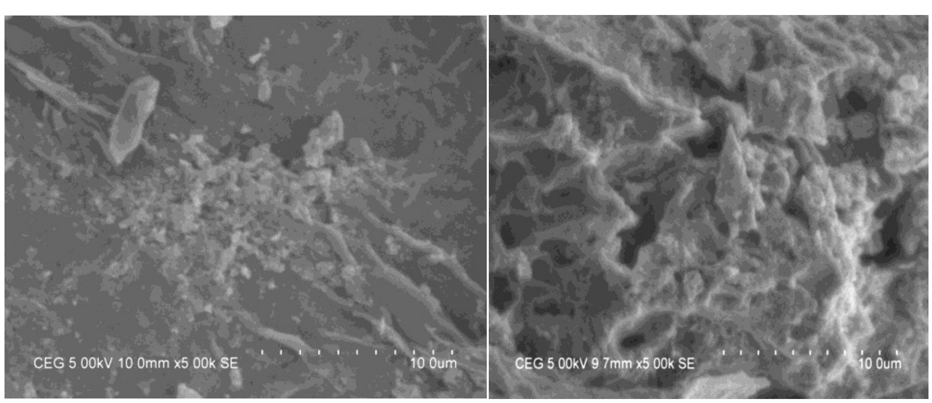
Functional group	S.P.	S.P.F.A
C-H(str)	2926	2933
C=C aryl (str)	1595	1597
O-H (str)	3433	3431
C-Cl (str)	734	773
C=O	1726	1512
Functional group	S.P.F.A.	S.P.F.A. After adsorption
C-H (str)	2926	2933
C=C aryl (str)	1598	1597
O-H (str)	3433	3739
C-Cl (str)	790	761

[E]. SEM Analysis:

The Strychnos potatorum seed powder and fly ash is to create pores and develop the longer surface area in the carbon material and thereby increase the adsorptive capacity. In addition, surface area and porosity value of the activated carbon are presented in Fig 8.a-d. It can be seen that the fly ash which was obtained from strychnos potatorum seed powder with a well developed pore structure. SEM micrographs spectra were obtained before and after Cr (VI) biosorption onto strychnos potatorum seed powder and fly ash. The SEM analysis made the Cr(VI) adsorption more visual between biosorbents and metal ions .It could be observed from SEM pictures that the surface of the strychnos potatorum seed powder having fibrous structure and bulkier particals present in the surface of the fiber than in the case of Cr(VI) adsorption. This observation is confirmed by the Cr (VI) molecules were filled by the porous.



(a) **(b)**



ISSN: 2278 – 7798

© (d))

Fig.8. SEM micrography of activated carbons a) Strychnos potatorum seed powder before adsorption b) Strychnos potatorum seed powder after adsorption of Cr (VI) and c) Fly ash before adsorption d) Fly ash after adsorption.

IV. Conclusion

The present study has shows that Strychnos potatorum seed powder and fly ash as effective removal of Cr (VI) from aqueous solution. Batch adsorption test showed that the extent of metal ion adsorption was dependent on initial concentration, contact time, pH and temperature. The maximum removals of the metal ions were observed at the pH 5. The scanning electron microscope shows that activated carbon has larger pore size than raw strychnos potatorum seed powder this study indicates that strychnos potatorum fly ash was highest removal of Cr (VI) compared with raw strychnos potatorum seed powder. The FT-IR spectral data shows the presence of different functional groups is involved in metal adsorption. The high value of correlation coefficient indicated that there was a good agreement between the kinetic data of adsorption and the pseudo second order model. This study also proves that the smaller particles of activation are the most effective in water parameter removal. Therefore it can be concluded that the powder strychnos potatorum fly ash is a good adsorber and potentially being used for Cr (VI) removal compared to the raw strychnos potatorum seed powder.

V. References

[1] K.Mubeena , G. Muthuraman , " Extraction and Stripping of Cr(VI) from aqueous solution by using solvent extraction" Desalination and Water Treatment pp.1-8, June 2014.

[2] K.Ravikumar , A.K.Prof.Sheeja , "Heavy metal removal from water using Moringaoleifera seed coagulant and double filtration" International Journal of Scientific & Engineering Research, Vol 4, Issue 5,pp.10-13, May 2013.

[3] Mohammed Mansour saleh saif, N.Siva kumar,M.N.V.Sivakumar, "Biosorption of cadmium by Strychnos potatorum seed proteins :Adsorption kinetics, Proteins, Nanoparticles for Enhancing Cd removal and relevance to wastewater treatment" Libyan Agricultural research center Journal International 3 pp.269-278,2012.

[4]Thomas binitha Mancy, Meby Mary Mathew and Shaleesha A Stanley, "Comparative Analysis of cost effective Biosorbents in the removal of Chromium and Iron from aqueous solution".Vol 12,issue12, 1June 2013.

[5] R.M.S.Radis mohammed, N.Abdul Rahman and A.H.Mohd Kassim, "Moringa oleifera and Strychnos potatorum seeds as Natural coagulant compared with synthetic common coagulant intreating car wash wastewater cash studies, "Asian journal of Applied Sciences, Vol.02,Issue 05, pp 693-700, October 2013.

[6] G.Muthuraman, S. Sasikala, "Removal of turbidity from drinking water using natural coagulants" Journal of industrial and Engineering Vol.20, pp1727-1731,August 2013.

[8]G. Muthuraman , S.Sasikala ,"Proteins from natural coagulants used as potential application of turbidity removal from drinking water". IJEIT Vol 3, pp.283-287, August 2013.

ISSN: 2278 – 7798