International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075, Volume-9, Issue-1, November 2019

Adsorption of Cr (VI) From Polluted Water using Activated Carbon Prepared from Vincarosea Apocynaceae

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Abstract*— The performance removal of chromium (VI) from polluted water is discussed in this paper. The sorption characteristic of Nitric Acid activated carbon derived from Vincarosea Apocynaceae plants through oxidation process and was proposed for the removal of Cr (VI) from polluted solutions. The surface chemistry characteristics of the prepared adsorbent were analysis by XRD, FTIR and SEM-EDAX. The effects are determined for removal of chromium they are initial concentration, PH level and adsorbent dose. The metal ion removal was pH dependent and, to a lesser extent, ionic strength. Kinetics data were found to follow the pseudo-second order kinetic model. Activation thermodynamic parameters, such as activation enthalpy (ΔH^*), activation entropy (ΔS^*), activation Gibbs free energy (ΔG^*) and activation energy(E), have been evaluated and the possible adsorption mechanism also was suggested.

***Key Words:* Vincarosea Apocynaceae Activated Carbon, Chromium (VI), Adsorption Isotherms and Kinetics.**

I. INTRODUCTION

Nowadays, heavy metals are among the most important pollutants in source and treated water and becoming a severe public health problem. The main problem in this entire world is heavy toxic metals are obtained while water is contaminated [1]. In the environment, the species of metallic are increased because of the domestic effluents, agriculture run off and mining activities [2]. Coming to aquatic water, it consists of four oxidation states they are di, tri, penta and hexa states. These states are combined to the trivalent chromium and hexavalent state. Trivalent chromium acts as the micro nutrients which is essential for glycolsis whereas hexavalent chromium is 500 times more toxic than the trivalent chromium. Thus, the presence of Cr (VI) ions in the environment is posing serious problems and causing great public concern [3]. These tissues will irritate the plan and animal's skin because of the oxidant agent is strong. This agent easily passes to the skin from the environments of aquatic [4]. According to USEPA, the permissible level of Cr (VI) in drinking water should be less than 100µg/L [5].

Many physical-chemical methods, included reduction [6], ion exchange [7], precipitation [8] and membrane separation [9], have been proposed for Cr(VI) removal from industrial effluent. However, these methods are often inefficient and/or cost disadvantageous when they are used to remove heavy metal ions from solution [10]. Adsorption methods were found to be more effective and attractive due to its lower costs and the higher efficiency of heavy metal ions removal from waste water [11].

To obtain good adsorbent in the water, mainly active carbons are used and consist of mainly adsorptive sites. To remove the chromium ions from polluted water, active carbons are used and active carbons plays important role in the adsorption process. There will be huge number of waste products and expensive natural materials to perform the operations. There will be no expensive regeneration for this disposed one. Hence the capacity of contaminant sorption is very high and available at low cost [13]. Here various types of studies are given, they are seaweeds [17], Eucalyptus Bark [15], Peanut Husks Carbon [19], Beech Sawdust [14], Bagasse Fly Ash, Coir Pitch [18], Green Algae [16], Activated Slag, Zeolite Tuff [20], Fabric Cloth, etc. All these studies need some high sate adsorbents. Here the operational cost is reduced by 36%, capital cost is reduced by 20% and at last the total cost is reduced by 28%.

Some adsorbents are required which are very effective in an economical way. Basically, to remove chromium (VI) an adsorbent is used, the adsorbent is named as Vincarosea Apocynaceae. This adsorbent is indicated in the literature survey. Vincarosea Apocynaceae belongs to the family of Vincarosea Apocynaceae which consists of Apocynaceae carbons. Hence from waste water the chromium is removed based on this Vincarosea Apocynaceae adsorbent. To estimate the behavior of adsorption in chromium (VI), thermodynamic functions are used. This is obtained at different temperatures. Here we investigate the parameters like temperature, pH concentration and agitation time. Classical methods are introduced by using new techniques. The new techniques are given as FT-IR, SEM, and EDX & XRD. By using NVAC, the chromium (VI) is removed from the polluted water.

II. MATERIALS AND METHODS

2.1 Chemicals And Reagents

By using the double stilled water, the investigation for chemicals and reagents is done. Based on the grade of A.R the entire investigation process is performed. Hence from this solutions are prepared.

2.2 Materials Of Adsorbent

In India, the evergreen shrub is growled by using the Cape periwinkle. sadabahar or Rosea periwinkle is the

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Revised Manuscript Received on September 05, 2019.

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domestic name of the Cape periwinkle. Vincarosea is the botanical name of Vinca Rosea and available from the family of Apocynaceae. Plantae kingdom and Magnoliophyta are the kingdom and division for the Vinca Rosea.

Basically, it is called as the flowering plant. This plant consists of ducotyledons and gentianales, which is mainly used for the purpose of medicinal.

Fig. 1: Home / Herbs Information / Vinca Rosea Information-Uses And Benefits

Basically, white layer form flower or Vincarosea is known as the Vincarosea. This is a type of flower, which is equal to the ever green shrub and charmed and grow in the south western and Eastern Madagascar. Here, it is a native plant. Ornamental property is introduced by the European colonist to recognize the invasion. In the tropical and sub tropical regions it is mainly grown.

The flower which is named as Vincarosea consists of oblong and oval in shape. This provides the covering of glossy and waxed. By using a pale midrib and short petiole, there will be arranged in the pairs. It mainly consists of five petals which are equal to loves.

The flower Vinca rosea will be grown in the regions of well drained soil and infertile regions. This flower will be dried in the cases of heavy fertile in the soil. Branching and full growth process is used for the purpose of pinching occasionally. After the process of blooming, the flower will not died. This flower is mainly used to treat the disease of Leukemia which is mainly occurred in the children. The leaf growth is reduced if the Phytoplasmas infection is occurred. It mainly consists of 70 different types of alkaloid which are mainly used for the types of indole. The alkaloids used in this are given as serpentine, reserpine vinblastine and ajamalicine.

2.3 Preparation Of Adsorbent

Activated carbons were prepared from Vincarosea Apocyanacea plant stem material. The earthy matter is removed from the raw material using double distilled water. After removing, this will cut in small pieces and dried. The activated material was ground and sieved in to desired particle sizes. By using concentrated nitric acid, activated carbons are prepared. The weight of acid volume is given as 1:1 for 24hrs. In double stilled water, the materials that charred are washed.

2.4 Adsorbate

By dissolving the potassium dichromate, the adsorbent obtains a stock solution. This process is done only in double distilled water. Different types of experiments are performed using the double distilled water.

2.5 Adsorbent Characterization

By using standard testing methods, parameters were analyzed. Due to adsorption and area is high; the activated carbons are most widely used. The activity of adsorption is determined by the chemical nature and pore structure. From table 1, the characteristics of physics and chemical are given.

Table 1: Physico-chemical Properties.
SAMPLE NAME: NVAC

S.NO	CHARACTER (UNITS)	RESULTS
1	Bulk Density in gm/cc	0.333
2	Moisture Content in %	6.503
3	Loss on Ignition in %	81.873
4	Ash Content in %	6.553
5	Particle Size in µm	75
6	pH	7.133
7	Point of zero charge	7.22
8	Water soluble Matter in %	3.627
9	Acid soluble Matter in %	41.54
10	Iodine Number mg/gms	487.667
11	Decolorizing Power in mg/gms	295.333
12	Surface Functional Groupr in %	
a)	Carboxyl	0.274
b)	Lactone	0.025
c)	Phenol	0.013
13	Total Basic Groups	0.716

2.6 Analysis Of FTIR

By using Fourier Transform Infrared Spectroscopy (FTIR), the examination of NVAC is done. Active carbons are mixed in the sample disc with 1mg and 500mg of NVAC of NVAC. By using all this the mortar is agate in vacuum by pressing the mixture which is resulted for 5 min as 6tones/cm^2 and again after 5 min as 10 tones/cm$^{2.}$. By using HATR Spectrum the 400-4000cm^{-1} value is measured having USA ID No: SN/LE-735/00735.

2.7 Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

By using the double-sided adhesive carbon tape, the NVAC is stubbed. Basically, NVAC is named the surface of powered carbonaceous material. It is coated using the platinum coater which obtained from the model of SEMSu1510 Hitachi. SEMSu1510 Hitachi model mainly consists a set of samples in the micro photographs. By using the accelerating voltage, the EDX is analyzed at 5kv. The resolution of this is maintained at 3nm and compared to the actual size, it is 3, 00,000 times greater.

Table 2: EDX - Elemental Analysis(Before)
SAMPLE NAME: NVAC 1

Composition	CK	NK	OK	Crk	Total
Energy (eV)	0.3	0.5	0.7	5.2	
Wt % (Mass ratios)	72.3	11.2	16.5	-----	100
At % (Atomic percentages)	71.1	13.0	15.9	-----	100

Table 3: EDX - Elemental Analysis(After)
SAMPLE NAME: NVAC 2

Composition	CK	NK	OK	Crk	Total
Energy (eV)	0.3	0.5	0.7	5.2	
Wt % (mass ratios)	63.5	9.3	12.1	15.1	100
At % (atomic percentages)	61.4	10.6	12.3	15.7	100

2.8 X-ray Diffraction (XRD) Analysis

By using the X Celebrator X', samples for the analysis of XRD is prepared. For the purpose of radiation, (0.150-54nm) is maintained for Monochromatized Cu KR1. The collection of diffraction is done only when the pattern is maintained from 45kV-40mA. The step scan rate maintains its level up to 3.00 min^{-1}. And the time taken for the process is given as 0.400 sec.

2.9 Chromium Ion Analysis

After the adjustments of total electronic strength, the measurement of chromium ion concentration is done. The value of pH is measured by using the Orion 3-star ion meter. The relationship of chromium ion removal is calculated as shown in below:

Percentage removal (%R) = C_i-C_e/C_i x100
Amount adsorbed (q_e) = (Ci-C_e/m)V
V= Vol.of Cr test solution in liters

The initial and final concentration of chromium (VI) is given as C_i and $C_{e.}$ The mass of the carbons available in chromium is given as m. the duplicate runs are analyzed based on the average values. To remove the error in data percentage is available between ± 1-2% and the amount of data is absorbed is ± 0.005-0.01 mg/g.

III. ANALYSIS OF RESULTS

From table 1 and 2, the different types of properties of NVAC, active carbons are shown. The surface area for NVAC of BET surface is given as 458m^2/g. from literature, it can be studied that it is more than the active carbons. The literature is given as Cornelian cherry (449m^2/g) Apricot shells (412m^2/g) and stone(369m^2/g).

From the process of adsorption, effectiveness is obtained in the features. The chromium (VI) will be on the surface of NVAC because there will be reduction the surface area from 458m^2/g to 390m^2/g. rin the same way the size of pore is reduced from 15.126 to 14.974^{0}A.in the surface of 1000x, the carbons are activated based on the magnification process and the micrographs of SEM is examined. From figure 2, the microspores are shown and identified. By using the Boehm's method, the specific acidic group is measured. Hence all these are compared with the results of activated carbons from bio adsorbents.

3.1 EDX Data

The EDX data is shown from figure (2) and tabular form (2). Before and after the adsorption process, samples of spectrum are compared. Hence small peak spectrum is noted from the chromium. This data is analyzed and shown in table 2. Here the concentration level of oxygen is decreased based on the process of adsorption. In the same way, the concentration of chromium (VI) also increased. Now, the ion of chromium is replaced with the ion of oxygen atom.

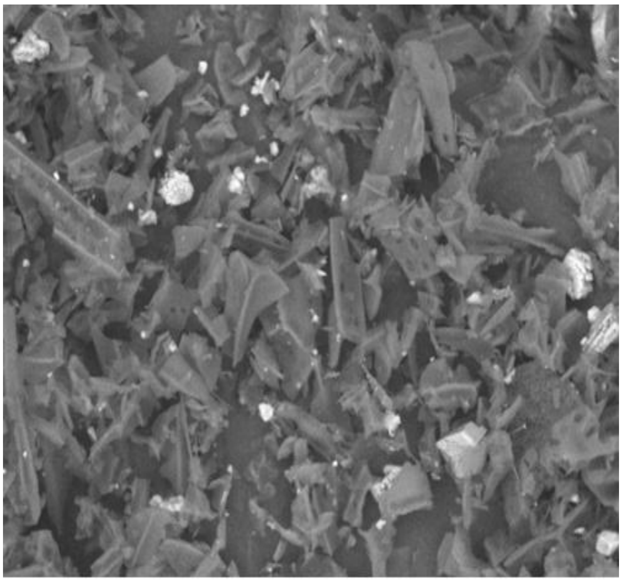

Fig. 2: SEM analysis of NVAC (before) at X50 magnifications

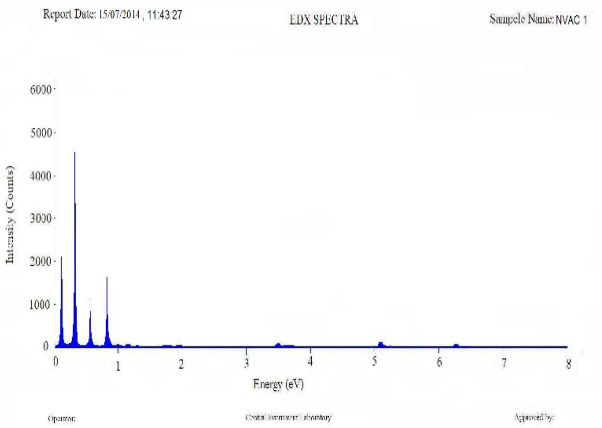

Fig. 3: Before Analysis Of Energy Dispersive X-Ray (EDX)

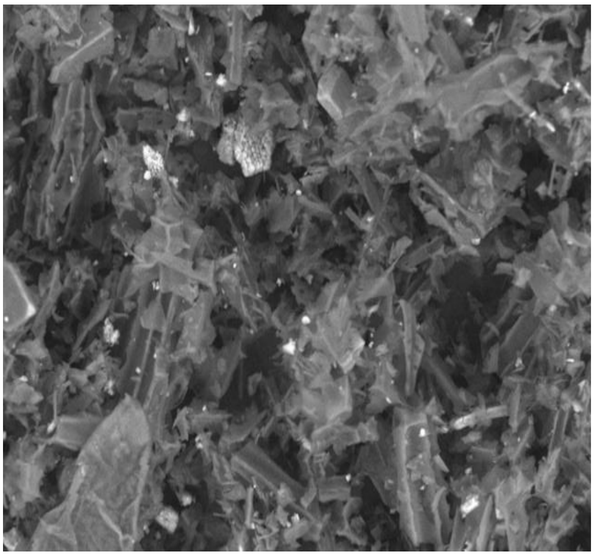

Fig. 4: SEM analysis of NVAC (After) at X50 magnifications

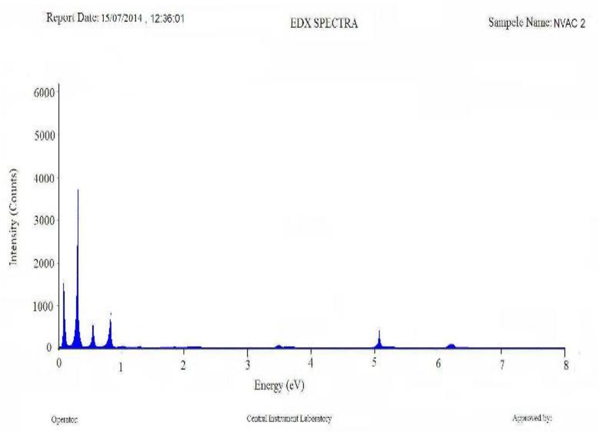

Fig. 5: After Analysis Of Energy Dispersive X-Ray

Based on the range of PH (2-7), the groups of carboxyl are dissociated. Near to the pH range, the chromium value is increased in the NVAC. From this it can be observed that the adsorbent level gives effective treatment for chromium ion containing water. Because of the oxidation of sulphuric acid, small amount of sulphur is added to the adsorbent. Therefore, the comparison of concentrations for nitrogen, hydrogen and oxygen is shown.

There will be change in the adsorption reactions from crystalline and molecular structure. Here valuable information is provided after the process of adsorption reaction. From fig 6, the patterns of XRD for NVAC are given before and after the process of adsorption. Without altering the structure of adsorbent, the NVAC is loaded into the chromium (VI). This will exhibit the variations of crystal in the structure. The chromium will be physical in nature by using batch absorption experiments, the observations are collaborated.

3.2 XRD

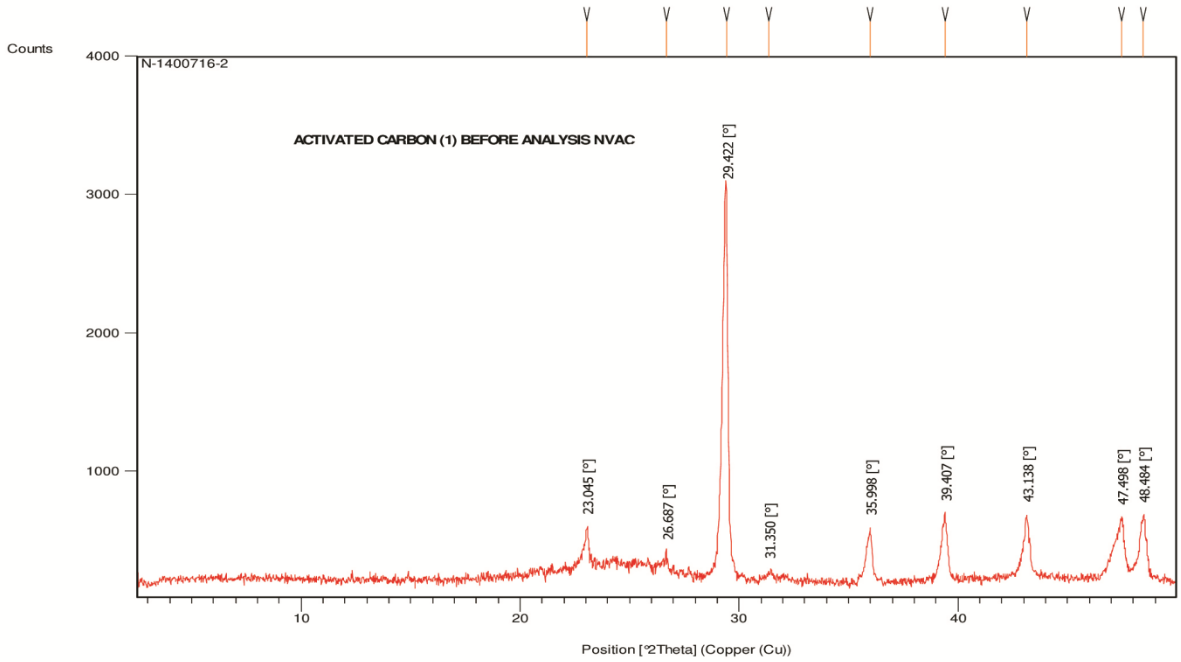

Fig. 6: Before Analysis Of XRD

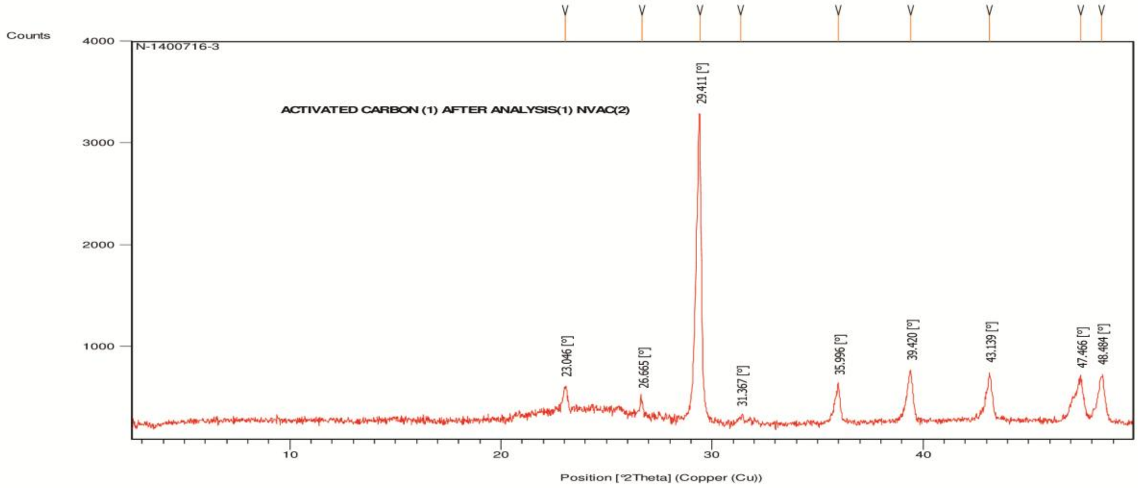

Fig. 7: After Analysis Of XRD

Basically, on the surface of carbon materials, Fourier transform infrared (FT-IR) spectroscopy is used. From figure 4, the bands which are assigned to the NVAC are observed and they are group of specific functions available in the literature. The sharp and intense band groups are obtained at 3736 cm^{-1}. This will vibrate and stretch of OH^{-} using the acids, alcohols and phenols. The range 3200 – 3600cm^{-1} is maintained for broad band and intense band which is centered at the 3393cm$^{-1.}$ By using amines and amides, the stretching and vibration of N-H is done. The mythylene group is used to stretch the C-H at 2922 cm^{-1}. In the same way the Amine group will stretch and vibrate the peak up to 2361 cm^{-1}[20 ir-11]. Because of aromatic and aliphatic stretching and vibrations, wide band range is set up to **1650-1600** cm^{-1}.

The –SO_3H group represents the exchange of ions mechanism and the band is maintained up to **1161 cm^{-1} - 1118** cm^{-1}. The C-O will stretch and vibrate up to the range of **1000-1068cm**$^{-1}$ by using the alcohols, ethers, phenols and esters. The stretching and vibration of the group S=O, the peak value is maintained at the **831** cm^{-1}. The C-S [ir-5] stretching and vibration is maintained their peak value up to **662**cm^{-1}. In the adsorption process the C-Cr peak value is absent.

3.3 FT-IR

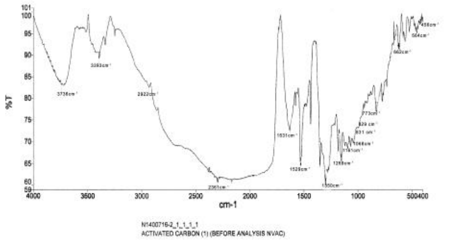

Fig. 8: Before Analysis Of FT-IR

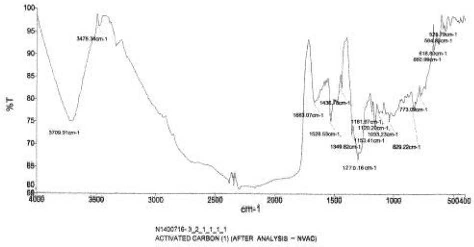

Fig. 9: After Analysis Of FT-IR

3.4 Effect Of pH

Basically, the solution of pH is mainly affected by the process of adsorption. The pH content is maintained from 2-10 in the adsorption process. This process is done only by using the solutions of HCl and NaOH which are diluted.

In the acidic media, the adsorption process will be processed in a metal and gives maximum value. By maintaining the pH value 2, maximum value of adsorption is obtained in the chromium. By using the both H^+ and OH^- ions, pH value are varied from high to very low. The adsorption will be decreased when the charged ions of positive and negative will be competed. Hence by maintaining the pH value from high to low, the metal gives adsorption value very low. Good absorption value is maintained when the ions of perception is taken from the hydroxide.

In bio-adsorbents, the functional groups and phenomenon of adsorption is related with the value of pH. By using the groups of amino acids, carbohydrates, carboxylic groups and hydroxide groups. At the various levels of pH value, the groups which are functioned will be associated. Hence in the adsorption process, surface chemistry plays an major role.

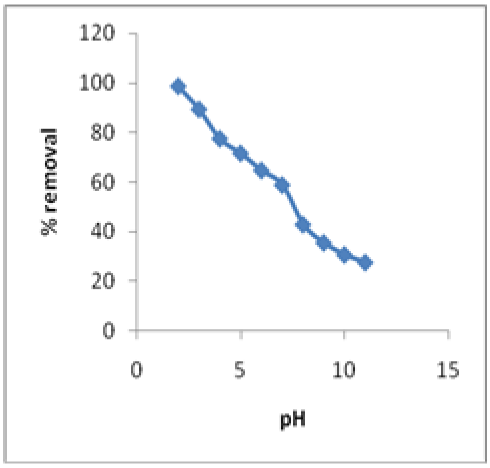

Fig. 10: plot of percentage removal of Cr(VI) as a function of pH

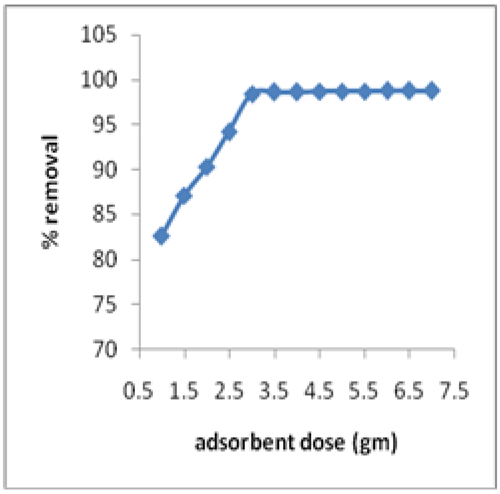

Fig.11: plot of percentage removal of Cr(VI) as a function of adsorbent dose

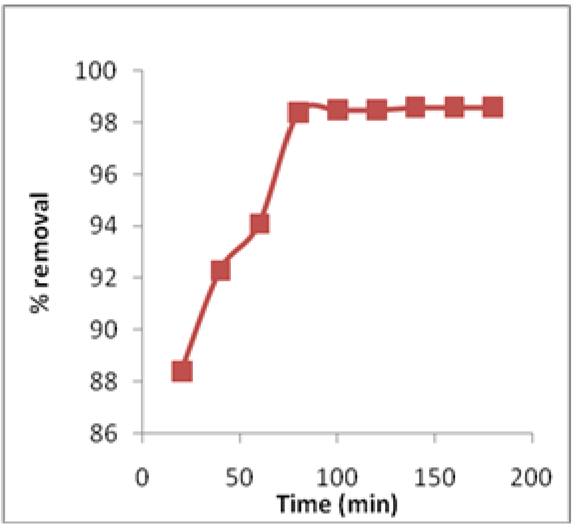

Fig. 12: plot of percentage removal of Cr(VI) as a function of contact time(min)

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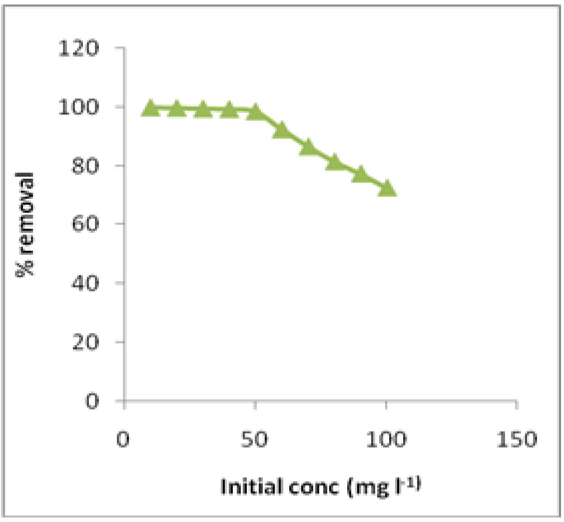

Fig. 13: plot of percentage removal of Cr(VI) as a function of ion solution

3.5 Effect Of Adsorbent Concentration (Dose)

By varying the dosage of adsorbent levels, the chromium percentage is removed. All this is mainly depends on the optimum condition and the value is maintained at 1.0g-3.0g/L. the chromium ion of initial concentration is maintained at 50mg/L. the time of contact of chromium is maintained at is 30^0C. There will be increase in the growth of adsorbent if the chromium percentage is removed. Here there will be increase of removal of percentage in the chromium ions if the number of sites increases.

3.6 Effect Of Initial Adsorbate Concentration

Here the amount of chromium ions is removed by using the adsorbent concentration in SAVAC. Here the dosage is fixed with 3.0g/L adsorbent of time 80 minutes at 30^0C temperature. The concentration is varied from the chromium ions between 10.0 to 50.0mg/L.

The initial concentration value of the chromium ions are decreased with increased value. This variation is occurred due to the less number of active sites in the chromium ions. Here the concentration of chromium is increased from 10.0 to 100.0 mg/L, and in the same way, the concentration of chromium is decreased from 100.0 to 72.50. if the concentration of chromium ions are increased in then there will be increase In value exponentially 2.5 to 3.0mg/L is changed from the fixed amount. This will increased from the 10 to 100 mg/L.

3.7 Adsorption Isotherms

To represent the equilibrium states in the system of adsorption, adsorption isotherm is used. Adsorbate concentration is interfaced with the solid solutions. In the design process, mainly isotherm data is developed by using an equation. To describe the isotherms of adsorption, some adsorption equations are introduced. Here the temperature is maintained constant for the treatment of water applications.

The equation for Freundlich isotherm equation is given below

$\mathrm{Log}(q_e) = \log K_f + (1/n) \log C_e$

The equation for linearization of Langmuir is given as

$q_e = k_L C_e/(1+a_L C_e)$

The isotherm model for the dimensionless constant is given as below equation

$R_L = 1/1+a_L C_i$

Here, the constants of Freundlich are represented by using the K_f and 1/n. The concentration of the chromium ion (VI) is represented by using C_i. The ions that are absorbed per unit weight of adsorbent is given by using the q_e(mg/g). The capacity and energy adsorption terms are represented by using the terms a and b.

Here the concentration is maintained at the linearity level, in the chromium ion (VI). This is equal to the model of isotherm by confirming the Freundlich applicability.

The separation factor, for the adsorption process in chromium ion is given as linear ($R_L = 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$), and favorable ($0 < R_L < 1$). This is introduced by the hall. Hence the removal of adsorption is favorable to the chromium ions which are removed from the adsorbent.

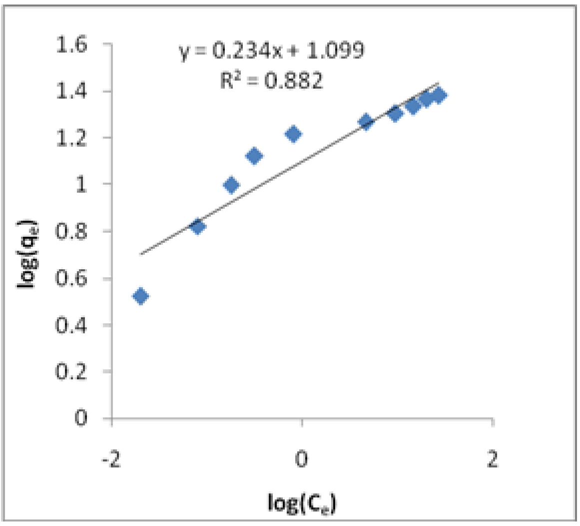

Fig. 14: Freundlich isotherm

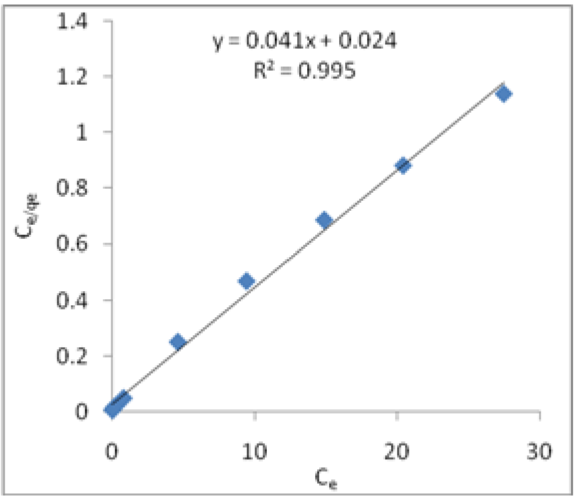

Fig. 15: Langmuir isotherm

3.8 Effect Of Agitation Time

In the adsorption kinematics, the calculation of agitation time plays an important role. Here the time is increased by maintaining the equilibrium condition for 80 minutes and because of this the removal of chromium ions are done.

3.9 Kinetic Study Of Adsorption Process

The adsorption reaction will give about the description of kinetic in adsorption. The efficiency of adsorption is obtained by maintaining the characteristics. The behavior of active carbons in NVAC is maintained by using the kinetics of adsorption. The below table shows the representation of kinetics and adsorption parameters.

Table 4. Kinetics and adsorption parameters

Adsorption Isotherm	slope	Intercept	R^2
Freundlich Isotherm	0.234	1.099	0.882
Langmuir Isotherm	0.041	0.024	0.995
Pseudo first order kinetics	-0.021	1.069	0.875
Pseudo second order kinetics	0.058	0.374	0.998
Weber and Morris intra particle diffusion model	0.451	11.29	0.589
Bangham's pore diffusion model	0.587	-0.974	0.854
Elovich model	2.090	6.389	0.730

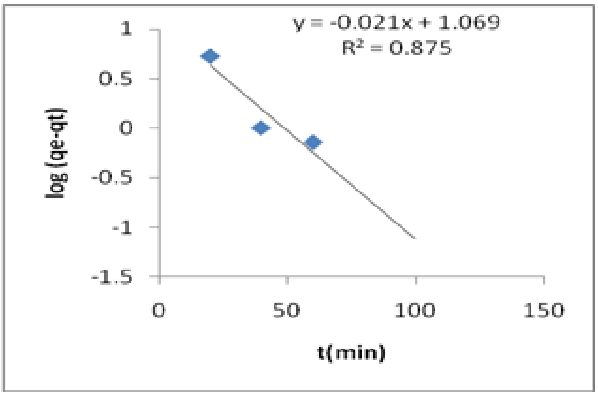

Fig. 16: Pseudo first order

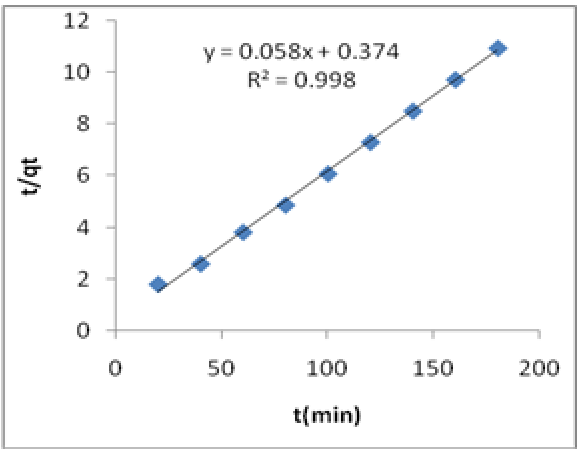

Fig. 17: Pseudo second order

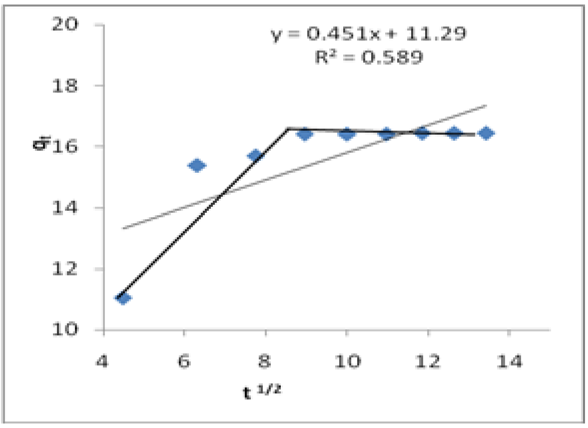

Fig. 18: Weber and Morris intra particle diffusion

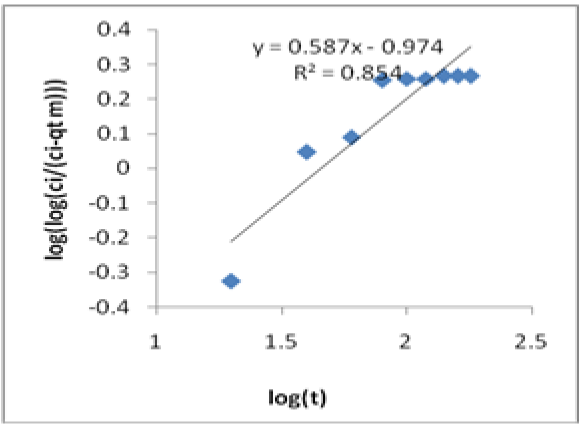

Fig. 19: Bangham's pore diffusion

IV. CONCLUSION

In this paper the removal of chromium ions from the polluted water is presented. Here different types of properties of chemical of chromium (VI) are studied. Here adsorption temperature, pH value and chromium ion concentration also investigated using active carbons. From results, we can observe that the introduced system will reduce the percentage of chromium ions from the polluted water. Hence, the reduction in pH solution will be apparent in nature.

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