REMOVAL OF IRON FROM AQUEOUS SOLUTION BY USING *LIMONIA* ACIDISSIMA (KAVATH) SHELL CARBON AND ACTIVATED CARBON AS AN ADSORBENT.

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ABSTRACT- Limonia Acidissima**(** Kavath) Shell Carbon(KSC) and Activated Carbon (KSAC) was utilized as an adsorbent to removal of iron from aqueous solution and Comparison of effectiveness of adsorbents is carried out. The effect of pH, contact time, temperature, and adsorbent dosage were investigated using batch adsorption experiments. Characterization of adsorbent was identified by FT-IR and XRD techniques. The pH dependence study of the adsorption process revealed that for charcoal pH for maximum iron removal was at pH 10 with percentage removal of 86.73%. For KOH activated carbon pH for maximum iron removal was pH 8 with percentage removal of 90.81%. The adsorption of iron on Limonia acidissima**(** Kavath) shell carbon and activated carbon increased as adsorbent dosage increases from 1gm/50ml to 5gm/50ml and also with the increase in contact time. The study showed that adsorbent had the potential for removal of iron from aqueous solution.

KEYWORDS: **Activated carbon, adsorption, batch adsorption experiments, Limonia acidissima (Kavath) shell, iron removal.**

INTRODUCTION

Iron is a common metallic element found in the earth's crust. Water percolating through soil and rock can dissolve minerals containing iron and hold them in solution. Occasionally, iron pipes also may be a source of iron in water. The main anthropogenic sources of Iron are various industrial sources, including present and former mining activities, Power plants combustion by – products, etc. It has adverse effects on the environment and human health and is toxic even at low concentration to human beings and other living and non living things. Iron in water is normally found in the ferrous state. Oxidation of dissolved iron particles in water changes to red-brown solid particles that settle out of the water. Iron that does not form particles large enough to settle out and that remains suspended and leaves the water with a red tint. The regulations regarding iron in drinking water were established as secondary standards, which mean the limits were set because of nuisance problems and aesthetic concerns.

Standards for Iron concentration in drinking water[1]

Standards	**Maximum Permissible Limit (mg/lit)**
BIS (IS 10500)	0.3
USEPA	0.3
WHO guidelines	*0.3, No health based guideline value is proposed*

Adsorption process is one of the easiest, safest and more effective methods for metal removal from industrial effluents [2,3] and this process is already established as a simple operation and an easy-handling process. Activated carbon is a commonly used adsorbent for the water and wastewater treatment. Previous research shows that there is growing interest of searching for a variety of materials as low cost adsorbents including cocoa shell[4], rice husk[5], modified sawdust of walnut[6], papaya wood[7], maize leaf[8], rice husk ash and neem bark[9], fly ash[10] and tea-industry waste[11]. Low cost and non-conventional adsorbents, including agricultural byproducts such as nut shells, wood, bone, peat processed into activated carbons and biomass have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater. The adsorbent like Sugarcane bagasse, Coconut coir having very good tendency for removal of total iron[12] the adsorption properties of coconut shell are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions[13]. Egg shell and Pongamia pinnata also known as Karanja tree bark is also used as an adsorbents for the removal of iron from groundwater[14].

MATERIALS AND METHOD

Limonia acidissima*(* Kavath)

It is the only species within the monotypic genus Limonia. It is found in the forest of Chandrapur and Gadchiroli district. Common names for the species in English include wood-apple and elephant-apple. It is a large tree growing to 9 metres (30 ft) tall, with rough, spiny bark. The fruit is a berry 5–9 cm diameter, and may be sweet or sour. It has a very hard shell which can be

difficult to break, and contains sticky brown pulp and small white seeds. It is used by the people to make jam and jelly. Kavath shells are wastes that are mainly disposed off after extraction of their inner contents. These wastes can be converted into useful activated carbon which in turn can be used to treat water. Water Treatment by Kavath Shells Activated Carbon (KSAC) is not yet reported to be done.

Fig 1-Limonia Acidissima(Kavath)

Preparation of Adsorbent - Limonia Acidissima**(** Kavath) Fruits are collected from nearby forest, after extraction of their inner contents shells were washed to remove soil and other substances and then sun dried for 1-2 days to eliminate moisture. Fruit shells are broken into smaller pieces. . It was then packed in an air tight in a cylindrical container with top completely sealed to prevent the entry of air during the process of charring. The sealed container was heated in furnace for 2hr.

Activation of carbon - The resultant charcoal obtained by above procedure was soaked in 2M KOH overnight. It was followed by washing with distilled water till the attainment of neutral pH, and then dried in the hot air oven at 80±5C temperature for 4 hrs to obtain activated carbon. The KOH saved as activating agent to introduce some functional groups and deepening micro pores.

Stock solution as Adsorbates - Iron solution was prepared by dissolving 49.78g of $FeSO_4.7H_2O$ dissolved in 1000ml distilled water to make water equivalent to ten g/lit and this served as a stock solution. A calibration curve was also plotted by analyzing the different concentrated solutions using UV-visible spectrophotometer

Adsorbent Characterization - The adsorbent was characterized by FTIR analysis. In chemical activation, activating agent is expected to significantly affect the properties of substance. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy analysis performed to determine the structural and surface properties.

Batch Experiments - Batch adsorption experiments were conducted to examine adsorption behavior of different adsorbent on iron removal under different adsorption condition. Adsorption studies were carried in different conditions namely adsorbent dose, initial concentration, contact time, pH and temperature. The adsorption experiments were conducted in 250 ml conical flasks. In each experiment, a known amount of adsorbent was contacted with 50ml of desired contaminated water with known pH and at a regular interval of time of 1 hour. pH of the solution was measured using pH meter and adjusted using 0.1N HCl and 0.1 N NaOH. The solutions were filtered by using Whattman filters and filtrates were collected for analysis.

RESULTS AND DISCUSSION

Characterization of Adsorbent: The pH values of Kavath fruit shell charcoal was 6.60 while that of activated charcoal was 8.00. The value of charcoal was less than 7.0 (i.e. acidic) may be due to the presence of acidic groups on the surface. It was found that pH of charcoal increased on activation by KOH. The acidic or basic nature of a charcoal or activated charcoal depends on its preparation, inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was subjected. The pH of the activated carbon affects the adsorptive property of the carbons, as highly acidic or basic carbons are undesirable for processing.

The FTIR technique is an important tool to identify the characteristic functional groups which are vital in adsorption of hardness ions. Fig.2 and Fig 3 shows FT-IR spectrum for Limonia acidissima**(** Kavath) Shell Carbon and Activated Carbon. Identified functional groups are likely to account for the adsorption of ions onto the adsorbent surface, hence high efficiency in iron removal.

X- ray diffraction pattern of the charcoal shows no peak, thereby indicating the amorphous nature of the adsorbent while activated carbon shows many peaks, thereby indicating the crystalline nature of the adsorbent. Peaks may be due to presence of inorganic and crystalline substance in the carbon. This shows carbon becomes more crystalline on activation.

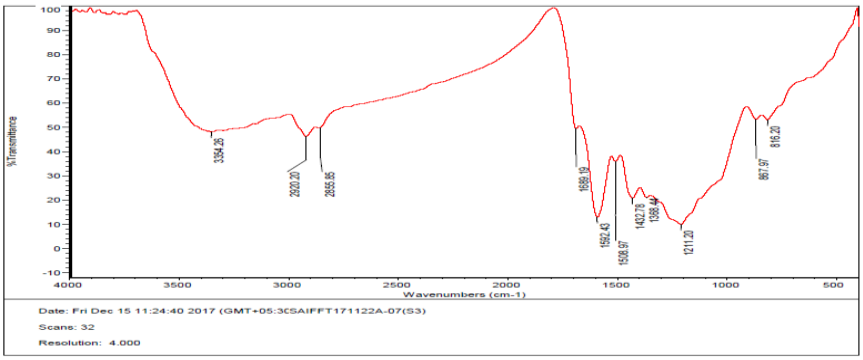

Fig-2 FTIR spectrum of **Limonia acidissima(** Kavath) shell charcoal

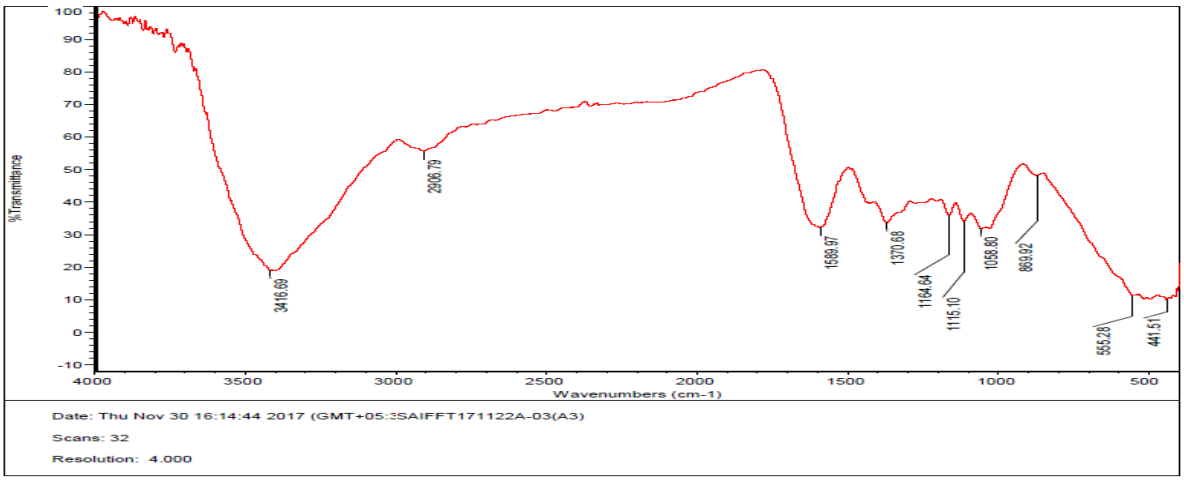

Fig-3 FTIR spectrum of KOH activated **Limonia acidissima***(* Kavath) shell charcoal

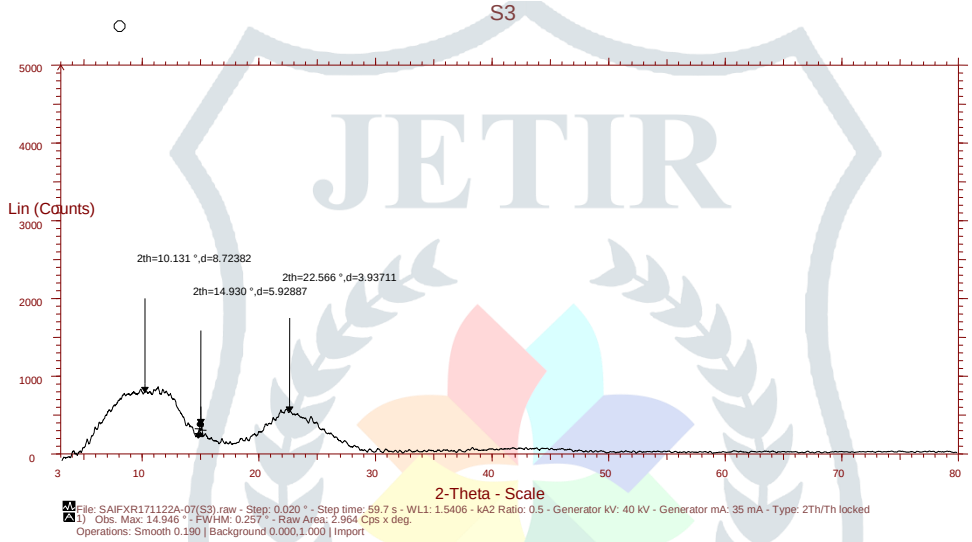

Fig-4 XRD of **Limonia acidissima***(* Kavath) shell charcoal

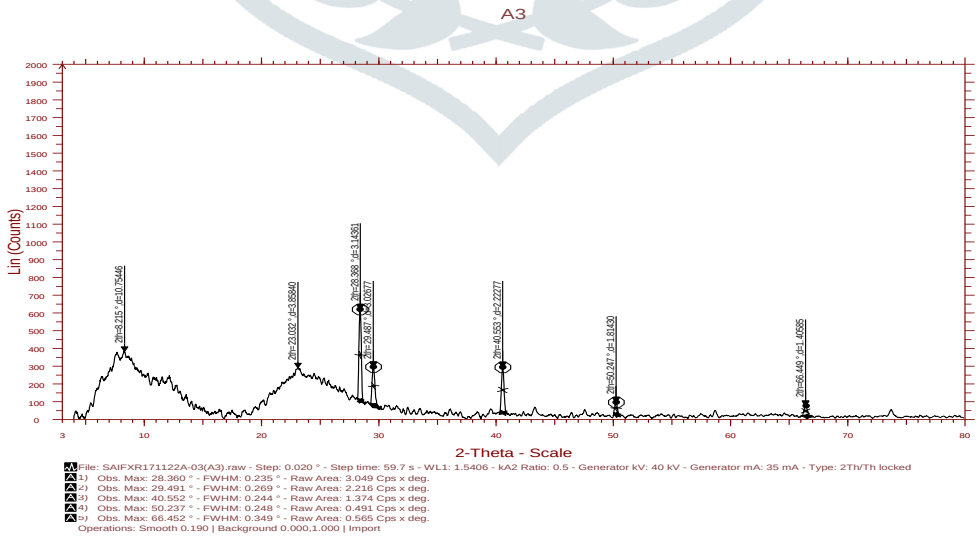

Fig-5 XRD of KOH activated **Limonia acidissima***(* Kavath) shell charcoal

Effect of pH on Iron Removal

Concentration = 4.8mg/l; Contact time = 60min,
Adsorbent dose = 1gm/50ml, Temperature = 30°C.

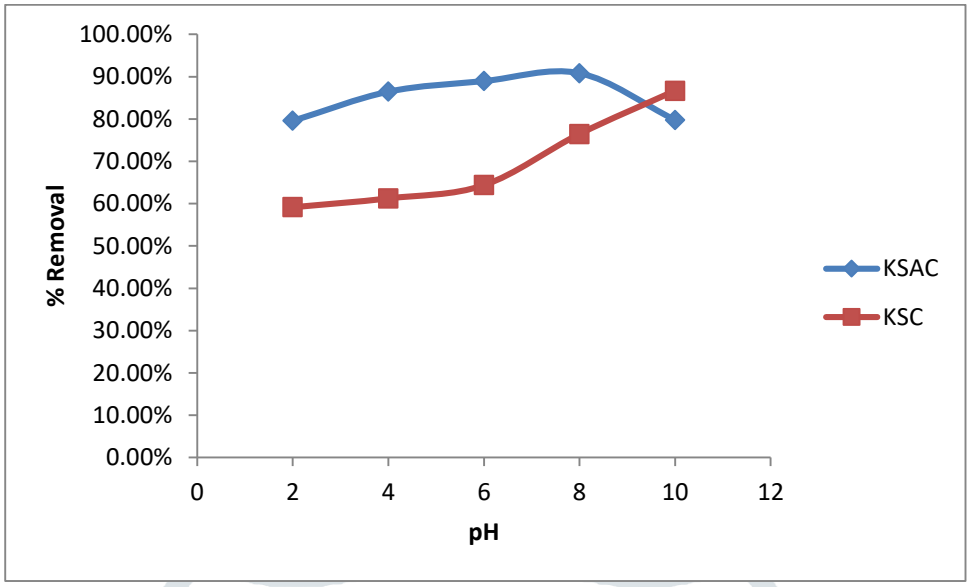

Fig 6 - Effect of pH on Iron Removal

Fig. shows effect of pH on adsorption onto KSC and KSAC. Key factor for the control of the adsorption of metal ions on the adsorbent is pH. The study was done in the pH range of 2 to 10. For Kavath fruit shell charcoal it was found that the adsorption of iron gradually increases as the initial pH of the solution is raised from 2 to 10. The maximum removal of iron was found to be 86.73 % at pH 10. For activated Kavath shell charcoal adsorption of iron gradually increases as the initial pH of the solution is raised from 2 to 8. On further increased pH to 10 shows decrease the percentage of adsorption. The maximum removal of iron was found to be 90.81 % at pH 8. Hence, pH of the iron solution was maintained at 8 for further study.

Effect of initial concentration on Iron Removal

Contact time = 60min, Adsorbent dose = 1g/50ml,
Temperature = 30°C pH = 8,

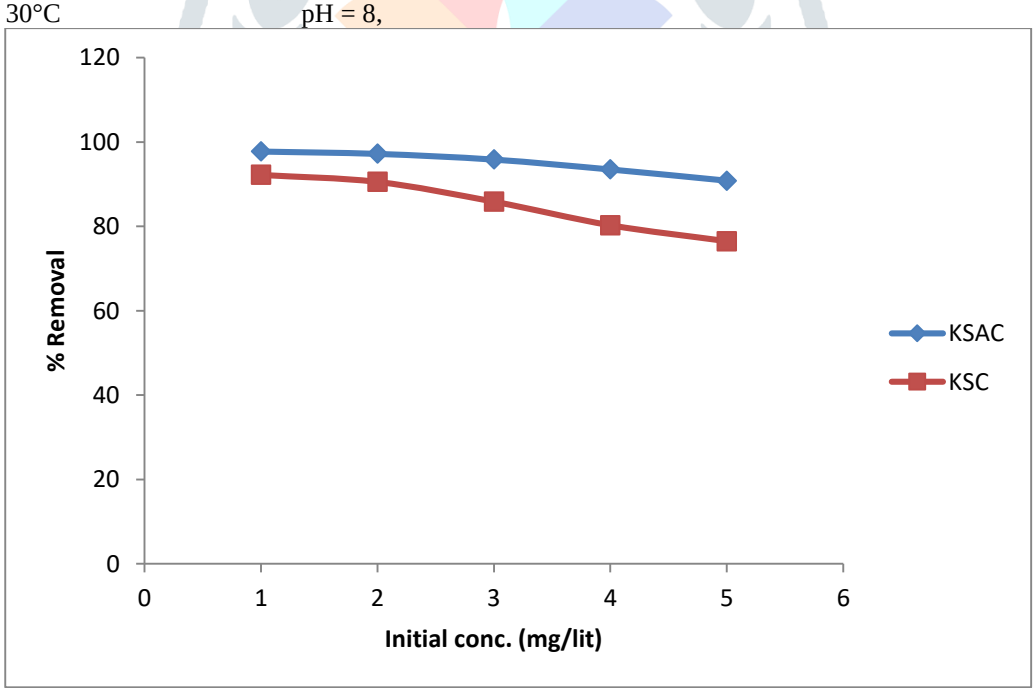

Fig 7 - **Effect of initial concentration on Iron Removal**

The effect of initial concentration of iron (II) ions on adsorption using Kavath shell carbon shows that Adsorption of irons (II) ions in solution increase significantly with decrease in the initial concentration of iron (II) ions in solution. The initial concentration of adsorbate varied from 0.9mg/lit to 4.8 mg/lit, the rate of adsorption for Kavath shell carbon decreased from 92% - 76% and for KOH activated Kavath shell it decreased from 97% - 91%.

Effect of Adsorbent dose on Iron Removal

Contact time = 60min, Temperature = 30°C,
Concentration = 4.8mg/l; pH = 8

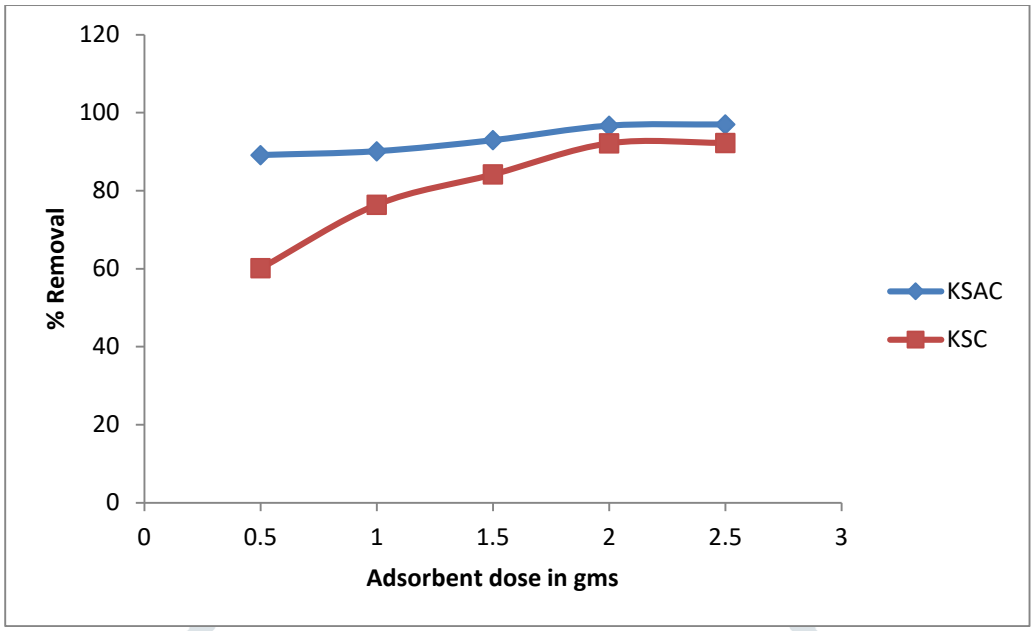

Fig 8 - **Effect of Adsorbent dose on Iron Removal**

The adsorbent doses were varied from 0.5 g to 2.5 g. It was observed that the removal of metal ion increased with the increase in dosage and attains a maximum at 2 g of dosage. It shows higher dose of adsorbent serves higher surface area provides greater number of binding sites for the metal ions. It is observed that, after dosage of 2 gm, there was no significant change in percentage of removal. It may be due to overlapping active sites at higher dosage. So, there was not any appreciable increase in the effective surface area resulting due to the accumulation of exchanger particles. For activated charcoal the maximum removal was 97.00% at 2.5g.

Effect of Temperature on Iron Removal

Contact time = 60min, Temperature = 30°C,
Concentration =4.8mg/l pH = 8,

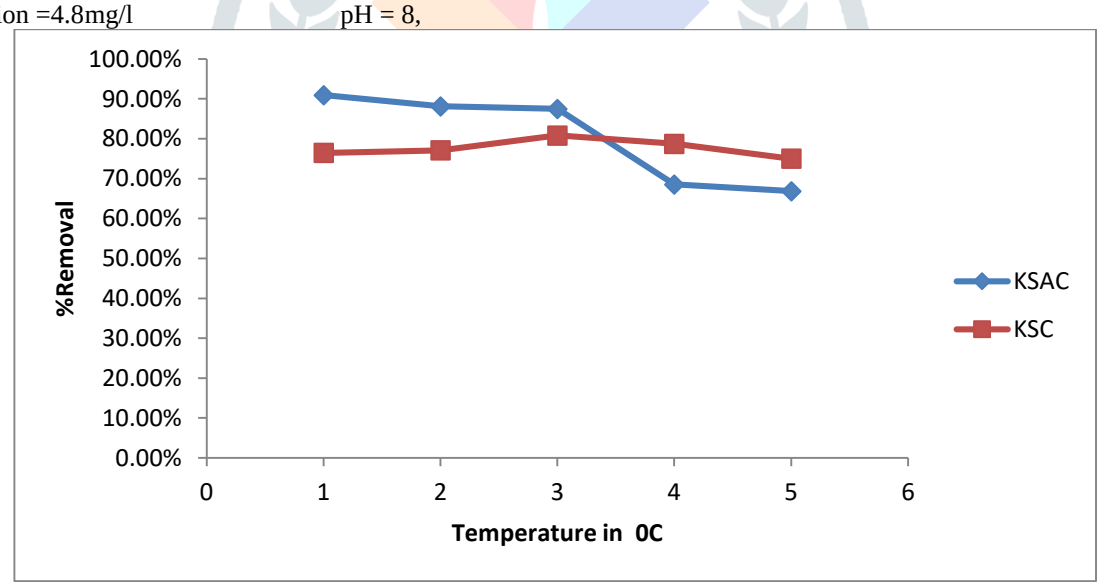

Fig 9- Effect of Temperature on Iron Removal

For Kavath shell charcoal initially the adsorption capacity and percentage removal are increasing with temperature. At 30^{0}**C**, adsorption percentage was 77.46 of adsorbent which increased to 80.83% when the temperature was increased up to 50^{0}**C and** decreases with temperature. Adsorption may be the chemical adsorption which can take place at all temperature. With the increases in temperature, Chemisorption first increases and then decreases. This may be due to at higher temperature, kinetic energy of the molecule is high which increase the mobility of molecule through the boundary layer hence molecule will get sufficient energy for adsorption. While activated charcoal shows decreases adsorption of hardness with increase in temperature.

Effect of Contact Time on Iron Removal

Concentration = 4.8mg/l; Adsorbent dose = 1gm/lit
Temperature = 30°C, pH= 8

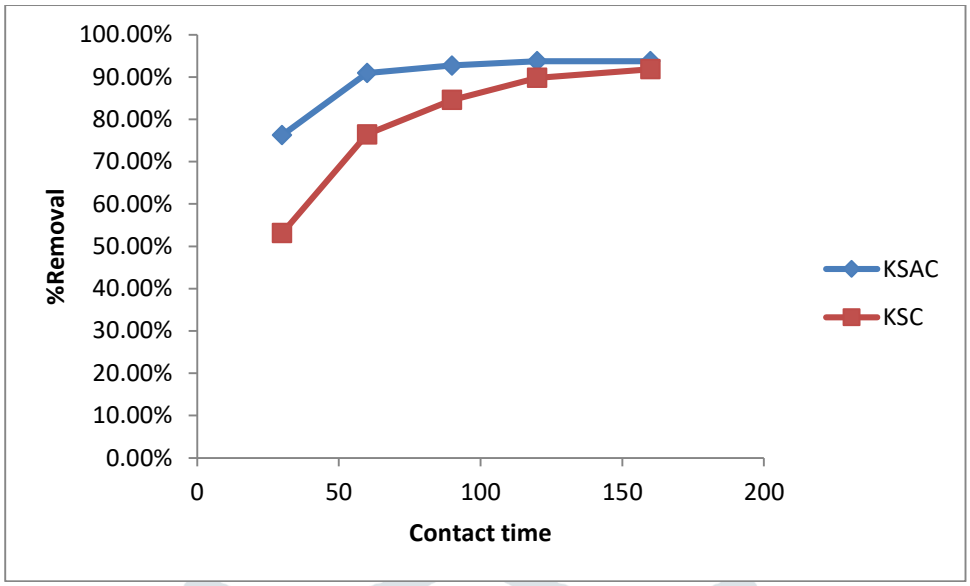

Fig 10- **Effect of Contact Time on Iron Removal**

Removal percentage was recorded at contact time of 30 min to 160 min. The results are shown in table indicates Kavath fruit shell carbon evidently, more than 50 % iron removal occurred within 30 min showing that initially the rate of adsorption of iron is very fast and gradually increases upto 160 min. For activated Kavath fruit shell charcoal initially the rate of adsorption of iron is very fast and gradually increases attaining a steady value after reaching the equilibrium at about 120 min.

Adsorption Isotherms Study

The Freundlich Isotherms - The Freundlich isotherms model is expressed by the following equation:

$\log x/m = \log K_e + 1/n \log C_e$

Where, x is the concentration of Iron adsorbed (mg/g), m is the mass of adsorbent, Ce is the equilibrium Iron conc. (mg/L), K_e and n are Freundlich constant indicating adsorption capacity and favorability of adsorption. Fig. 11 and 12 shows Freundlich isotherm curve for adsorption of iron (II) onto adsorbent.

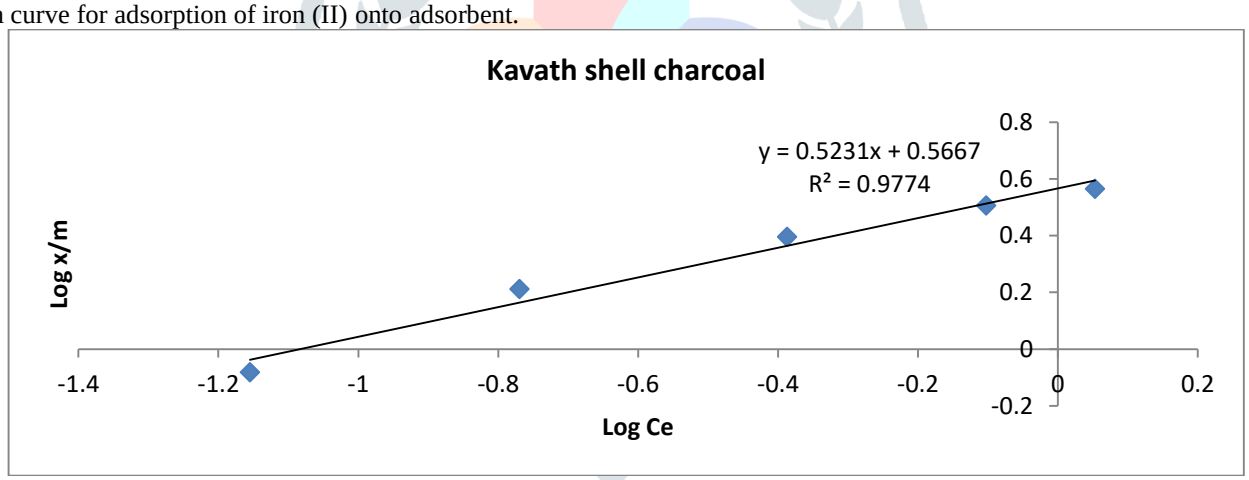

Fig 11 - Freundlich isotherm curve for adsorption on Kavath shell charcoal

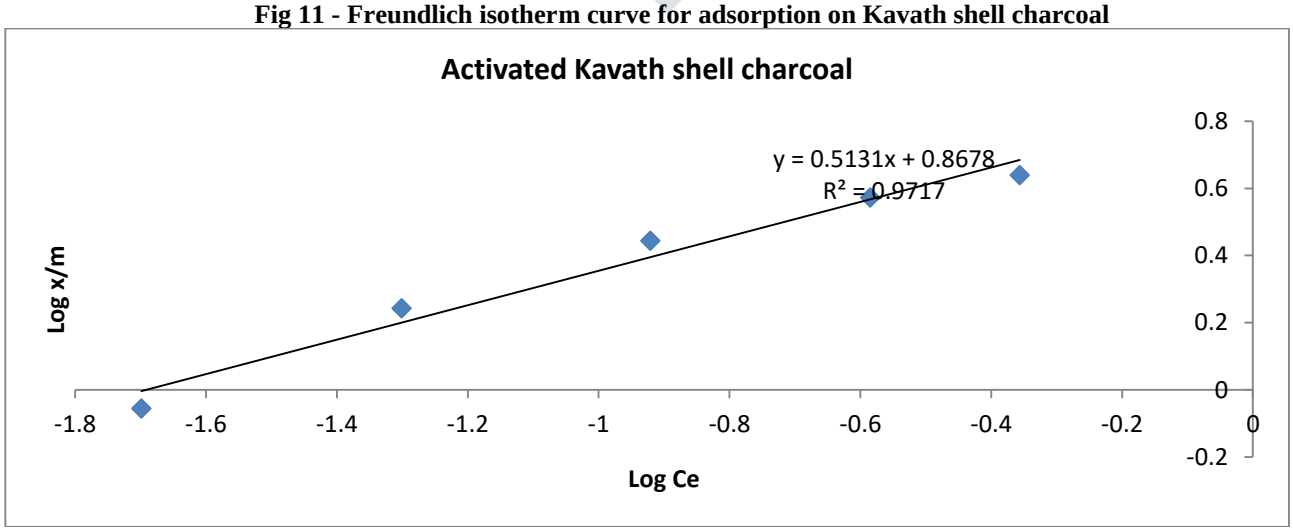

Fig 12-Freundlich isotherm curve for adsorption on Activated Limonia acidissima(Kavath) shell charcoal

Table 1 – Calculation of Freundlich Constants

Sr. No.	Adsorbent	1/n	n	Log k	Adsorption capacity k
1	KSC	**0.523**	1.912	**0.566**	3.681
2	KSAC	**0.513**	1.949	**0.867**	7.362

Value of n and K obtained for all other adsorbent indicate that the adsorbent are good for uptake of Iron from aqueous solution. The high Correlation coefficient of Freundlich curves shows good linearity for adsorbent and also indicates strong binding of ions to the surface of adsorbent.

Langmuir Isotherm - Langmuir isothermal model is described by the following equation:

$q_e = abC_e/(a+ bC_e)$

Where, qe is the amount of Iron adsorbed (mg/g), and Ce is the equilibrium Iron conc. (mg/L), a and b are Langmuir constants related to capacity and energy of adsorption respectively. The Langmuir model deals with monolayer adsorption and constant adsorption energy.

The linear form of Langmuir equation was applied for adsorption equilibrium is

$$Ce/qe = 1/Q_o b + Ce/Q_o$$

The plot of Ce/qe against Ce gave a straight line with a slope $1/Q_0$. The dimensionless constant separation factor RL can be used to define essential features of Langmuir isotherm model. RL is expressed by the following Equation

$R_L= 1/1+bC_e$

Where, Ce is the initial hardness (mg/L) and 'b' is the Langmuir constant (in g/L).

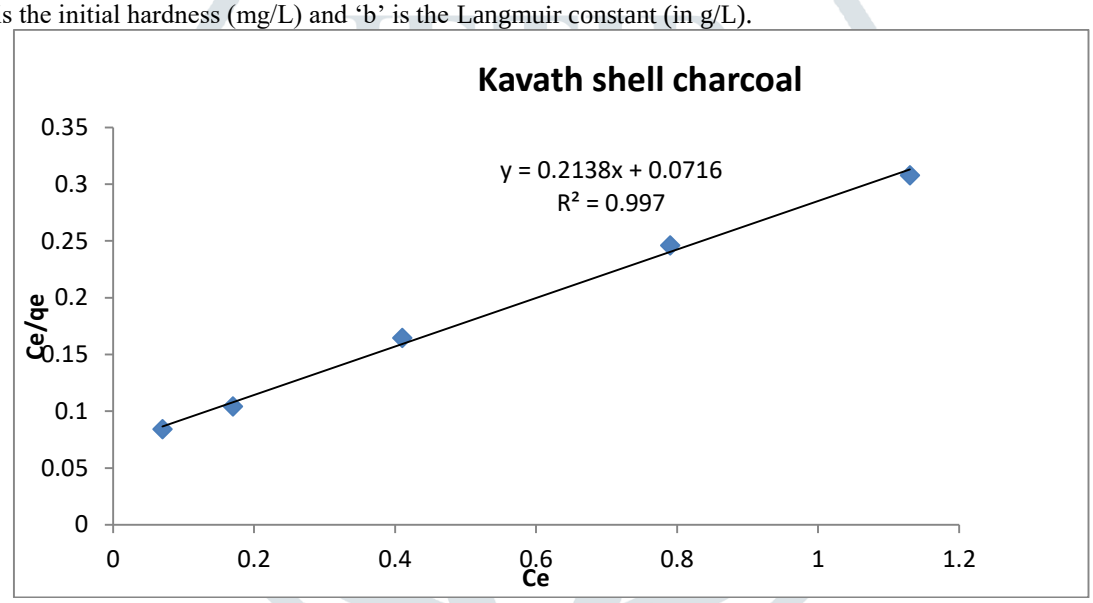

Fig 13- Langmuir isotherm curve for adsorption on Limonia Acidissima (Kavath) shell charcoal

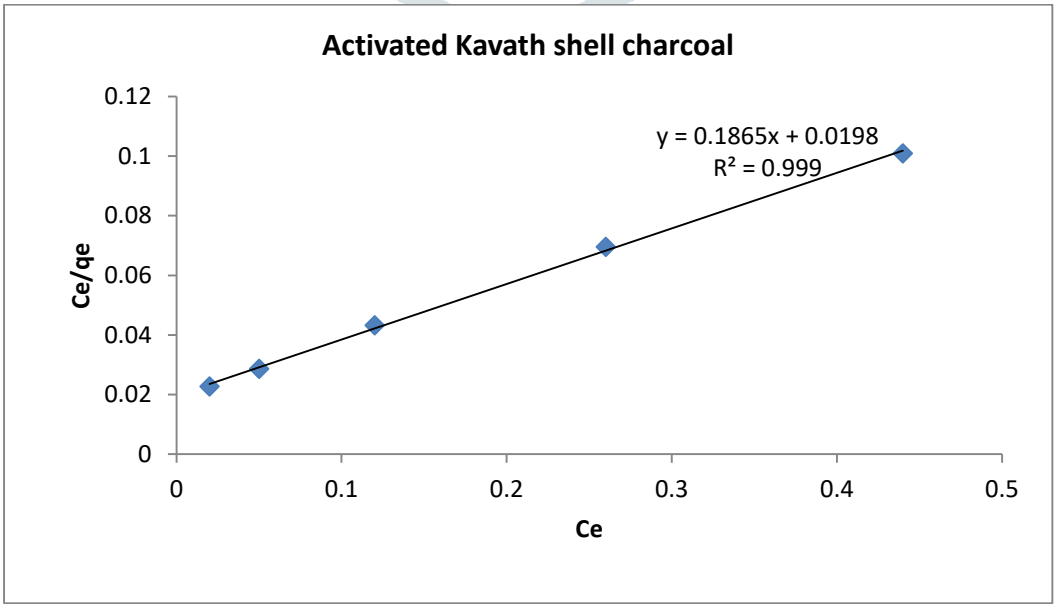

Fig 14- Langmuir isotherm curve for adsorption on Activated Limonia Acidissima (Kavath) shell charcoal

Table 2 -Langumuir Constants

Sr. No.	Adsorbent	B	Q_0
1	KSC	3.0000	4.6948
2	KSAC	9.7895	5.3763

The plots Ce/qe as a function of Ce for the adsorption was found linear suggest applicability of Langmuir model in present adsorption system. The higher adsorption capacity Q_0, b values obtained for KSAC indicate higher adsorption capacities and good performance.

CONCLUSION

Result clearly shows that adsorption of Fe^{2+} on to carbon and activated carbon was favored. The optimal dose was found to be 2.5gm and the maximum removal was seen within 120 and 160 minutes of contact time for KSC and KSAC respectively. Based on the results obtained in the present study, it is clear that Kavath shells carbon and activated carbon both are effectively removed iron from aqueous solution. Since the Kavath shells are locally available, especially in forest regions of Chandrapur district, this adsorbent is expected to be economically feasible for removal of iron from groundwater.

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