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Comparitive Adsorption Studies of Water Hardness Removal 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 remove water hardness ions from hard water 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 hardness removal was 10 with percentage removal of 81%. In this case pH below 10 shows negligible efficiency of adsorption. For KOH activated carbon pH for maximum hardness removal was 10 with percentage removal of 96%. However, for the safety of softened water, preferable pH is 7 which yield 82% removal efficiency for water hardness removal. Temperature study reveals that the KOH activated carbon shows adsorption is exothermic as removal decreases with the increase in temperature while in case of charcoal adsorption is endothermic as efficiency increases with the increase in temperature. The adsorption of hardness ions on Limonia acidissima(Kavath) shell carbon and activated carbon increased as adsorbent dosage increases from 1gm/50ml to 5gm/50ml and with the increase in contact time. The study showed that adsorbent had the potential for hard water softening.

Keywords: Activated carbon, adsorption, batch adsorption experiments, Limonia acidissima **(** Kavath) shell, water hardness removal.

Introduction

Rapid urbanization, population growth, industrial expansion and waste generation from domestic and industrial sources have released wastewaters which are hazardous to man and other living organisms. Many industries discharge untreated or inadequately treated wastewater into water ways. As water of good quality is a necessary, it has become very important to treat wastewater for removal of pollutants. A number of technologies have been developed over the years to remove pollutants, organic matter, etc. from industrial wastewater. The most important technologies include biological treatment, physical treatment, and chemical treatment and these methods are generally expensive and requires skilled personnel. Among all the treatment methods, adsorption is one of the more popular methods for the removal of pollutants, metal ions, or dyes from the wastewater. Adsorption process is one of the easiest, safest and more effective methods for metal removal from industrial effluents[1, 2] 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[3], rice husk[4], modified sawdust of walnut[5], papaya wood[6], maize leaf[7], rice husk ash and neem bark[8], fly ash[9] and tea-industry waste[10]. 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. **A**mong the various known forms of water contaminants, Calcium and Magnesium salts are of great apprehension since they lead to water hardness. Water hardness problem is reported to exist in various parts of state, the reason behind is rock type, which is rich in Calcium and Magnesium. These ions dissolve easily in to the groundwater and make them hard. In daily uses, hard water is associated with number of challenges that include scaling in boilers, washing machines and pipes[11], difficult lathering with soap, objectionable spots on sinks and clothes as well as toughening of skin and hair. Hard water is said to cause serious health problems like urolithosis, cardiovascular disorder, kidney problems, anencephaly and cancer[12]. Additionally, WHO reports that excess intake of calcium is associated with kidney stones and that of magnesium leads to diarrhea and laxative effect due to change in bowel habit. Because of the challenges raised by hardness in water, immediate actions to soften water are to be expected. Water softening by adsorption using agricultural wastes based activated carbon as adsorbent seems to be potential in the sense that the agricultural wastes are locally and cheaply available.

Calcium and magnesium play vital roles in the structure and functions of the human body. High intake of calcium and magnesium in drinking water could result in symptoms of toxicity such as a kidney stones, gastric and breast cancer, low blood pressure, muscle weakness, confusion and abnormal cardiac rhythm[13]. Therefore, the need to purify water which is not suitable for human consumption such as hard water cannot be overemphasized. It is obvious that hard water treatment methods required high capital operations. Hence, finding cheap and effective developed processes remains a major concern. For the purpose of removing hardness ions from water, various adsorbent materials have been used such as Moringa oleifera[14], Peanut hull[15], pumice[16] and Phyllanthus emblica[17]. The equilibrium time required for the adsorption of Ca^{2+} is less compared to the time required for Mg^{2+} removal. The reason for that is likely to be due to the smaller hydrated radius of Ca^{2+} ions compared to that of Mg^{2+}ions which leads to Ca^{2+} ions to be adsorbed faster than Mg^{2+} ions[18], Similar finding observed when natural pumice stone used as adsorbent and found it is a better material for removing Ca ions than Mg ions from water[16].

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. The fruit looks similar in appearance to the Bael fruit *(Aegle marmelos)*. . 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 - Synthetic hard water was prepared as reported by Window on State Government (1996) whereby 1.19g of CaCl2 and 1g of MgSO4 were dissolved in a litre of deionized water to make a water with hardness of 1214.8 mg/L as CaCO3 and this served as a stock solution[19].

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 transforms 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 different water hardness 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 hardness ions onto the adsorbent surface, hence high efficiency in water softening.

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.

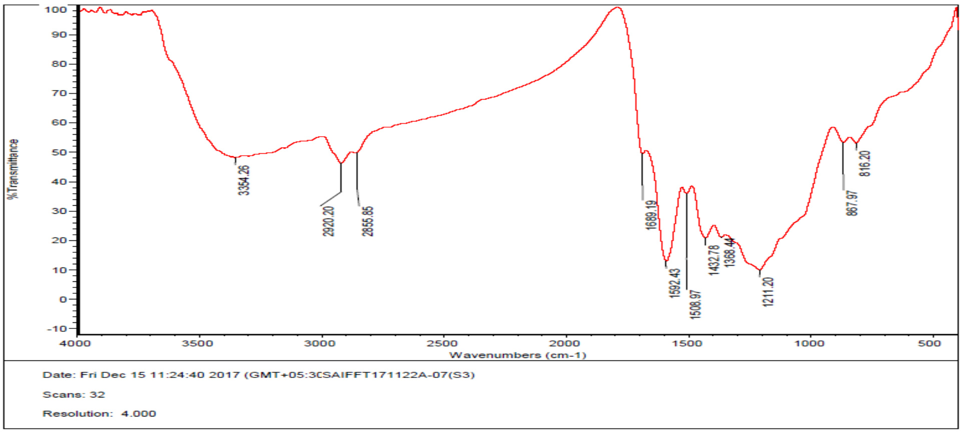

Fig-2 FTIR spectrum of **Limonia acidissima*(*** Kavath) shell charcoal

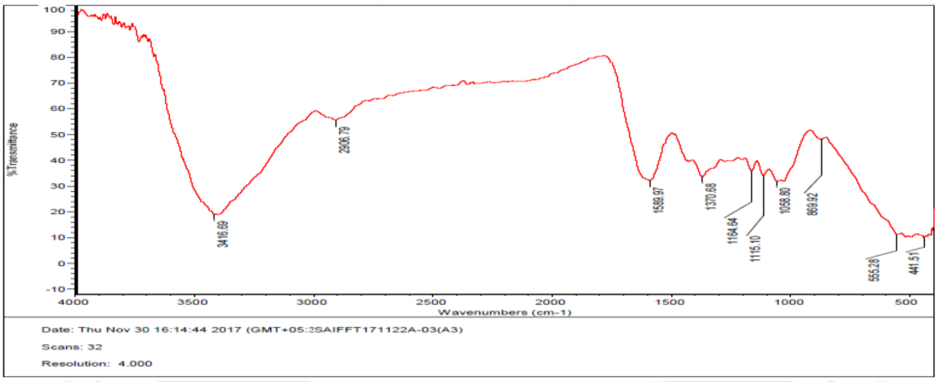

Fig-3 FTIR spectrum of KOH activated **Limonia acidissima*(*** Kavath) shell charcoal

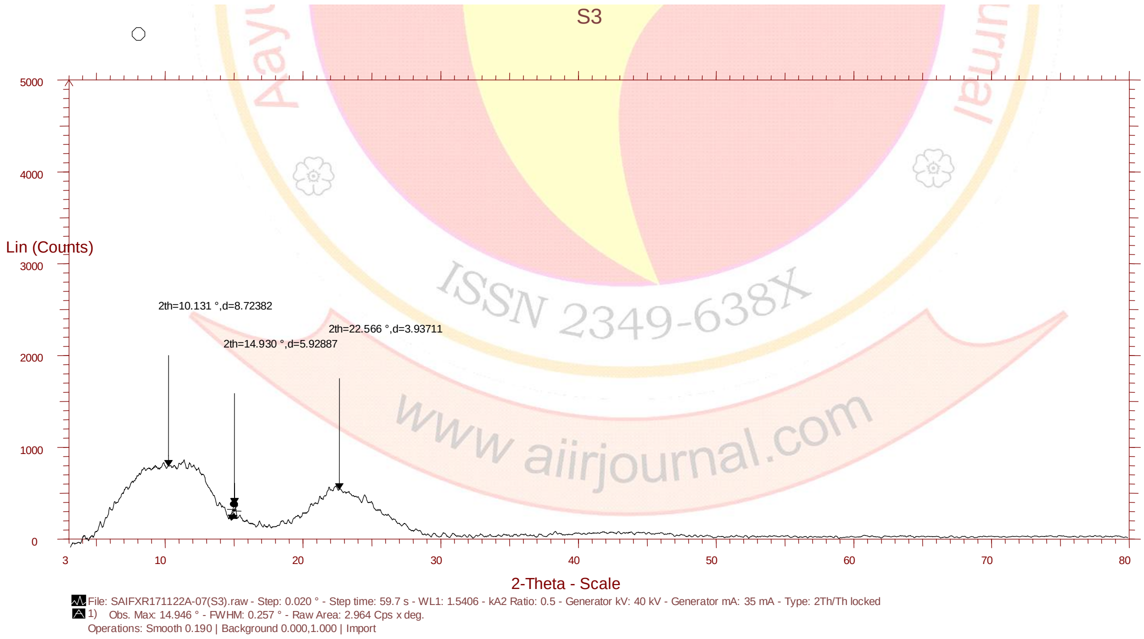

Fig-4 XRD of **Limonia acidissima*(*** Kavath) shell charcoal

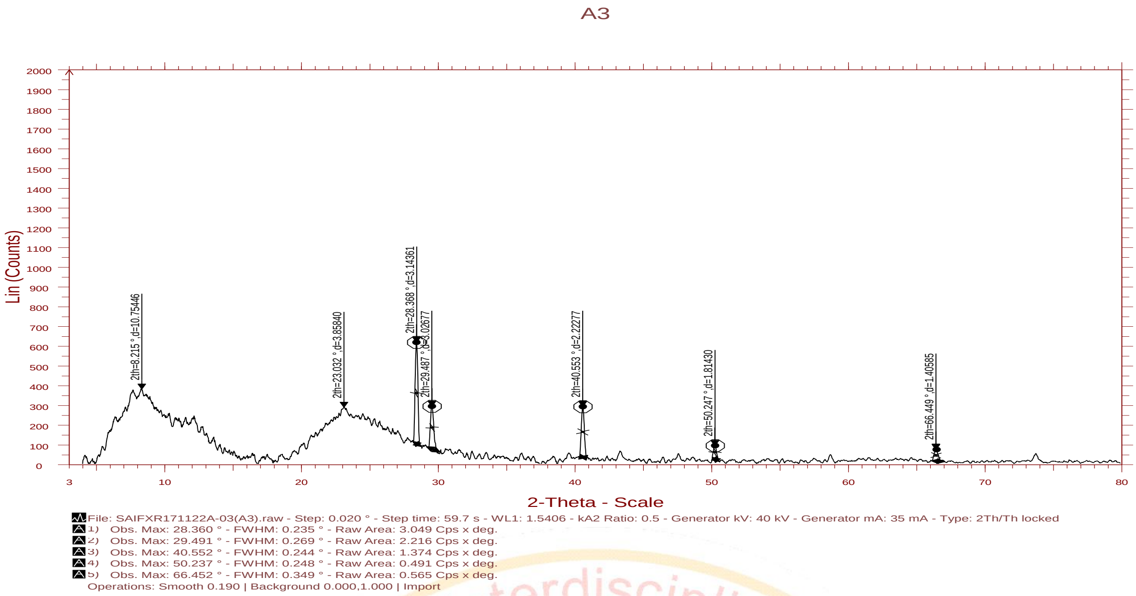

Fig-5 XRD of KOH activated **Limonia acidissima(** Kavath) shell charcoal

Effect of pH on Hardness Removal

Concentration = 820mg/l; Contact time = 60min,

Adsorbent dose = 1gm/50ml, Temperature = 30°C.

pH = KSC -10, KSAC - 7

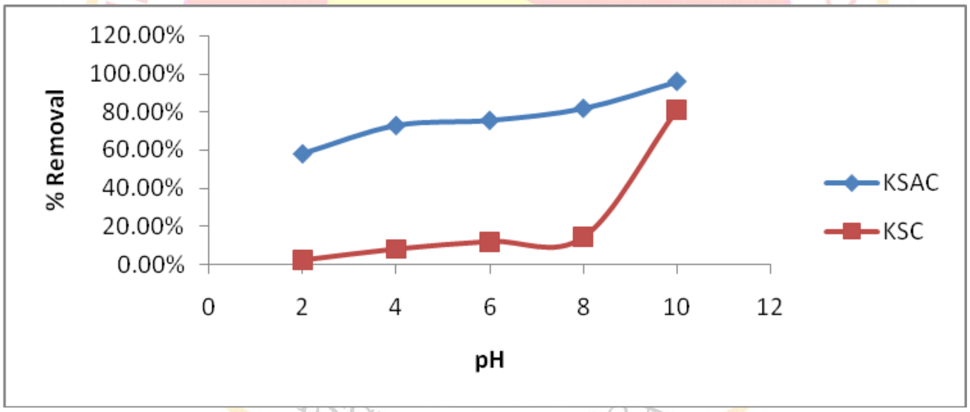

Fig 6 - Effect of pH on Hardness Removal

Fig. shows effect of pH on adsorption onto KSC and KSAC. During this study, results revealed that the removal of water hardness ions was strongly dependent on the pH of the solution. The initial pH of water samples was varied from 2 to 10. In case of KSC; from the pH of 2 to 8 hardness removal efficiency is very low and was observed to be almost constant, but exponential increase of removal efficiency was observed at the pH of 10. Highest removal efficiency was 81.46% that was achieved at the pH of 10. When pH of the solution of pH 10 checked after adsorption it was found to decrease in the pH value at some extent, might be due to substance have good adsorbing sight for OH^- ions.

In case of KSAC hardness removal efficiency is very high at all range of pH and there was an increase in efficiency from the pH from 2 to 10. This might be due to that, as pH increases the competition between hydroxonium ions, H_3O^+ and positively charged metal ions on the surface of adsorbent decreases[20]. Highest removal efficiency was 96.10% that was achieved at the pH of 10. For the sake of providing safe water in an economical and safe way, it is important to consider softening efficiency at neutral pH. From the data, it was found that around neutral pH, efficiency was constant with the average removal efficiency of 82%

Effect of initial concentration on Hardness Removal

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

pH = KSC -10, KSAC - 7,

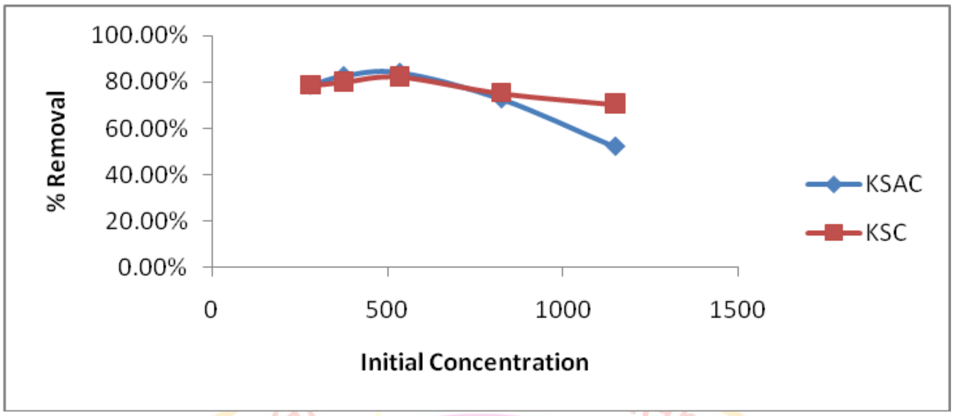

Fig 7 - Effect of initial concentration on Hardness Removal

The effect of initial concentration on adsorption of hardness by Kavath shell carbon and activated charcoal was studied by varying the concentration shows that adsorption capacity was found to increase with initial concentration and reaches maximum 82.24% at 535mg/L for KSC, 84.11% at 535mg/L for KSAC, increase in the value may be due to the higher concentration difference reduces the mass transfer resistances between adsorbent and adsorption media. On further increase in concentration the percentage of adsorption was observed to decrease. This may be due to saturation of the surface and available active sites of the adsorbent.

Effect of Adsorbent dose on Hardness Removal

Contact time = 60min, Temperature = 30°C, Concentration = 840mg/l;

pH = KSC - 10, KSAC - 7,

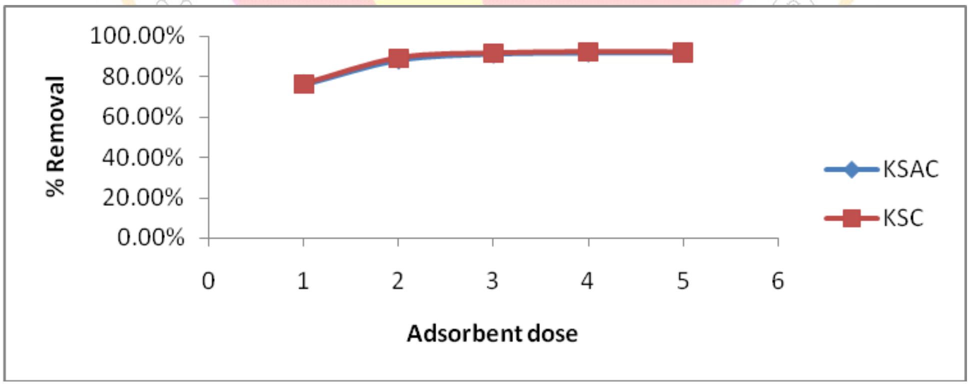

Fig 8 - Effect of Adsorbent dose on Hardness Removal

Study of effect adsorbent dose on adsorption of hardness ions was indicated that removal efficiency for activated charcoal of KSC and KSAC increases with increase in the adsorbent dose up to 3 gm/50 ml. After a this dose of adsorbent, may be the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of dose of adsorbent. That's why beyond 3gm the adsorption found to be almost constant.

Effect of Temperature on Hardness Removal

Contact time = 60min, Temperature = 30°C, Concentration =675mg/l
pH = KSC -10, KSAC - 7,

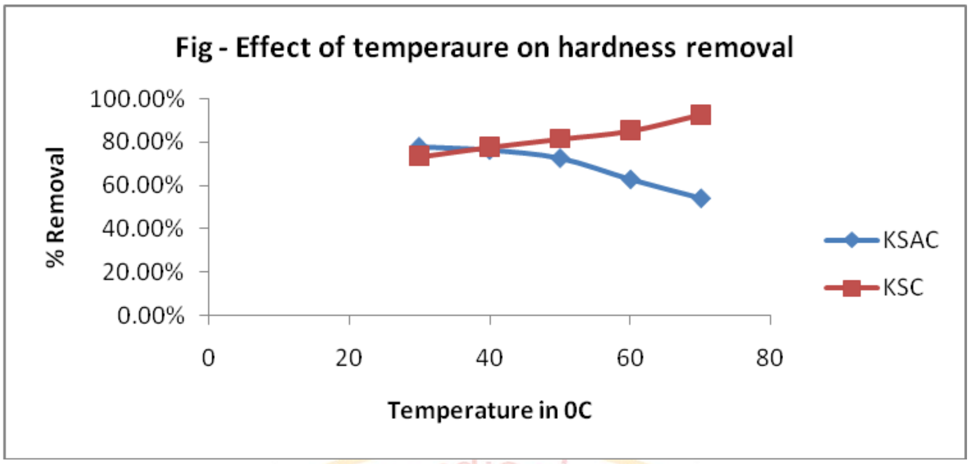

Fig 9- Effect of Temperature on Hardness Removal

Effect of temperature on adsorption of the hardness ions onto kavath shell charcoal at pH 10 was indicated that adsorption of hardness ions increases with the increase in temperature. Hardness increases up to 92.52%. This may be due to more active sites available with increase in temperature for hardness ions adsorption and process is endothermic. While activated charcoal shows decreases adsorption of hardness with increase in temperature this may be due to this may be due to adsorption of Ca^{2+} and Mg^{2+} ions on adsorbent surface is physical adsorption and may be due to exothermic reaction.

Effect of Contact Time on Hardness Removal

Concentration = 900mg/l; Contact time = 60min, Temperature = 30°C,
pH= KSC –10, KSAC - 7,

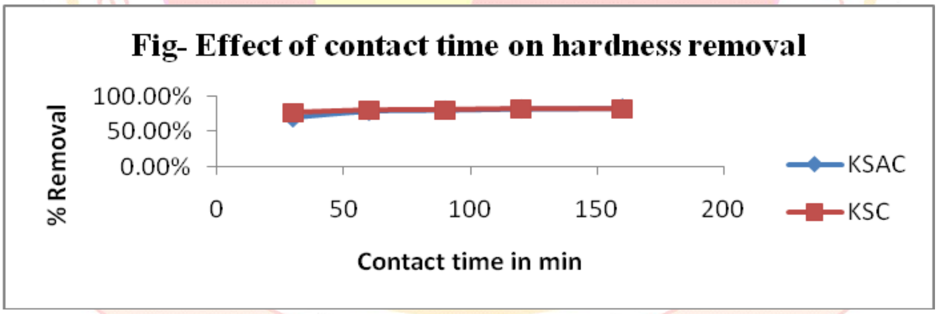

Fig 10- Effect of Contact Time on Hardness Removal

The effect of contact time was studied at 30°C, at intervals of 30 min. Observation shows that the removal of hardness ions by Kavath shell charcoal which studied at pH 10 increased with increasing contact time. The percentage hardness removal approached equilibrium at120 min. Further increase in contact time did not show change in hardness concentration. On the other hand adsorption of by activated Kavath shell charcoal shows constantly and slowly increased with increase in contact time, this may be due to equilibrium time is not still reached up to 160min with activated charcoal. Adsorption increased with increase in contact time, might be due to the fact that, large numbers of vacant surface sites are available for the adsorption during the initial stage. After some times, repulsive forces between solute molecules on solid phase and liquid phase may create difficultness for the solute molecules to occupy remaining vacant surface sites.

Adsorption Isotherms Study

For the purpose of understanding the distribution of Ca^{2+} and Mg^{2+} ions between the liquid phase and the solid phase, the Langmuir and Freundlich isotherm models were used.

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 hardness adsorbed (mg/g), m is the mass of adsorbent, Ce is the equilibrium hardness (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 hardness ions onto adsorbent.

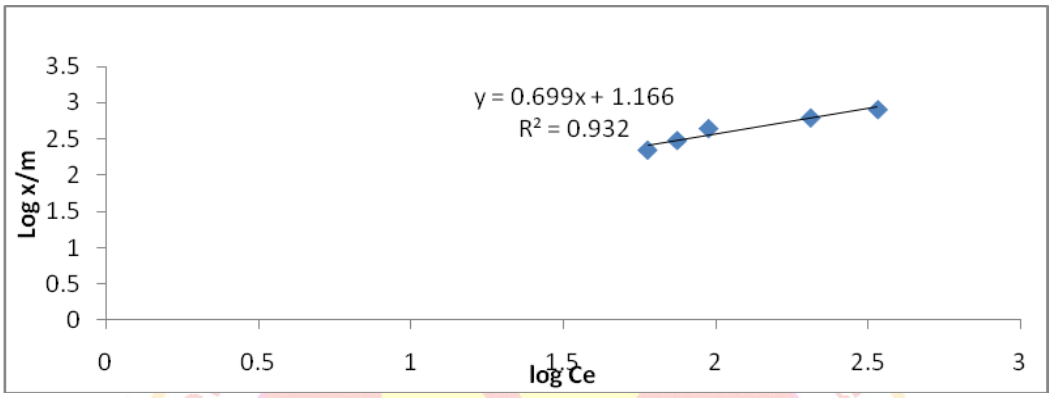

Fig 11 - Freundlich isotherm curve for adsorption on Kavath shell charcoal

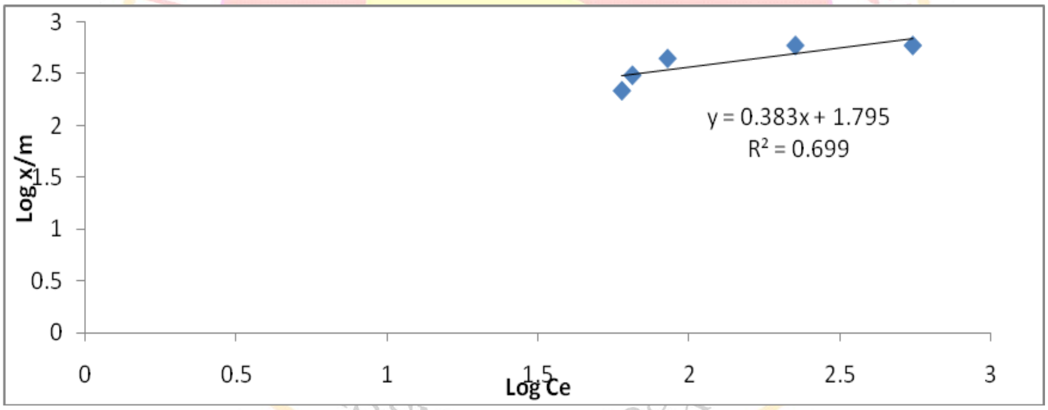

Fig 12-Freundlich isotherm curve for adsorption on Activated Limonia acidissima (Kavath) shell charcoal

Table 1 – Calculation of Freundlich constants for hardness ions

Sr. No.	Adsorbent	1/n	n	Log k	Adsorption capacity k
1	KSC	0.699	1.431	1.166	14.655
2	KSAC	0.383	2.611	1.795	62.373

Value of n and K obtained for all other adsorbent indicate that the adsorbent are good for uptake of Hardness from aqueous solution. The high Correlation coefficient of Freundlich curves for KSC 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 hardness adsorbed (mg/g), and Ce is the equilibrium hardness (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).

The separation factor RL indicates the isotherm's shape and the nature of the adsorption process, that is, unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible (RL = 0).

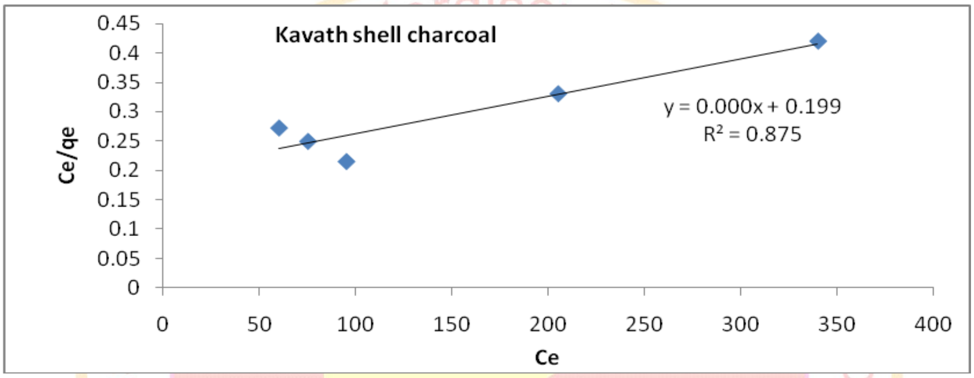

Fig 13- Langmuir isotherm curve for adsorption on Limonia Acidissima *(* Kavath) shell charcoal

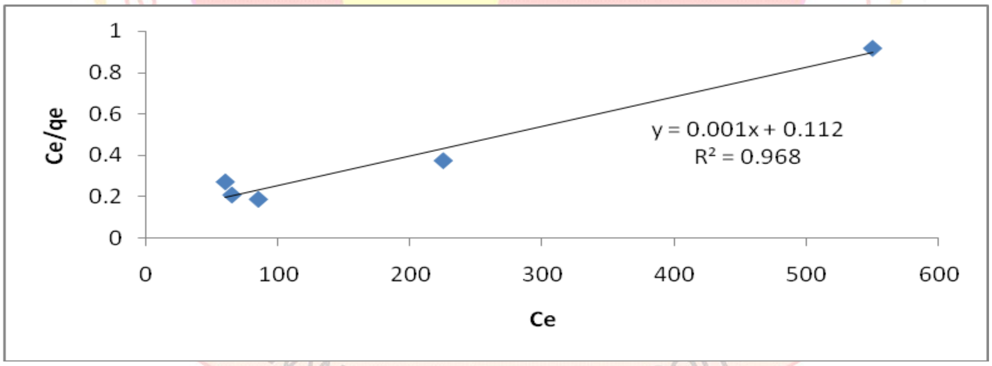

Fig 14- Langmuir isotherm curve for adsorption on Activated Limonia acidissima*(* Kavath) shell charcoal

Table 2 -Langumuir constants for hardness ions

Sr. No.	Adsorbent	b	Q_0	R_L
1	KSC	-----	---	---
2	KSAC	0.0089	1000	0.286 - 0.089

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 and R_L values which are between 0 to 1 indicate favorable adsorption.

Conclusion

Removal of hardness (Ca^{2+} and Mg^{2+}) by Application of operational conditions such as contact time, adsorbent dose, pH and concentration of adsorbate led to increase of hardness removal for both carbon and activated carbon. Temperature shows increase in hardness removal for carbon and increase with activated carbon. Result clearly shows that adsorption of Ca^{2+} and Mg^{2+} on to carbon and activated carbon was favored. The optimal dose was found to be 3gm 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 effective in water softening. Since the Kavath shells are locally available, especially in forest regions of Chandrapur district where hardness problem is prevailing, then, this adsorbent is expected to be economically feasible for removal of hardness from groundwater. Materials we used are reported as an adsorbent very first time.

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