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REMOVAL OF FLUORIDES IN DRINKING WATER USING BIOCHAR

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ABSTRACT

Agriculture is the predominant occupation in India, accounting for about 52% of employment. Major agricultural products include rice, wheat, oilseed, cotton, jute, tea and sugarcane. Maharashtra is a major state in the Indian Union. Vidarbha is the eastern region of Maharashtra state. It occupies 31.6% of total area and holds 21.3% of total population of Maharashtra Vidarbha accounts 25% of total production of crops in Maharashtra. Annually, around 59,55,579 Tons of agricultural crop is produced. After harvesting the crop, large quantities- about 1,15,61,204 Tons - of residue is generated.

40% of agricultural residues are used as domestic fuel while a large amount is simply burnt in the field. This burning of residue in the field not only increases pollution but also wastes the biomass energy. The residues' cellulosic mass can be converted into useful products like bio-char, bio-oil, bio-chemicals etc. by pyrolysis.

We have used pyrolysis to convert the biomass available in the form of agricultural residues to useful products – mainly biochar. The process has been optimized in terms of temperature and time of pyrolysis as also the size of the feed material. The biochar produced has been characterized through techniques like SEM, BET surface area values.

High fluoride levels in drinking water has become a critical health hazard of this century as it includes intense impact on human health including skeletal and dental fluorosis. The current

methods for removal of fluoride are chemical precipitation with calcium and aluminum salts, ion exchange using polymeric resins, adsorption on activated carbon, reverse osmosis and electrodialysis. Activated biochar has been reconsidered as a potential adsorbent for defluoridation of drinking water because of its high fluoride adsorption capacity.

We have studied adsorption of fluoride and find that fluoride can be effectively removed from water solutions by adsorption on activated char produced from agricultural residues. The adsorption process has been optimized. We find that maximum defluoridation occurred with contact time of 120 minutes at a dosage of 3 mg/litre to effect removal of 73 % of fluoride content in drinking water.

Key Words:-Fluorides, Biochar , Agricultural residue.

1.0 Introduction

Agriculture usually plays a vital role in the economy of every nation. Not only for the reason that it tends to feed the entire population of a country but also in the respect that agriculture correlates and interacts with all the related industries of that country. A country is usually considered to be a socially and politically stable nation if it possesses a very stable agricultural base..

India's large service industry accounts for 57.2% of the country's GDP while the industrial and agricultural sector contribute 28% and 14.6% respectively[1]**.**Agriculture is the predominant occupation in India, accounting for about 52% of employment. The service sector makes up a further 34 % and industrial sector around 14%[2] Major agricultural products include rice, wheat, oilseed, cotton, jute, tea, sugarcane, potatoes, cattle, water buffalo, sheep, goats, poultry and fish. Major industries include stele communications, textiles, chemicals, food processing, steel, transportation equipment, cement, mining, petroleum, machinery, information technology enabled services and pharmaceuticals.

Vidarbha is the eastern region of Maharashtra state made up of Nagpur Division and Amravati Division. It occupies 31.6% of total area and holds 21.3%[3] of total population of Maharashtra Vidarbha's economy is primarily agricultural and also the region is rich in forest and mineral wealth Agriculture is the predominant occupation in Vidarbha accounting for about 50% of employment.

The main cash crops of the region are cotton, sugarcane and soya beans. Traditional crops are sorghum (jowar), pearl millet (bajra) and rice. Amaravati is the largest orange growing district. Yawatmal is the largest cotton growing district. Gondia is the largest rice growing district.

The production of crops (Percentage) in Vidarbha is given in Table 1.1[4]

SR.NO.	NAME OF CROP	%
01	COTTON	18.17
02	JOWAR	8.12
03	MAIZE	2.51
04	PEAGON PEA	5.31
05	RICE	5.23
06	SAFFLOWER	2.00
07	SOYABEAN	18.43
08	SUGERCANE	14.32
09	SUNFLOWER	3.0
10	WHEAT	3.31
11	OTHER	19.34

Table 1.1

Vidarbha accounts 25% of total production of crops in Maharashtra. Around **59,55,579 Tones**[5] Of agricultural crop produced. With this crop large quantity of residue is also generated. Near about **1,15,61,204 Tones** [6] of residue generated per year.

2.0 Materials and Methods

The activated charcoal was prepared from agricultural residue of cotton and pegon pea. The residue of cotton and pegon pea first cut into smaller pieces about 2cm. and then pyrolysed at

400 ^{oc} in Muffle furnace The resulting product is cooled to room temperature and crushed . Then it is sieved to the desired particle size 106-150 mesh. This Agricultural Residue Charcoal (ARC) /Biochar is then used for further experiment.

3.0 Analysis of Biochar

3.1 Proximate analysis of Biochar

3.2 BET

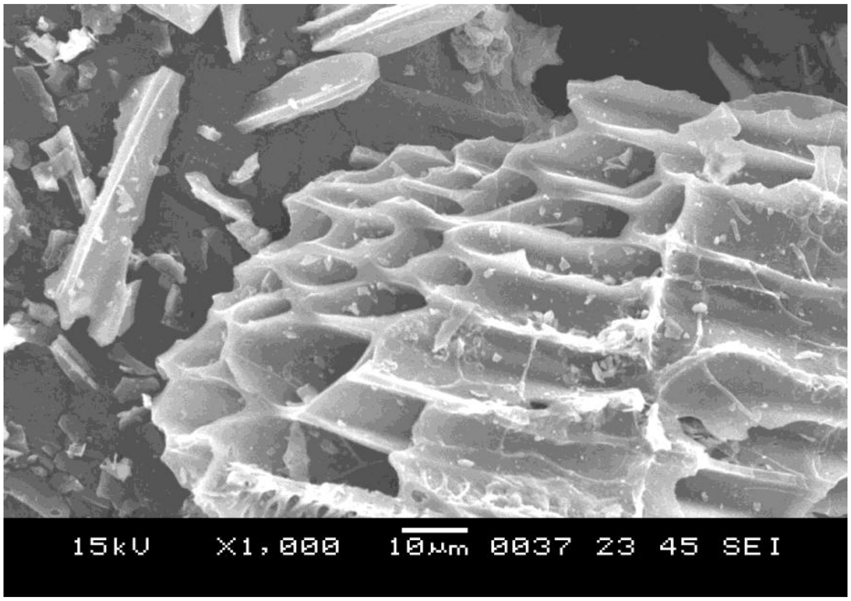
Sample	Moisture	Volatile matter	Ash%	Fixed Carbon %
Biochar From ARC	**5.52**	**5.82**	**11.84**	**76.82**

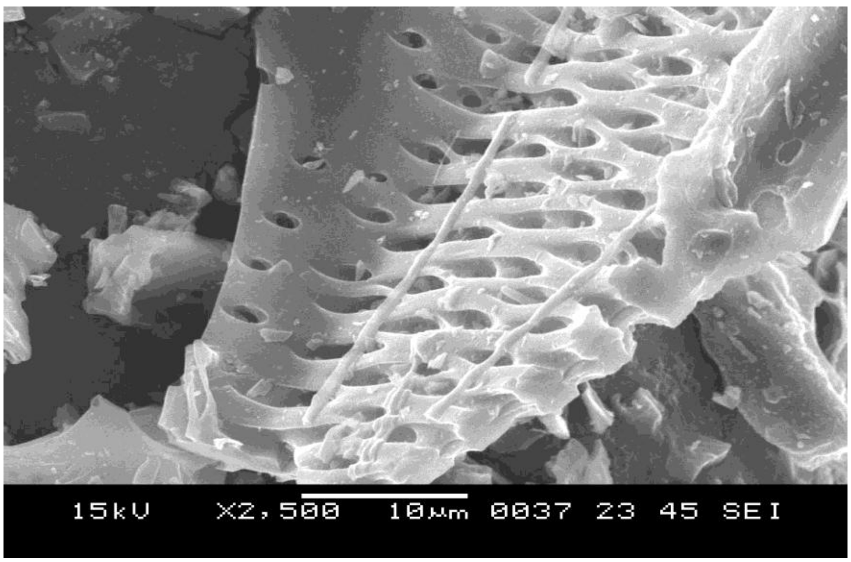
The BET surface analyzer is used to determine the surface area of activated carbon sample. The result obtained is shown below.

Sample	BET surface area m^2/gm
Biochar From ARC	**395**

3.3 Scanning Electron Microscopy (SEM)

As can be seen, the size of the carbon particles produced is in the range of 10 to 100 µm. The particles are all porous. The tubular structure of the carbon can also be seen.



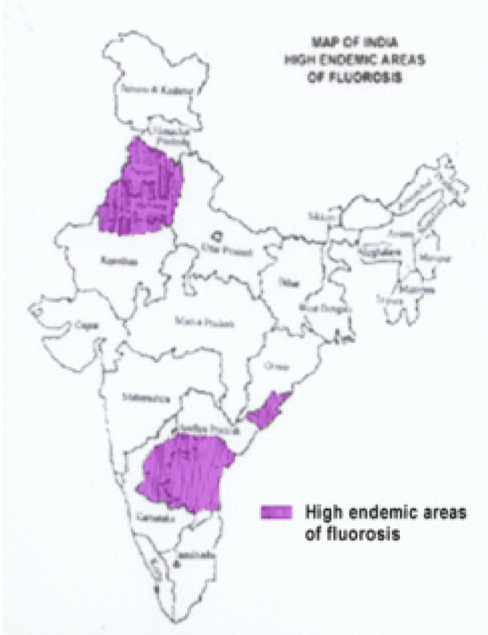


4.0 Fluorides

Fluoride is the anion F^{-}, the reduced form of fluorine when as an ion and when bonded to another element. Both organofluorine compounds and inorganic fluorine compounds containing are called fluorides. Fluoride, like other halides, is a monovalent ion (−1 charge). Its compounds often have properties that are distinct relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxide ion. Fluorine-containing compounds range from potent toxins such as saran to life-saving pharmaceuticals such as efavirenz, and from inert materials such as calcium fluoride to the highly reactive sulfur tetra fluoride. The range of fluorine-containing compounds is vast because fluorine is capable of forming compounds with all the elements except helium and neon.. Compounds containing fluoride anions and in many cases those containing covalent bonds to fluorine are called fluorides.

High fluoride levels in drinking water has become a critical health hazard of this century as it includes intense impact on human health including skeletal and dental fluorosis. Though fluoride is an essential constituent for both human and animals , it can either beneficial or detrimental to human health depending upon the level of fluoride in drinking water.**Dental fluorosis** is a health condition caused by a child receiving too much fluoride during tooth development. The critical period of exposure is between 1 and 4 years old; children over age 8 are not at risk. In its mild form, which is the most common, fluorosis appears as tiny white streaks or specks that are often unnoticeable. In its severest form, which is also called mottling of dental enamel, it is characterized by black and brown stains, as well as cracking and pitting of the teeth.[7]

The severity of dental fluorosis depends on the amount of fluoride exposure, the age of the child, individual response, as well as other factors including nutrition. Although water fluoridation can cause fluorosis, most of this is mild and not usually of aesthetic concern. Severe cases can be caused by exposure to water that is naturally fluoridated to levels well above the recommended levels, or by exposure to other fluoride sources such as brick tea or pollution from high fluoride coal.Dental fluorosis is an irreversible condition caused by excessive ingestion of fluoride during the tooth forming years. It is the first *visible* sign that a child has been overexposed to fluoride. Fluoride causes dental fluorosis by damaging the enamel-forming cells, called ameloblasts. The damage to these cells results in a mineralization disorder of the teeth, whereby the porosity of the sub-surface enamel is increased. High-endemic areas of Fluorosis – India [8]



This map indicates the regions that have an high and endemic incidence of fluorosis. It shows that the problem is most severe in Rayalseema and Coastal regions of Andhra Pradesh, North and East Karnataka, North Rajasthan, Punjab and Haryana, and parts of Orissa.

Several methods have been applied to remove fluoride from drinking water.
The current treatment methods are chemical precipitation with calcium and aluminum salts, ion exchange using polymeric resins, adsorption on activated carbon, reverse osmosis and electro dialysis .Now a days, activated char has been reconsidered as a potential adsorbent for DE fluoridation of drinking water because of its high fluoride adsorption capacity. Adsorption of fluoride on activated char has been studied and it has been reported that fluoride can be effectively removed from water solutions by adsorption on activated char .

5.0 Fluoride Adsorption Experiments

All the chemicals used for this experiment are of analytical grade. The stock Fluoride solution of 1,00mg/L was prepared by dissolving 221 gm of anhydrous Sodium fluoride (NaF) in in distilled water and make it up to 1000ml using distilled water. Solutions of desired concentration were prepared by diluting the stock solution stepwise. A calibration graph of absorbance versus concentration was constructed using systronics spectrophotometer (model 169) at maximum wavelength of 570nm.[9]

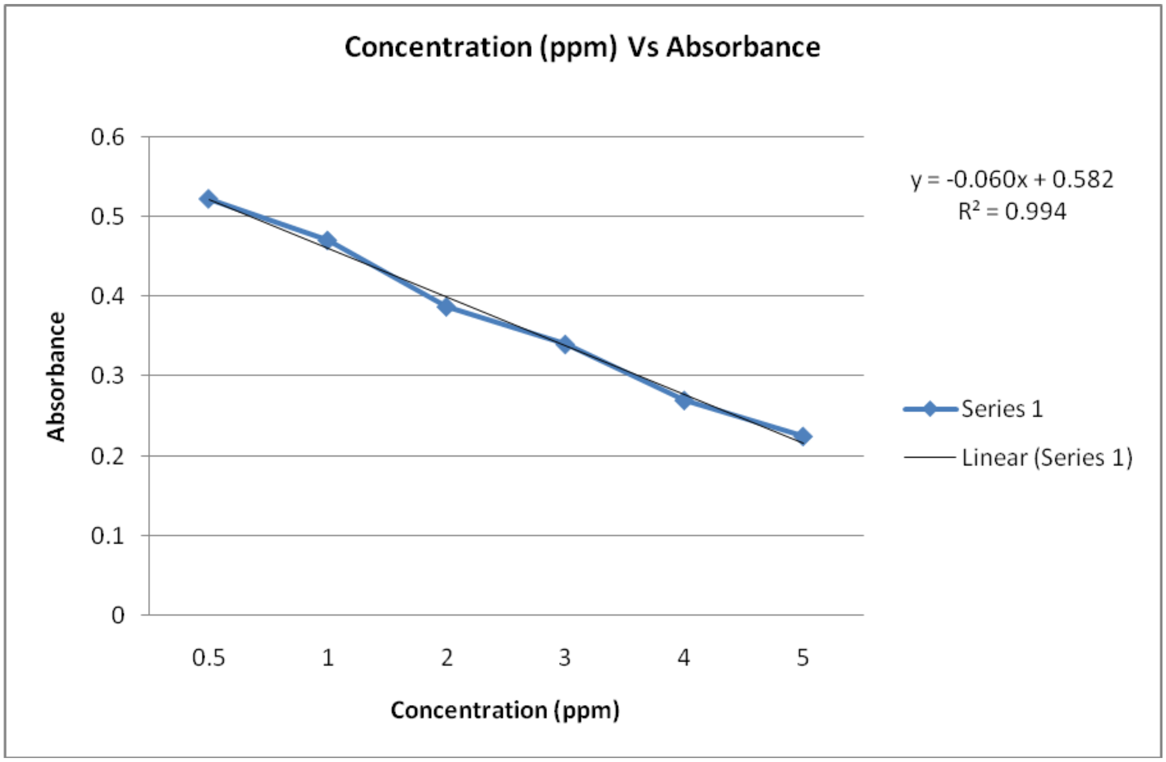


Figure (1):- Concentration verses Absorbance

The sorption isotherms and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 0.3gm (obtained by the study effect of adsorbent dose)of sorbent with 100ml of sodium fluoride containing 3mg/L as initial fluoride concentration. The mixture was agitated in a water bath shaker at a speed of 200 rpm at room temperature. The de fluoridation studies were conducted for the optimization of various experimental conditions like contact time , initial fluoride concentration adsorbent dose.

The effect of different initial fluoride concentration like 2,3,4,5, 5.5 6,7mg/L at a room temperature were studied by keeping the mass of sorbent at 0.3gm and volume of solution as 100ml .

The amount of fluoride adsorption at equilibrium qe (mg/g) was calculated using the following equation

$qe = (C0 - Ce)/W$-----------------------(1)

Where Co is the initial concentration Ce (mg/L) is the liquid phase concentration of fluoride at equilibrium and qe is the adsorption capacity (mg/g) at equilibrium

6.0 Adsorption isotherm models

An adsorption isotherm is the relationship between the adsorb ate in the liquid phase and the adsorb ate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption isotherm is very important to design the adsorption systems. For solid-liquid systems, several isotherms are available.

The Langmuir isotherm takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent; according to the following equation

$$q_e = \frac{q_m K_a C_e}{1+K_a C_e} \qquad \text{-------------(2)}$$

where Ce is the equilibrium concentration (mg/L); qe is the amount of fluoride adsorbed (mg/g); qm is qe for a complete monolayer (mg/g); and Ka is adsorption equilibrium constant (L/mg). [10]

To evaluate the adsorption capacity for a particular range of adsorb ate concentration the above said equation (eq, 2) can be used as a linear form as follows

$$\frac{Ce}{qe} = \frac{(1)Ce}{qm} + \frac{1}{Ka.qm} \quad \text{--------------------------------(3)}$$

The constants qm and Ka can be determined from a linearised form of eq.(3) by the slope of the linear plot of Ce/qe Verses Ce.

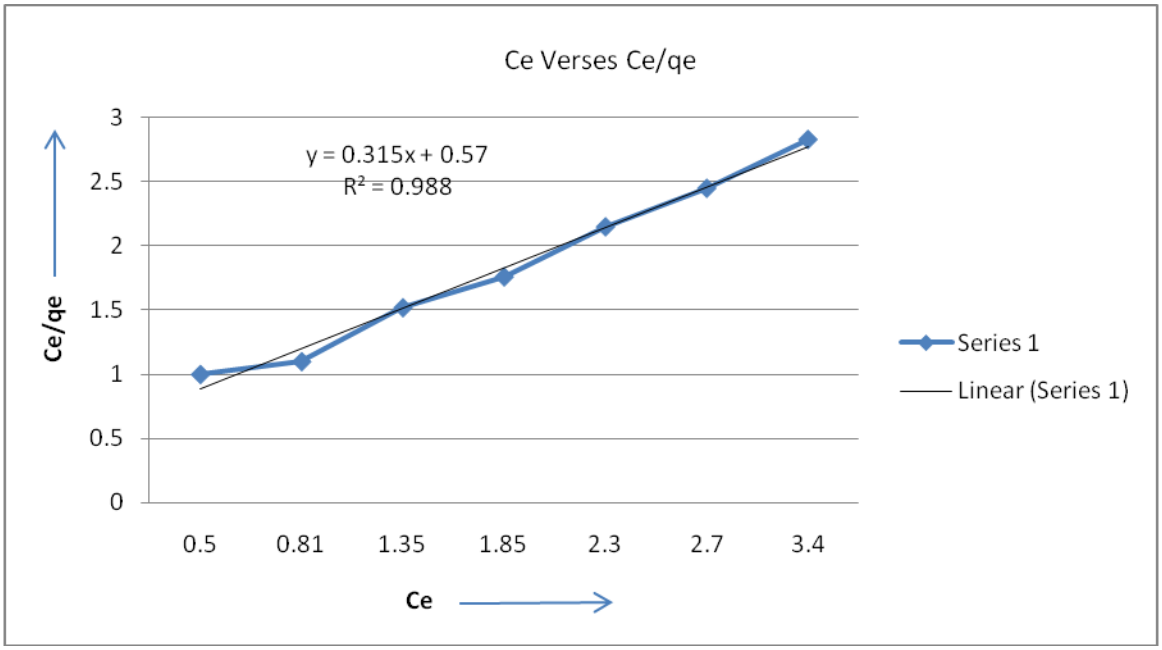


Figure (2):- Langmuir isotherm

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system .The equation is given below

$qe = Kf * Ce\ 1/n$ -----------------------(4)

Where qe is the amount of dye adsorbed (mg/g) ; Ce is the equilibrium concentration (mg/L) Kf and 1/n are the empirical constants indicating the adsorption capacity and adsorption intensity, respectively .The eq.(3) can be converted to a Llinear form by taking Logarithms

$$Log\ qe = Log\ Kf + (1)/(n)(Log\ Ce)$$ ---------(5)

The plot Log qe versus Log Ce Of eq(5) should result in a straight line. From the slope and intercept of the plot , the values of n and Kf can be obtained which are the Freundlich isotherm constants. [11]

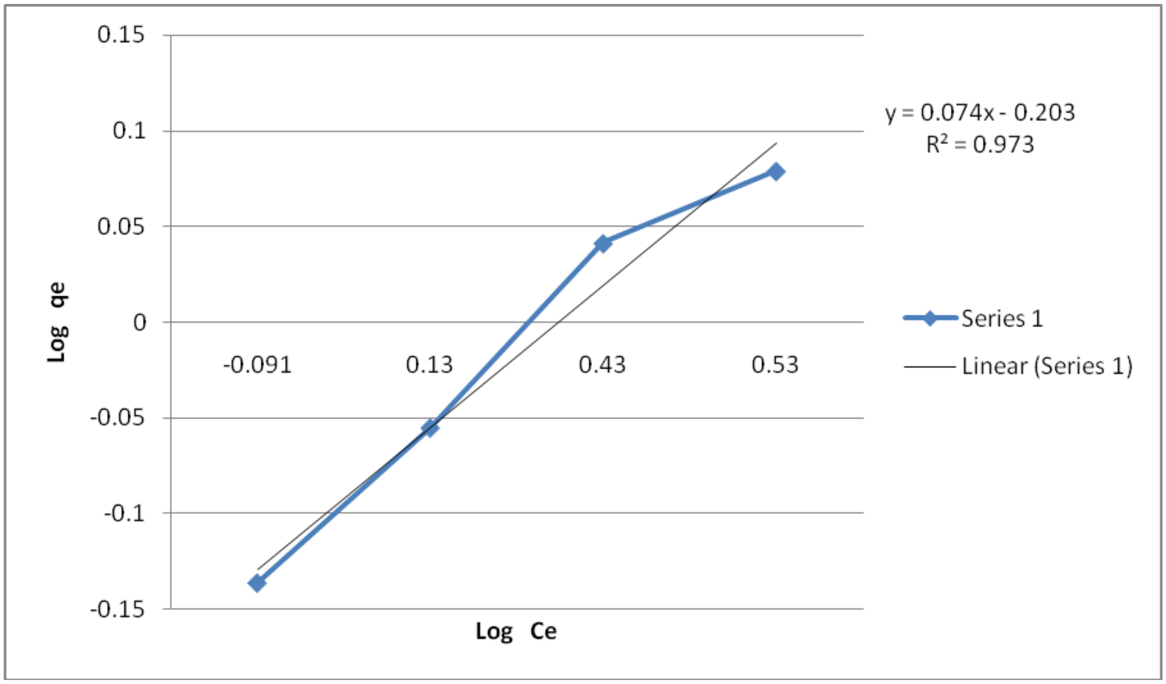


Figure (3) :-Freundlich isotherm

7.0 Effect of contact time and initial dye concentration

Contact time plays a very important role in adsorption dynamics. The effect of contact time on adsorption of Fluoride onto agricultural residue charcoal (ARC) is shown in fig(4) .Batch adsorption studies using the concentration 2,3,4,5,5.5,6 and 7 mg/L of Fluoride solution and with 3 gm/L of the adsorbent were carried out at temperature 303 K as a function of time to evaluate the % removal and adsorption constants.

The adsorption of Fluoride increases with time and gradually attains equilibrium after 120 minutes. From fig.(4) the time to reach equilibrium conditions appears to be independent of initial dye concentrations. Therefore 120 minutes was fixed as a minimum time for the maximum dye removal. It was also observed that the removal curves are smooth and continuous indicating the possibility of the formation of monolayer coverage of coverage of fluoride ion at the interface of adsorbent.

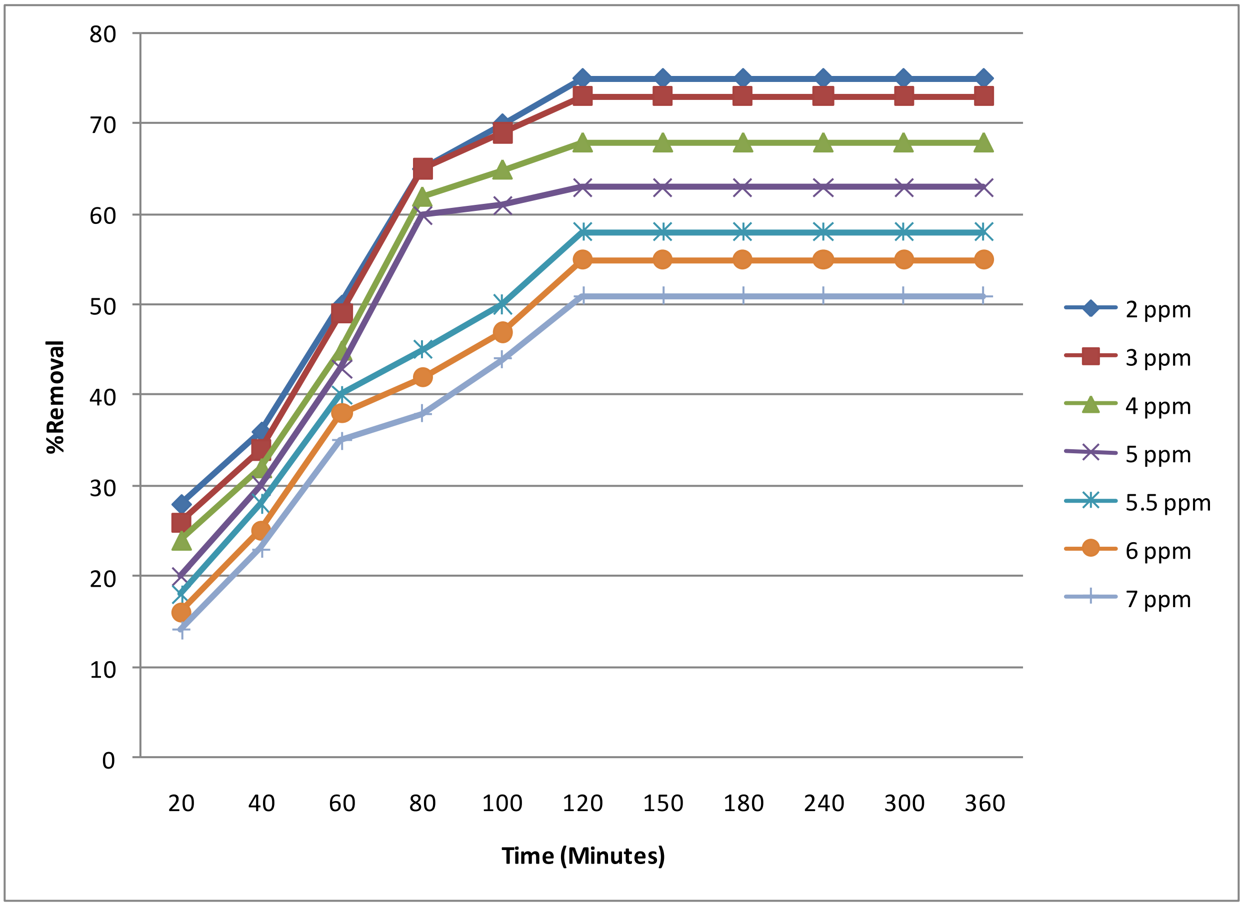


Figure (4) :- percentage of fluoride removal verses time for different initial fluoride concentration

8.0 Influence of Adsorbent dose

The influence of varying concentrations of adsorbent on the adsorption of fluoride at room temperature is shown in fig (5) . While increasing the adsorbent dose proportional removal observed for fluoride until some extent. After that , the curve laps as flat indicating the higher fluoride adsorption occurs at 3gm/L and following remains constant.

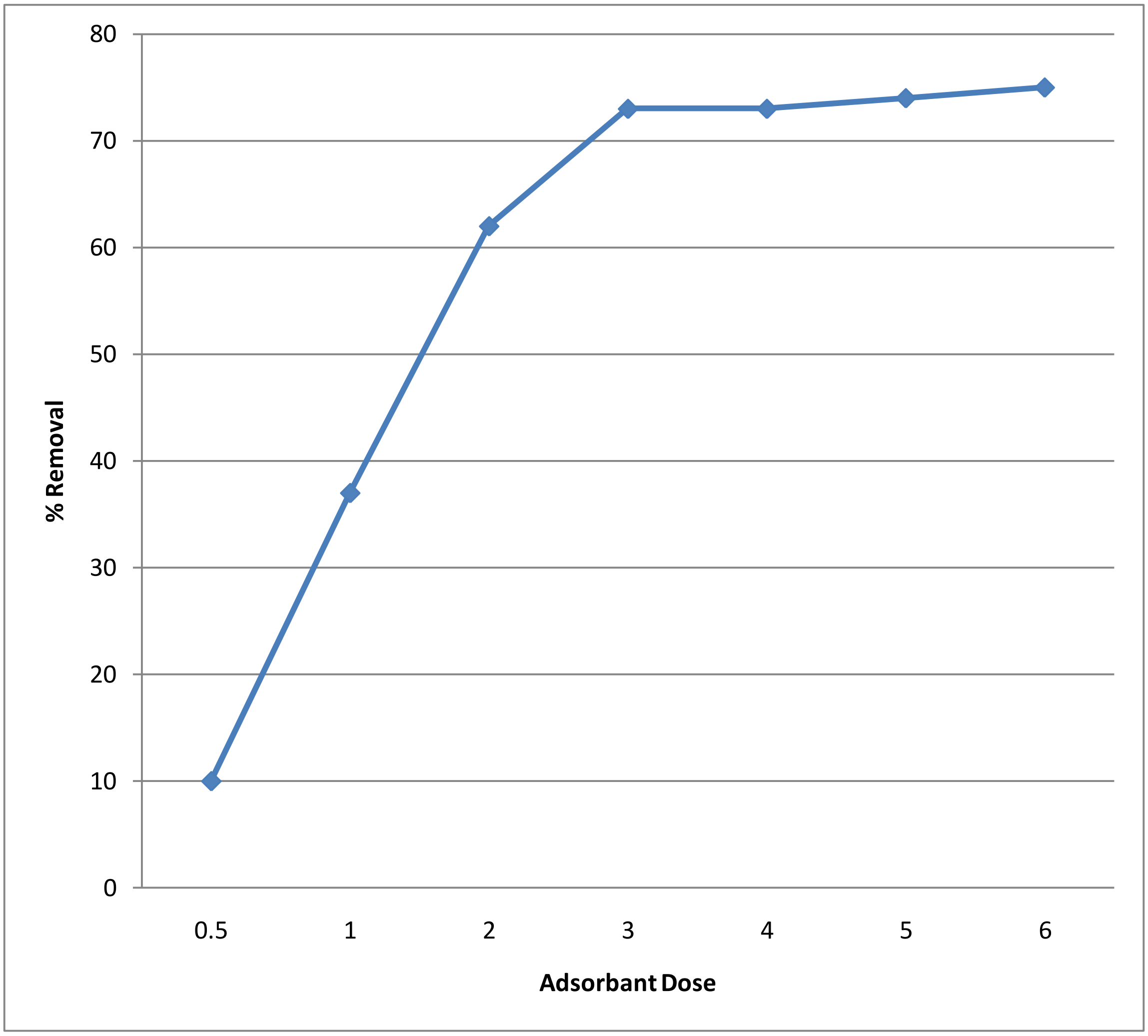


Figure (5) :- Variation of fluoride removal for different doses at constant temperature

9.0 Isotherm analysis

The equilibrium data isotherm analysis for fluoride adsorption onto the agricultural residue charcoal at room temperature are shown in figure. Result indicate that the adsorbent has a high affinity for fluoride adsorption under these conditions. The equilibrium data has been analyzed by linear regression of isotherm model equations viz. Langmuir Fig (2) and Freundlich Fig (3). The related parameters obtained by calculations from the values of slope and intercepts of the respective linear plots are shown in Table 2

Isotherm	Parameters	Value
Langmuir Isotherm	q_m	3.17
	K_a	0.55
	R^2	0.988
	K_R	0.603
Freundlich Isotherm	K_F	0.626
	n	13.5
	R^2	0.973

The present data fit the Langmuir (R^2 =0.988) isotherm. The average monolayer adsorption capacity (qm) obtained for ARC is 3.17 mg/gm

Freundlich isotherm model based on multilayer adsorption described the data fairly well (R^2 =0.973) . The Freundlich adsorption constants (K_F) obtained for the linear plot is o.626. The Freundlich coefficient (n) is obtained from plot is 13.57 that supports the favorable adsorption of fluoride on to the adsorbent.

10.0 Conclusion

From statistical data 1,15,61,204 Tons of residue is generated per year in Vidrbha, out of which some residue is used as a animal food some residue used as a raw material for industry and some residue is burned in the field or used as fuel. The net amount of residue that is burned in the field or used as a fuel is 63,58,662 Tons. This agricultural residue is easily available and cost of this residue is very less. If agricultural residues are properly utilized, more economic opportunities can be offered to maintain the healthier rural environment. In this study we have used pyrolysis to convert the biomass available in the form of agricultural residues to useful products – mainly biochar. The process has been optimized in terms of temperature and time of pyrolysis as also the size of the feed material. The biochar produced has been characterized through techniques like SEM, BET surface area values.

The defluoridation studies of the adsorbent (Biochar) have been carried out in batch mode. The most excellent defluoridation occurred at the optimum time 120 minute to get a success rate of 73% of fluoride removal while keeping 3.0 gm/L of dosage of absorbent. Thus it shows the superior adsorptive efficiency.

Based on above description Biochar from agricultural residue could be used to remove Fluoride from aqueous solution.

References

1-2 Indian Economy Datt, Ruddar and Sundarman. S. Chand publications. page 976

3-4 Maharashtra state Gazetteers Volume 04 part 04.Directorate of Govt. print Stationery and publications 1987.

5 Special data dissemination standard Division, Directorate of Economics and Statistics, Ministry of Agricultural Govt. of India.

6 Paper published on “Agricultural And Forest Residues- Generation, Utilization and Availability "at the Regional consolation on Modern Application of Biomass Energy in Kaula Lumpur . Author Auke Koopmans and Jaap Koppejan (Wood Energy conversion specialists) page 16 to 20.

7 Hand Book of Environmental Analysis : Chemical Pollutants In Air ,Water, Soil and Solid Waste , Pradyot Patnaik 2nd Edition , Lewis Publications page 167 to 230.

8. htpp://www.indiawaterportal.org/sites/images/6112

9 Paper published on “ Adsorption Isotherms on Fluoride Removal ; Batch Techniques” Archives of Applied Science Research 2010 (Scholars Research Library) G.Alagumuthu , V. Veeraputhiran and R. Venketaraman

10-11 Water Quality Control Hand Book by E. Roberts Alley. 2 nd Edition , Mc Graw Hill publications page 9 to 68.