International Journal of Research in Engineering and Applied Sciences (IJREAS)
Available online at : http://euroasiapub.org
Vol. 6 Issue 9, September - 2016, pp.99~111
ISSN(O): 2249-3905, ISSN(P) : 2349-6525 | Impact Factor: 6.573 | Thomson Reuters ID: L-5236-2015

Adsorption Of Methylene Blue using Charcoal produced from Agricultuter Residue

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ABSTRACT

Maharashtra is a major state in the Indian Union. Vidarbha is the eastern region of Maharashtra state. In Vidarbha 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. *L*arge amount of residue is simply burnt in the field. This burning of residue wastes the biomass energy. We have used pyrolysis to convert the biomass available in the form of agricultural residues to useful products – mainly biochar. The charcoal produced has been characterized through techniques like SEM, BET surface area values.

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents. The presence of Methylene Blue, can cause eye injury for both human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea ,vomiting, profuse sweating, diarrhea, gastritis and mental confusion .

We have studied adsorption of methylene blue and find that methylene blue can be effectively removed from effluents by adsorption on activated char produced from agricultural residues. The adsorption process has been optimized. We find that maximum adsorption of methylene blue occurred with contact time of 100 minutes at a dosage of 2mg/liter to effect removal of 80% of Methylene Blue from industrial effluent.

Key Words:- Methylene blue, Charcoal , Agricultural residue, adsorption, pyrolysis.

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 [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

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.

Dyes are important hazardous substances found in textile industry, food industry, pharmaceutical industry, paper industry and plastics industry. Their presence in water bodies reduces light penetration and this consequently thwarts the photosynthesis of aqueous flora [7] [8]. Similarly, this makes the water objectionable for drinking. Dyes in water stream causes allergy, dermatitis, skin irritation, which, at extreme cases, provoke cancer and mutation in humans [9]. Furthermore, the colour and the non-biodegradable nature of the spent dye baths constitute serious environmental problems.

Various treatment methods for the remove dyes from wastewater have been investigated and these methods can be classified as chemical coagulation/flocculation, ozonation, oxidation processes, chemical precipitation, ion exchange, reverse osmosis, and ultra-filtration [10]. However, most of these methods for the removal of dyes from dye containing wastewater have serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements [11] [12]. Therefore, the development of efficient, low-cost and environmentally friendly technologies to reduce dye content in wastewater is extremely necessary. Adsorption is rapidly gaining prominence among the treatment technologies and [13] has noted that adsorption can produce high-quality water while also being a process that is economically feasible. The physical characteristics of the adsorbents such as surface area, porosity, size distribution, density and surface charge have high influence in the adsorption process [14]. As a result, there has been a great interest in developing new adsorbent materials with diverse compositions, properties and functionalities. Although commercial activated carbon is the most widely used adsorbent for dye removal, it is too expensive [15]; consequently, numerous low-cost alternative adsorbents have been proposed including chemically modified sugarcane bagasse lignin [16], pistachio hull waste [17], coffee husk-based activated carbon [18], pine cone [19], rice husk [20], synthetic calcium phosphates [21], natural untreated clay [22], pillared clays [23], and swelling clays [24].

2.0 Materials and Method

2.1 Preparation of Adsorbent

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.

2.2 Analysis of Charcoal

2.2.1 Proximate analysis of Charcoal

Proximate analysis of charcoal is done to record, moisture content, volatile matter ,ash % and fixed carbon % in charcoal. The analysis is done by Indian standard methods of tests for coal and coke.

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

2.2.2 BET

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**

2.2.3 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.

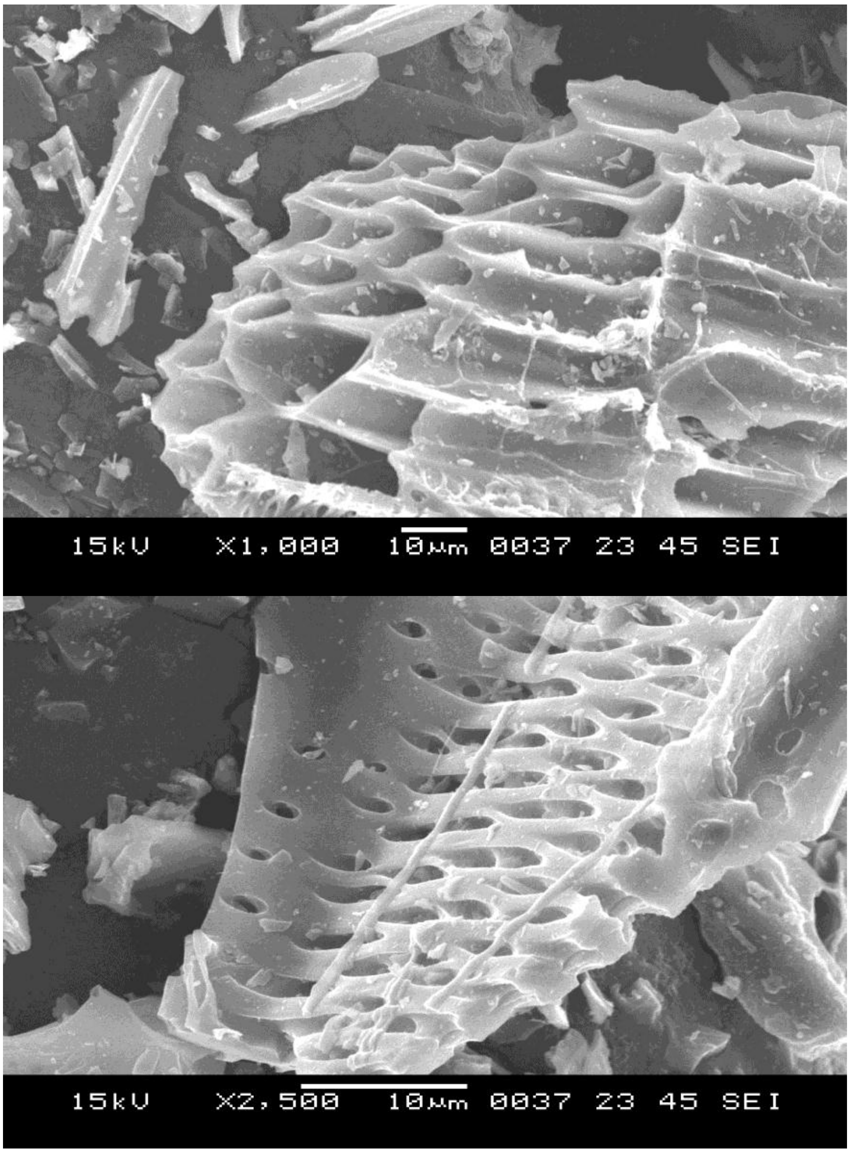

Figure (1) Scanning electron Microscope Of Charcol

2.3 Preparation of basic dye solution

Methylene Blue, C16H18N3SCI.3H2O, is a cationic dye. It was chosen in this study because of its known strong adsorption onto solids. The structure of this dye is shown in Figure. The dye is not regarded as acutely toxic, but it can have various harmful effects.

Figure.(2) Structure of Methylene Blue

Basic dye, Methylene Blue, was used without further purification. Methylene Blue was dried at 110°C for 2h before use. All of the Methylene Blue solution was prepared with distilled water. The stock solution of 1000 mg/l was prepared by dissolving Methylene Blue in 1000 mI distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

3.0 Methylene Blue Adsorption Experiments

The adsorption experiments were carried out in a batch process by using aqueous solution of Methylene Blue. Variables parameters are , initial Methylene Blue concentration, adsorbent amount, and contact time. Standard solutions containing 10-250 mg/l ..Methylene Blue were prepared by dilution of dye stock solution containing 1000 mg/l of metal ion. All experiments were performed by using beakers of 100 mI capacity containing 1-6 g/l of charcoal suspended in 50 mI of dye solution. The suspensions were mixed at predetermined periods (20-360 min) at constant temperature (25°C) in a shaker at 200 rpm until equilibrium was reached. The solution reaction mixture was centrifuged at 2800 rpm for 10 min and the absorbance of dye solution was determined by a spectrophotometer (Systronics Model 169) at 630 nm wavelength, at which the maximum absorbency occurred [25]. The amounts of dye adsorbed were calculated from the concentrations in solutions before and after adsorption.

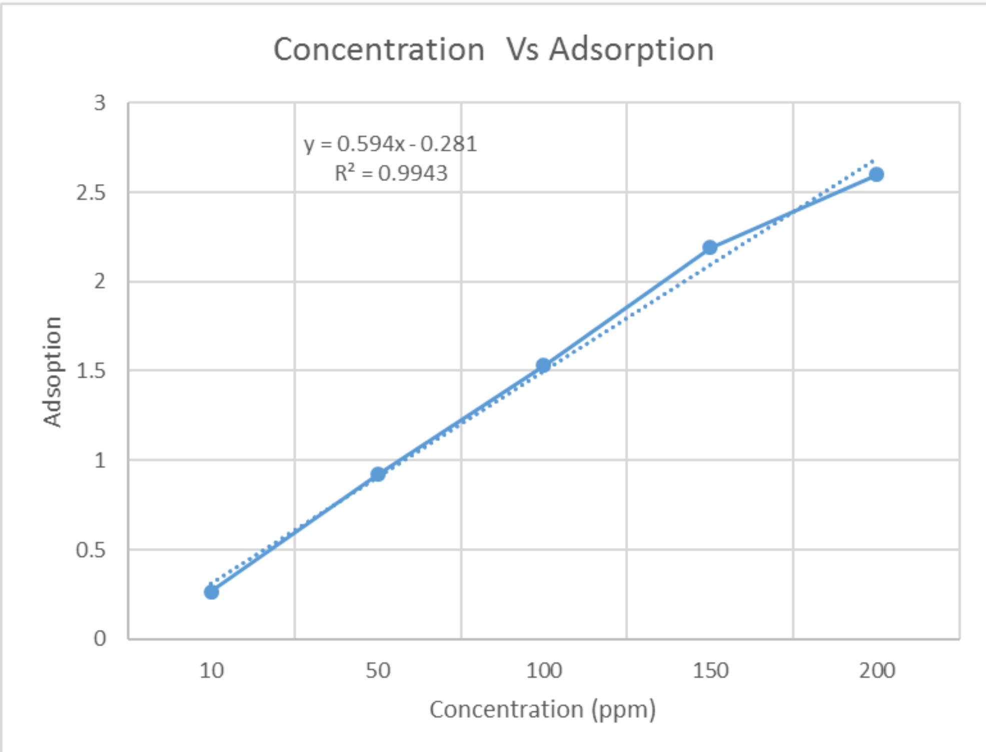

Figure (3):- Concentration verses Absorbance

The sorption isotherms and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 2gm (obtained by the study effect of adsorbent dose)of sorbent with 100ml of solution containing 100 ppm as initial methylene blue concentration. The mixture was agitated in a water bath shaker at a speed of 200 rpm at room temperature. The adsorption studies were conducted for the optimization of various experimental conditions like contact time, initial methylene blue, adsorbent dose.

The effect of different initial methylene blue concentration like 50,100,125,150,175,200mg/L at a room temperature were studied by keeping the mass of sorbent at 2.0gm and volume of solution as 100ml .

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

$$qe = (C0 - Ce)/W \text{-----------------------(1)}$$

Where Co (mg/L) 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

4.0 Adsorption isotherm models and Results

An adsorption isotherm is the relationship between the adsorbate 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.

4.1 Langmuir isotherm

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 Methyelene Blue adsorbed (mg/g); qm is qe for a complete monolayer (mg/g); and Ka is adsorption equilibrium constant (L/mg) [26]

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 :

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

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

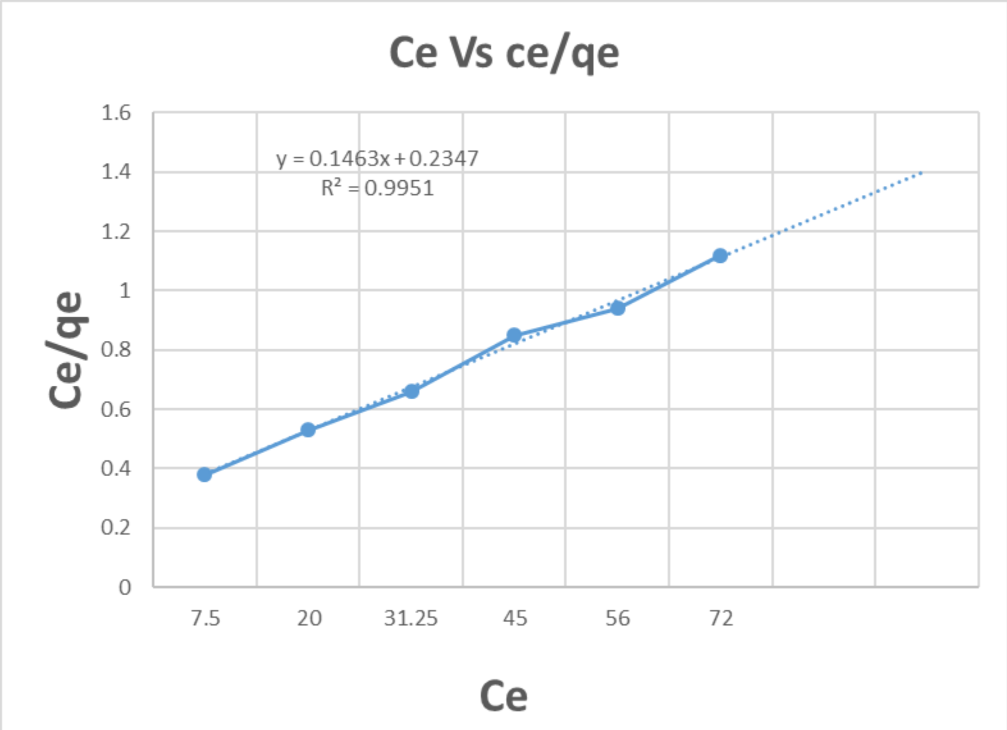

Figure (4):- Langmuir isotherm

4.2 Freundlich 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. [27]

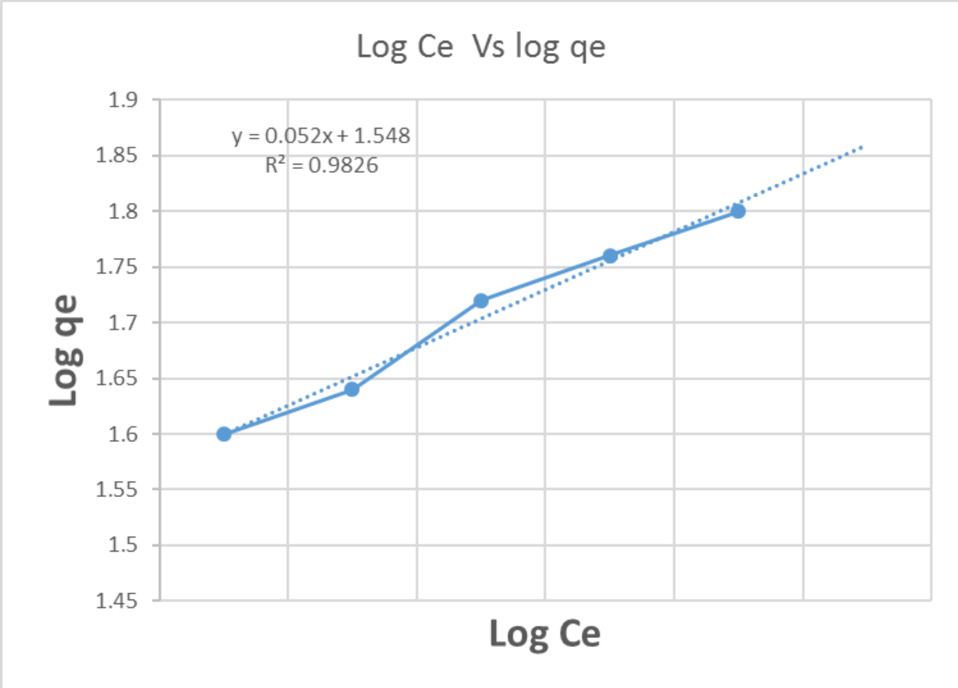

Figure (5) :-Freundlich isotherm

4.3 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 dye onto agricultural residue charcoal (ARC) is shown in fig(6) .Batch adsorption studies using the concentration 50,100,125,150,175,200mg/L of Methylene blue and with 2 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 Methylene blue increases with time and gradually attains equilibrium after 100 minutes. From fig.(6) the time to reach equilibrium conditions appears to be independent of initial dye concentrations. Therefore 100 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 Methylene Blue fluoride ion at the interface of adsorbent.

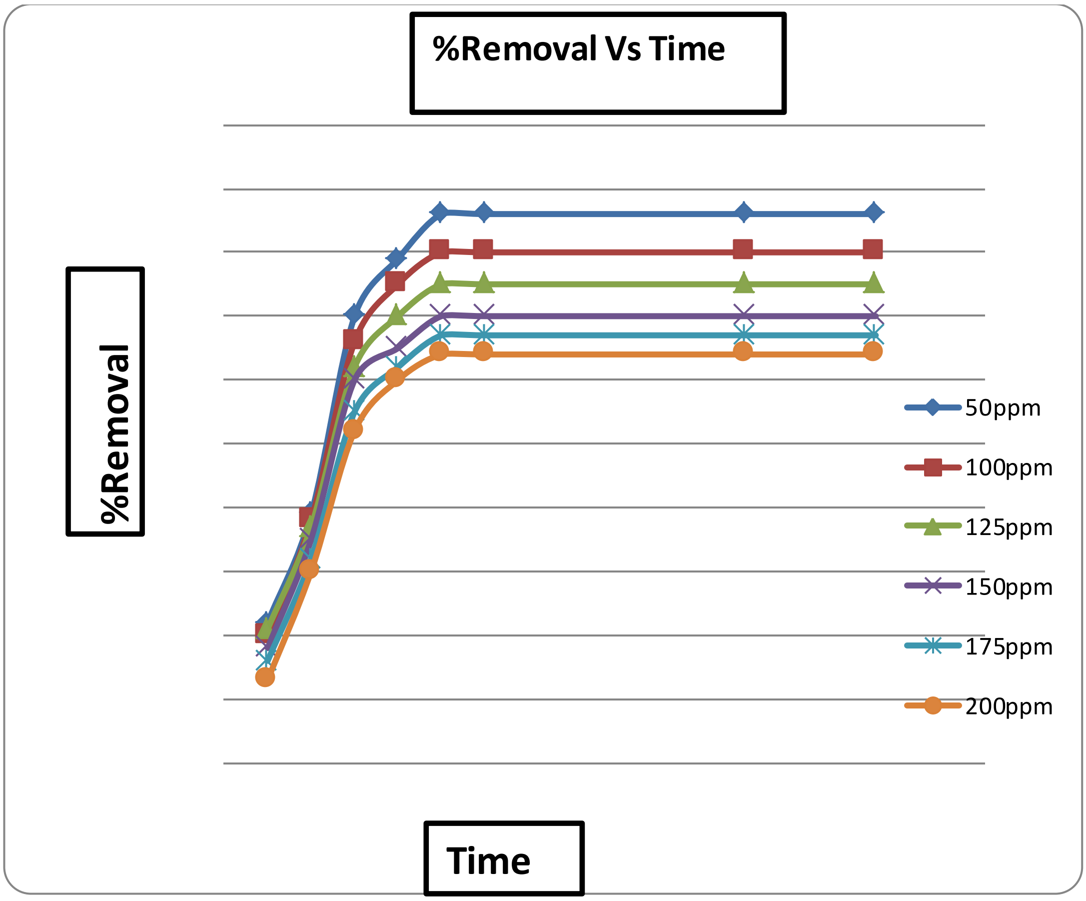

Figure (6) :- percentage of Methylene Blue removal verses time for different initial Methylene Blue concentration

4.4 Influence of Adsorbent dose

The influence of varying concentrations of adsorbent on the adsorption of Methylene blue at room temperature is shown in fig (7) . While increasing the adsorbent dose proportional removal observed for Methylene blue until some extent. After that , the curve laps as flat indicating the higher Methylene blue adsorption occurs at 2gm/L and following remains constant.

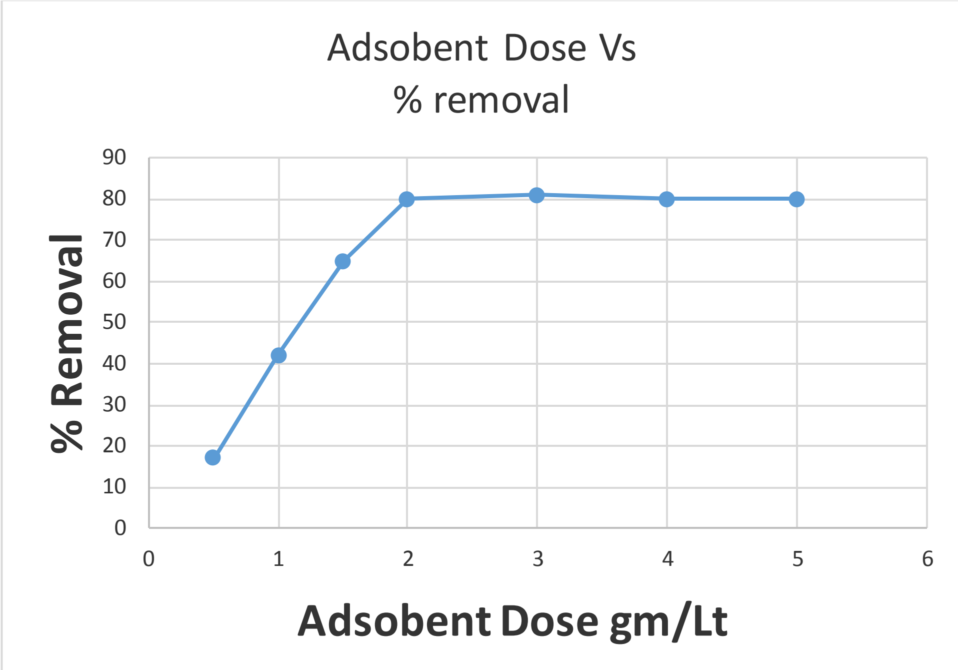

Figure (7) :- Variation of Methylene Blue removal for different doses at constant temperature

5.0 Isotherm analysis

The equilibrium data isotherm analysis for Methylene blue adsorption occurs at 2gm/L and following remains constant. Adsorption onto the agricultural residue charcoal at room temperature are shown in figure(7). Result indicate that the adsorbent has a high affinity for Methylene blue adsorption under these conditions. The equilibrium data has been analyzed by linear regression of isotherm model equations viz. Langmuir Fig (4) and Freundlich Fig (5). 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	$q_{m\ (mg/gm)}$	6.83
	$K_{a\ (L/gm)}$	0.623
	R^2	0.995
	K_R	0.0157
Freundlich Isotherm	K_F	35.31
	n	19.23
	R^2	0.982

Table 2.

The present data fit the Langmuir (R^2 =0.995) isotherm. The average monolayer adsorption capacity (qm) obtained for ARC is 6.83 mg/gm

Freundlich isotherm model based on multilayer adsorption described the data fairly well (R^2 =0.982) . The Freundlich adsorption constants (K_F) obtained for the linear plot is 35.31. The Freundlich coefficient (n) is obtained from plot is 19.23 that supports the favorable adsorption of fluoride on to the adsorbent.

6.0 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 Charcoal produced has been characterized through techniques like SEM, BET surface area values.

The adsorption of Methylene blue studies for the adsorbent (Biochar) have been carried out in batch mode. The most excellent adsorption occurred at the optimum time 100 minute to get a success rate of 80% of Methylene blue removal while keeping 2.0 gm/L of dosage of absorbent. Thus it shows the superior adsorptive efficiency.

Based on above description Charcoal from agricultural residue could be used to remove Methylene blue from aqueous solution.

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