ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

Dye Removal from Waste Water Using Low Cost Adsorbents

[1] A.G.Deshmukh, [2] P.S.Randive, [3] P.S.Deshmukh, [4] S.Bakhade
[1] Assistant Professor, Department of Civil Engineering, KDKCE, Nagpur
[2] Assistant Professor, Department of Civil Engineering, KDKCE,Nagpur
[3] Assistant Professor, Department of Civil Engineering, KDKCE,Nagpur
[4] Assistant Professor,Department of Civil Engineering, KDKCE,Nagpur

Abstract: **-- This study is designed to investigate the performance of Low cost adsorbents for removal Methylene Blue Dye. The adsorbents are synthesized in the laboratory, form the agricultural waste like Orange peel and Rice Husk. The study is conducted by batch treatment method for various pH levels and dye concentration. The dye concentrations were measured using a spectrophotometer. The comparative study is done by plotting the adsorption isotherms for the materials under study and conventionally used activated carbon.Through the experimental results, it was found that Efficiency of PAC as an adsorbent for MB dye remains near about same at all the pH values. Removal of MB dye is significantly affected by pH of the system. In the present investigations, maximum removal of dye was found at pH 9 for RHAC and pH 8 for OP Hence it is always better to work with other sorbents instead of with costlier PAC. All adsorbents followed Freundlich adsorption isotherm. Removal of dye is as high, as near to 100% depending on pH for all.**

***.Key Words*: - Adsorption, Mthylene Blue Dye, Low Cost Adsorbents ,Oarange Peel, Rice Husk, PAC, Spectrophotometric Method, Adsorption Isotherm.**

I. INTRODUCTION

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc., to color their products. The dyes are invariably left as the major waste in these industries. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be decolorized once released into the aquatic environment (Sharma et al,2008). Many of the organic dyes are hazardous and may affect aquatic life and even the food chain (sheikh et al, 2009). Release of these dyes in water stream is aesthetically undesirable and has serious environmental impact. Due to intense color they reduce sunlight transmission into water hence affecting aquatic plants, which ultimately disturb aquatic ecosystem; in addition they are toxic to humans also. The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Many carbonaceous materials such as bark, coal, lignite, coconut shells, wood, dead biomass, seaweed, pecan shell and peat are used in the production of commercial activated carbons. The adsorption process has been widely used for color removal. Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in wastewater treatment. This process being very low cost method and most simple method for containing these pollutants is being used in this study. The main objectives of this study were to determine the effectiveness and feasibility of some low cost agricultural waste materials in the removal of Methylene Blue Dye.

II. MATERIALS AND METHODS

COLOR MEASUREMENT

The intensity of color in water is measured on an arbitrary scale. The unit of color on cobalt scale is the color produced by one milligram of platinum cobalt in a liter of distilled water. Another method is spectrophotometric method. In this method dye solutions of different concentration are prepared. Absorbance of each sample is measured at its max absorbance wave length λmax . .calibration curve is plotted.

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

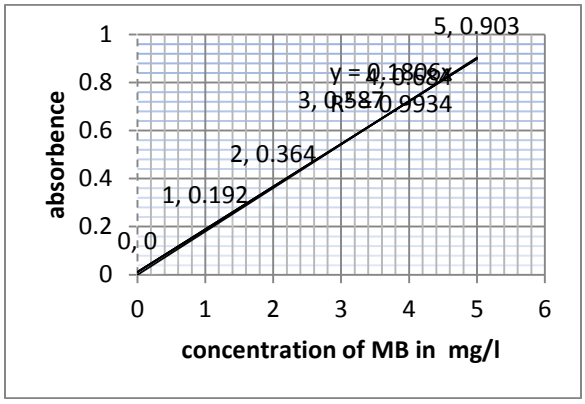

Figure 3.1 Calibration curve for MB dye

ADSORPTION THEORY

Among the unit operations in water and waste water treatment adsorption occupies an important position. It is used for taste, odor and color removal. But more important is adsorption of dissolved organic impurities on activated carbon. The non biodegradable organics can be removed by activated carbon. Adsorption is a physical phenomenon by which molecule of solutes are attracted towards the surface of adsorbent material

ADSORPTION ISOTHERMS

Equilibrium is established between the molecules adsorbed and molecules in the solution .The position of equilibrium in adsorption are given by adsorption isotherm.

.Langmuirs Adsorption Isotherm:

This is derived mathematically from rational considerations.

$$\frac{X}{M} = \frac{abc}{(1+bc)}$$

Or $\frac{c}{\left(\frac{X}{M}\right)} = \frac{c}{a} + \frac{1}{b}$

Where, x/m and c are same as above,

a = Langmuir constant

b = Monolayer coverage value

Freundlich Adsorption Isotherm:

This is based on practical experience and no mathematical proof is available.

$$\frac{x}{m} = kc_e^{1/n}$$

Which represents the relation between amount of solute adsorbed per unit weight of adsorbent and the concentration of solute in aqueous solution, here

x/m = Weight of adsorbate removed per unit weight of adsorbent.

Ce = Equilibrium concentration of solute.

K, n = Freundlich parameters, which represents the adsorption capacity and intensity of adsorption respectively. Freundlich adsorption isotherm is empirical one. In addition this equation is a parabola and can't explain the almost rectilinear rise in adsorption which does not depend on concentration. The almost rectilinear region of an isotherm which corresponds to low pressure or concentrations may be obtained by means of Freundlich's equation only when 1/n = 1, while horizontal part corresponds to 1/n = 0. Hence 1/n should be the function of p or c. But here 1/n is assumed to be constant (0.1- 0.5)

Bruner, Emmeett and Teller Isotherm (BET Isotherm):

The basic principles of the BET theory are

The adsorbent surface has a definite number of active centers are equivalent energetically and are capable of retaining the adsorption the molecule.

1. The interaction of the neighboring adsorbed molecules in the first and subsequent layers is neglected both of these allowances correspond to Langmuir's adsorption on a homogeneous surface without the interaction of adsorbed molecule.

2. Each molecule of the first layer is a possible centre for adsorption and formation of second adsorbed layer. Each molecule of the second layer is the possible centre for adsorption in the third and so forth.

3. It is assumed that all the molecules in the second and subsequent layers have the same partition function as in the liquid state. Hence the adsorbed phase may be represented as molecular chains which are started by adsorbent surface. No energy exchange occurs between the chains. According to bet theory, it is assumed that every molecule of a liquid has only two close neighbors (i.e. from the top and from the bottom in a chain) while the molecule of the real liquid is surrounded with much more adjacent molecules.

Nevertheless the theory turned out to be very useful.

$$\frac{X}{M} = \frac{Bcq_0}{(C-c)(1+(E-1)\left(\frac{c}{C_S}\right))}$$

Where Cs = saturation concentration of solute in the solvent,

Q_0 = no of moles of solute adsorbed per unit weight of adsorbent in forming a mono layer of the surface.

Factors Affecting Adsorption:

i) Surface area of adsorbent : As surface area is increased, adsorption increases.

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

Rate of adsorption is. $\propto \frac{1}{dia}$

Rate of adsorption is. $\propto \frac{1}{dia^n}$

For granular carbon, The parameter n is there because of porous structure of granular carbon, n = 1.85 or 2.

ii. Nature of solute (adsorbate)

a) Solubility of solute :

Adsorption $\propto \frac{1}{solubilities}$ Of solute in given solvent. Because of solubility is higher, the bonds between solute and solvent molecule are better and stronger which makes adsorption slower.

b) Chain length of molecules:

As chain length increases, solubility decreases.

So adsorption $\propto$ *chain length of molecule*

c) Molecular size of solute :

An increase in molecular size of solute favors the adsorption. The effect is evident when comparing compound of similar chemical nature.

d) Geometry of molecule :

Branches - lesser tendency to get removed. Coiled – more easily removed because they are easily entrapped in the interstices.

e) Degree of ionization :

Natural species are more easily removed.

$$\text{Adsorption} \propto \frac{1}{dissociation\ constant}$$

ii) pH : The effect is quite specific and depends on chemical nature of solvent solute system. Morris and Webber have observed that the effect of pH reduction on adsorption of adsorbate.

iii) Temperature: rate of adsorption decreases with increase in temperature.

iv) Solute concentration: from equation it is appeared that at the low concentration of solute the value of $\frac{X}{M}$ is large as compared to that at the higher solute concentration.

v) Time of contact: the effect of this on rate of adsorption is to be found out by laboratory taste.

ADSORBATE

Methylene Blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{l6}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of Methylene Blue. Its stock solution was prepared in double-distilled water. All the test solutions were prepared by diluting the stock with double- distilled water. Details about MB dye are given in table 1.

Table 1: Physicochemical properties of the Methylene Blue

Molecular weight 319.85 g/mol

Molecular weight	319.85 g/mol
Molecular formula	$C_{l6}H_{18}N_3SCl$
Absorption maxima	664 nm

1gm of Methylene Blue was dissolved in 1lit. of double distilled water to obtain stock solution. Later it was diluted by using distilled water according to the concentration required and pH was adjusted by adding 0.1 M NaOH solution and 0.1 M HCl solution according to the conditions

ADSORBENT

i. Powdered activated carbon was supplied by Central Scientific Company laboratory supplies, The adsorbents were used directly without any further grinding and sieving. Following specification are given by the manufacturer :pH value 5-8, loss on drying less than 20%.

ii. Adsorbent materials used in the present research work are waste materials, available easily and abundantly first material is rice husk. It was obtained from local rice mill of Bhandara .The husk was first dried thoroughly to remove dirt and other impurities. It is then chemically activated. The procedure involves carbonization of husk in furnace for two hrs in a range of 250-3000C by this means organic and inorganic matters are driven off .it's charred and heated strongly in the furnace with stirring once in 60 min . After carbonization it is treated with alkali. Char is added in 5% caustic soda solution and boiled with constant stirring of 2 hrs. The alkali react with silica in the char forming sodium silicate. carbon obtained is washed thoroughly to remove alkali completely. The carbon powder obtained thereby is stored in air tight container for use as an adsorbent.

iii. Orange peels were obtained from a local fruit stall. The Peels were dried, crushed, and washed thoroughly with distilled water repeatedly to remove the natural color of peel and the adhering dirt. They were air dried in an oven at 100–1200C for 24 h. After drying, the adsorbent was sieved through a 5mm mesh size.

BATCH ADSORPTION STUDY

Black carbon prepared from Rice husk, OP, and PAC was used as adsorbent of Methylene Blue dye. MB and PAC was purchased from central scientific company (PAC was used without further purification). The stock solution of 1000 mg/l Methylene Blue (MB) was prepared using double distilled water. Solutions of desired concentration were prepared by diluting the stock solution. A calibration graph of adsorption verses concentration of MB was obtained using Visiscan Systronics Spectrophotometer (model 167) at λmax 665 nm.

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

Batch experiments were conducted using screw cap closed containers and Orbitek shaker at 300 rpm. The required initial pH of the dye solution was obtained by using HCl (0.1 N, 0.01 N, and 0.001 N) and NaOH (0.1 N, 0. 01 N, and 0.001 N).Effect of dose of adsorbent was studied by using 50 ml of 50 mg/l dye solution (pH = 7±0.05) for 2 hours shaking. Effect of pH was studied by taking adsorbent dose of 1g, agitation time 60 min and initial dye concentration 10mg/l after equilibrium time, the residual concentration of the dye (the activated carbon was separated by using Whatman filter paper) was analyzed using spectrophotometer at a wavelength of 665 nm. All the experiments were carried out at 25ºc.

ANALYTICAL DETERMINATION OF MB

MB in the aqueous solution was analyzed using UV spectrophotometer. A standard solution of the MB was scanned to determine the wavelength λmax corresponding to maximum absorbance. The wave length corresponding to maximum absorbance was 665 nm. Once the wavelength found dye solutions of 1,2,3,4,5 mg/l was scanned at absorbance for each was found. The best fitted graph of dye solution concentration and correspondence absorbance was plotted which is used as calibration cure. If the absorbance of dye solution is know by using spectrophotometer, the concentration of dye in that particular sample can be calculated using equation of the line showing figure1.

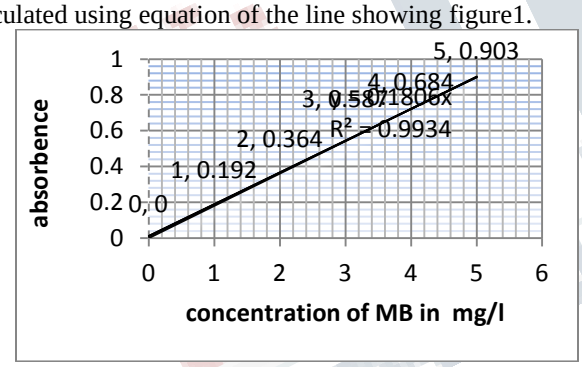

Figure 1 Calibration curve for MB dye

III. OBSERVATIONS, RESULT AND DISCUSSION

Maximum removal of dye was achieved by varying parameters like pH, agitation time, dose of adsorbents, and initial dye concentration, thus optimum values of those parameters were obtained.

Dye Removal by RHAC

i. Effect of pH

For RHAC: (rice husk activated carbon) from fig 2 it can be observed that as pH was increased from 1 to 11 it was seen that adsorption again increased. Maximum dye removal was obtained at pH 9. From The results of this study it is evident that while using low cost adsorbents (RHAC) without much treatment, the removal of dyes are more at higher pH because the surface of activated carbons are negatively charged. The decrease in adsorption capacity in the low pH region would be expected as the acidic medium would lead to an increase in hydrogen ion concentration which would then neutralize the negatively charged carbon surface thereby decreasing the adsorption of the positively charged cation because of a reduction in the force of attraction between adsorbent and adsorbate. pH would affect both aqueous chemistry and surface binding sites of the adsorbents. At Lower pH , H+ ions may compete with dye ions for the positive sites of the orange peel waste thereby Inhibiting the adsorption

ii. Effect of agitation time

Fig. 4. represents the effects of agitation time on the adsorption of MB by the all three adsorbents. In case of RHAC it was found that the adsorption increases with an increase in the agitation time and attains equilibrium after some time, up to an initial agitation period of 140 min more than 72% adsorption has been observed.

It was found that the adsorption increases with an increase in the agitation time and attains equilibrium after certain limit Similar results have been reported in literature for removal of dyes. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the adsorbate species form the outer sites to interior sites of the adsorbent.

iii. Effect of Dose of adsorbent

From fig 5 adsorption of MB by RHAC was found to be increased by increasing the sorbent dose. This study showed that minimum 2.5 g of RHAC was required for maximum removal (74 %) of dye from 50 ml of MB dye Solution (50 mg/l).The effect of adsorbent dose for the uptake of MB by adsorbents was found to be increased by increasing the sorbent dose, due to the introduction of the more activate sites available for sorption, but it is very obvious that for economical treatment only those adsorbents can be used which give more dye removal with minimum dose.

iv. Effect of Initial Dye Concentration

From the observation and fig. no 4, it is evident that for lower initial concentration percent removal of MB is higher i.e.90%. As the dose of adsorbent is kept constant, with increase in initial dye concentration adsorption decreases i.e.65%. So at lowest initial dye concentration i.e 10 mg/l adsorption was found maximum. Results also show that increase in initial concentration of dye results in faster attainment of equilibrium but higher residual dye.

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

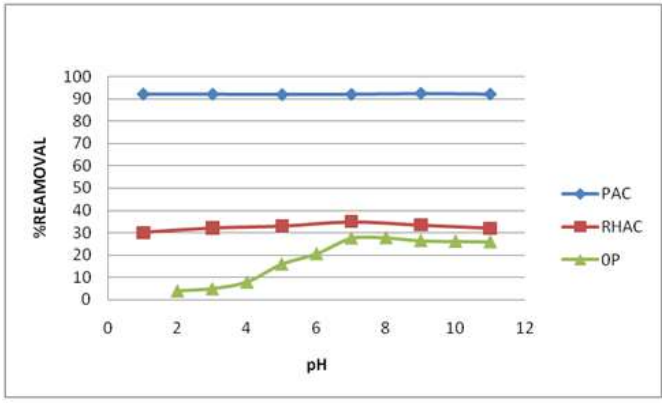

Figure 2: Effect of pH on Dye Removal

Dye Removal by OP

i. Effect of pH

As shown in fig 2,in case of OP (orange peel powder)increase in pH from 2 to 6 there was less quantity of dye adsorbed .when dye concentration further increased from 6 to 12 there was significant increase in adsorption .optimum adsorption was found at 7. There after it was near about constant.

Solution pH would affect both aqueous chemistry and surface binding sites of the adsorbents. At lower pH, H+ ions may compete with dye ions for the positive sites of the Orange peel waste thereby inhibiting the adsorption. From the above results it is evident that the removal of dyes are more at higher pH because the Surface of activated carbons are negatively charged, the decrease in adsorption capacity in the low PH region would be expected as the acidic medium would lead to an increase in hydrogen ion concentration which would then neutralize the negatively charged carbon surface thereby decreasing the adsorption of the positively charged cation because of a reduction in the force of attraction between adsorbent and adsorbate.

ii. Effect of agitation time

Fig. 4. represents the effects of agitation time on the adsorption of MB by the all three adsorbents. Extent of removal of Methylene Blue by orange peel powder was found to increase, with increase in contact time. It almost become constant with increase in contact time, after 110 Min. Based on these results, 110 min was taken as the equilibrium time in adsorption Experiments.

Extent of removal of Methylene Blue by orange peel powder was found to increase, with increase in contact time. Similar results have been reported in literature for removal of dyes. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the adsorbate species form the outer sites to interior sites of the adsorbent.

iii. Effect of Dose of adsorbent

As shown in fig 5 The effect of carbon dose for the uptake of MB by adsorbents was found to be increased by increasing the adsorbent dose. This study showed that minimum 2.75 g orange peel powder was required for maximum removal MB which is found as (84%).,due to the introduction of the more activate sites available for sorption. This study will be very useful to find out the optimum amount of carbon required for the removal of dye from the solution.

iv. Effect of initial dye concentration

From the fig. no 3, it is evident that for lower initial concentration percent removal of MB is higher i.e.90%. As the dose of adsorbent is kept constant, with increase in initial dye concentration adsorption decreases i.e.70%. The maximum dye removal was found at lowest initial dye concentration i.e 10 mg/l.

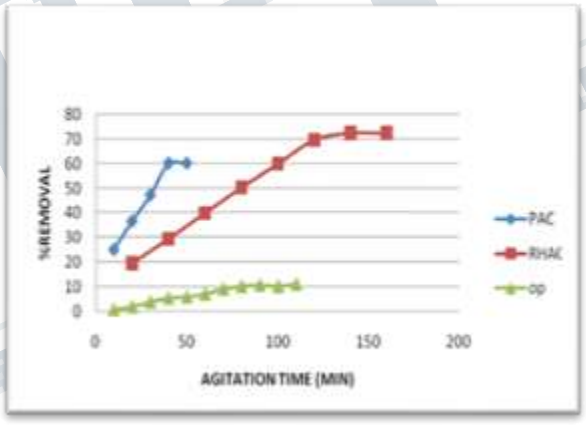

Fig.3:Effect of agitation time on Dye Removal

STUDY OF ADSORPTION ISOTHERM

Adsorption data for a wide range of adsorbate concentration and adsorbent dose shave been analyzed using Langmuir and Freundlich isotherms and constants of their equation in order to find the adsorption capacity of activated carbon prepared from Orange peel and activated rice husk. Isotherm constants are shown in table no.2 The linear plots of Langmuir isotherms will determine whether the activated carbon prepared from activated rice husk can be used as low cost adsorbent by calculating the separation factor rl by using Langmuir equation. The linear graph of Langmuir isotherms also represents the correlation coefficient and the value of intercept that is interpreted in table. The linear plots of log qe and log ce show the strength of adsorption capacity. The adsorption data was analyzed with the help of the following linear forms of Freundlich and Langmuir isotherms:

Freundlich isotherms: log qe = log kf + (1/n) log ce

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

Langmuir isotherms:(ce / qe) = (1/qo b) + (ce / qo)
Where; log kf = the adsorption capacity,
1/n = an indicator of adsorption effectiveness,
Qe = amount of dye adsorbed per unit mass of adsorbent (in mg/g)
Ce = the equilibrium concentration of dye (in mg/l),
Qo and b were the Langmuir constants, which measures of monolayer (maximum) Adsorption capacity (in mg/g) and energy of adsorption (in g/l), respectively. The valuesof Freundlich and Langmuir parameters were obtained from the linear correlations between the values of:

i. Log qe and log ce (Freundlich)
ii. (ce /qe) and ce (Langmuir)

The observed statistically significant (at 95% confidence level) linear relationships as evidence by Rl values (close to unity) indicate the capability of these two adsorption isotherms. The characteristics of separation factors can be referred in table 2.Other essential characteristics of the Langmuir isotherms can be described by a separation factor RI; defined by the following
equation:
Rl = 1/(1 +b ci)
Where;
Ci = initial concentration of dye (in ppm or mg/l) and
b = the Langmuir constant (in g/l).
The applicability of the Langmuir isotherm shown in fig. 6 with the Rl values showed to be in the range of 0-1 indicates that the adsorption process is favorable as low cost adsorbents. Langmuir isotherm is based on the assumption that maximum adsorption corresponds to saturated monolayer of dye molecules on the adsorbent surface. The energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface of activated carbons. The Freundlich isotherm shown in fig 7 describes equilibrium on a heterogeneous surface where energy of the adsorption was not equivalent for all adsorption sites, thus allowing multi-layer adsorption. The larger the value of adsorption capacity, kf , the higher the adsorption. The more heterogeneous the surface will bring the 1/n value closer to zero (tsai et al., 2001; azira et al., 2004). Values of kf and n were calculated from the slope and intercept of the Freundlich plots in fig 7 respectively.
The magnitude of the exponent ‘n’ gives an indication of the favorability and kf the capacity of the adsorbent/adsorbate system. Result from this experiment shows then values ranging between1and 10, indicating beneficial adsorption.

Table 1: Characteristics of Separation Factors

Rl value	**Adsorption process**
Rl > 1	Unfavorable
Rl= 1	Linear
0< Rl >1	Favorable
Rl= 0	Irreversible

Table 2: Study of Isotherm constants

Dye	**Langmuir isotherm**				**Frundlich isotherm**		
Methylene Blue	Qo (Mg/g)	b (g/l)	Correlation factor (r)	Rl	Intercept (kf)	Slop (1/n)	Correlation factor(r)
PAC	200.00	0.052	0.966	0.885	13.18	0.674	0.990
RHAC	71.429	0.034	0.836	0.922	2.366	0.806	0.870
OP	21.739	0.126	0.931	0.760	7.499	0.224	0.945

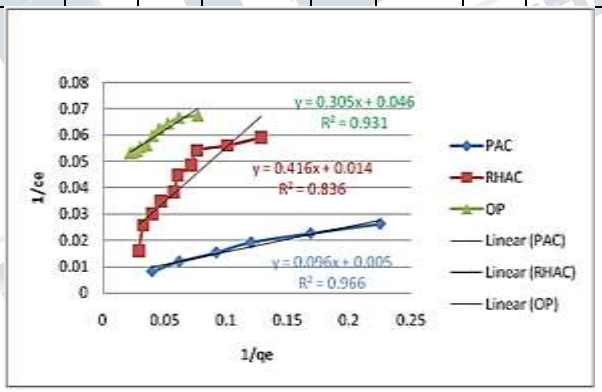

Figure 6: Langmuir Isotherm

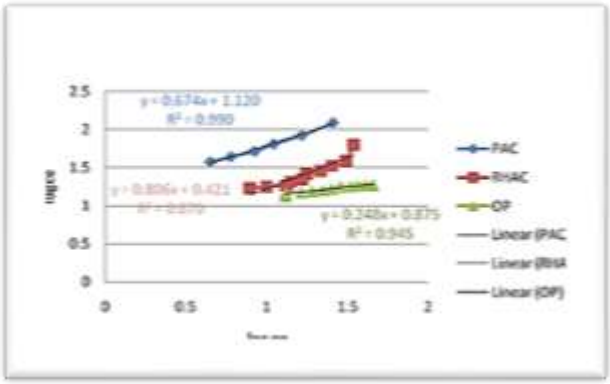

Figure 7: Freundlich Isotherm

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 1, January 2018

IV. CONCLUSION

1) Rice Husk activated carbon showed better performance than Orange Peel next to PAC for the treatment of removal of dye.
2) Efficiency of PAC as an adsorbent for MB dye remains near about same at all the pH values.
3) Removal of MB dye is significantly affected by pH of the system. In the present investigations, maximum removal of dye was found at pH 9 for RHAC and PH 8 for OP Hence it is always better to work with other sorbents instead of with costlier PAC.
4) All adsorbents followed Frundlich adsorption isotherm.
5) In all the cases of adsorbents more than 60% removal of dye was observed at an initial concentration was 50 mg/1.
6) Removal of dye is as high, as near to 100% depending on pH for all adsorbent.

BIBLOGRAPHY

- APHA, (1992): Standard method for the examination of water and wastewater. 18th edition, American Public Health Association, Washington, D.C.1992
- Amit Bhatnagar & A K Minocha (2006) Conventional and non-conventional adsorbents for removal of pollutants from water – A review Department of Chemistry.
- O. Yavuz, A. H. Aydin (2005) Removal of Direct Dyes from Aqueous Solution Using Various Adsorbents Dicle University, Faculty of Science and Art, Deparment of Chemistry, TR 21280, Diyarbakir, Turkey.
- V K Verma & A K Mishra (2007) Removal of dyes using low cost adsorbents Chemical Engineering Department, H. B. Technological Institute, Kanpur.
- S. Saiful Azhar, A. Ghaniey Liew, D. Suhardy, K. Farizul Hafiz, M.D Irfan Hatim (2005) Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse School of Materials Engineering, Northern Malaysia University College of Engineering (KUKUM)
- T. Murugan, A. Ganapathi And R. Valliappan. (2010) Removal of Dyes from Aqueous Solution by Adsorption on Biomass of Mango (Mangifera Indica) Leaves
- Ruey-Shin Juang, Duu-Jong Lee (2008) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions Gurusamy Annadurai.
- Indian Journal of Chemical Technology Vol. 15, pp. 140-145.
- American Journal of Applied Sciences 2 (11): 1499-1503, 2005 ISSN 1546-9239.
- http://www.e-journals.net 2010, 7(3), 669-676.
- Bhalki (2004) Preparation of Activated Carbon from Rice Husk Dept of Chemical Engineering REC.