

Adsorption Capacity of Activated Carbon Prepared by Chemical Activation of Lignin for the Removal of Methylene Blue Dye

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Abstract: *Currently much of the lignin produced in paper and pulp industry is consumed as a waste which is generally used only for its fuel value; therefore it can be of interest to prepare a high value and low cost product such as activated carbon from lignin. High surface area activated carbon was obtained by chemical activation of industrial waste lignin with H_3PO_4 . To optimize the preparation method, the effect of the main process parameters such as H_3PO_4 /lignin impregnation ratio, activation temperature and activation time on the iodine number and N_2 -BET surface area were studied in detail. The activated carbon obtained were analyzed by its proximate and elemental analysis, FTIR characterization and SEM analysis. The surface textural properties were determined by surface area determination by N_2 -BET isotherm and pore volume. The lignin based activated carbon with maximum surface area ($\sim 1343.98 \text{ m}^2/\text{g}$) and pore volume ($\sim 0.6950 \text{ cm}^3/\text{g}$) was obtained with H_3PO_4 -to-lignin impregnation ratio of 1:1, the activation temperature 800°C and the activation time 1 h. The adsorption capacity of prepared activated carbon has been tested for the decolourization of wastewater containing organic pollutant such as methylene blue dye. The effect of system variable such as concentration, pH, contact time and adsorbent dosage are investigated. The adsorption data was fitted with both Langmuir and Freundlich adsorption isotherms models.*

Keywords: *Industrial waste lignin, H_3PO_4 , Activated carbon, Adsorption, Isotherms.*

1. INTRODUCTION

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Textile industry use dyes and pigments to color their product. Dyes and pigments are emitted into wastewaters from various industrial branches mainly from dye manufacturing, textile finishing [1], food coloring, cosmetics, papers, carpets and tannery industries [2]. There are various conventional methods of removing dyes including coagulation and flocculation, electrolysis, oxidation [3] or ozonation and membrane separation. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used.

Activated carbon [4] is the commonly used adsorbent for removal of dyes and phenolic compounds. Activated carbons are the amorphous form of carbon characterized by high internal porosity and consequently high adsorptivity. Adsorption capacity of activated carbon mainly depends on its porosity and surface area. The textural property of activated carbon depends on the method of preparation and starting material [5]. Activated carbons are versatile adsorbents. Their adsorptive properties are due to their high surface area, a microporous structure, and a high degree of surface

reactivity. They are therefore used to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to permit recovery and to filter, remove, or modify the harmful constituents from gases and liquid solutions. The world demand for activated carbon is about 4.28 million metric tons and is expected to increase by more than ten percent over the next five years[6]. However, commercially available activated carbon is expensive and might not be economical for wastewater treatment. For an economical wastewater treatment purpose, therefore the development of activated carbon from low cost or waste materials acquired locally is an interesting option. Some 80-85% of the total production of activated carbon claimed to be derived from non-renewable coal-based resources. The remaining production is derived from renewable resources, such as wood and coconut shell, the later being dominant[7]. Agricultural waste are promising source of AC because of their low cost and abundance. Presently, quite a lot literature has reported the use of nut shells [8-9], Bamboo[10], rice husk[11], plant stem[12] etc. as a raw material for AC owing to their high carbon content. The high carbon contents of lignin make it a potentially attractive feedstock. As a polyaromatic hydrocarbon macro molecule and molecular structure similar to bituminous coal with carbon content between 61-66%, lignin may provide the high carbon yield required for commercial manufacture of AC.

Lignin is the second most abundant natural raw material and nature's most abundant aromatic (Phenolic) polymer whose main function is to cement the cellulose fibers in plant (Unlike cellulose lignin is a highly cross linked polyphenolic polymer without any ordered repeating units). Though the total lignin content varies widely from plant to plant, it is estimated that a total of 30% of the organic carbon in plant biomass is contained in lignin [13]. The conversion of wood chips to pulp for manufacturing paper generates huge quantities of by-products lignin. It is generally obtained from black liquor, a waste discharged from paper mills in large quantities, which poses a major disposal problem. As lignin is a three dimensional branched polymer with aromatic phenolic units, it degrades slowly and leads to the formation of char as a major degradation product[14].

Thus one of the potential applications of lignin is as a precursor for the preparation of activated carbon. Many researchers have investigated and reported about using kraft lignin to produce activated carbon with H_3PO_4 , $ZnCl_2$ [15], KOH , K_2CO_3 [16] or water vapour [17]. The chemical activation enhances the surface characteristics of the activated carbon.

Therefore, in the present research work the industrial waste lignin was subjected to chemical activation by activating agent H_3PO_4 . The pyrocatalytic degradation has produced activated carbons (ACs) with various surface area and micropores. Therefore it was thought to utilize the AC with maximum surface area for the adsorption of methylene blue dye.

2. MATERIALS AND METHODS

2.1. Reagents

All reagents used were of analytical grade including sulphuric acid, ortho-phosphoric acid, sodium hydroxide, hydrochloric acid, methylene blue (MB). Double distilled water was used to prepare experimental solution.

2.2. Precipitation of Industrial Waste Lignin

Concentrated black liquor obtained from Bilt Graphic Paper Products (Unit- Ballarpur), Ballarpur, MS, India, was acidified with dilute H_2SO_4 to precipitate the lignin, which was filtered and washed with plenty of distilled water to remove traces of acid. It was subsequently dried in oven for overnight at $80^\circ C$ and weighed. Pure lignin was obtained for the preparation of activated carbons. It was then crushed and sieved to the uniform and desired size (72 micron) for further procedure.

2.3. Preparation of Char from Lignin (In Absence of H_3PO_4)

The experiment was carried out in a cylindrical muffle furnace, in which a chromel/alumel thermocouple was placed inside, to measure the temperature. Purified industrial waste lignin (20g) was treated as a starting material. Thermal degradation of lignin in absence of catalyst was studied at the temperature $800^\circ C$ with the heating rate of $5^\circ C \text{ min}^{-1}$. After the final temperature was reached, the lignin sample was held for 1 hr at that temperature. The exhaust pipe was used to discharge the generated gases, such as CO_2 . At the end of the experiment, the product obtained was identified as 'char'. The char weighed 4.042g.

2.4. Preparation of Activated Carbon from Lignin (In Presence of H₃PO₄)

Industrial waste lignin was mixed with H₃PO₄ in various impregnation ratios (acid to lignin ratio such as 0.5:1, 1:1, 1.5:1 and 2:1) on wet basis in a beaker. Then it was boiled on electric heater using water bath until it turns into semisolid form. The semisolid slurry set into porcelain crucible and was left at room temperature for 24 hrs in air, and then transferred to a electric muffle furnace where activation was carried out under air atmosphere. The furnace was heated for 1 hr, at temperature 150°C with the heating rate of 10°C min⁻¹, to allow the free evolution of water. Afterwards the furnace was heated at 5°C min⁻¹ up to the final temperature (600°C, 700°C, 800°C and 900°C) where it was held for 1 hr. To study the effect of impregnation ratio and activation temperature on the development of the porous structure, four impregnation ratios have been checked and at each ratio different activated carbons were prepared at temperature ranging from 600 to 900°C (See Table 1). After activation, the AC was taken out of the reactor and cooled to room temperature. The ACs were extensively washed with 1M HCl firstly and afterwards with hot distilled water until a neutral pH was met (a multi parameter meter of Eutech Instruments, Oakton PCSTestrTM 35 India) [18]. Then, the samples were dried overnight in an oven at 110°C and the yield of activated carbons were calculated with the equation:

$$Y = (M_1/M_2) \times 100\%$$

where, M₁ is the weight of the activated carbon and M₂ is the weight of oven-dried powdered lignin; (x) Finally, all sample were pulverized and passed through 72 mesh for characterization analysis.

2.5. Iodine Number

Iodine number of lignin char and activated carbons prepared were determined on the basis of Standard Test Method ASTM Designation: D 1510-57 T. As iodine number gives as indication of microporosity (pores less than 1 nm in diameter), higher iodine numbers reflect better development of the microporous structure and higher adsorption abilities for low-molar-mass solutes [19].

2.6. Characterisation of Activated Carbon with Highest Iodine Number (ACHP 1/800)

2.6.1. Proximate and Ultimate Analysis

The proximate analysis of lignin, lignin char and the activated carbon (AC_{HP 1/800}) obtained by thermal degradation was carried out by standard method [20] to find out the percentage of moisture, volatile matter, ash and fixed carbon.

Elemental analysis of C, H, N, S and O content of lignin, lignin char and the activated carbon (AC_{HP 1/800}) was done using vario MACRO cube V3.0.3, CHNSO Elemental analyzer. Oxygen was calculated by difference. For the analysis, all the carbon samples were sieved to 0.212 μ in size. Before testing, all the samples are air dried by spreading thinly overnight so that the sample is equilibrated in the laboratory humidity condition.

2.6.2. Surface Area and Porosity

Single point BET surface area and total pore volume of samples was determined by Smart sorb 93 Surface Area Analyzer (Smart Instruments Pvt Ltd, Mumbai). All samples were pre-treated in the flow of pure nitrogen gas at 50 ml/min, 250°C for 1 h before the surface area measurements. A dynamic method has been used for surface area measurement in which gas mixture (30% N₂ + 70% He) continuously flows over the catalysts samples. Then the sample was dipped in liquid nitrogen having temperature (-196°C). In this flow, gas gets adsorbed on the surface and forms a mono layer on the surface. This adsorbed N₂ is allowed to desorb by bringing the sample at room temperature. The desorbed nitrogen is proportional to the surface area and so measured to calculate surface area. A dynamic method was used for total pore volume measurement in which gas mixture (95% N₂ + 5% He) continuously flows over the sample. Pore volume is measured at higher partial pressure i.e. above 0.35 for multilayer formation and filling of pores. Partial pressure of 0.95 was chosen to include largest radius pores in the measurement so that the pores smaller than 150° Å are filled.

2.6.3. FT-IR

The presence of various functional groups of lignin, lignin char and activated carbon were analyzed with Fourier Transform Infrared Spectroscopy (FTIR-2000, Perkin Elmer). The wave number was found to vary between 4000 and 400 cm⁻¹. All the spectra were compared according to the

assignments [21-22] given to the peaks so as to see the structural changes occurred in lignin during thermal degradation.

2.6.4. SEM Analysis

The surface morphology of lignin, lignin char and activated carbons obtained from thermal degradation of lignin was studied by SEM. The SEM images were recorded with Scanning Electron Microscope (JEOL; JSM-6380A) equipped with an electron probe analyzer system (accelerating voltage 30KV).

2.7. Optimization of Adsorption Parameters

2.7.1. Optimization of Adsorbent Dose

To optimize the ACs dose for maximum removal, studies were carried out for removal of dyes on activated carbon AC_{HP1/800} which is having maximum surface area amongst all prepared ACs. A dye solution was prepared in a volumetric flask with dye conc. 100 mg/L. Amount of AC_{HP1/800} adsorbent ranging from 0.01, 0.02, 0.025, 0.05 to 0.1g was agitated with 100ml standard solution of methylene blue dye in each BOD bottles. All the bottles were put inside the Remi orbital incubator shaker at 30 ± 1 °C for 48 hr. Then the supernatant dye solution was separated from the adsorbent with the help of a micropipette after centrifuged by centrifuge machine. The final dye concentration readings were taken using Elmer Lambda 35 UV/VIS spectrophotometer. The dye removal percentage was calculated using the following relationship.

$$\text{Percentage removal} = \frac{(C_0 - C_e)}{C_e} \times 100$$

where C₀ and C_e are the initial and equilibrium concentrations (mg/L) of dye respectively.

2.7.2. Optimization of pH

For determination of pH range for maximum removal, the batch type adsorption experiments were carried out at various solution pH (range: 2-11) by adding the required volumes of 1M HCl or NaOH solution. 0.05 g of AC_{HP1/800} was agitated with 100ml standard solution of methylene blue dye in each BOD bottles. The pH of the dye solution was measured by using digital pen type pH meter. Adsorption experiments were carried out and the dye removal percentage was calculated using the relationship as mentioned earlier.

2.7.3. Optimization of Contact Time

For determination of effect of contact time on adsorption study, the adsorption experiments have been conducted by varying the agitation time from 6 hr to 72 hr hours until equilibrium reaches. Activated carbon AC_{HP1/800} was taken in each BOD bottle containing 100 ml of the prepared dyes solution. 0.05 g of AC was agitated with 100ml standard solution of methylene blue dye in BOD bottles. Adsorption experiments were carried out and the dye removal percentage was calculated using the relationship as mentioned earlier.

2.8. Adsorption Experiments

Adsorption isotherm of methylene blue were carried out using AC_{HP1/800} adsorbent. Adsorption isotherm are indicative of the efficiency of an adsorbent for a particular adsorbate removal. A stock solution of 100 mg/L of MB dye solution was prepared by dissolving it in 1000 mL of double distilled water. It was soaked slowly to make sure all the dye powder has been dissolved in distilled water. In this method the time required for the adsorbate-adsorbent system to reach equilibrium was much longer as the liquid film diffusion resistance to mass transfer of solute to adsorbent surface could not be eliminated. All the isotherm studies were conducted at 30⁰C temperature and the fluctuations in the temperature of the adsorbate solution were no more than ±2⁰C. While performing adsorption equilibrium studies, stock solution was diluted to appropriate concentrations as and when required using distilled water. Concentration ranging from 1 mg/L to 180 mg/L of the solution prepared and difference of initial and final concentration of dye solution was measured by UV/VIS spectroscopy by measuring the optical density of the components at their respective wavelengths of maximum absorbance.

The adsorption capacity of AC_{HP1/800} for methylene blue at the equilibrium Q_e (mg/g) was calculated by mass balance as follows:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where, C_0 and C_e is the initial and final concentration of MB dye in solution(mg/l), V is the volume(l) of dye solution for adsorption experiments and m is the adsorbent mass(g) respectively.

3. RESULTS AND DISCUSSION

3.1. Influence of H₃PO₄ /Lignin Impregnation Ratio on Yield and Iodine Number of AC

The effects of the H₃PO₄/lignin ratio was studied at different temperature ranging from 600 to 900 °C for activation time of 1 hr. In this study, the ratio H₃PO₄-to-lignin was varied as 0.5:1, 1:1, 1.5:1 and 2:1 which is mentioned in Table 1. The effect of H₃PO₄/lignin ratio on the yield showed that the yield of activated carbon decreases with increase in impregnation ratio continuously (See Fig. 1). This indicates the pyrocatalytic degradation becomes more intense with increase in impregnation ratio. The iodine number of AC increases with increase in impregnation ratio from 0.5:1 to 1:1 but decreases after further increase in impregnation ratio from 1.5:1 to 2:1(See Fig.2). This indicates at 1:1 ratio the activation reaction was more intense, enhancing the adsorption capacity of iodine. At higher impregnation ratios, the pore would be widened and burnt off which decreases the adsorption capacity of iodine.

Table1. Activation conditions, iodine number and yield of the prepared ACs using H₃PO₄

Sr. No.	Sample code	Impregnation ratio (H ₃ PO ₄ : Lignin)	Temperature	Time	% Yield	Iodine number (mg/g)
1	AC _{HP} 0.5/600	0.5 : 1	600°C	1 hr	58.42	540.27
2	AC _{HP} 1/600	1 : 1		1 hr	51.64	780.52
3	AC _{HP} 1.5/600	1.5 : 1		1 hr	49.81	741.87
4	AC _{HP} 2/600	2 : 1		1 hr	44.32	624.117
5	AC _{HP} 0.5/700	0.5 : 1	700°C	1 hr	50.12	991.28
6	AC _{HP} 1/700	1 : 1		1 hr	44.67	1157.62
7	AC _{HP} 1.5/700	1.5 : 1		1 hr	38.31	1059.57
8	AC _{HP} 2/700	2 : 1		1 hr	31.63	1038.28
9	AC _{HP} 0.5/800	0.5 : 1	800°C	1 hr	39.94	1189.05
10	AC _{HP} 1/800	1 : 1		1 hr	31.79	1300.08
11	AC _{HP} 1.5/800	1.5 : 1		1 hr	29.98	1281.56
12	AC _{HP} 2/800	2 : 1		1 hr	22.78	1215.26
13	AC _{HP} 0.5/900	0.5 : 1	900°C	1 hr	30.84	1146.69
14	AC _{HP} 1/900	1 : 1		1 hr	23.35	1270.85
15	AC _{HP} 1.5/900	1.5 : 1		1 hr	20.2	1212.26
16	AC _{HP} 2/900	2 : 1		1 hr	15.54	1187.12

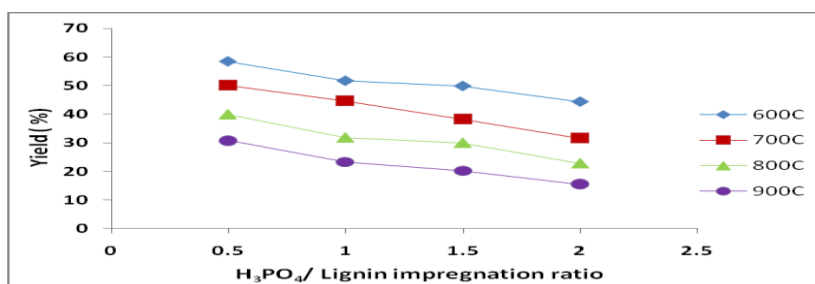


Fig1. Influence of impregnation ratio on yield

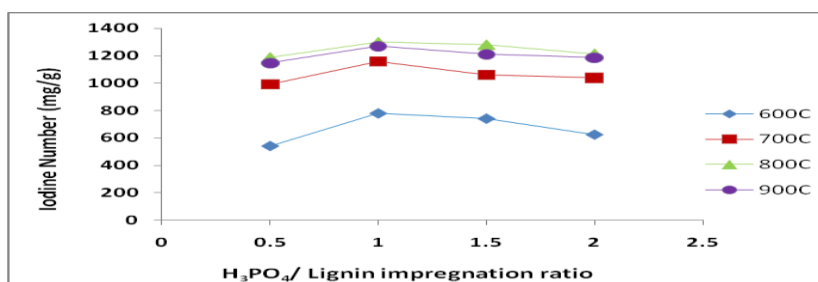


Fig2. Influence of impregnation ratio on iodine number

3.2. Influence of Activation Temperature on Yield and Iodine Number of AC

The effects of different activation temperature ranging from 600 to 900 °C on yield of activated carbons prepared using H_3PO_4 activating agent is illustrated in Fig. 3. The experimental data provided in Table 1 shows that the yield of activated carbon decreased progressively with increasing activation temperature. This indicates the pyrocatalytic degradation becomes more intense with increase in activation temperature.

It has been observed that the iodine number of AC increases with increase in temperature from 600 to 800 °C, but decreases at 900 °C (See Fig. 4). This shows that the H_3PO_4 activation is highly effective at 800 °C in the present study. During initial stage of degradation, due to acid attacks and there is a cleavage of aryl ether bonds of the lignin [23]. This reaction may be accompanied by secondary reactions such as degradation and condensation. During this low temperature treatment, there is an extensive evolution of CO/CO_2 and methane (which would not occur under the heat treatment without H_3PO_4). This process also leads to a decrease in the volume of the particles. When the temperature is increased, during the second heat treatment, towards the final temperature, the rate of weight loss decreases significantly and the structure begins to dilate, developing porosity[24]. The decrease in iodine number with the increase in activation temperature above 800 °C may be suggested due to the collapse of walls of the smaller pores which then combine to form larger pores. Beyond 800°C, the micro and mesopore areas experience a decrease, which is accompanied by a contraction of the particles. These changes are accompanied by a shrinkage of the pore size distribution.

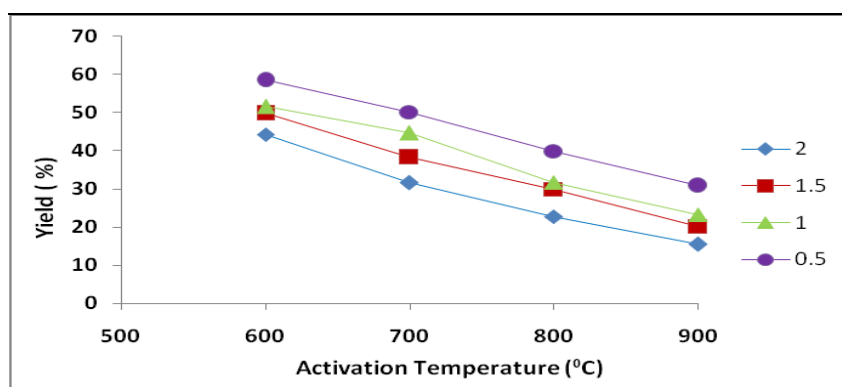


Fig3. Influence of activation temperature on yield

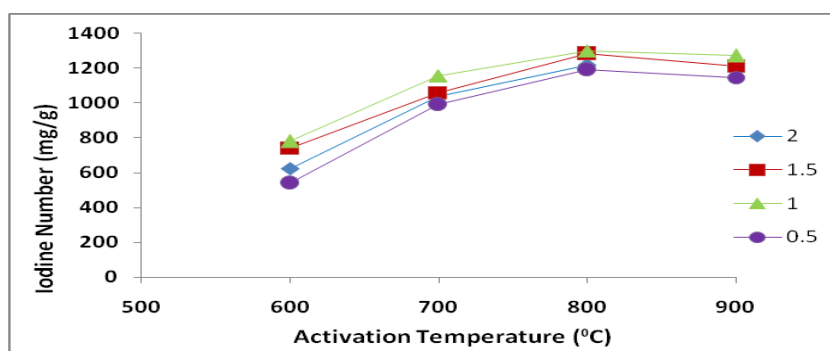


Fig4. Influence of activation temperature on iodine number

3.3. Characterisation of Activated Carbon with Highest Iodine Number (ACHP 1/800)

3.3.1. Proximate and Ultimate Analysis

Proximate analysis of lignin, lignin char and the prepared activated carbon ($AC_{HP\ 1/800}$) shows the difference in percentage of moisture, volatile matter, ash and fixed carbon (See Table 2). Results shows that the percentage of fixed carbon is highest in the AC obtained from lignin in presence of H_3PO_4 as compared to lignin char. In ultimate analysis (See Table 3) higher carbon content of $AC_{HP\ 1/800}$ indicates that aromatic structure becomes dominant after degradation in the presence of H_3PO_4 as compared to lignin char. It can be explained as, due to activation, the organic substances have degraded into volatile gases and liquid, where the solid carbonaceous residue left behind with high carbon content. However, the low hydrogen and low oxygen content in the ACs may be due to breaking of molecular chain.

peaks related to C-OH, CH, CH₂, CH₃, CO and C=O group were considerably reduced in the prepared AC. The low absorption in the region 800-1000 cm⁻¹ indicates a lower content of substituted aliphatic groups on the aromatic ring.

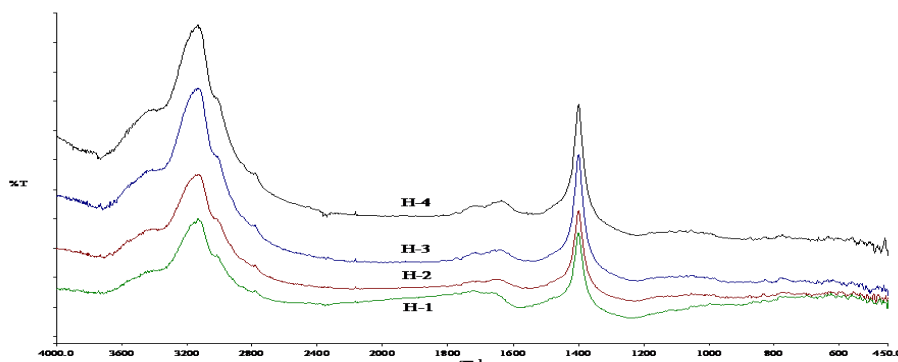
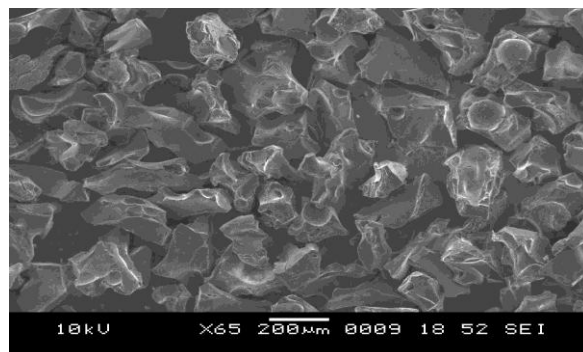


Fig6. Comparative FTIR spectra of activated carbons in presence of H₃PO₄

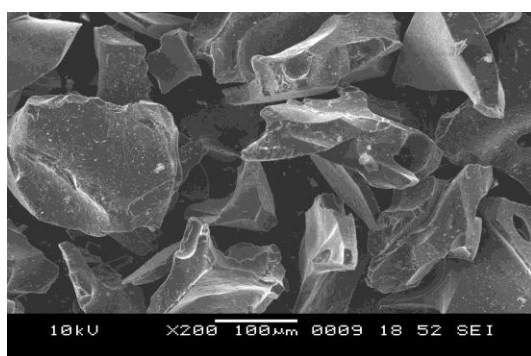
(H1=600^oC, H2=700^oC, H3=800^oC and H4=900^oC)

3.3.4. SEM Analysis

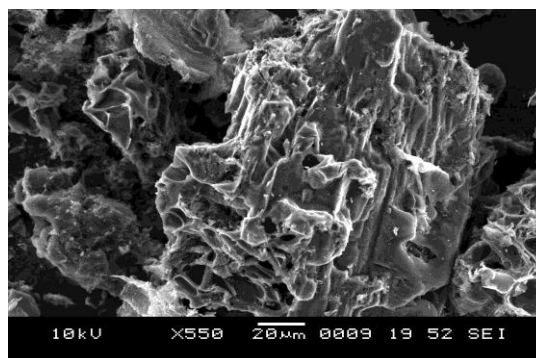
The SEM analysis of the lignin, lignin char and activated carbon (AC_{HP 1/800}) was recorded as shown in Fig. 7 to study effect of degradation process on the surface morphology of AC. SEM observations of ACs obtained from chemical activation of lignin revealed its complex and porous surface texture. The SEM images of lignin shows its amorphous nature. The SEM images shows a few pores on the rough surface of carbonized lignin prepared without catalyst, however a large number of various sizes and shapes pores observed on the irregular, heterogeneous and grainy surface of AC_{HP 1/800} which may contribute to the relatively high surface area. While compared with raw lignin material and lignin char, AC seems to have much more porosity showing large number of micropores and mesopores, which might have been the result of volatile gases released from the softened lignin matrix during activation process.



SEM image of lignin



SEM image of lignin char



SEM image of AC_{HP 1/800} using H₃PO₄ catalyst

Fig7. SEM images

Researchers suggest that the mentioned pores represent active sites of the adsorption process. Moreover, remarkably porous material having a high specific surface area should play an important

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role for providing the suitable binding sites for dyes, organic species and heavy metal molecule in the process of removal from aqueous solution.

3.4. Optimization of Adsorption Parameters

3.4.1. Effect of Adsorbent Dose

The percentage removal capacity of activated carbon is due to their porous structure and pore size distribution, and it depends on the polarity, solubility and molecular size of adsorbate. From the Fig. 8 it is observed that the optimum dose of adsorbent $AC_{HP1/800}$ for the removal of methylene blue dye from aqueous solution is 0.05g/100ml. Though at 0.1g/100ml, there is slight increase in Q_e value but if we get nearly the same result as we get at adsorbent dose of 0.05g/100ml, then going for 0.1 g/100ml will be expensive and loss of adsorbent. It is obvious that with increasing amount of the active sites, there is an increase in removal efficiency. As the process of chemical activation enhances porosity of the AC formed, hence it is evident that percentage removal of $AC_{HP1/800}$ for MB dye is 94.10% when using 0.05g of adsorbent dose.

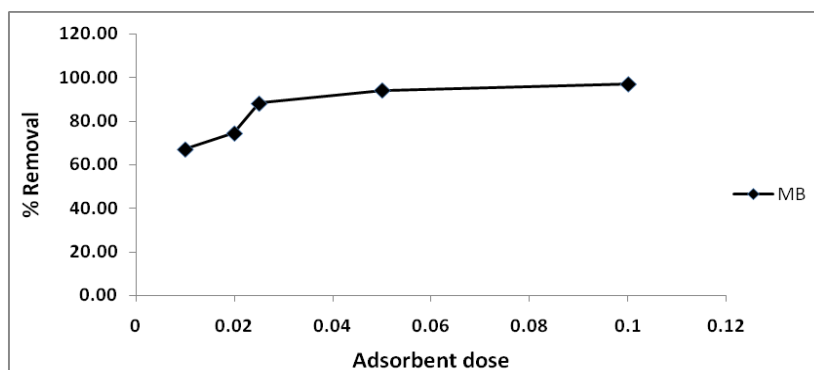


Fig8. Effect of adsorbent dose on removal of dye

3.4.2. Effect of pH

The effects of initial pH on the percentage removal of MB dye solution having concentration 100 mg/L, were investigated by varying the pH from 2 to 11. The removal capacity is largely dependent on pH of the dye solution. At pH 2 the percentage removal was minimum but it increased along with increasing initial pH of dye solution. Fig. 9 shows that in case of MB higher the pH, greater is removal by adsorption. It is evident that the percent adsorption of MB dye increases from 78.67 to 93.10 percent for MB as the pH increases from 2 to 10 [25]. Since the surface of activated carbons are generally considered to be 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 dye cation because of a reduction in the force of attraction between adsorbent and adsorbate.

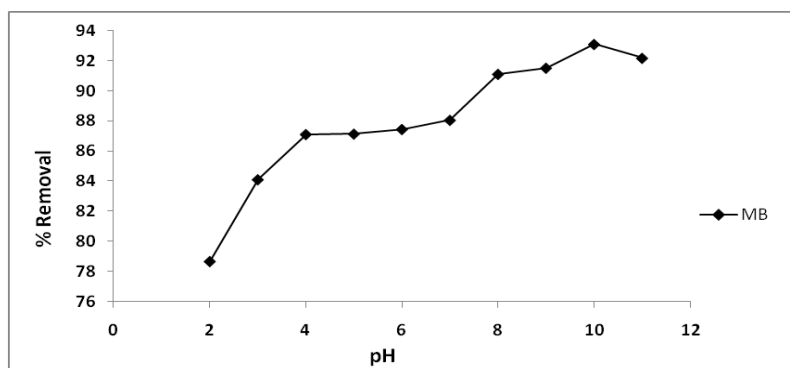


Fig9. Effect of pH on removal of dye

3.4.3. Effect of Contact Time

For a 100 mg/L concentration of MB dye and a 0.05g of adsorbent ($AC_{HP1/800}$) mass, the retention of dyes increased with increasing contact time which is shown in Fig 10. It was observed that the initial

removal percentage of dye is quite rapid, 51.34% of MB reached within first 6 hrs but the optimal removal efficiencies reached within 48 hrs and it was 94.08%. The removal efficiencies reached a steady value with increasing contact time after equilibrium had been reached. The final dye concentration did not vary significantly after 48 hours from the start of adsorption process. This shows that equilibrium can be assumed after 48 hours. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high, later the percentage removal rate of dye was decreased significantly resulted from saturation of $AC_{HP1/800}$ surfaces with dye molecules followed by adsorption and desorption processes that occur after saturation, it indicates the possible monolayer formation of dye molecules on the outer surface [26].

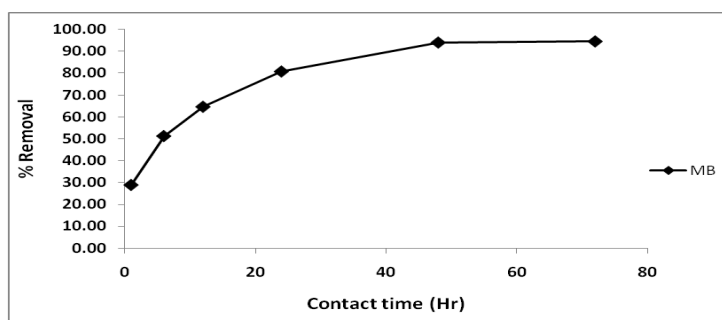


Fig10. Effect of contact time on removal of dye

3.5. Adsorption Experiments

Experimental isotherms are useful for describing the capacity of an activated carbon for an adsorbate to facilitate evaluation of feasibility of an appropriate carbon, and for preliminary determination of carbon requirement. Moreover, the equilibrium isotherm plays an important role in predictive modeling procedure for analysis and design of carbon system. Langmuir (Eq.1) and Freundlich (Eq.2) were introduced to analyze the experimental equilibrium data in this study and the model equations are listed below:

$$C_e/Q_e = (C_e/Q^0) + (1/Q^0b) \quad (1)$$

$$\text{Log}(Q_e) = \text{Log} K_f + 1/n \text{Log}(C_e) \quad (2)$$

Where Q_e = Amount adsorbed per unit weight of adsorbent, mg/g at equilibrium, C_e = Equilibrium concentration of adsorbate in solution, mg/l, Q^0 = Monolayer capacity of adsorbate, mg/g, b = Langmuir constant, K_f and n = Freundlich constants

The parameters of both models were calculated and summarized from the plots of $1/C_e$ Versus $1/Q_e$ and $\text{Log} C_e$ versus $\text{Log} Q_e$ shown in Fig. 11 and 12. The adsorption equilibrium data were analysed for their adherence to Langmuir and Freundlich plots by applying the method of linear regression over the concentration range for which the isotherms adhered to linearity. The values of the regression coefficient, R^2 , for all the adsorbent-adsorbate systems were mostly around 0.93 – 0.99. It was observed that the Langmuir and Freundlich adsorption isotherm models described the adsorption accurately with higher R^2 , indicating the identical affinity for the adsorbates and no transmigration of the adsorbates on the surface of $AC_{HP1/800}$. The validity of Langmuir equation was much better and over a larger equilibrium concentration range as compared to the Freundlich equation. The value of $1/n$ was found to be less than 1 which means the adsorption is favorable. The capacity of $AC_{HP1/800}$ was found to be 166.66 mg/g and 21.6271 mg/g for Langmuir and Freundlich model respectively for removal of methylene blue dye.

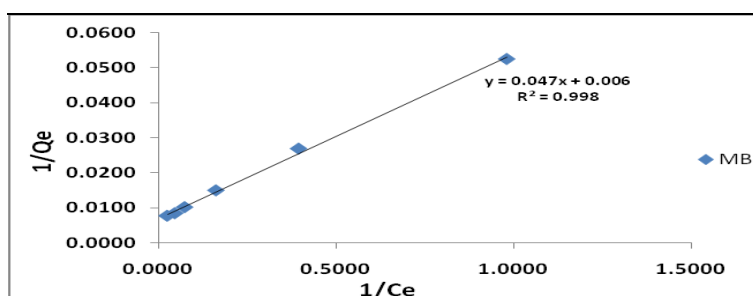


Fig11. Langmuir adsorption isotherm of MB dye

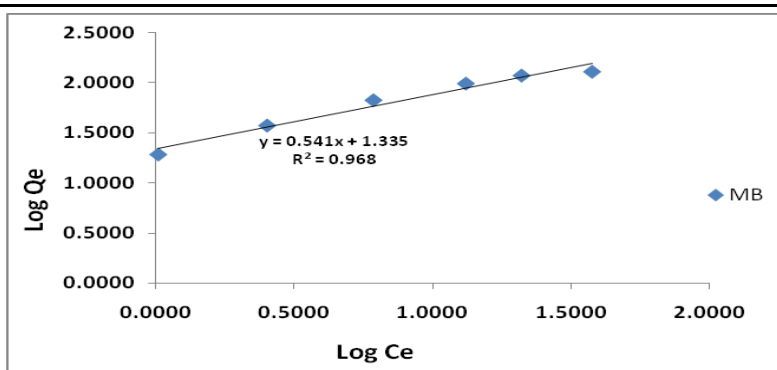


Fig12. Freundlich adsorption isotherm of MB dye

Table5. Adsorption isotherm parameters for adsorption of dyes on AC_{HP1/800}

Dyes	Langmuir Model			Freundlich Model		
	Q _e (mg/g)	b (L/mg)	R ²	K _f (mg/g(L/mg) ^{1/n})	1/n	R ²
Methylene Blue	166.66	0.1276	0.99	21.6271	0.541	0.99

4. CONCLUSION

This study indicates that properly sequenced treatments can ensure greater and better utilization of industrial waste lignin. Since large amount of renewable industrial waste alkali lignin is available, instead of isolating it from a particular species, the use of industrially produced lignin is considered more practical and rational for the purpose. In the present study, sixteen different activated carbons were prepared by chemical activation of industrial waste lignin, using H₃PO₄ activating agents for the optimization of impregnation ratio and activation temperature. The optimum activation conditions for porosity development of lignin derived ACs were found to be, impregnation ratio 1:1, activation temperature 800⁰C and activation time 1 hr. At activation temperature above 800⁰C, there is a decreases in N₂-BET surface area of activated carbon due to shrinkage of pores. The adsorption of methylene blue dye is fast, and the adsorption isotherm data fitted well to Langmuir as well as Freundlich isotherms. The obtained adsorption capacity are 166.66 mg/g and 21.6271 mg/g for Langmuir and Freundlich model respectively which is much higher than the earlier reported values [27]. These study confirms the suitability of activated carbon prepared from the industrial waste lignin for removal of toxic dyes and organic pollutants present in waste water.

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