Adsorption of methyl blue with activated carbon derived from peanut shell

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ABSTRACT

In this study we synthesized activated carbon (AC) sourced from peanut shell, an agricultural waste, for the adsorption of methyl blue from its aqueous solution. AC was produced via chemical activation method and was characterized using various tools like XRD, FESEM and Raman spectroscopy. Adsorption experiments were carried in different batches with varying initial concentration, adsorbent dose, contact time, pH and temperature. The optimized parameters for adsorption were found to be that of initial dye concentration of 150 mg/L, adsorbent dose of 120 mg/L, temperature equals to 50°C, contact time of 50 minutes and pH equals to 8. Adsorption data were used to figure out isotherm models, kinetics as well as thermodynamics of the process. It was concluded that maximum adsorption capacity is coming to be 714.28 mg/g, and the adsorption is favoring the Tempkin isotherm model. Also it was observed that the process is endothermic and spontaneous in nature.

KEYWORDS

Activated carbon; Methyl blue; Adsorption; Thermodynamics; Isotherms; Kinetics

HIGHLIGHTS

- The maximum adsorption capacity for this material was found to be 714.28 mg/g.
- The adsorption process highly increased in the basic medium.
- The adsorption followed Tempkin isothermal model and is spontaneous in nature.

1. INTRODUCTION

Water pollution has emerged as one of the major global concerns in last few decades. Effluents from industries contain acids, heavy metals, toxic organic compounds, etc., when dumped into the water bodies, causes severe ecological damage and contamination. It is estimated that more than 7×10^5 MT of dyes are commercially available across the globe, annually and majority of them are used in different industries, like that of textile, leather, paper, plastic, and cosmetics.[1] Moreover about nine million tons of colored wastewater are generated annually, when thrown away into water, causes severe ecological menaces.[2]These colored water not only blocks the sunlight penetration into the water, but many of them are toxic, both for human and animal. For human, prolonged contact with some dyes can cause nausea, vomiting, toxicity and organ failure. Removal of dyes from wastewater has become a significant issue with the increasing concern on environment protection. Many methods have been tried to removing these contaminations from water including electro-coagulation using solar energy [3], biological treatments [4], coagulation, [5], adsorption, [6], etc. Adsorption is considered as the one of the best method for water purification due to its simplicity of design, low cost and ease of operation.

Many adsorbents have been reported for removal of some of the common dyes, such as sawdust [7], fly ash [8], agricultural waste [9], carbon nano-tubes [10], graphene [11], and activated carbon from various sources like textile sludge [12], plant seeds [13] and various agricultural wastes [14]. Activated carbon due to its large surface area and economical production, considered as one of the best adsorbing media, mainly for the purification and separation of liquids and gases [15].

Activated carbon is a highly porous adsorptive medium composed primarily of carbon atoms. The basic chemical structure is closely approximated by the structure of pure graphite. It is also composed of layers of fused hexagons held by weak van de Waals forces. Although it is in the disorganized form, i.e. layers are randomly oriented and thus making it an amorphous substance. There are commonly produced by chemically activating the residues obtained from plants or animal, by treating it in alkaline medium, and then charring it high temperature. [16]

Peanuts are widely grown for their seeds as the agricultural output, while its shell is generally considered as waste. Due to its porous structure and high carbon content, it is viable to use it for the production of activated carbon. In this study, we have generated activated carbon from peanut shell and experimented to adsorb methyl blue, a common dye, mainly used for staining in histology and other scientific works. The optimal parameters for dye removal were obtained as well as desorption of adsorbents for recycling was also studied. Isothermal models like that of Langmuir, Freundlich, Tempkin were also realized. Also kinetics and thermodynamics for the adsorption were studied.

2. Materials and methods

2.1. Adsorbents

Peanut was purchased from a local market in Jaipur, India. Its shell was separated and washed with DI water twice to remove any dirt particles. It was then dried at 110°C in an oven. 40 gm of KOH was dissolved in 160 ml of water and 200 grams of dried shell was added to the solution and kept for 18 hours in a cool place. After then the shell was taken out and washed for several times with DI water to remove excess of KOH from its surface. It was then again dried for 12 hours in an oven at 110° C. Dried shell was then crushed with hand and placed in crucibles and heated in muffle furnace at 450° C for 75 minutes. After cooling, it was taken out to obtain a black colored substance. This was then crushed with a mortar pestle and the powder was then filtered with 5% HCl water solution for several times for the removal of silicate and other impurities. The activated carbon thus obtained is then dried overnight at 150°C in an oven and then kept in airtight lids.

2.2. Adsorbate

Methyl blue was purchased from Merck India and was used to make solutions of different concentrations by dissolving it in DI water. It was made sure to avoid the contact of light to the solution by wrapping the beaker with aluminum foil to prevent light degradation.

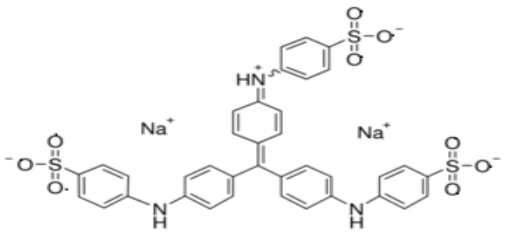


Figure 1Molecular structure of methyl blue

2.3. Experimental protocol

The batch adsorption experiments were carried out in a set of 200 ml glass flask with varying amount of solution, concentration, doses, time and pH. The flasks were agitated in an isothermal water-bath shaker at 120 rpm. After decantation and filtration, the concentrations of dye in the solution were measured at 590 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 0.1N HCl and 0.1N NaOH solutions. The amount of dye adsorbed and percentage removal of MB were calculated using equations (1) and (2), respectively:

$$q_e = (C_i - C_e) * V/M \quad (1)$$

$$\% \text{ Removal} = (C_i - C_e) / C_i \quad (2)$$

Where,

q_e = amount of dye in mg per gram of adsorbent.

C_i and C_e are initial concentration and concentration at a particular point in sorption respectively for the dye

V = Volume of the solution

M = Mass of the adsorbent

3. Result and Discussion

3.1. Characterization of activated carbon

3.1.1. XRD

XRD spectrum for the activated carbon was obtained as shown in figure 2. A peak at around 25° and one at around 43° can be seen, representing (002) and (101) planes of graphite, confirming the sample consist of carbon bonded with each other in the lattice structure similar to that of graphite. Although the broadness in peaks are because of the random orientations of the carbon sheets and thus shows the amorphous nature of the substance. The pattern observed in this case is quite similar to that of few previous works of synthesis of activated carbon [17-18].

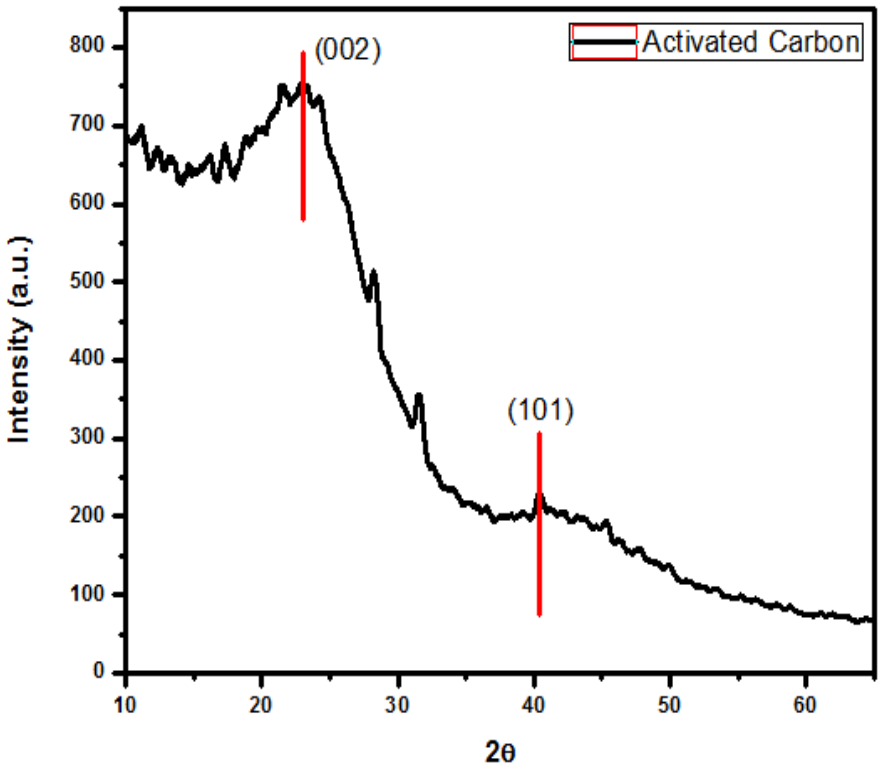


Figure 2XRD pattern obtained for the activated carbon

3.1.2. FESEM

FESEM was performed for the sample for the morphological analysis. It can be seen from the figure 3 that the material is highly porous in nature, containing of micro-pores of varying dimensions. Also it can be seen that the pores distributed over it having diameter in the range of 100- 300 nm. These pores on the surface effectively increase the surface area and acts as the sites for trapping the adsorbate molecules.

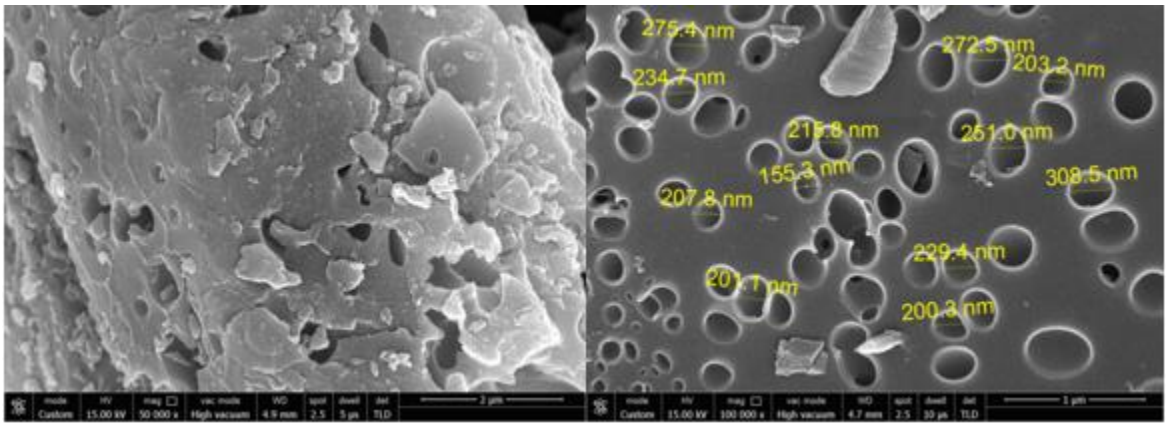


Figure 3 Images obtained for the activated carbon seen under high resolution SEM

3.1.3. Raman spectroscopy

Raman spectroscopy is done for carbonaceous material, as for them, two bands namely G and D-band appears. G-band which appears at around 1550 cm^{-1}, arises from the stretching of the C-C bond in graphitic materials, and is common to all sp2 carbon systems. D-band which appears at around 1350 cm^{-1}, represents the magnitude of structural disorder i.e. deviation from pure graphene. The ratio I_d / I_g is uses to estimate defects in the sample, which is 0.73 in this case, showing less structural defects developed during synthesis of the material.

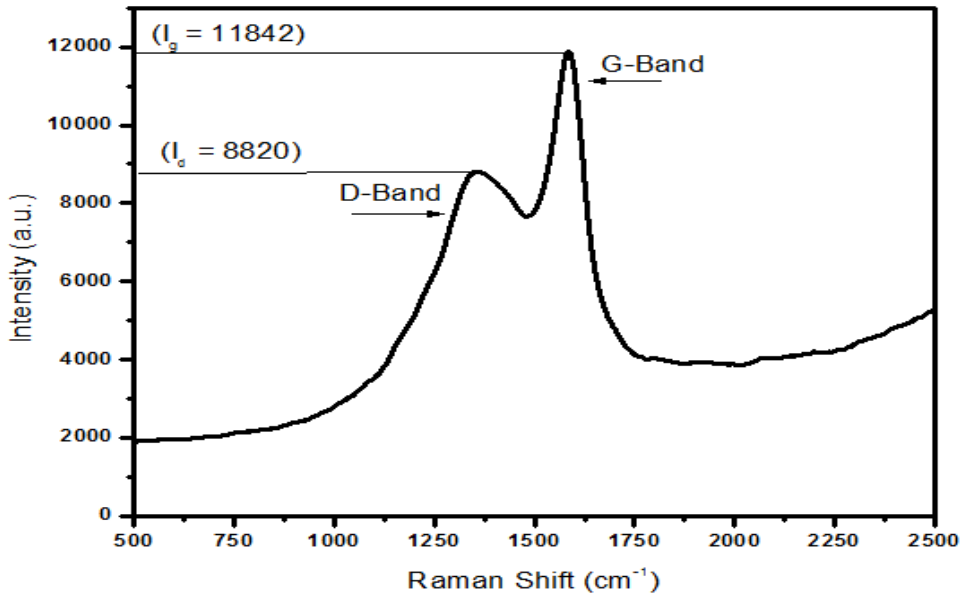


Figure 4 Raman Spectroscopy obtained for the activated carbon

3.2. Removal of methyl blue

3.2.1 Effect of initial concentration of the dye

The effect of initial concentration of the dye in adsorption process can be seen in fig 5.50 ml of dye solutions with varying initial concentration were taken and treated with 10 mg of activated carbon for 20 minutes. It can be seen that initially the percentage removal increases with the increase in dye concentration. This may be due to the fact that with increase in dye concentration, mass transfer rate also increases. Also at lower concentration, there would be more availability of active sites than at higher concentration, hence the amount adsorbed becomes almost constant at higher concentration and hence the percentage removal decreases.

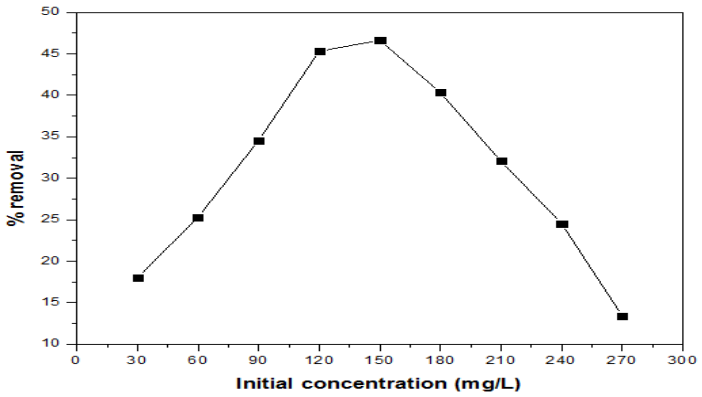


Figure 5 Effect of initial concentration of the dye in the removal

3.2.2 Effect of adsorbent doses

Adsorbent doses were varied from 3 mg to 24 mg for 100 ml of solution of 100 mg/l concentration. As shown on figure 6, initially percentage removal increases with increase in dose amount and after a certain dose it becomes almost constant. This may be due to the fact that initially there would be increasing availability of active sites with increase in the amount but afterwards, due to conglomeration of adsorbent particles, net surface area available remains same.

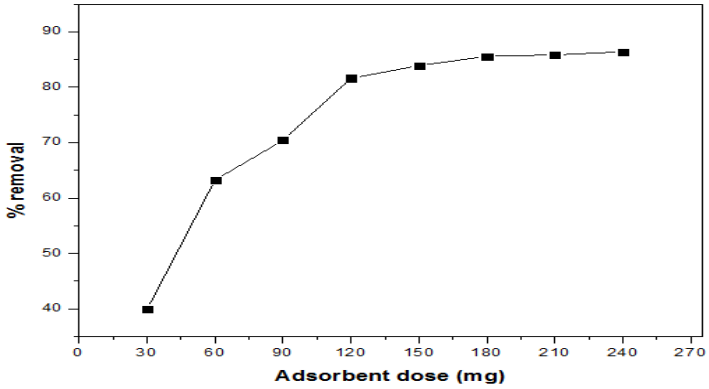


Figure 6 Effect of adsorbent dose in the removal

3.2.3. Effect of contact time

For this experiment dye concentration in the solution as well as adsorbent dose were kept same i.e. 140 mg/l, and 35 mg respectively and contact time were varied from 10 minutes to 90 minutes. From the figure 7, it can be seen that initially percentage removal increases sharply with increase in time, before being constant. This may be due to the fact that till 40 min, there were availability of active sites in large amount. Also concentration gradient was quite high initially, which came down and hence lessen the adsorption rate. Removal percentage becoming constant also indicates the formation of monolayer on the surface of adsorbent. The equilibrium is supposed to reach at 90 min.

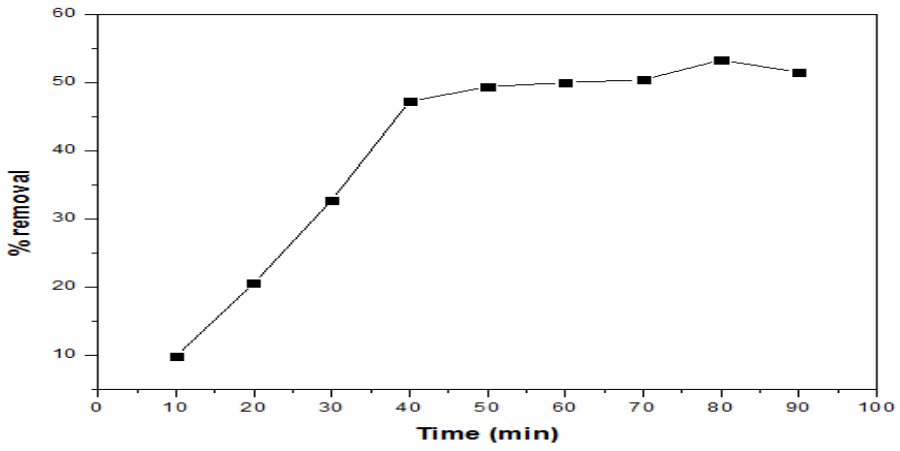


Figure 7 Effect of contact time in the removal

3.2.4. Effect of temperate

We can see the effect of temperature on the adsorption process as shown in figure 8. The adsorption of methyl blue increases sharply with the increasing temperature in the range of 10°C (283K) to 40°C (313K). This may be due to pore size enlargement and activation of sorbent surface with the rise in temperature.

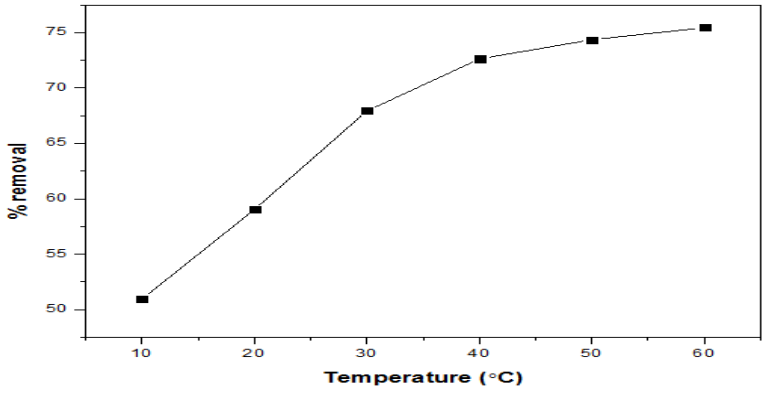


Figure 8 effect of temperature in the removal

3.2.5. Effect of pH

From figure 9, we can see the effect of pH on adsorption. The removal increases and reaches to maximum as the medium turns basic. Since the dye which is basic in nature itself, become positively charged ions when dissolved in water. Thus, in acidic medium the positively charged surface of adsorbent opposes the adsorption of the cationic adsorbate. When pH of the solution is increased negative charge develops over the surface of adsorbent, there by resulting in an increased adsorption of the dye due to an increase in the electrostatic attraction.

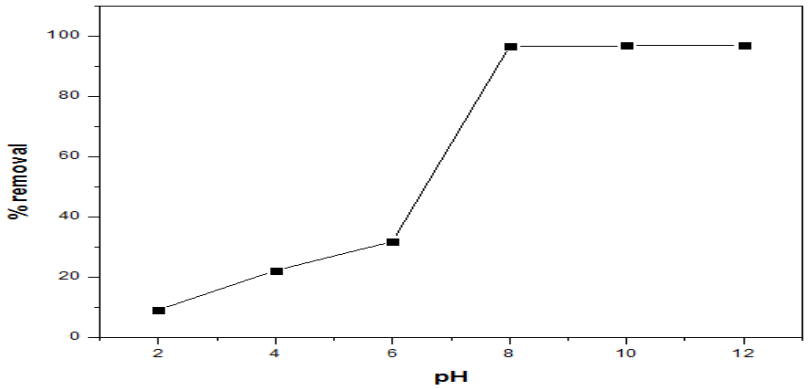


Figure 9 Effect of pH in the removal

3.3. Adsorption isotherms

Three isothermal models namely Langmuir, Freundlich and Tempkin models were studied. The Langmuir model is applied to the equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites.

Langmuir equation is written as:

$$1/q_e = 1/q_m + 1/K_L q_m C_e$$

The Freundlich equation, which is studied for heterogeneous surface energy system, is given as:

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

The Tempkin equation is given as:

$$q_e = \beta \ln\alpha + \beta \ln C_e, \text{ where } \beta = RT / b$$

Here K_L is the Langmuir's constant, K_F and n are Freundlich constants, b is the Tempkin constant, q_e is the dye concentration on sorbent at equilibrium, C_e is the dye concentration in the

solution at equilibrium and q_m is the dye concentration when monolayer forms on the adsorbent. R and T are the universal gas constant and absolute temperature respectively. Plotting the linear slopes for all these three equation, we get the values of unknown constant, by knowing the values of slopes and intercepts.

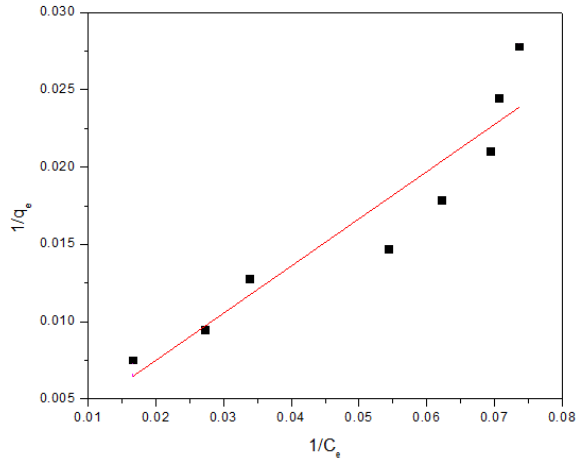
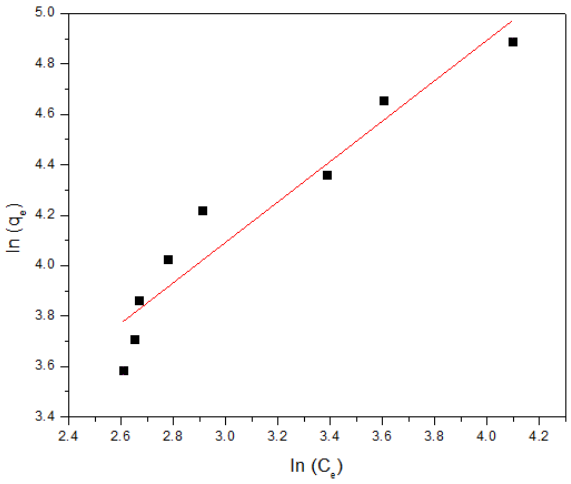


Figure 10 Langmuir modeling plot for the adsorption



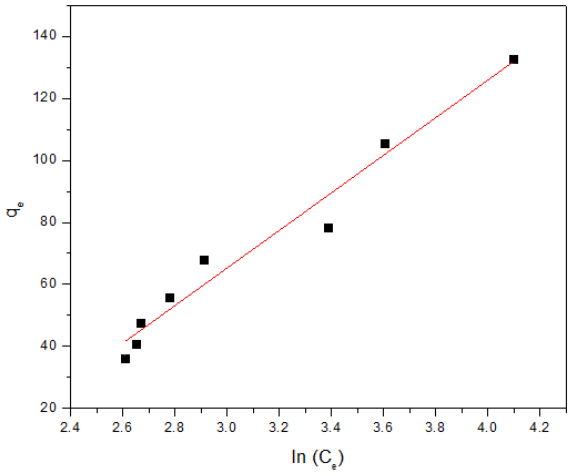


Figure 11 Freundlich modeling plot for the adsorption **Figure 12 Tempkin modeling plot for the adsorption**

Table 1 Different isothermic constants obtained for the process is tabulated below

Models	Isothermal Constants			
Langmuir	q_m = 714.28 mg/g	K_L =0.0045 L/mg		R^2 = 0.890
Freundlich	n = 1.24	K_F = 5.407 mg/g		R^2 = 0.920
Tempkin	β = 60.687 L/g	α = 6.851 mg/L	b = 40.825 J/mg	R^2 = 0.968

Figure 10, 11 and 12 are the plots for Langmuir, Freundlich and Tempkin models. It can be concluded that the adsorption is not fitting well in the Langmuir model (R^2 = 0.890) and hence apart from forming monolayer on the surface, internal diffusion of adsorbate in the sorbent is also evident. The adsorption capacity is coming to be 714.28 mg/g, which is quite high and hence it can be accepted as an ideal adsorbent for methyl blue adsorption. The adsorption is not

fitting well in Freundlich model (R^2 = 0.920) than the other, although smaller value of n indicates favorability of methyl blue adsorption on activated carbon. Tempkin isothermal model is well describing this process (R^2 = 0.968), and the value of b indicates the heat of adsorption which is coming to be 40.825 J/mg.

3.4. Adsorption kinetics

The pseudo first order rate equation is given as :

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$$

Here q_e and q_t are the amount of dye adsorbed on the adsorbent (mg/g) at equilibrium and at time = t respectively. K_1 is the first order rate constant. A graph between $\log(q_e-q_t)$ and t, gives us a linear relationship from which k_1 and q_e can be obtained.

Pseudo second order equation in its linearized form can be written as [19]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

Here q_e and q_t have same meanings. K_2 is the pseudo second order rate constant (g/mg min). A graph of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept [20].

The intra-particle diffusion equation is given as:

$$q_t = K_d t^{1/2} + C$$

here K_d is the intra-particle diffusion rate constant.

Table 2 Result obtained after applying the adsorption values to the pseudo first and second order kinetic models and intraparticle diffusion model

Pseudo first order model K_1 = 0.631 (min^{-1})	q_e = 364.921 (mg/g)	R^2 = 0.962
Pseudo second order model K_2 = 0.002 (g / mg-min)	q_e = 48.543 (mg/g)	R^2 = 0.671
Intra particle diffusion model K_d = 27.44 (mg / g-min)	C = -25.007 (mg/g)	R^2 = 0.869
Thermodynamic parameters ΔH° = 17518.429 (J/mol)	ΔS° = 72.986 (J/mol-K)	ΔG° = - 4961.26 (J/mol)

The correlation coefficient (R^2) for the first order is much greater than that of the second order and of inter particle diffusion model. Moreover it is close to unity hence it can be said that the adsorption is governed by pseudo first order kinetic model.

Also it can be observed that in the graph of intra-particle diffusion model, the plot is not passing through origin. This confirms that the adsorption was a multiple step process in which firstly there was adsorption on the surface then the diffusion in the interiors of the adsorbent [1, 21].

3.5. Adsorption thermodynamics

van't Hoff equation for the adsorption is given as:

$$\ln (q_e/q_c) = \Delta S°/R - \Delta H°/RT$$

Here q_e is the dye concentration on activated carbon at equilibrium (mg/g) and q_c is the dye concentration in the solution at equilibrium (mg/l), at a given temperature T.

ΔG°,ΔH° and ΔS° are changes in Gibbs free energy, enthalpy and entropy respectively.

R is the universal gas constant and is equal to 8.314 J / mol-K.

Values of ΔH° and ΔS° were calculated from the slope and intercept of the plot of ln K_D versus 1/T.

Gibbs free energy change of sorption was calculated by the equation:

$$\Delta G° = \Delta H° - T\Delta S°$$

Value of ΔH° (17.518 kJ / mol), which is positive, indicates that the adsorption of the dye onto activated carbon is an endothermic reaction. The calculated value of ΔG° (−4.96 kJ/mol) indicates spontaneous nature of the adsorption process. Also, the positive value of entropy change, ΔS° (72.986 J/mol K) shows the affinity of adsorbent for the dye.

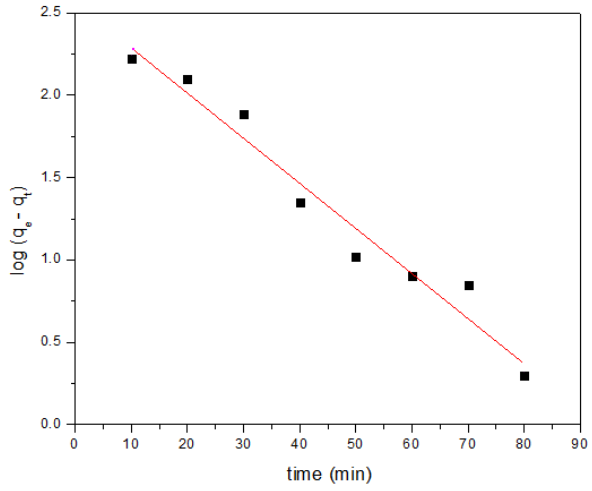


Figure 13 van't Hoff equation plot

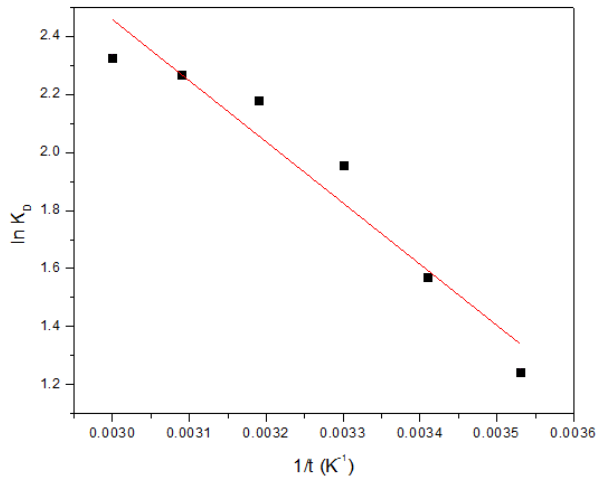


Figure 14 Enthalpy and entropy determination

3.6. Desorption of the adsorbate

Desorption study was carried out for recycling of the adsorbate. For this experiment we first carried out an adsorption experiment with standard solution. Adsorbent was then filtered out and washed with DI water. It was then divided into four equal parts and the three were treated with 1% (w/w) solution of HCl, HNO3 and NaOH and fourth one with acetone. Four of them were again washed and an adsorption experiment was carried out with these four individually with the same standard solution. The second time removal was compared with the initial removal amount to get the percentage desorption.

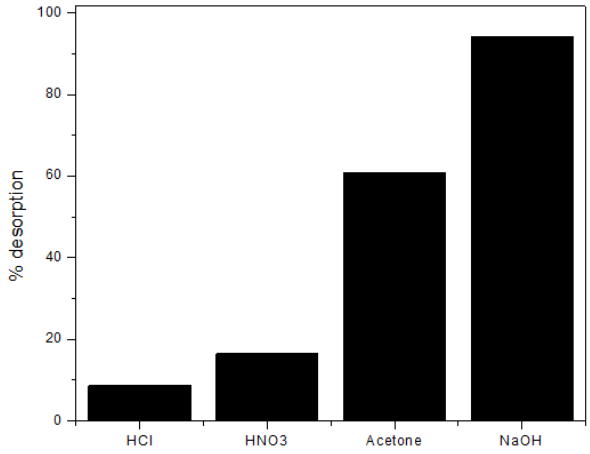


Figure 15 Percentage desorption after treating with different media

4. Conclusion

In this study, it was concluded that activated carbon derived from peanut shell is a promising candidate for adsorption of methyl blue from its solution. The maximum adsorption capacity was found to be 714.28 mg/g. The optimal parameter for dye sorption were the initial concentration of dye 150 mg/l, adsorbent dose of 120 mg/l, time of 50 minutes, temperature of 50°C and pH of 8. It was observed that NaOH solution is a favorable media for desorption. It was concluded that the rate of adsorption follows pseudo first order kinetics and the adsorption process is best fitting into Tempkin isotherm model. Moreover the negative value of Gibbs free energy ($\Delta G°$) indicated that the adsorption was spontaneous process. And the positive value of change in enthalpy ($\Delta H°$) specified the endothermic nature of sorption.

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