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Methylene Blue removal from aqueous solutions by activated carbon prepared from *N. microphyllum* (AC-NM): RSM analysis, isotherms and kinetic studies

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Abstract

This study was conducted to remove Methylene Blue (MB) from aqueous solution using activated carbon prepared from *N. microphyllum* (AC-NM) as a new, cheap, and non-toxic. Design of experiments based on Response Surface Methodology (RSM) conducted to investigate the effect of variables namely; initial dye concentration, pH, contact time and absorbent dosage. An empirical model was developed applying ANOVA analysis. The interaction effects of all factors and their optimization have been carried out using RSM. Dye removal efficiency increased to more than 90% with increasing pH and initial concentration of dye from 3 to 11 and 10 to 210 mg/L, respectively under 1.1 to 1.4 g/L of absorbent dosage. Among factors, initial concentration of MB known as an important factor with P-value <0.0001. The experimental data are fitted with Freundlich model based on multilayer adsorption states (R^2=0.99). The adsorption kinetics well described by second order model with R^2 = 0.98. This novel absorbent has different advantages such as low cost, high ability to absorb pollutants and easily available that can be suggested for water and wastewater treatment.

Keywords: Absorption, Activated Carbon, Decolorization, Methylene Blue, *N. microphyllum*

1. Introduction

Nowadays, one of the major challenges for environment and human life due to their adverse effects is synthetic dyes (Hayat *et al.*, 2015; Tan *et al.*, 2015). Synthetic dyes are intensely compounds having general applications in different industries such as chemical and dye manufacturing, textile, paper, leather and plastics (Özer and Dursun 2007; Low *et al.*, 2011; Albadarin and Mangwandi 2015; Mitrogiannis *et al.*, 2015) with structural diversity including: acidic, basic, reactive, azo, anthraquinone-based, and metal complex dyes (Rohilla, 2012). Those aforementioned dyes have different effects on environment; for example, they can be cause of reduction of sunlight penetration, oxygen transfer limitation, and also are stable chemical and toxic for fauna and flora, when release into environment. Furthermore, they cause irreversible damages on human health such as mutagenic, teratogenic and carcinogenic effects (Bouaziz *et al.*, 2015; Dotto *et al.*, 2015; Yuan *et al.*, 2016).

Amongst these dyes, the Methylene Blue (MB) is widely used for dying wood, cotton and silk (Hameed *et al.*, 2007; Li *et al.*, 2013) which can be cause of methemoglobinemia, nausea, vomiting and mental confusion(Mitrogiannis *et al.*, 2015). For this reason, removal of it from effluent containing dye is necessary. However, there are chemical and biological methods (like coagulation/flocculation, advanced oxidation processes, membrane filtration and ozonation) for treatment of dye effluents but these effluents are hardly treated by conventional biological wastewater treatments (Zhang *et al.*, 2010; Li *et al.*, 2013). At the present time, adsorption is reliable to be a simple technique and successful in water and wastewater treatment process and the success of the method largely depends on the evolution of a capable adsorbent (Khashij *et al.*, 2016). Variety of absorbents has been studied to removal of MB from water and wastewater such as Clay, Clinoptilolite, Almond Gum, Rice Husk, Fly Ash and etc (Fernandes *et al.*, 2007; Hameed *et al.*, 2007; Özer and Dursun 2007; Almeida *et al.*, 2009; Ghaedi *et al.*, 2012; Liu *et al.*, 2012; Li *et al.*, 2013; Bouaziz *et al.*, 2015). Recently, agricultural waste as low cost adsorbent, availability and non-toxicity is noteworthy. In the meantime, *N. microphyllum* is widespread as an aquatic plant species and activated carbon prepared (PAC) from it can be considered in removal of Methylene Blue and other pollutants (Almasi *et al.*, 2017).

The removal efficiencies of dye in adsorption systems are often influenced by many parameters such as dosage of adsorbent, concentration of absorbate, contact time, and

pH (Cui *et al.*, 2016). Therefore, using of the method for optimization of parameters is necessary. Recently, one of the methods for optimization is RSM technique (Liu *et al.*, 2012). RSM is a collection of mathematical and statistical technique that involves experiments based on the multivariate non-linear model and it can be used for studying the effect of several factors (Mousavi *et al.* 2014; Mousavi and Ibrahim, 2014). In this model, all parameters are varied overset of experimental runs; RSM can make simple and efficient modeling utilization (Bezerra *et al.*, 2008). *N. microphyllum* had perennial growing as well as there is no information in the literature regard to the use of *N.microphyllum* originating from this type of geographical location, a fact which confirms without doubt the novelty of this work. So, the objective of this study was to determine the effectiveness of AC-NM as a novel adsorbent in removing MB dye and optimization of independent factors with RSM.

2. Experimental

2.1. Material and Reagents

For experiments, Methylene Blue ($C_{16}H_{18}N_3SCl$) with 98% purity – (Merck) was used for preparing the stock solution. All the reagents were prepared with deionized water. All runs have been conducted by using solution from stock solution at the desired concentration.

2.2. Preparation of Absorbent

The AC-NM that was obtained from Gilangharb (city of Kermanshah in Iran). Initially, *N. microphyllum* plant was washed with distilled water and cut to desired size of 5 cm. Then, raw materials were dried at150 °C for 2 hours using an oven model Memert 854- Germany. Samples were sieved to obtain mesh of 50 (0.2 mm). After that sieved plants carbonized in oven at 500 °C for 4 hours. Activation was conducted in a furnace under purified nitrogen (99.99%) flow of 150 ml/min to make an inert atmosphere. Finally, absorbent was dried at ambient temperature and stored in a capped bottle.

2.3. Adsorbent Characterization

AC-NM was characterized using SEM analyses. SEM images of all samples were taken to determined surface textures of PAC, using scanning electron microscope (XI-30 ESEM-FEG Company, USA). The FTIR spectra of the AC were analyzed between 4000 and 600 cm^{-1} in a Perkin-Elmer 1720 spectrometer and samples were prepared by mixing carbon powder and KBr at the weight ratio of 1:400. Also, the specific surface area and total pore volume (V_{tot}) were determined by N_2 adsorption isotherms (BET) via the nitrogen uptake at relative pressure of 0.88 and ambient temperature of 298 K by SA-9600 analyzer (HORIBA, Germany).

2.4. Batch Adsorption Studies

The experiments were carried out in a glass beaker with total volume of 250 mL. The reactor consisted of a 7 cm diameter by 9 cm height. Homogeneity achieved by applying magnetic shaker (JENWAY SELECTA 1000, UK) at 150 rpm for all tests, when temperature was 25±2 °C. Batch experiments were done with four factors namely initial pH (3-11), Dosage of adsorbent (0.2-1.4 g/L), initial concentration (10-210 mg/L) and contact time (10-50 min). Subsequently, samples were centrifuged at 3800 rpm for 5 minutes.

2.5. Isotherm, Kinetic and Experimental Modeling

Interaction between MB with adsorbent toward surface properties is described with different isotherm and kinetic models. Isotherm models and parameters are illustrated in Table 1. In addition, the design of experiments (DOE) in order to eliminate errors systematically was conducted.

Table 1. Isotherms and Kinetic models of adsorption

Isotherms	Equation	kinetics	Equation
Freundlich	$\log q_e=\log k_f+\frac{1}{n}\log c_e$	First-Order	$\frac{dq_t}{dt}=k_1(q_e-q_t)$
Langmuir	$\frac{C_e}{q_e}=\frac{1}{bQ_{max}}+\frac{c_e}{Q_{max}}$	Second-Order	$\frac{dq_t}{dt}=k_2(q_e-q_t)^2$
Temkin	$q_e=\frac{RT}{b}\ln K_tC_e$	Intraparticle diffusion	$q_t=kt^{1/2}$
Redlich–Peterson	$q_e=\frac{K_{RP}C_e}{1+\alpha C_e^{\beta}}$	Elovich	$q_t=\frac{1}{b}\ln ab+\frac{1}{b}\ln t$
Parameter	**Description**	**Parameter**	**Description**
q_e	Adsorption equilibrium rate (mg/g)	a	Initial adsorption rate (mg/(g min)
q_{max}	Dye adsorbed (mg/g)	1/b	Number of sites available(mg/g)
K_F	Constant (mg/g) $(L/g)^{-1/n}$	K_t	Temkin equilibrium constant
b	Langmuir constant (L/mg)	b	Energy of adsorption(j)
n	Freundlich constants	T	Absolute temperature in K (°C)
C_e	Final concentration (mg/g)	R	Ideal gas constant (8.314 J mol^{-1} K^{-1})
k	Intraparticle diffusion constant	α	Redlich–Peterson constant
C	Boundary layer thickness(mg/g)	β	Redlich–Peterson constant

This technique has the ability to optimization of the experiments and designed to test an empirical model. The most common way for optimization of multivariables is optimizing the individual variable while the other variables are constant. Because cases like time-consuming and disregarding the reaction between variables, this method not been paid to optimal results. For this reason, a statistical method for determine the effects between dependent and independent variables is designed. Among such methods, the response surface methodology (RSM) is a statistical technique for modeling of experiments. Modeling by this method is able to determine the effective independent variables namely concentration (factor A), adsorbent dosage (factor B), pH (factor C), contact time (factor D), and their interactive influences on MB adsorption at a limited number of designed runs, that is by using the central composite design (CCD) via Design-Expert (ver, 8.0) software relationships between the variables will be provided. The reasonable range of MB dye (actual value = 10, 50 and 200 mg /L) and adsorbent dosage (AC-NM; actual value = 0.2, 1 and 1.4 g/L) were selected according to the previous studies that the coded value term was used to represent the independent variables at two levels, which consist of –1 (low level), and +1 (high level).

Table 2. Level of various independent variables at coded values of CCD

Symbol	Independent variables	Coded levels	
		High	Low
A	Concentration, mg/L	200	10
B	Dosage, g	1.4	0.2
C	pH	11	3
D	Contact Time, min	50	10

As shown in Table 2, the experimental conditions for adsorption process based on CCD with a factorial matrix of 78 steady state runs were designed. After accomplishing the experiments at a set value of independent variables (concentration, dosage of adsorbent, contact time and pH), the experimental data according to Table 1 were used to develop empirical models based on actual factors (AF) and coded factors (CF), using analysis of variance (ANOVA). The significance of the variables was recognized based on the confidence levels above 95% ($P < 0.05$) in the polynomial model. The quadratic model based on Eq. (1) was used to estimate the coefficients of the statistical model:

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i x_i+\sum_{i=1}^{k}\beta_{ii}x_{ii}^2+\sum_{i<j}^{k}\sum\beta_{ij}x_i x_j+e \quad (1)$$

Where *i* represents linear coefficient, *j* stands for the quadratic coefficients, *β* is the regression coefficient, *x* represents independent variables, *k* is the number of studied and optimized factors in the experiment and *e* is the random error.

2.6. Analysis Procedure

The concentration of MB is determined by the 2120 C standard methods spectrophotometer method(Federation and Association 2005). The samples measured at 675 nm in a UV- visible spectrophotometer (Jenway6305-Germany). The results were analyzed using analysis of variance (ANOVA) (Design Expert Software). Decolorization percentage was determined using the (2) formula:

$$\text{Decolorization}(\%)=\frac{(C_i-C_f)}{C_i}\times 100\% \quad (2)$$

Where, C_i is the initial concentration of dye (mg/L), C_f is the final concentration (mg/L).

3. Results and discussion

3.1. Characterization of carbon

SEM images of activated carbon are shown in Figure 1. The activated carbon has crevices, cracks and various sizes of crystals in large pores that can be due to activation of adsorbent. This result is also in good accordance with the BET results, leading to relatively high BET surface area of 1940 m^2/g. FTIR spectroscopy before and after activation is shown in Figure 2.

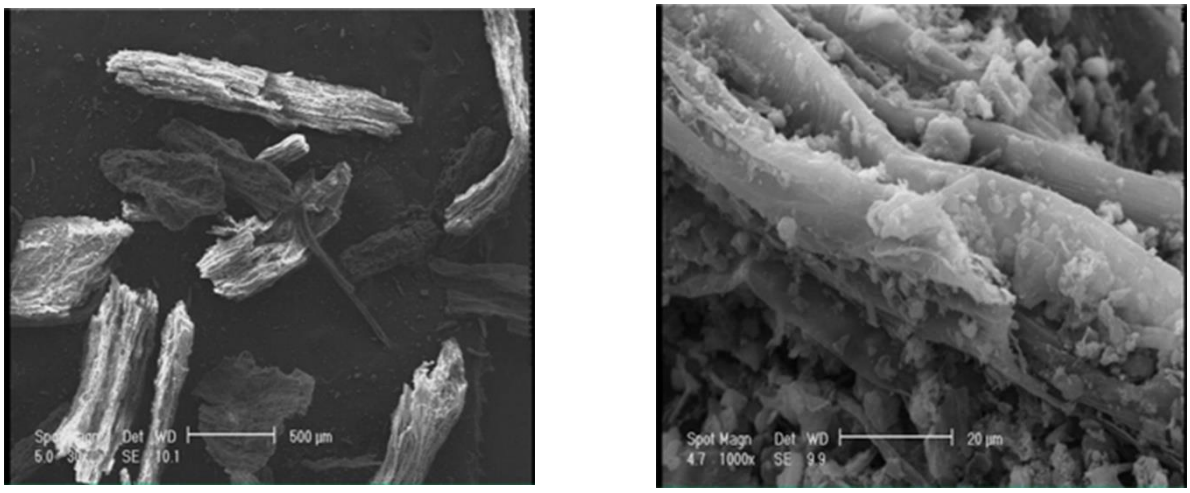

Figure 1. SEM of activated carbon prepared from *N. microphyllum (AC-NM)*

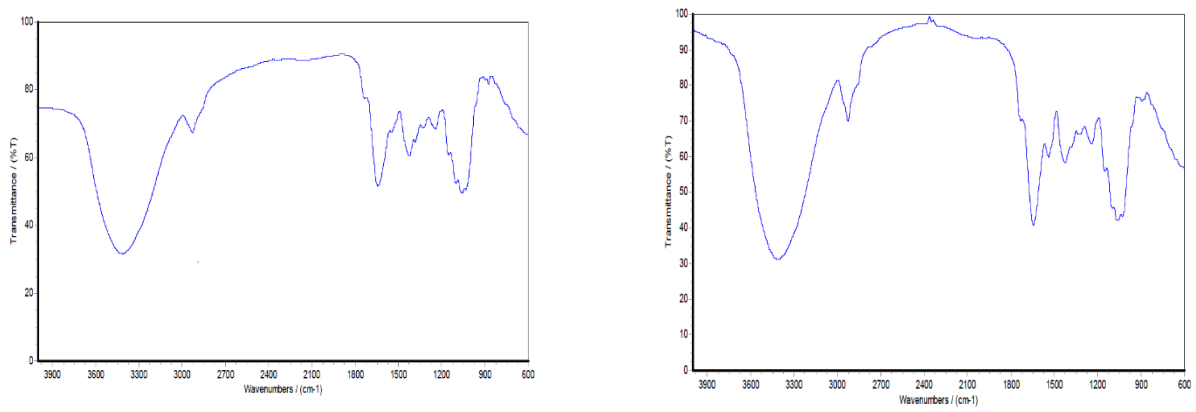

Figure 2. FTIR spectroscopy before (a) and after (b) activation

Based on FTIR spectra, there are different types of functional groups on adsorbent surface (Vickers *et al.*, 2000). These functional groups are assignments to four main groups (Carboxylic acids, Phenolic groups, Pyridine-like groups and Nitro groups). The band at 3200 to 3600 cm^{-1} corresponded with O-H stretching vibration of hydroxyl functional groups. The peak at 1700 to 1800 cm^{-1} associated to C=O stretching of the carboxyl groups(Jia *et al.*, 2002). The intensity of this peak gradually increases with activation of adsorbent. So that, the peak about 1400 cm^{-1} and 1500 cm^{-1} is associated to carboxyl structures (Siriwardane *et al.*, 2005). For example, carboxylic groups such as C=O and C–O have the peak at 1400 cm^{-1} which it can be corresponded to oxygen containing functional groups. Also, there is weak peak attributed C–O group in phenol, alcohol, ether at about 1150 cm^{-1} (Drage *et al.*, 2007). It could also be attributed to carboxylic groups (Carrott *et al.*, 2001), including $–CO_3$ group and the phenolic –OH group (Plaza *et al.*, 2009). The peak at about 960 cm^{-1} may be due to C–C or C–H groups stretching vibration. All the functional groups on activated carbon depending on the solution pH can have positive or negative charge in the surface (Plaza *et al.*, 2009). In additions, the capacity of PAC towards MB dye was compared with those of other activated carbon from different sources, as summarized in Table 3.

Table 3. Maximum adsorption capacities and surface area of different adsorbents for MB

Adsorbent	Maximum adsorption capacity (mg/g)	Surface area (m^2/g)	References
Activated carbon prepared from chitosan flakes	143.53	318.4	(Marrakchi *et al.*, 2017)
Activated carbon of rattan hydrochar	359	1135	(Islam *et al.*, 2017)
Activated carbon from Fox nutshell	75.37	2869	(Kumar and Jena, 2016)
Commercial activated arbon	221	514	(Martins and Nunes, 2015)
This work	67.5	1940	-

3.2. Statistical analysis and development of mathematical model

Results of ANOVA showed that the regression model for MB removal is tabulated in Table (4). The factorial designs are used when the curvature in the response surface is concerned. Also, with the number of large factors, the factorial design can be as alternative approach (Wu *et al.*, 2012). The empirical model based on aforementioned parameters is valid (Eq. (3)):

$$\%R_{MB}=30.07-30.77(A)+2.17(B)+3.20(C)+0.84(D)+1.67(AB)+2.49(AC)+0.52(AD)-0.24(BC)-0.16(BD)+1.39(CD)+14.20(A^2)+10.41(B^2)+15.15(C^2)-2.99(D^2) \quad (3)$$

From Eq. (3), it can be seen that the dose of adsorbent, pH and contact time have positive effect on the adsorption efficiency and initial concentration has negative effect on the efficiency. The positive value of variables points out an effect that favors the optimization, whereas a negative value presents an inverse relationship between the factors and the responses. The coefficient value (R^2) determines the fitness of the models. The R^2 (Adj) and R^2 (pred) should be within approximately 0.2 of each other to be in reasonable agreement. The close correspondence between R^2 adj and R^2 indicates unnecessary variables have not been included. Beside P-value is used to determine the effects in the model that are statistically significant. P-value being closer to zero was used to data significance (Srinivasan and Viraraghavan, 2010). when p-value is less than 0.05, the interaction effects of each factors are statistically

significant (Demim *et al.*, 2014). As can be seen from Table 3, the p-values of A (concentration) is 0.0001, which indicates that this variable is significant on the removal of MB by PAC but the p-values of B (PAC), C (pH) and D (time) indicates that these variables are not significant in MB removal (p>0.05). Factors considered affect on response differently. So, factor with high value lead to higher mean responses except factor of time for MB removal. Alternatively, the factors A to have a greater effect on the responses by PAC, with a steeply slope. In other hand, lack-of-fit is useful for model adequacy by comparison between pure and residual error which that lacking significance is desirable when F-value is small (Mousavi *et al.*, 2012). As noted in Table 3, lack-of-fit for all factors was not significant (p>0.05) except A (p<0.0001).

Table 4. Developed models and ANOVA results using Design Expert 8.0.0 for studied responses

Source	Sum of squares	df	Mean square	F value	p-ValueProb>F
Model	25496.2	14	1821.1	36.03	<0.0001
A	15618.5	1	15618.5	309.01	<0.0001
B	77.91	1	77.91	1.54	0.23
C	169.4	1	169.4	3.35	0.08
D	11.37	1	11.37	0.28	0.63
AB	44.46	1	44.46	0.88	0.36
AC	99.25	1	99.25	1.96	0.18
AD	4.34	1	4.34	0.086	0.77
BC	0.96	1	0.96	0.019	0.89
BD	0.42	1	0.42	0.0082	0.92
CD	31.00	1	31.00	0.61	0.44
A^2	33.58	1	33.58	0.66	0.42
B^2	18.04	1	18.04	0.36	0.55
C^2	38.21	1	38.21	0.76	0.39
D^2	1.48	1	1.48	0.029	0.86
Residual	758.16	15	758.16		
Lack of fit	580.22	10	580.22	1.63	0.30
Pure error	177.94	5	177.94		
Cor total	26254.4	29			
R^2=0.97	**R^2(Adj)=0.94**		**R^2(pred)=0.90**		

3.3. Effect of pH and Contact Time

Adsorption experiments were carried out to investigate the combined effect of initial solution pH and contact time on the dye removal (Figure 3).

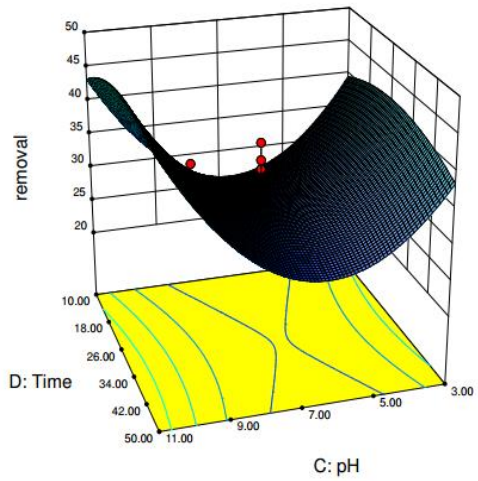

Figure 3. Effect of pH and contact time on the removal of MB

The MB removal increases with pH from 3 to 11 and maximum removal obtained 45% with 0.8 g/L of PAC and 110 mg/L of initial dye concentration. It is evident that both variables have a strong influence on the MB removal. Results showed that when pH was increased from 3 to 11 under constant concentration of 110 mg/L and 0.8 g/L of adsorbent dose, the static repulsion force decreases and the MB adsorption increases. When pH value increased from 3 to 11, the surface of PAC was negatively charged which resulted to a higher adsorption capacity (Turan Beyli *et al.*, 2015). Indeed, positive charge and electrostatic force because of protonation phenomena of functional group at low pH is high and PAC have a high absorption capacity (Ghaedi *et al.*, 2012).

On the other hand, by reducing the electrostatic force between the adsorbate and the electrical double layer surrounding the adsorbent, MB acts as a proton conjugate. So, when the pH is greater than pKa (pH> pKa), the pollutant converted to anionic state. Considering that pKa of MB is 3.8, the removal of it in alkaline pH is increased. This results due to reduction of repulsive forces between positive groups and negative hydroxyl ions (Veličković *et al.*, 2016).

Also, the sorption capacity of the MB was increased at the high contact time due to the enough time and more availability of binding sites for the sorption. Thus, due to these two factors, raised of pH and contact time, increased of removal MB in solution.

3.4. Effect of initial concentration and carbon dosage

The combined effects of PAC dosage (0.2-1.4 g/L) and concentration (10-210 mg/L) on MB removal are shown in Figure 4. It was observed that percentage removal of MB increased (85%) with increasing the amount of concentration as well as PAC at a constant time of 30 min and pH=7. This means that higher values of MB removal can be obtained by simultaneous increase in PAC and initial concentration of dye. This may be due to the saturation of the adsorption sites at higher MB concentrations. The MB concentration provides an important driving force to overcome all mass transfer resistance but this issue in contrast of Ghaedia *et al.*, (2012) study because of saturation of PAC surface pores (Hayat *et al.*, 2015).

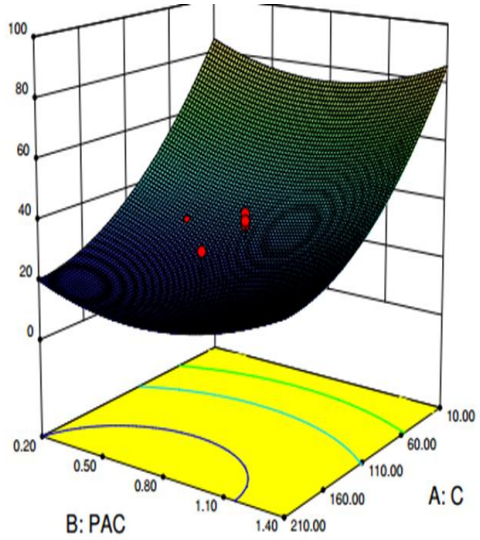

Figure 4. Effect of PAC dosage and dye concentration on the removal of MB

3.5. Effect of PAC dosage and time

Figure 5 illustrates the interaction effects of PAC dosage and contact time in the response process. The time showed a little effect, while a remarkable effect of PAC dosage on the removal of MB by PAC is shown in Figure 5.

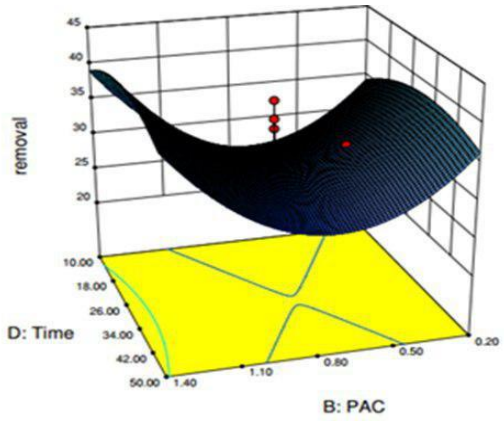

Figure 5. Effect of PAC dosage and contact time on the percentage removal of MB

In addition, the removal of MB decreased with the time increased. That is probably because the saturation of the adsorption sites at higher time (Hayat, Mahmood *et al.* 2015). As shown in Figure 3, the MB removal increased from 25% to 38% at a concentration of 110 mg/L and contact time of 10 -50 min, with an initial solution pH = 7.

3.6. Optimization of experimental conditions

A multiple method was used for the optimization of any combination of four goals (pH, contact time, concentration and removal of MB). So for achieving the best quality of effluent each input variable and response can be selected through this method. However, PAC dosage, pH and concentration increasing has ability to higher abortion of MB dye but detection of mentions factors optimized value is useful. Figure 6 shows the overlay plot which highlighted the optimum areas for achieved dye discharged standard. However, there is maximum allowable of color concentration for countries but based on global effluent guideline, offensive color is not accepted for wastewater discharged to surface waters (STRAUSS, 2007).Therefore, by conducting seeking at 3 starting points for MB, the best local maximum response was found to be at initial solution pH=3, concentration 10 mg/L and contact time of 10 min with absorbent dosage of 0.2 g/L. The maximum response (MB removal) was 97%. So, this result to make for achieving dye discharge standard under optimum condition is utilizable and verified that the model was able to make an acceptable prediction for the optimum conditions.

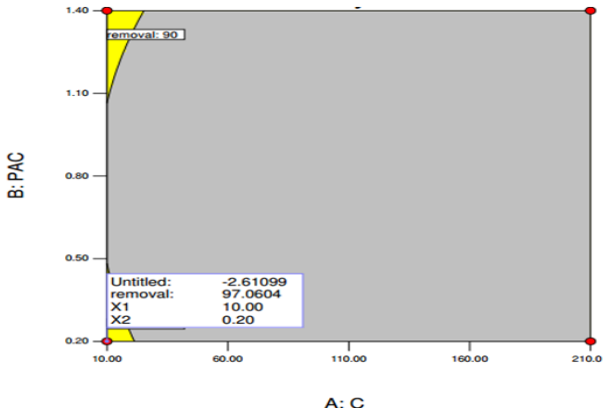

Figure 6. Overlay plot in order to optimization of MB removal

3.7. Adsorption isotherms and kinetics

The results in Table 5 showed Freundlich isotherm states the best interpretation of MB adsorption with R^2=0.99. The high correlation to Freundlich isotherm implies the multilayer adsorption that in direct to Hameed *et al.*, (2007) study (Hameed *et al.*, 2007) but this study does not support the findings of Ghaedia (2012), Rodriguez(2009), Tan (2008) and Ozer (2007) studies (Özer and Dursun, 2007; Tan *et al.*, 2008; Rodríguez *et al.*, 2009; Ghaedi *et al.*, 2012). Whatever Freundlich constants (n and k) is greater, demonstrated that uptake of MB by adsorbent increased. Furthermore, the absorption kinetics correspond with the Zhang *et al.*, (2010) study showed Freundlich adsorption

isotherm due to external surface adsorption as well as intraparticle diffusion (Zhang *et al.*, 2010).

Table 5. Absorption isotherms parameters and kinetics study for MB adsorption by AC-NM

Isotherms											
Freundlich			Langmuir			Temkin			Redlich–Peterson		
R^2	n	k	R^2	b	$q_{(max)}$	R^2	b_t	K_t	R^2	α	K_{RT}
0.99	0.17	39.5	0.92	0.04	43.3	0.06	0.14	0.07	0.02	0.01	15.6
Liner Equation											
Y= 5.61X - 13.94			Y= -0.2856X + 7.068			Y = 2.103X + 14.09			Y= -0.001X + 0.064		
Kinetics											
First-Order			Second-Order			Intraparticle diffusion			Elovich		
K_2	R^2		K_1	R^2		C	R^2		a	R^2	
0.001	0.94		0.02	0.98		0.01	0.23		0.007	0.069	
Linear Equation											
Y=-0.0013X + 3.630			Y = 0.1151X+ 0.7045			Y = 2.1033X + 14.095			Y = -4.0105X + 67.5		

Also, to elucidate of adsorption mechanisms was tested kinetics such as pseudo first-order and pseudo second-order and data shown in Table 5. The adsorption kinetics well described by second order model with R^2 = 0.98 that supported with Ghaedi *et al.*, (2012) for Kinetic and isotherm study for removal of Methylene blue (Ghaedi *et al.*, 2012). Liao *et al.*, applied consecutive step consist of

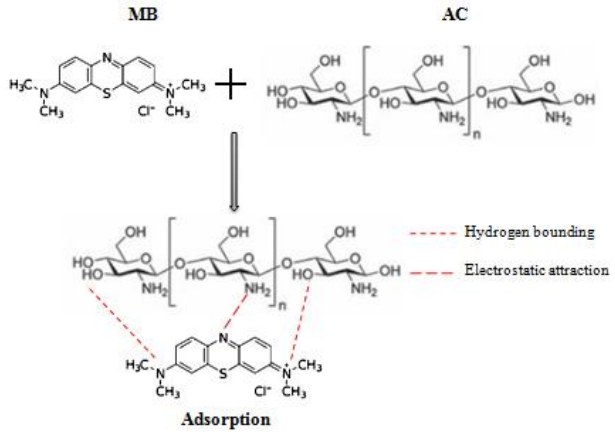

Figure 7. Mechanisms of MB de adsorption onto AC-NM

Also, the MB adsorption occurs possibly through surface exchanges until the functional sites are completely unavailable; subsequently, dye molecules diffuse into PAC for more interactions possibly hydrogen bonding and hydrophobic interactions. This subject developed by else investigator that indicates intraparticle diffusion can be rate controlling step(Hizal *et al.*, 2015). As noted in Table 4, k constant in second-order was obtained 0.02. Thus, raise of this value indicated that increased in MB absorption due to a greater driving force.

4. Conclusions

In this study, RSM is demonstrated to be effective and reliable to develop a matematical model ans statical analysis of experimental data. The results of experimentals at the differents values of pH, contact time, adsorbent dosage and dye concentration showed that, the adsorption conditions have significant effects on the removal of MB. The quaderatic mathematical model was developed and intraparticle diffusion, external diffusion, and adsorption for MB absorption process that these steps under control kinetics models (Liao *et al.*, 2015). Indeed, in first step external diffusion and adsorption is dominant mechanism but with increasing in time, intraparticle diffusion will be predominance (Fig. 7).

the isoterms studies indicate that the Fre-undlich isotherm was best fit with experimental data. Different kinetic models were also examined, and the results indicate that the adsorption kinetics follow the pseudo-second-order rate. This study conformed that the *N. microphyllum* has comparatively high adsorption capacity and can be used as cost effectiveness natural absorbant.

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