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Removal of Methylene Blue Dye from Aqueous Solutions by Adsorption onto Casuarina Charcoal.

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Removal of Methylene blue Dyestuff from Aqueous Solutions by Adsorption onto Casuarina Charcoal

إزالة صبغة الميثيلين الأزرق من المحاليل المائية بالامتزاز على الفحم المنتج من اشجار الكازورينا

Ibrahim Gar Al Alm Rashed, *Mustafa Kameran Alsendi, Ahmed Alsarawi* and Waleid Azmy Shehap

KEYWORDS:

Adsorption; Methylene blue; Casuarina; Charcoal

الملخص العربي:- يتناول هذا البحث تطبيق عملية الإمتزاز (Adsorption) باستخدام الفحم المنشط المنتج من المخلفات الناتجة عن تقليم بعض الأشجار، حيث إختيرت أشجار الكازورينا كنموذج لأشجار الطرق والتي تستخدم لإنتاج الفحم النباتي في مكامير الفحم. تم إستجلاب عينات من الفحم النباتي الناتج من إحدى مكامير الفحم بكفر سعد (محافظة دمياط)، وتم سحقها وتنشيطها بالتسخين عند درجة حرارة 850 درجة مئوية بمعزل عن الهواء ولمدة 3 ساعات. وتم توصيف البنية الداخلية للفحم الناعم المنشط باستخدام الميكروسكوب الإلكتروني (SEM)، وكذلك تحديد المجموعات الوظيفية باستخدام تحويل فورير الطيفي (FTIR). إستخدمت صبغة أزرق الميثيل (Methylene Blue, MB) كمادة ممتزة (Adsorbate) على الفحم الناعم المنشط كمادة مازة (Adsorbent). وأهم ما توصلت إليه الدراسة أن أنسب الظروف للإمتزاز بكفاءة عالية في الأوساط المائية عند قيمة رقم الأس الهيدروجيني (pH =6) ، كما تم توفيق نتائج عملية الإمتزاز مع نماذج الإمتزاز التقليدية وهي نموذجي لانجمير (Langmuir isotherm) وفروندليتش (Freundlich isotherm). كما تم دراسة حركية الإمتزاز، وتبين أن حركية عملية الإمتزاز تتوافق مع حركية الرتبة الثانية (Pseudo 2ed order kinetics).

Abstract— In this work, batch adsorption experiments were carried out for the removal of methylene blue as a basic dye from aqueous solutions using powdered activated carbon (PAC) prepared from Casuarina trees. PAC was prepared by activation through roasting at high temperature (850 °C) for 3hrs. The prepared PAC was used for removal of basic methylene blue with different concentrations and under different conditions of pH mediums revealing that the appropriate removal efficiency was at pH 6. The experimental results were fitted to kinetic models of pseudo 2nd order. Freundlich and Langmuir isotherms were

applied to describe the equilibrium relationship at different conditions.

I. INTRODUCTION

ACTIVATED carbon is extensively used as efficient and versatile adsorbents for purification of water, air, many chemical and natural products. Water treatment is, by far, the largest outlet for activated carbon, and powdered activated carbon (PAC) is more commonly used than granular activated carbon (GAC) to control taste, color and odor in drinking water treatment. Color is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Residual dyes are the major contributors to color in wastewaters generated from textile and dye manufacturing industries, etc. [1]. Color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms. Most of the used dyes are

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stable to photo degradation, bio-degradation and oxidizing agents [2].

Currently, several physical or chemical processes are used to treat dye-laden wastewaters. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. The advantages and disadvantages of some methods of dye removal from wastewaters are given in Table (1) [3]. The adsorption process has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon (powdered or granular) for organic compounds even from dilute solutions, but commercially available activated carbons are very expensive [4].

TABLE (1):
ADVANTAGES AND DISADVANTAGES OF THE METHODS USED FOR DYE REMOVAL FROM INDUSTRIAL EFFLUENTS [3].

Physical/chemical methods	Advantages	Disadvantages
Fentons reagent	Effective decolourisation	Sludge generation
Ozonation	No change in effluent volume	Short half life (20 min)
Photochemical	No sludge generation	Formation of byproducts
NaOCl	Initiate azo-bond cleavage	Release of aromatic amines
Electrochemical	Non-hazardous end products	High cost of electricity
Activated carbon	Highly effective for various dyes	Very expensive
Peat	Good adsorbent	Surface area is low
Silica gel	Effective for basic dyes	Side reactions in effluent
Membrane filtration	Removes all dyes	Concentrated sludge production
Ion exchange	No adsorbent loss	Not effective for all dyes

Various carbonaceous materials, such as coal, lignite, coconut shells, wood and peat are used in the production of commercial activated carbons [5]. However, the abundance and availability of agricultural byproducts make them good sources of precursors for activated carbons. Agricultural byproducts are renewable sources of raw materials for activated carbon production because the development of methods to reuse waste materials is greatly desired. Residues from agriculture and agro-industries are the non-product outputs from the growing and processing of raw agricultural products such as rice, corn, beans and peanuts [6]. Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to adsorbents, such as activated carbon, represents a possible outlet.

Casuarina is widely distributed in Africa, where five species have been introduced in Algeria, Benin, Burkina Faso, Cameroon, Central African Republic, Chad, Congo, Ivory Coast, Democratic Republic of Congo, Djibouti, Egypt, Eritrea, Ethiopia, Gabon, Gambia, Ghana, Guinea, Guinea-Bissau, Kenya, Liberia, Madagascar, Malawi, Mali, Mauritania, Niger, Nigeria, Senegal, Sierra Leone, Somalia, South Africa, Sudan, Tanzania, Togo,

Uganda and Zimbabwe. In some countries, including Senegal, Egypt, Benin, Kenya, South Africa, and Madagascar Casuarina is widely planted, whereas in others its presence is much reduced and is limited to decoration [7]. In Egypt, Casuarina is mostly used for its significant ecological roles such as crop protection, shelterbelt, irrigation stabilization, drainage canal banks, land reclamation and protection of buildings. In the Nile Delta and in the Nile Valley, Casuarina trees were planted to provide shade, to limit border effects, and as a windbreak. In Egypt, this species plays an important economic role in the production of fuel timber, charcoal, wood for industry and for the manufacture of particle board [7]. The main objectives of this work is to investigate the performance of powdered activated carbon (PAC) prepared from charcoal originated from Casuarina trees for the removal of methylene blue dye from aqueous solutions. The influences of different conditions such as pH of the medium, contact time, PAC dose were investigated. Langmuir and Freundlich isotherm models were used to describe the equilibrium relationship

II. THEORY

2-1 Adsorption Isotherm

To simulate the adsorption isotherm, two commonly used models, the Langmuir and Freundlich, were selected to explicate dye – Casuarina charcoal interaction [8].

Langmuir Isotherm The linearized form of Langmuir can be written as

$$(1/q_e) = (1/Q_0) + (1/K_L Q_0) (1/C_e) \quad (1)$$

The Langmuir constants, Q_0 (maximum adsorption capacity; milligrams per gram) and K_L (litres per milligram) values for Langmuir constant related to the energy of adsorption are predicted from the plot between $(1/q_e)$ and $1/C_e$.

Freundlich Isotherm: The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed as:

$$\ln(q_e) = \ln(K_F) + (1/n) \ln(C_e) \quad (2)$$

Where q_e is the amount of dye adsorbed per unit of adsorbent at equilibrium time (milligrams per gram) and C_e is equilibrium concentration of dye in solution (milligrams per litre). K_F and n are isotherm constants which indicate the capacity and the intensity of the adsorption, respectively

2-2 Adsorption Kinetics

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behavior of the dye adsorption process was analyzed using the pseudo-first-order, and pseudo-second-order [8].

Pseudo-First-Order Model:

Pseudo-First-Order Model according to Lagergren takes the form:

$$dq/dt = k_1 (q_e - q_t) \quad (3)$$

The integral form of the pseudo-first-order model generally expressed as:

$$\text{Log}(q_e - q_t) = \text{log } q_e - (k_1 t / 2.303) \quad (4)$$

Where: q_t and q_e represent the amount of dye adsorbed (milligrams per gram) at any time t and at equilibrium time, respectively, and k_1 represents the adsorption first-order rate constant (min^{-1}) and t is the contact time (minute).

The adsorption rate constant k_1 is calculated from the plot of $\text{log}(q_e - q_t)$ against t .

Pseudo-Second-Order Model

The adsorption data is then analyzed in terms of pseudo-second-order mechanism, described by the following equation:

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (5)$$

Where: k_2 is the pseudo-second-order rate constant (grams per milligram minute).

Integrating and applying boundary conditions $t=0$ to $t=t$ and $q=0$ to $q=q_t$ gives:

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e) t \quad (6)$$

A plot between (t/q_t) and t gives the value of the constants k_2 (grams per milligram min), and also q_e (milligrams per gram) can be calculated.

The constant k_2 is used to calculate the initial sorption rate h , at $t \rightarrow 0$, as follows:

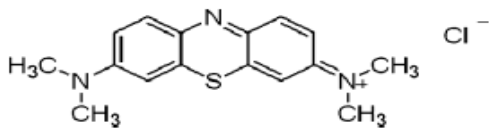
$$h = k_2 q_e^2 \quad (7)$$

Thus, the rate constant k_2 , initial adsorption rate h and predicted q_e can be calculated from the plot of (t/q_t) versus time t using Eq.(6).

III. MATERIALS AND METHODS

3-1 Materials

Methylene blue (MB), supplied by Sigma Aldrich, and was used as an adsorbate. The MB was chosen in this study because of its known strong adsorption onto solids. The dye stock solution was prepared by dissolving accurately weighted methylene blue in distilled water. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to the required initial concentrations. MB has a molecular weight of 373.5 g/mole and its chemical formula is $C_{16}H_{18}ClN_3S$. Its structural formula as:



The cationic MB dye produces an intense molecular cation (C^+) and reduced ions (CH^+) in the aqueous solution [9]. Different concentrations of stock solutions were prepared (50,100,150 and 200 mg/L) to be used in the experiments. Liquid samples of known initial concentration were put in Erlenmeyer flasks (500 ml). This mixture was flustered by a magnetic agitator for a time interval of 3, 6, 9, 12, and 15 minutes to observe the adsorption kinetics of the process. The mixture before stirring was retained to the required pH, the

volume of the blend is 250 ml. MB concentration in the sample solution was determined using a UV-VISIBLE SPECTROPHOTOMETER (UV-160 1PC SHIMADZU).

Charcoal was brought from carbonization kilns located at "Kafer Saad, Damietta Governorate" which using dried branches of casuarina trees as precursor for production of charcoal. To prepare (PAC) from casuarina charcoal, polishing paper was used for grinding the charcoal to produce powder carbon. This powder was put in a dish and inserted in the muffle at temperature 850 °C for 3 hours. After activation, the furnace was allowed to cool to room temperature. The pyrolysed carbon was leached with 1% HCl (v/v) for 2-3 hours and washed several times with distilled water until a neutral pH was achieved. Later the carbon paste was dried in an oven at 110 °C for at least 24 hours before application [10]. These techniques activate the sorbent by increasing active surface area and improving chemical reactivity by formation of surface functional groups which helps to chemically bond with the adsorbate molecules [11]. Samples of the prepared activated carbon were taken before grinding, after activation process, and at the end of adsorption process. These samples were scanned by Scanning Electron Microscope SEM, using JEOL JSM-6510LV, (at Electron Microscopy Unit, Faculty of Agriculture- Mansoura University). Also, these samples were characterized by Fourier Transform Infrared Spectroscopy Analysis (FTIR) using Thermo- Scientific Nicolet iS10 (at Faculty of Science- Mansoura University).

3-2 Experimental Methods

Using different concentrations processed by adding pure water to the dye solution in a flask 500 ml. PAC blended with solution, and placed on magnetic stirrer. The pH of the experiment solutions was adjusted by addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions. pH measurements were done using Orient pH meter. The stirring began with adding the PAC with dosages ranged from 0.2 to 1.6 gm. /L. Samples were drawn at different time intervals to follow the effect of contact time. The adsorbed mass of MB at time t , q_t (mg/g), was determined by the following relation:

$$q_t = (C_o - C_t) V / W \quad (8)$$

Where: C_o (mg/L) is the initial liquid-phase concentration of methylene blue, C_t (mg/L) is the dye concentration at time t , V (L) is the solutions volume and w (gm) is the dry carbon mass used. Also, the equilibrium dye concentrations on solid phase (q_e) and in liquid phase (C_e) were determined by the following relation:

$$q_e = (C_o - C_e) V / W \quad (9)$$

Where: C_e (mg/l) is the liquid phase concentration at equilibrium time (t_e)

IV. RESULTS AND DISCUSSION

4-1 Characterization of PAC by SEM and FTIR

The visible observation of the surface texture and porosity of the samples using scanning electron microscopy (SEM) gives better understanding of the nature of adsorption process and is given in Fig. 1. Rough surface with some pores were visualized before activation (Fig. 1a). After activation the structure is finer with larger number of pores (Fig. 1. b) as an indication of larger surface areas capable of high adsorption. After adsorption (Fig. 1c) smooth surface covering the pores can be observed.

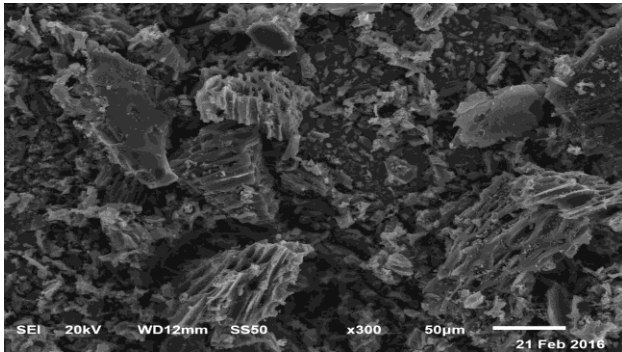


Fig 1.a before activation

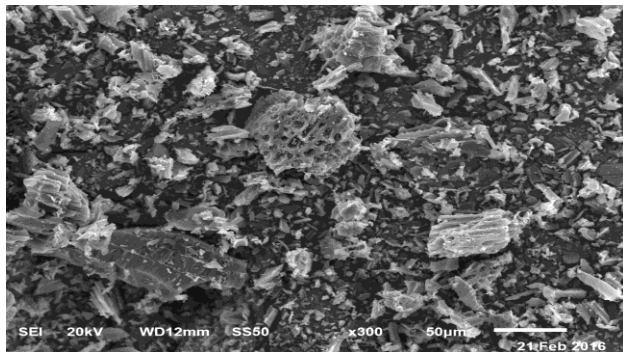


Fig 1.b after activation

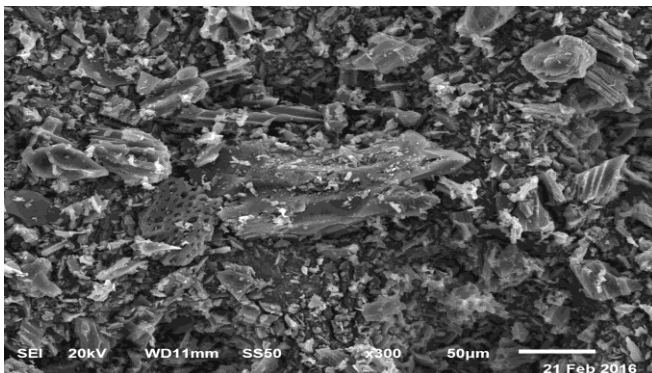


Fig 1.c after adsorption of Methylene Blue

Fig. (1): SEM image of charcoal from *Casuarina* trees as precursor for production of PAC

- (a) Before activation
- (b) After activation
- (c) After adsorption of Methylene Blue

FTIR spectra were performed to identify the active functional groups responsible for the adsorption (Fig.2). FTIR spectra for the samples before activation, after activation, and after adsorption are demonstrated in Fig (2.a), Fig (2.b), and Fig (2.c) respectively.

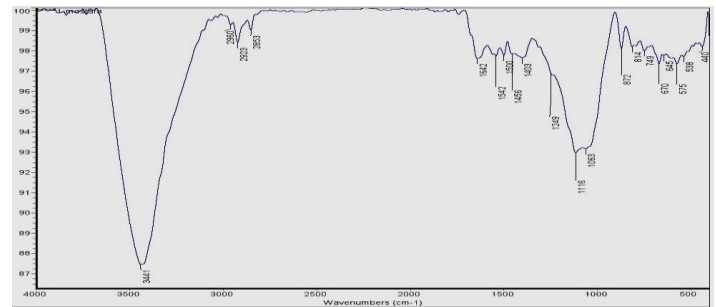


Fig 2.a before activation

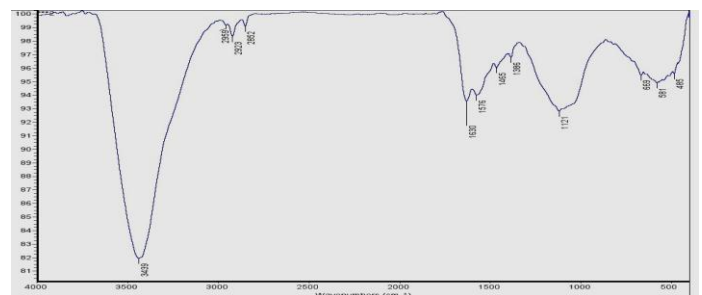


Fig 2.b after activation

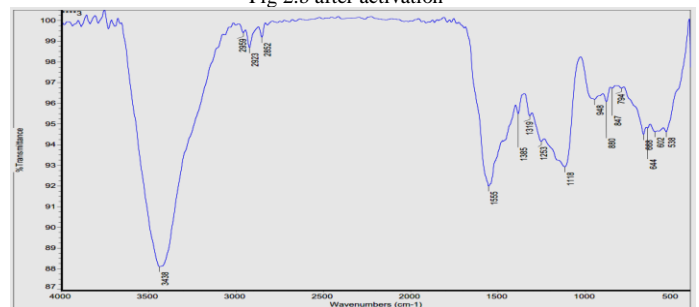


Fig 2.c after adsorption of Methylene Blue

Fig. (2): FTIR of charcoal from *Casuarina* trees as precursor for production of PAC.

- (a) Before activation
- (b) After activation
- (c) After adsorption of Methylene Blue

Table (2) displays the wave numbers of the peaks appears in the FTIR spectra for the samples before activation, after activation, and after adsorption. The interaction of MB molecules with functional groups of *Casuarina* charcoal was confirmed by the reduction and appearance or disappearance of several peaks. FTIR spectra can be summarized with the following peak assignments; a broad and strong band around 3440 cm^{-1} is attributed to the intra- and inter-molecular hydrogen-bonded (OH) stretching that occurs in cellulose, the peaks observed around 2923 and 2853 cm^{-1} were assigned to the presence of C-H asymmetric stretching of CH_3 and CH_2 groups. The peaks at approximately 1116 - 1121 cm^{-1} may represent the C-O-C stretching vibration of lignin and the C-O stretching of cellulose and hemicellulose, respectively [12].

TABLE (2)

WAVE NUMBERS FROM THE FTIR OF CHARCOAL FROM CASURAINA TREES AS PRECURSOR FOR PRODUCTION OF PAC. (CM-1)

(A) BEFORE ACTIVATION (B) AFTER ACTIVATION
(C) AFTER ADSORPTION OF METHYLENE BLUE

before activation	after activation	after dsorption	before activation	after activation	After Adsorption
3441	3439	3438			1253
2960	2959	2959	1116	1121	1118
2923	2923	2923	1063		
2853	2852	2852			948
1642	1630		872		880
1542	1576	1555	814		847
1500			749		749
1456	1465		670	669	668
1403			645	581	644
	1386	1385	538	485	602
1249		1319	440		538

4-2 Effect of contact time and initial concentration

The average of sorption of MB on the PAC is displayed in (Fig. 3) for five different initial concentrations. The adsorption fractions for all MB concentrations began rapidly from the interval (0-4) minutes, then reduced after 6 minutes and

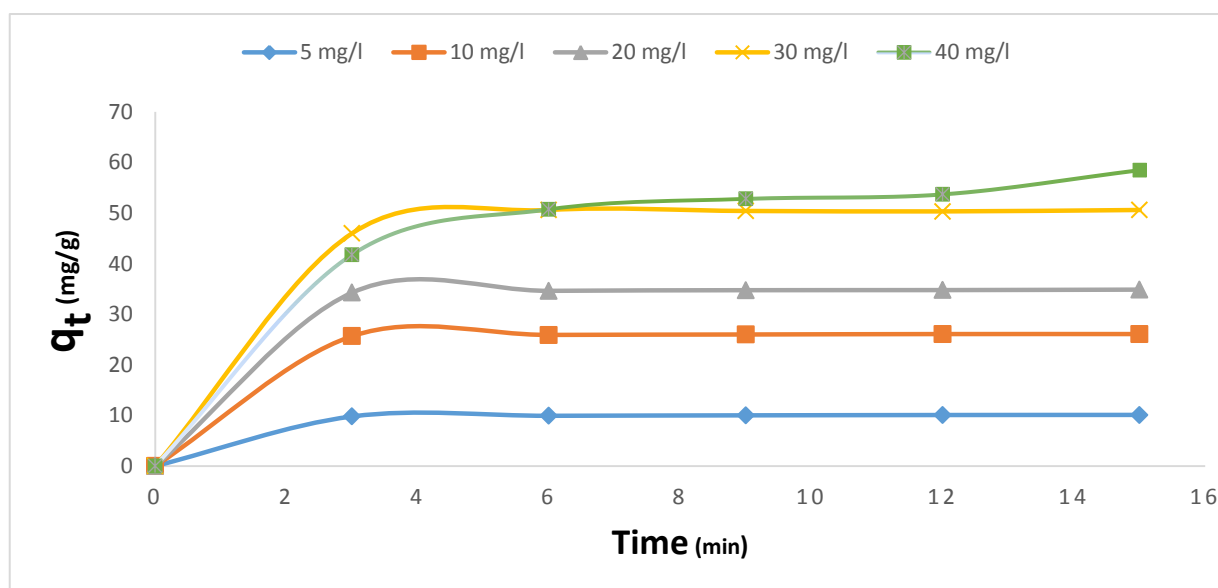


Figure.3 Effect of contact time and initial concentration of MB on adsorption

4-1 Effect of pH

To study the effect of pH on methylene blue (MB) adsorption, 0.1 g of the prepared activated carbon was added to solutions of volume 250 ml containing on concentration of 20 mg/lit of methylene blue. The initial pH values were adjusted from 4–10 using 0.1M HCl and 0.1M NaOH. After the suspensions were shaken for different times reached to about 20 min to ascertain the attainment of the equilibrium time, at room temperature (about 25 °C), they were filtered using Whatman no. 1 filter paper and analyzed for residual methylene blue concentration. Figure 4 shows the effect of pH of the medium on the attainment of the equilibrium time, demonstrating none significant effect. In the same figure higher adsorption of methylene blue at weak acidic medium (pH = 6) may be due to increased protonation by

approached to the equilibrium. The equilibrium time reached for all initial concentration at about 6-8 minutes. The equilibrium time is independent on the initial concentration. Generally, the equilibrium adsorbed dye concentrations on the adsorbate (q_e) increases with the increase in the initial dye concentration in solution (C_o). The significant increase was observed from $C_o = 5$ to $C_o = 10$ mg/lit. Also increasing was observed from $C_o = 10$ to $C_o = 20$ mg/lit, $C_o = 20$ to $C_o = 30$ mg/lit and $C_o = 30$ to $C_o = 40$ mg/lit. Increasing the initial dye concentrations from 5 to 40 mg/lit did not demonstrate the same rate of increasing in q_e . This may be attributed to that the first step leads to surface adsorption and the second step leads to Intraparticle transport from bulk fluid to the external surface of the porous adsorbent [10]. This trend is in accordance with the report of other investigators [13]. The stages of sorption of methylene blue on activated carbon might be controlled by the diffusion process from bulk to the surface or the heterogeneous nature of the adsorbent

neutralization of the negative charges at the surface of adsorbent. But for $pH < 6$, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cation due to electrostatic repulsion [13]. Even though some authors have reported that methylene blue adsorption usually increases as the pH is increased [14, 15], in the undertaken adsorbent the adsorption of Methylene blue was slightly decreased with the increase in pH (pH 9 to pH 10), as demonstrated in Table (3), which may deserve further investigation for the point of zero charge (pH_{PZC}) of the adsorbent, where it is an important parameter at which the surface of adsorbent has zero net charge (neutral) [16]. When solution $pH < pH_{pzc}$, the surface of the adsorbent is predominately positive whereas when solution $pH > pH_{pzc}$,

the adsorbent's surface will be predominately negative. Generally, positively charged molecule or ion will be attracted to negatively charged surface and positively charged surface

will attract negatively charged molecule or ion via electrostatic interaction

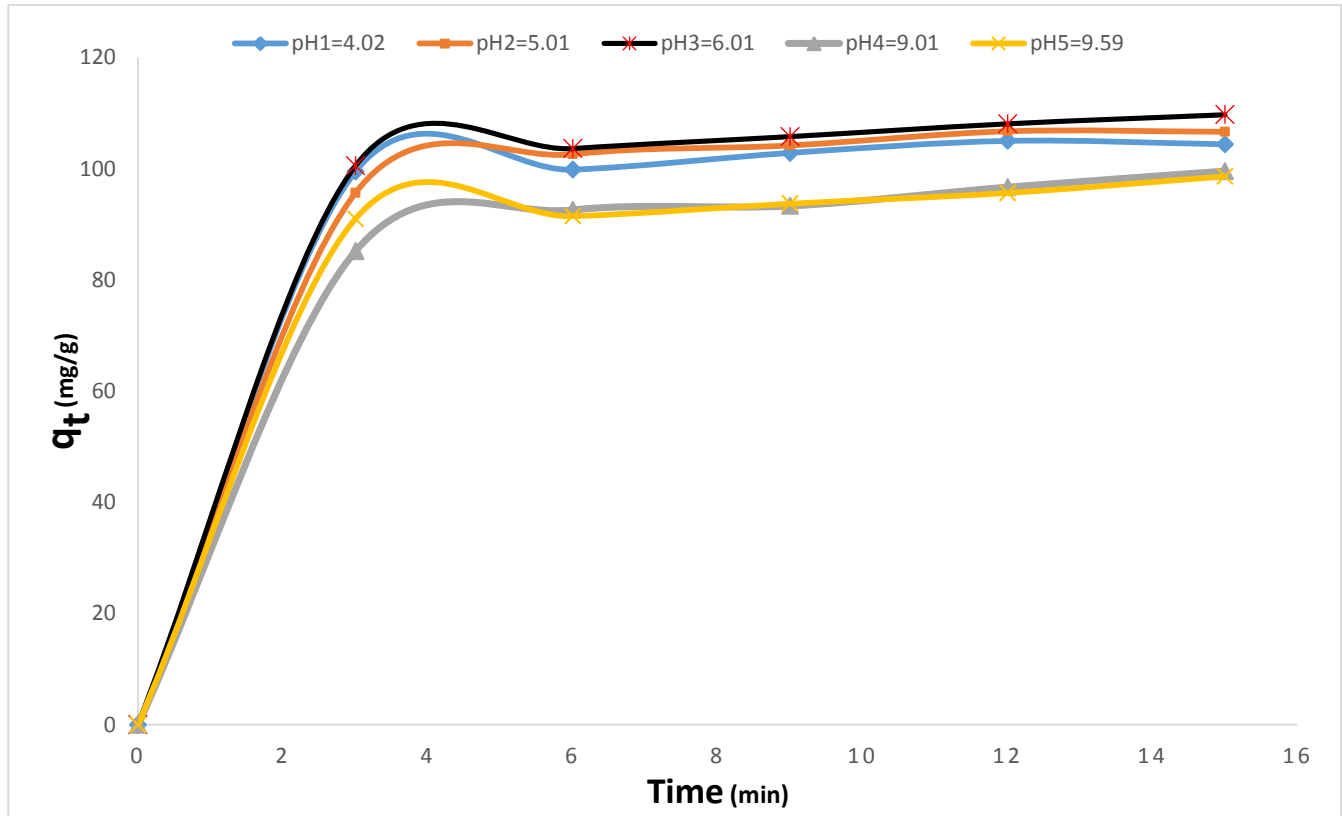


Figure 4 Effect of pH on adsorption

TABLE (3)
VALUES OF THE EQUILIBRIUM VALUES OF THE ADSORBED METHYLENE BLUE ON PAC, (q_e) AT DIFFERENT PH VALUES.

pH	4.02	5.01	6.01	9.01	9.59
q_e (mg/gm)	104.4	106.6	109.7	99.5	98.6

4-1 Effect of adsorbent dose

The equilibrium concentration in both liquid phase (C_e) and solid phase (q_e) are dependent on the adsorbent dose (w). Figure (5) shows that the equilibrium concentration of the

adsorbate on the adsorbent, q_e (mg adsorbate/gm adsorbent), was decreased from 109.78 mg/gm to 36.076 mg/gm for the change in the adsorbent dose from 0.2 gm/lit to 0.4 gm/lit, while it was found to be 28.987 mg/gm for the adsorbent dose of 0.8 gm/lit. A similar behavior was observed for methylene blue adsorption onto pine cone biomass of *Pinus radiata* [8], on perlite [17], on rice husk [18], on cashew nut shell [19] and on oak sawdust [20].

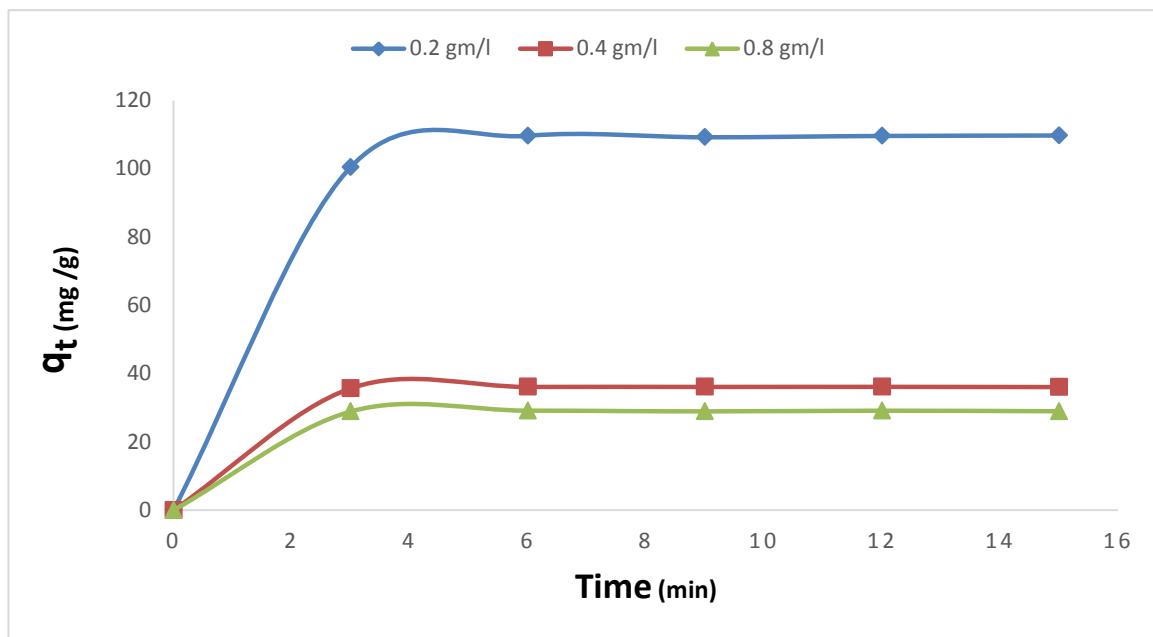


Figure 5: Effect of adsorbent dosages on the extent (percent) of adsorption of methylene blue: volume of dye solution=250 ml; initial dye concentration=20 mg/lit; pH=6.; temperature =25 °C

4-1 Equilibrium modeling

Equilibrium adsorption studies were conducted by contacting 250 ml of dye solutions of different initial concentration of 5, 10, 20, 30, and 40 mg/lit with about 0.1g of powdered activated carbon prepared from Casuarina charcoal in 500 ml conical flasks for a period of 1 h which was more than sufficient to equilibrium time. The method was as Section 3.2. Adsorption isotherm is used to represent the relevance

between the amounts of adsorbed substance at dynamic equilibrium (q_e) and the equilibrium concentration of the adsorbate in liquid phase C_e . Figure (6) presents the adsorption isotherm of Methylene blue (MB) at pH 6 as the relationship between the amount of dye adsorbed per unit mass of the adsorbent (q_e) and the equilibrium concentration of MB in solution (C_e).

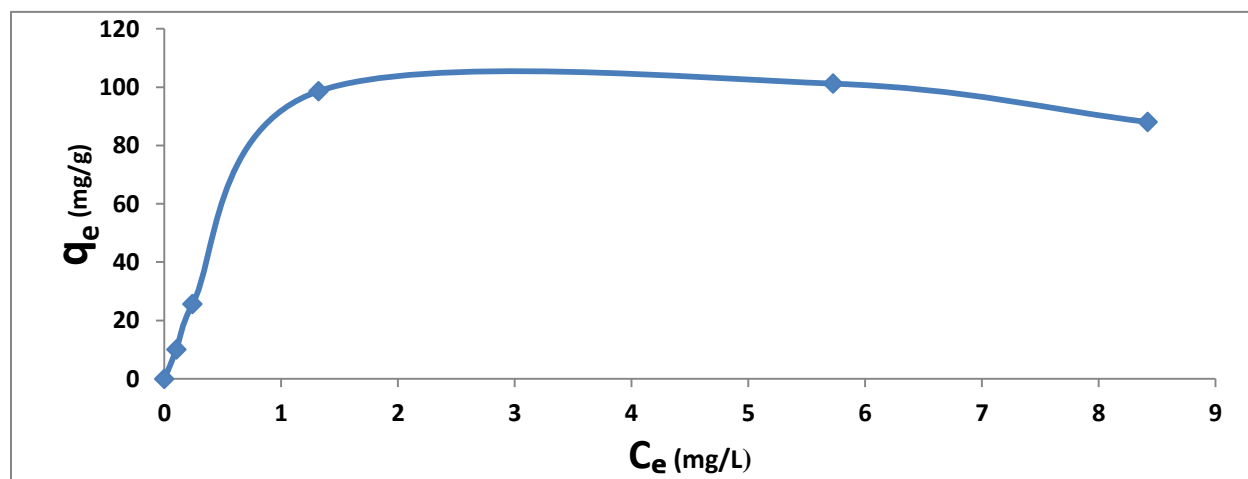


Figure (6): Adsorption isotherm of MB adsorbed by on PAC prepared from *Casuarina* charcoal (equilibrium time = 1 h, dosage = 0.1 g, pH = 6, temperature = 25 °C)

To simulate the adsorption isotherm, the two commonly used models, presented in 2.1, that are well known as the Langmuir and Freundlich isotherms, were selected to explicate dye – Casuarina charcoal interaction [8]. Adsorption isotherms were analyzed according to the linear form of Langmuir and

Freundlich models using Eqs. (1) & (2), respectively. The experimental data were plotted as $(1/q_e)$ vs $(1/C_e)$ as shown in Fig (7) to fit Langmuir isotherm. Whereas in Fig (8) the equilibrium data is plotted as $\ln(q_e)$ vs $\ln(C_e)$ to fit Freundlich isotherm and the parameters, Q_o , K_L of the

Langmuir and K_F , n of the Freundlich were determined and listed in Table (4). The lower determination coefficients R^2 of the Freundlich model (0.8296), suggests that the Langmuir equation can be used to fit the experimental adsorption data and evaluate the maximum dye adsorption capacities of the adsorbent. The results also indicate that the adsorption of MB by the adsorbent takes place in a monolayer adsorption manner [21, 22]. Compared with previous studies as reported

in the literature [22-28], the activated carbon prepared in this work showed comparatively reasonable adsorption capacity of 164 mg/g. At the same time, the parameters of both Langmuir and Freundlich isotherm models of MB adsorption on PAC prepared from *Casuarina* charcoal, Q_o , K_L , n , and K_F are compared well with that found for the adsorption of MB on different types of adsorbents as predicted by different authors as demonstrated in Table (4).

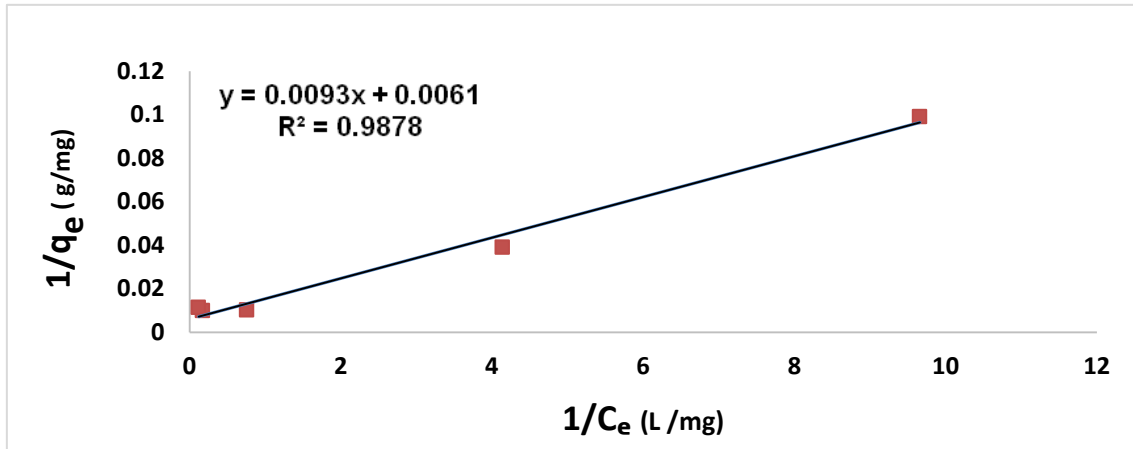


Figure 7: Langmuir isotherm of adsorption

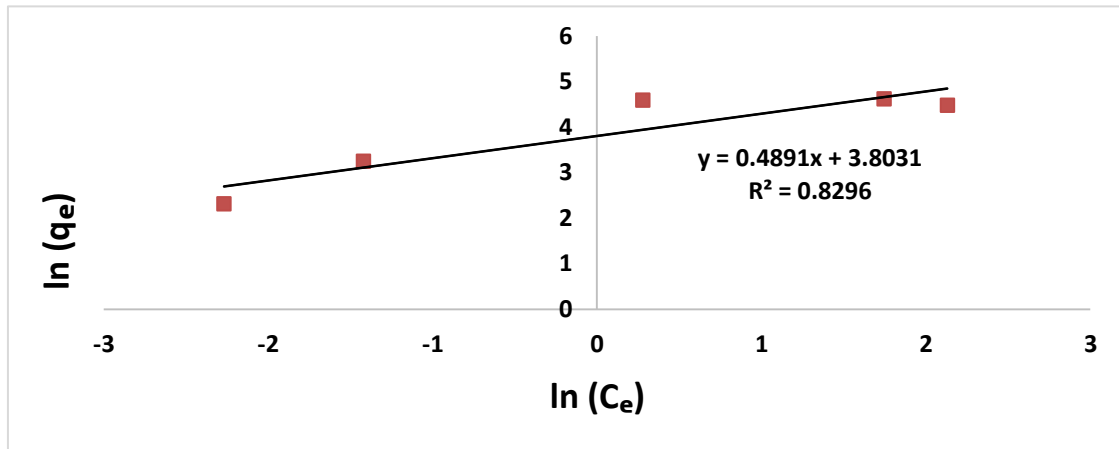


Figure 8: Freundlich adsorption isotherm

TABLE (4)

PARAMETERS OF BOTH LANGMUIR AND FREUNDLICH ISOTHERM MODELS OF MB ADSORPTION ON PAC PREPARED FROM CASUARINA CHARCOAL COMPARED WITH PREVIOUS STUDIES AS REPORTED IN THE LITERATURE [22-28].

Ref.	Langmuir Isotherm				Freundlich Isotherm		
	T(K)	Q_o (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) (L/mg) ^{1/n}	n	R^2
Under-taken study	298	164	0.656	0.988	44.84	2.040	0.83
23	293	363.6	1.004	0.999	220.4	8.773	0.96
22	298	270	1.23	0.996	236	3.72	0.79
27	303	68.72	0.201	0.981	23.82	4.325	0.94
28	298	271.00	0.385	0.993	142.52	7.364	0.93
24	303	418.15	1.13	0.999	196.11	5.200	0.81
25	298	149.2	966.4	0.990	36.15	3.030	0.93
26	303	60.61	0.108	0.976	1.424	2.829	0.99
	313	59.95	0.114	0.979	1.41	2.928	0.99
	323	62.11	0.114	0.976	1.41	2.938	0.99
	333	62.50	0.122	0.974	1.40	2.990	0.99

4-7 Adsorption kinetics

The prediction of batch adsorption kinetics is necessary for the design of industrial adsorption columns. The nature of the adsorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions. In the present study, the applicability of the pseudo-first-order (Eq. 4) and pseudo-second-order model

(Eqs. 6) was tested for the adsorption of methylene blue onto the activated carbon, developed from the Casuarina's charcoal, for the data displayed in Figure (3). The values of $[\log (q_e - q_t)]$ are plotted versus time (t) in (Fig. 9) for the application of the 1st order kinetic model, whereas the values of (t/q_t) were plotted versus time (t), as demonstrated in Fig. (10)

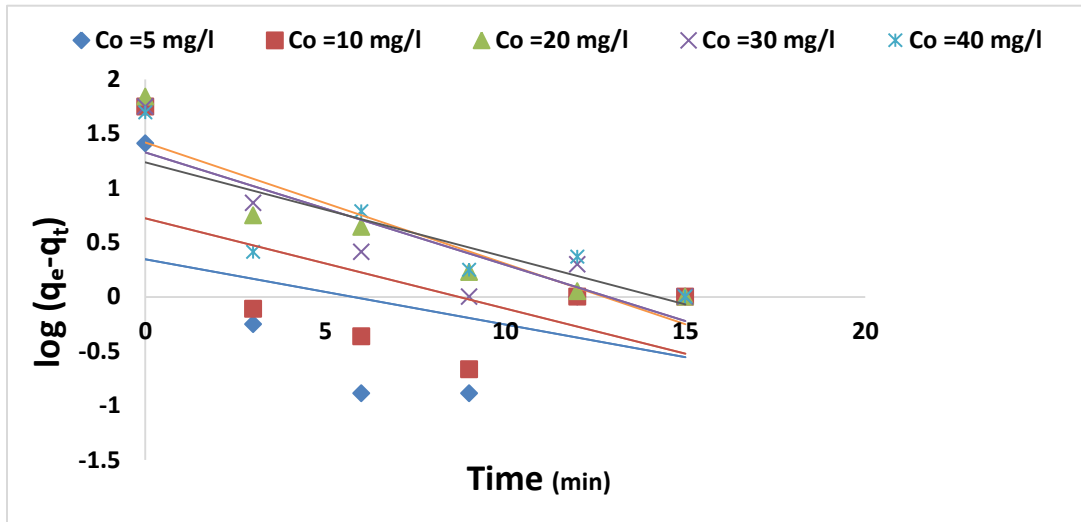


Figure 9: Kinetics of Pseudo 1st order for MB adsorption

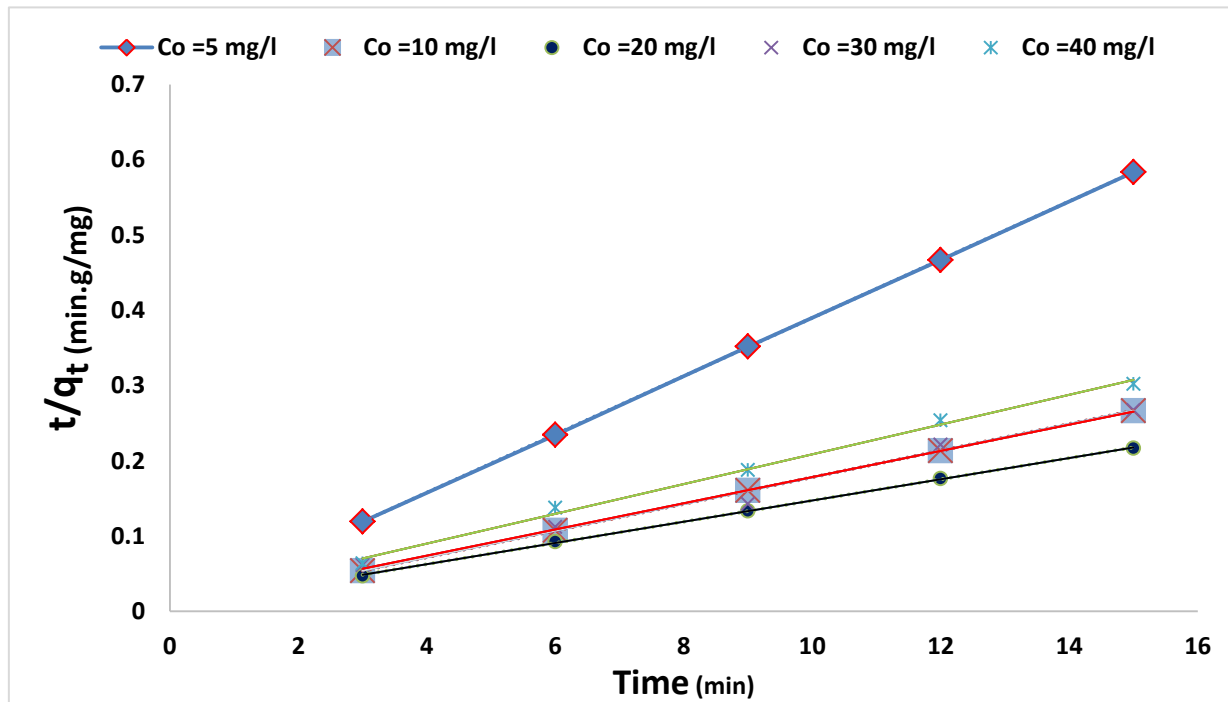


Figure 10: Kinetics of Pseudo 2nd order for MB sorption

To obtain theoretical q_e , k_1 , and correlation coefficient R^2 , Linear regression was applied and the results are showed in Table (5).

The model of pseudo1st order showed lower value for R^2 and the pertinent values of predicted for q_e contrasted to experimental q_e values. Whereas, the model of pseudo2^{ed} order

showed higher value for R^2 and the pertinent values of predicted for q_e are compatible with the corresponding experimental values of q_e . These results suggested that the adsorption process followed the model of pseudo2^{ed} order kinetics.

TABLE (5)
KINETIC PARAMETERS OBTAINED FROM FITTING PSEUDO 1ST ORDER AND PSEUDO 2ST ORDER MODELS

Co (mg/l)	Pseudo 1st order				Pseudo 2nd order		
	qe experimental (mg/g)	qe theoretical (mg/g)	k1 (g.mg-1.min-1)	R2	qe theoretical (mg/g)	k2 (g.mg-1.min-1)	R2
5	25.7094	2.2228	1.13818	0.1589	25.8400	0.4992	1
10	56.2500	5.3027	0.1913793	0.3027	56.4972	0.2848	1
20	69.1909	26.3876	0.2570148	0.8297	70.9220	0.0311	0.9996
30	56.1206	21.3304	0.2381302	0.7571	57.4713	0.0644	0.9841
40	49.6501	17.3460	0.2008216	0.6624	50.7614	0.0343	0.9952

V. CONCLUSIONS

The present study demonstrated that Powdered Activated Carbon (PAC) prepared from Casuarina charcoal can be used as an effective adsorbent for the removal of Methylene blue from aqueous solutions. In the studied pH range from 4 to 10, the loading capacity was found to be highest at pH 6, amounting 109.7 mg/gm. Freundlich and Langmuir models were used to describe the isotherm and the Langmuir model was shown to provide the best fitting. The results indicate that the adsorption of MB by the adsorbent takes place in a monolayer adsorption manner. Compared with previous studies as reported in the literature, the activated carbon prepared in this work showed comparatively reasonable adsorption capacity of 164 mg/g. The kinetics studies show that the experimental data can be well fitted by the pseudo second order rate equation

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