A Comparative Investigation on Adsorption of Methylene Blue Dye on Activated Carbon and Activated Carbon/Chitosan Composites

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(Received 5 / 2 / 2019. Accepted 10 / 7 / 2019)

□ ABSTRACT □

In this study, commercial activated carbon and activated carbon/chitosan composites; AC(0.25-0.5), AC(0.5-1), AC/CS(0.25-0.5),AC/CS(0.5-1)mm, were used as an adsorbents to remove methylene blue dye from dilute solution. Three experimental parameters of the adsorption were studied by factorial design . The three factors were, initial concentration of the dye in the solution, presence of chitosan as a coating agent and granular size of the activated carbon. The ANOVA table indicates that the initial concentration of the dye is the most significant adsorption parameter. The maximum value of qt was 7.78mg/g at initial concentration10ppm of the dye. The adsorption data fitted Langumir isotherm .The kinetic study indicate that the adsorption fitted Pseudo-second-order for three adsorbents; AC(0.25-0.5), AC/CS(0.25-0.5), AC/CS(0.5-1). The results confirm the nature of the adsorption as chimosorption for these adsorbents.

Keywords: adsorption, activated carbon, chitosan, methylene blue.

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دراسة مقارنة لامتزاز صباغ أزرق الميتلين على الفحم الفعال وخليط فحم فعال\اكيتوزان

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(تاريخ الإيداع 5 / 2 / 2019. قُبِل للنشر في 10/ 7 / 2019)

□ ملخّص □

درس امتزاز صباغ أزرق الميتلين على حجمين حبيبين من الفحم الفعال التجاري وعلى خلائطهما مع بوليمير عضوي هو الكيتوزان

AC(0.25−0.5), AC(0.5−1), AC/CS(0.25−0.5),AC/CS(0.5−1)mm

تم تصميم تجربة عاملية لدراسة الظروف الأمثل لامتزاز أزرق الميتلين على المواد المازة المدروسة بأخذ ثلاثة عوامل بالاعتبار هي : التركيز الابتدائي للصباغ في المحلول ، وجود الكيتوزان كعامل تغليف ، الحجم الحبيبي للمادة المازة . بين جدول تحليل التباين ANOVA أن للتركيز الابتدائي للصباغ أكبر تأثير على عملية الامتزاز. كانت أعظم قيمة لتركيز الصباغ في الطور الصلب qt هي 7.78mg/g عند التركيز الابتدائي 10ppm . وافقت بيانات الامتزاز نموذج لانغمویر التوازني كما بينت الدراسة الحركية أن امتزاز أزرق الميتلين على , ,AC(0.25−0.5) AC/CS(0.25−0.5),AC/CS(0.5−1)يتبع نموذج بسيدو من 33المرتبة الثانية وهذا يؤكد أن الامتزاز له طبيعة كيميائية على هذه المواد المازة.

الكلمات المفتاحية: امتزاز، الفحم الفعال، الكيتوزان، أزرق الميتلين.

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Introduction:

In the last few decades, rapid industrialization and population growth have caused serious environmental pollution. Water pollution with elevated contaminants such as toxic heavy metal ions, inorganic anions, organic compounds is serious and has been widely reported.[1]

Annually, 7 × 107tons dyes are manufactured worldwide and a significant amount is lost during processing and dying, which ultimately mixed with water bodies [2].

Synthetic organic dyes have been treated as a class of serious pollutants in surface water due to their wide applications in the textile, leather, paper, and printing industries. These dyes could cause environmental problems and are toxic for humans, and non-biodegradable. Thus, it is necessary to remove these dyes from wastewaters. Methylene blue (MB) is a typical organic dye with toxicity, which could be found easily in dye wastewaters [3]

Current available water treatment technologies, such as conventional adsorption treatment, ion exchange, coagulation and flocculation ,membrane treatment ,advance oxidation, electrochemical degradation and biodegradation are usually proposed [4]

Adsorption is the method for separation of mixtures on a laboratory and industrial scale where it is a surface phenomenon that can be defined as the increase in concentration of a particular component at the interface between two phases. Adsorption of dyes depends on the properties of the dye and the surface chemistry of the adsorbent [5]

The new trend of greater interest is the synthesis of novel adsorbents, tuning their properties on the specific pollutant-target and/or achieving a different engineeration of adsorbent form. A new simplified adsorbent coating, as a thin and flexible coated layer, can be conceived. The adsorbent coating modify the classical adsorption concept with simpler synthesis procedure and working application afterwards. The coating can be formulated as an amphoteric charge coating so that it can excellently adsorb both cationic and anionic pollutants. Such characteristic is highly required to meet the demand of versatile treatments able to face the typical complexity of industrial effluents, especially when dealing with dyes effluent [4], [5] .

Activated carbons are non-hazardous carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of undesired species from the gaseous or liquid phase in order to affect the effect purification [6], [7].

use of commercial activated carbon is limited, because of its relatively high cost. The coating of activated carbon with biological origin material is new method for the modification of activated carbon properties. By this modification, much lower quantities of activated carbon will be needed in adsorption process and removal process has been changed to a cost-effective and environmentally benign process. One of biological origin materials is chitosan. Chitosan, poly D-glucosamine, is the deacetylated form of chitin (a natural polymer found in several sources such as crustaceans and fungal cell walls) that has a great variety of applications including in biochemistry, pharmacy, medicine, agriculture, as well as wastewater treatment.[8]

The amine and hydroxyl groups of chitosan are able to sorb metals through several mechanisms including chemical interactions (such as chelation) and electrostatic interactions (for example ion exchange or the formation of ion pair). In recent years, chitosan and its derivatives such as cross linked chitosan, chitosan beads and chitosan composite, has been studied as an adsorbent for the removal of dyes and heavy metal ions from aqueous solutions [9], [10].

Cationic dyes are widely used in acrylic, wool, nylon and silk dyeing. These dyes include different chemical structures based on substituted aromatic groups. This group of dyes is considered as toxic colorants and can cause harmful effects such as allergic dermatitis, skin irritation, mutations and cancer. These dyes are also called basic dyes and depend on a positive ion, which are generally hydrochloride or zinc chloride complexes [11].

Cationic dyes carry a positive charge in their molecule, furthermore it is water soluble and yield colored cations in solution. Acid dyes are used with silk, wool, polyamide, modified acrylic and polypropylene fibers. Acid dyes have good water solubility; on the other hand they have a harmful effect on human beings since they are organic sulphonic acids [12].

Anionic dyes depend on a negative ion. Anionic dyes includes many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g., azoic, anthraquinone, triphenylmethan and nitro dyes) but possess as a common feature, water-solubilizing, ionic substituents. The anionic dyes also include direct dyes, and from the chemical standpoint the group of anionic azo dyes includes a large proportion of the reactive dyes [5].

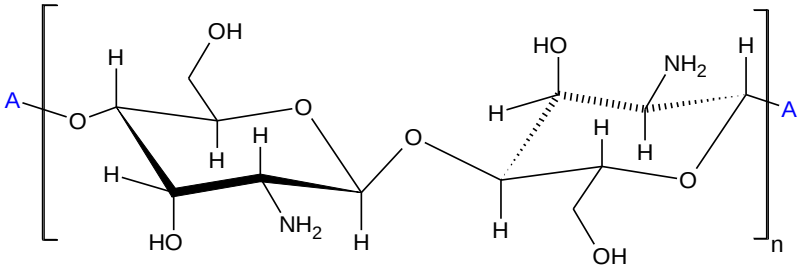
Over the century, various researchers have proposed their own equilibrium isotherm models such as Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory- models has few fundamental hypothesis and assumptions and they have been formulated to provide simple parameter interpretation, which often do not have any physical significance. Moreover, the hypotheses are rarely applicable or in very specific cases, but not absolutely relevant in many others [13]–[15].

This study aimed to evaluate the performance of commercial activated carbon and chitosan/activated carbon composite for cationic dye (methylene blue) removal from dilute aqueous solutions.

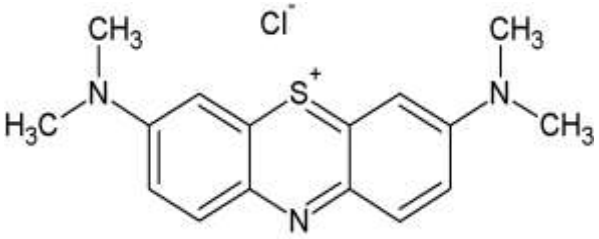
Materials and methods:

1. Materials

Tow granular sizes of commercial activated carbon, which was used as adsorbent, was purchased from POCH(Polonia) with particle diameter of 0.2-0.6mm and density of 2g/cm^3, (AC)(250-500) (500-1000)µm were used as the adsorbent.. Low molecular weight of Chitosan with 80% degree of deacetylation and medium molecular weight (120,000)Da that was purchased from Sigma Aldrich (USA).,was used as coating agent as it is a biopolymer with functional group NH_2.



Oxalic acid (0.2 M) and NaOH (0.7 M) were used to coating of AC with CH (preparation of biobased CH/AC composite. hydrogen chloride (HCl, 4%V/V). Methylene blue was obtained from TECHNO PHARMCHEM HARYAN(India), with molecular formula $C_{16}H_{18}ClN_3S$ and molecular weight 319.851g/mol.



2. Preparation and characterization of adsorbents

2.1. Preparation of chitosan/activated carbon composite

The chitosan/activated carbon composite (CH/AC) was prepared by following method: 10 g AC of every granular size was poured in 0.2 M oxalic acid for 4 h. AC was washed with deionized water after filtration and dried in oven at 70 C° for 12 h. CH (5 g) was added to 0.5 L of 0.2 M oxalic acid solution under continuous stirring at 45–50 C° to facilitate the formation of gel. About 20 g of acid treated AC was added slowly to the CH gel and stirred for 16 h at 45–50 C°. The CH/AC composite (CH/AC) beads were then prepared by drop wise addition of activated carbon gel mixture into a 0.7 M NaOH precipitation bath. The beads were filtered from NaOH bath, and washed several times with deionized water to a neutral pH. The beads are dried in an air oven (50 C°) [9], [10], [16]

2. 2. Effect of adsorption parameters

response surface methodology (RSM) explores the relationships between several explanatory variables and one or more response variables. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response, this model is only an approximation, but it used because such a model is easy to estimate and apply, even when little is known about the process.

RSM can be employed to maximize the production of a special substance by optimization of operational factors, the interaction among process variables can be determined by statistical techniques.

The experiment by using RSM was designed to study three factors, dye initial concentration in five levels (1,2,3,4,10ppm), particle size of the adsorbent in two levels((0.25-0.5mm),(0.5-1mm)), presence of chitosan as coating agent in two levels (present, not present) (Table 1). This method determined the effectiveness of parameters and identified the optimum operation conditions by using software statistic program Minitab 16.

Table 1: Arrangement of parameters in factorial array.

Size of adsorbate	Chitosan presence	Initial Concentration(mg/l)
0.25-0.50	-	1
0.25-0.50	-	2
0.25-0.50	-	3
0.25-0.50	-	4
0.25-0.50	-	10
0.25-0.50	+	1
0.25-0.50	+	2
0.25-0.50	+	3
0.25-0.50	+	4
0.25-0.50	+	10

0.50-1.00	-	1
0.50-1.00	-	2
0.50-1.00	-	3
0.50-1.00	-	4
0.50-1.00	-	10
0.50-1.00	+	1
0.50-1.00	+	2
0.50-1.00	+	3
0.50-1.00	+	4
0.50-1.00	+	10

2.3. Batch adsorption experiments

Dye removal experiments were performed in batch manner by adding a measured weight of AC and CH/AC with known particle size in 50 mL of dye solution
in 100 mL Erlenmeyer flasks. These samples were shaken at room temperature using an orbital shaker at 250 rpm for 24h for methylene blue dye. Adsorption experiments were performed at their original .pH. The dye concentration in the solution was analyzed using an UV–vis spectrometer by monitoring the absorbance changes at the wavelength of maximum absorbance (λmax =616nm). The removal (%) and adsorption capacity q_t (mg/g) were obtained using Eqs (1) and (2):

$$removal(\%) = \frac{C_o - C_t}{C_o} x100\% \quad (1)$$

where C_o and C_t (mg /l) are the concentration of dyes at initial time, and at time t [18].

$$q_t = \frac{(C_o - C_t)v}{w} \quad (2)$$

where C_o and C_t (mg /l) are the concentration of dyes at initial time, and at time t , v (ml) is the volume of solution and w (mg) is the amount of the adsorbent [19].

2.4. Kinetic studies

The kinetic of adsorption was conducted by placing 0.05 g adsorbent (AC, and CH/AC) in flasks containing 50 mL of dye solution with initial concentration 10ppm. The contents of the flasks were agitated on an orbital shaker at 250 rpm for prescribed periods of time (24hr) at room temperature. The dye concentration was determined in defined time intervals(10-15min) for about 5hours using Spectrophotometric instrument (SHIMADZU – UV-1700) to determine the maximum ultraviolet wavelength absorbance of each dye using scanning procedures to define the appropriate wavelength.
Pseudo-first-order expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where:
q_t: the adsorbed amount at time t.
k_1 :the first order rate constant.
q_e:the adsorbed amount of adsorbate at the equilibrium ,which is calculated by plotting the $\log(q_e - q_t)$ versus (t)
The pseudo-second-order-equation based on equilibrium adsorption may be expressed as

$$\frac{t}{q_t} = \frac{1}{\vartheta_0} + \frac{1}{q_e} t \quad (4)$$

Where:

q_t.:the adsorbed amount at time t.

$$v_o = \frac{1}{K_2 q_e^2} \quad (5)$$

k_2: the second order rate constant.

q_e:the adsorbed amount at equilibrium.

The values of ϑ_0, q_ecan be calculated by plotting t/q_t versus t [20].

Intra-particle equation :

$$q_t = k_p t^{0.5} \quad (6)$$

where *k*p is the intra-particle rate constant (g mg^{-1} $min^{-0.5}$)

the intra-particle rate constant k_p is a function of equilibrium concentration in solid phase *q*e and intra-particle diffusivity *D* in the following way:

$$K_p = (6q_e/R)(D/\pi)\text{ ^0.5} \quad (7)$$

were *R* is the particle radius [21]

The liquid film diffusion model is given by:

$$\mathrm{Ln}(1 - \mathrm{F}) = \mathrm{K_{fd}}.\mathrm{t} \quad (8)$$

where F = qt/qe and kfd is the constant rate (min^{1-})[9]

2.5. Adsorption isotherm

The three most widely used adsorption isotherms are the Langmuir, Freundlich and Dubinin –Radushkevich (D–R) isotherms. The Langmuir adsorption isotherm equation on linear form is:

$$\frac{1}{q_e} = \frac{1}{q_{\ max}.k_L}.\frac{1}{C_e} + \frac{1}{q_{max}} \quad (9)$$

where q_{max} is maximum adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir constant related to energy of adsorption (L/mg). K_L and q_{max} can be calculated from the slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$. Other important parameter, R_L, called the separation factor was calculated to identify whether an adsorption system is favorable or unfavorable:

$$R_L = \frac{1}{1+K_L.C_o} \quad (10)$$

If the R_L value is between 0 and 1, the adsorption process is favorable.

Linear form of Freundlich model is:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \quad (11)$$

in this equation, K_f is the Freundlich constant related to adsorption capacity of adsorbent (mg $^{1\_(1/n)}$ L $^{1/n}$/g) and 1/n is the Freundlich exponent related to adsorption intensity [9].

The Dubinin –Radushkevich (D–R) isotherm was applied to distinguish the nature of adsorption as physical or chemical. The linear form of Dubinin–Radushkevich isotherm is:

$$lnq_e = lnq_m - ßC^2 \quad (12)$$

where q_m is the theoretical saturation capacity (mol/g), ß is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), and C is the Polanyi potential which is related to the equilibrium concentration as follows:

$$C = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (13)$$

where R is the universal gas constant (8.314 J/mol K), Ce is the equilibrium concentration of adsorbate in solution (mol/L) and T (K) is the absolute temperature. A plot of lnqe versus C^2 is used to determine the D–R constants q_m and ß.

The constant ß gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E = \frac{1}{(2ß)^{0.5}} \qquad (14)$$

This parameter gives information whether adsorption mechanism is ion-exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ/mol, the adsorption process follows by ion-exchange (chemical nature), while for the values of E < 8 kJ/mol, the adsorption process is of a physical nature [22].

Results and discussion:

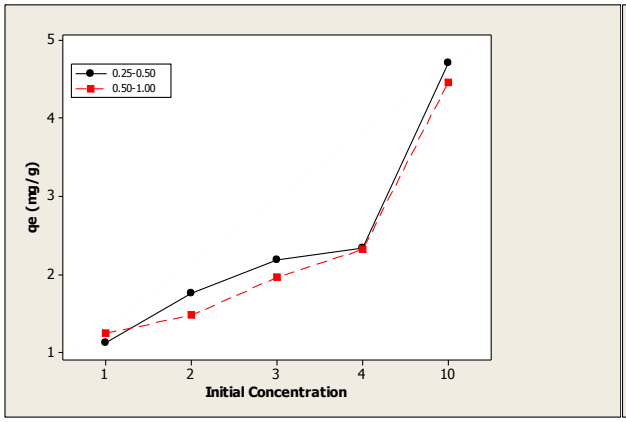
1. Surface analysis

Adsorption–desorption isotherm of N_2 at 77 K was examined. Geminii 2375 surface area analyzer was used to determine this parameter by applying the 3-point BET (Brunaeur–Emmet–Teller). The pore diameter was calculated depending on BET. It was found that the studied activated carbon was mesoporous as the pore diameter average was 28.1856A° and its specific surface area was736.189$m^2.g^{-1}$ at relative pressure p/po=0.3 and. Activated carbon/chitosan composite was found to be mesoporous material with average pore diameter was 25.4357A° and the specific surface area decreased to 290.822$m^2.g^{-1}$after coating. The surface area decreasing after coating although the pore average diameter didn't actually change can be interpreted by the fact that the micropore<2nm, which contribute to surface area increasing had blocked after coating. [17]

2. Responding surfaces

The ANOVA table was calculated by MINITAB 16 through responding surfaces method,

b



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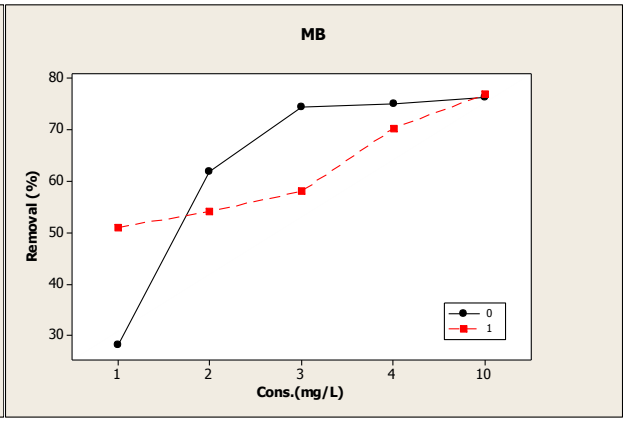


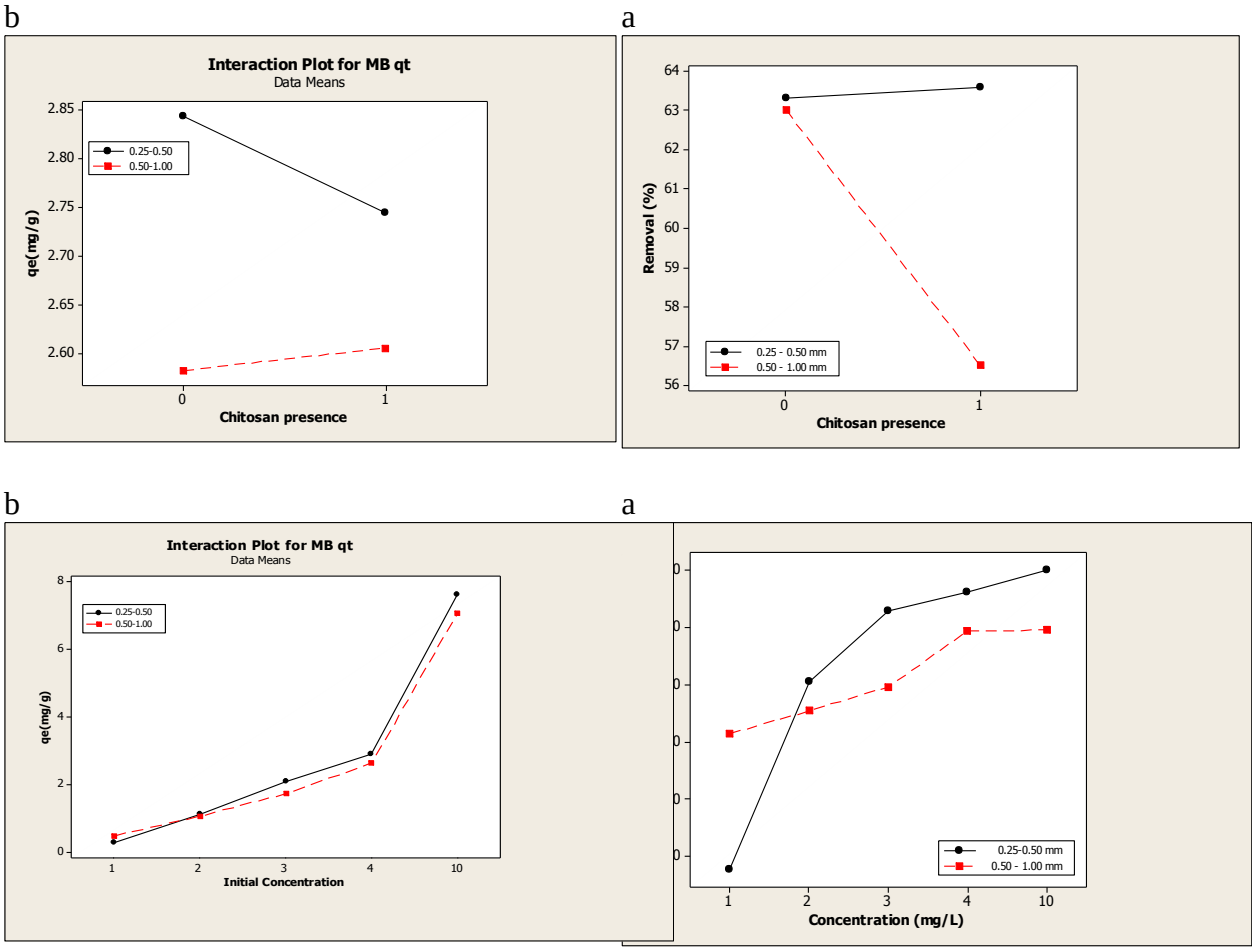


Figure 1: The interaction between three adsorption parameters (initial concentration of the dye, granular size of activated carbon and presence of chitosan) in term of a, removal percentage%. b, solid phase concentration qt.

Table (2) for methylene blue dye concentration in the solid phase and removal percentage, indicate that the initial concentration of the dye in the solution is the most significant removal parameter. The solid phase concentration for adsorbents AC (0.25-0.50), AC (0.5-1.00), AC/CS (0.25-0.50), at MB initial concentration 10 ppm, were 7.78, 6.47, 7.40, 7.78 mg/g respectively.

Table 2 Analysis of Variance for MB qt

Source	DF	SS	MS	F	P
Size of adsorbate	1	0.200	0.200	1.72	0.212
Chitosan presence	1	0.007	0.007	0.06	0.808
Initial Concentration	4	119.476	29.869	256.58	0.000
Error	13	1.513	0.116		
Total	19	121.196			

Where:
DF: degree of freedom
SS: sum of squares
MS: the variance
F: variance between data (MS_b)/variance of error (MS_w)

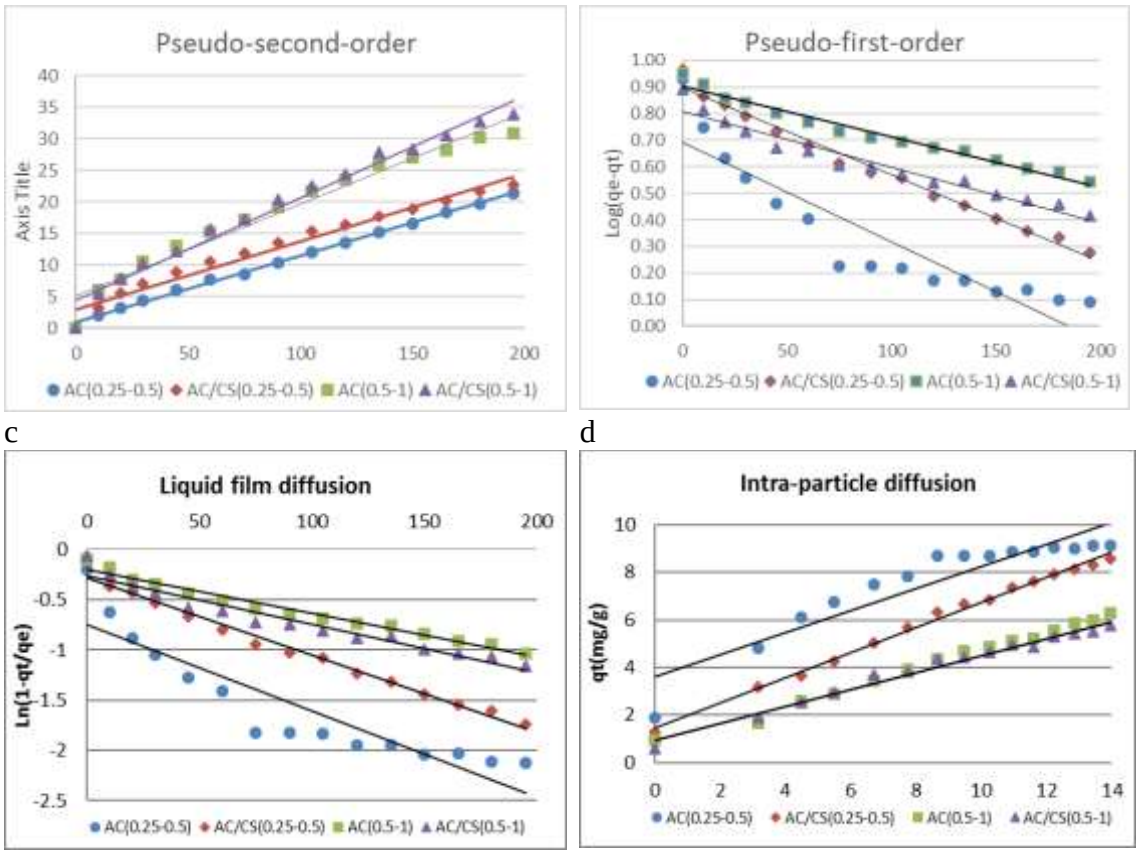
P: probability of rejecting zero hypothesis.

3. Kinetic study of methylene blue adsorption

Linear plots of kinetic models for methylene blue adsorption onto activated carbon and activated carbon/chitosan are shown in figure 2

Constants and regression coefficient for kinetic models Pseudo-first-order, Pseudo-second-order, film diffusion and intra particle diffusion models for methylene blue adsorption onto four adsorbents: AC(0.25-.5), AC/CS(0.25-0.5), AC(0.5-1) and AC/CS(0.5-1) are shown in table 3

a b



c d

Figure 2: Linear plots of kinetic models a: Pseudo-first-order, b: Pseudo-second-order, c:film diffusion, d: intra particle diffusion for methylene blue adsorption onto four adsorbents, AC(0.25-0.5), AC/CS(0.25-0.5), AC(0.5-1), AC/CS(0.5-1).

Table 3: Constants and regression coefficient for kinetic models.

Kinetic models													
adsorbent	qe-exp	Pse-first-order			Pse-second-order			Film-diffusion -model			Intra-particle diffusion		
		R2	K1	qe	R2	K2	qe	R2	Kfd	inters	R2	Kid	inters
AC(0.25-.5)	10.38	0.831	0.009	4.902	0.998	95.278	9.533	0.831	0.009	-0.750	0.862	0.465	3.610
AC/CS(0.25-0.5)	10.45	0.974	0.004	8.000	0.963	9.367	6.878	0.987	0.008	-0.285	0.994	0.527	1.452
AC(0.5-1)	9.78	0.986	0.008	7.861	0.974	28.698	9.328	0.974	0.004	-0.201	0.993	0.395	0.768
AC/CS(0.5-1)	8.38	0.944	0.005	6.445	0.977	8.769	6.146	0.944	0.005	-0.262	0.981	0.359	0.908

The table 3 indicates that the kinetic of adsorption of methylene blue dye follow Pseduo-second-order for the three adsorbents AC(0.25-.5), AC/CS(0.25-0.5)and AC/CS(0.5-1) according to the high values of R^2 and the very closely similarity of qe to the experimental ones, so the mechanism of adsorption is chemisorption. But the mechanism of adsorption of the dye is physisorption for the adsorbent AC(0.5-1) as the rate of adsorption is controlled by Pseduo-first-order. Film diffusion and intra particle diffusion don't play a role in the adsorption as the plots of qt versus $t^{0.5}$ and ln(1 - qt/qe) versus t do not pass through the origin(inters(crossing Y axis) don't equal to zero.

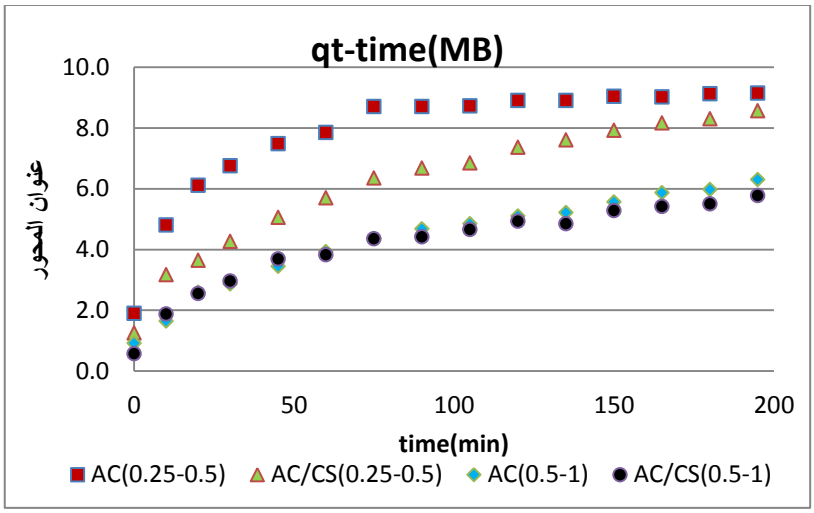


Fig. 3. Solid phase concentration qt by time for the adsorption of methylene blue dye on four adsorbents:.□: AC (0.25-0.5), ◊: AC (0.5-1), ○: AC/CS (0.5-1), Δ: AC/CS (0.25-0.5).

As shown from figure 3, the activated carbon AC(0.25-0.5) reached equilibrium within 100 minutes while its composite AC/CS(0.25-0.5) reached equilibrium in 150 minutes. In case of AC(0.5-1) and its composite AC/CS(0.5-1), they reached equilibrium at the same time , in 150 minutes.

4. Adsorption equilibrium

Linear plots of three isotherms are shown in figure 4. Constants parameters and regression coefficient for Langmuir, Freundlich and Dubinin–Radushhkevich , are shown in table 4.

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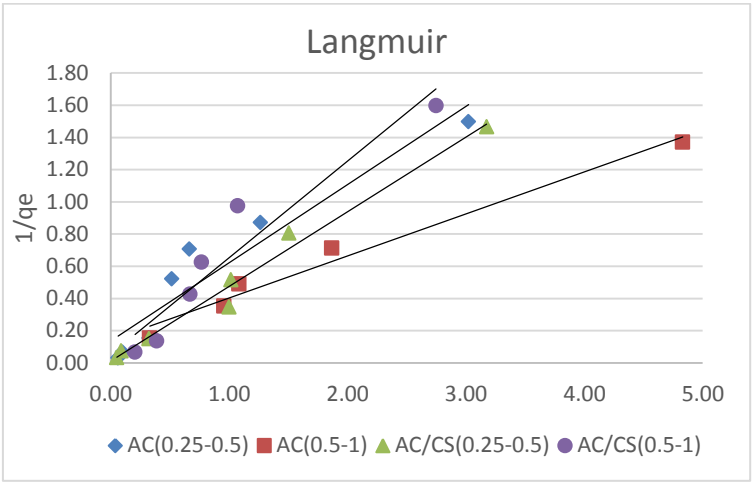

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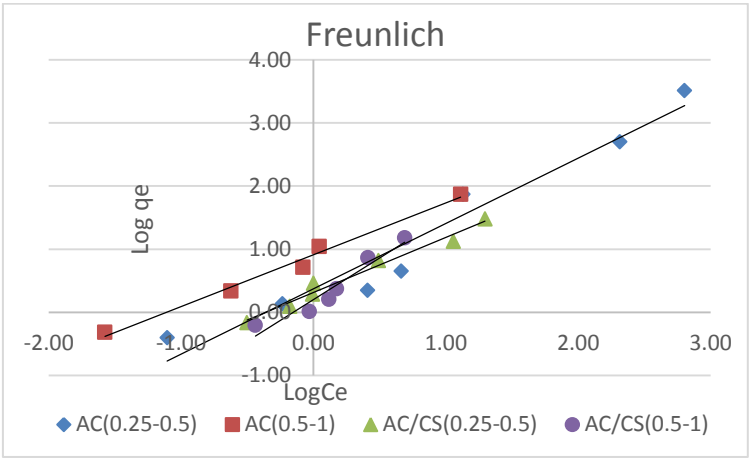

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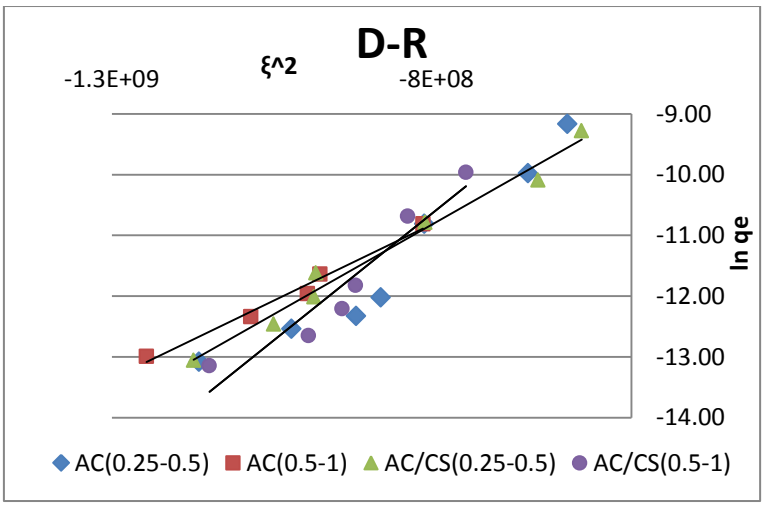

Figure 4 : Linear plots of isotherms. a:Langmuir, b: Freundlich, c: Dubinin-Radushkevich, for methylene blue adsorption onto four adsorbents, AC(0.25-0.5), AC/CS(0.25-0.5), AC(0.5-1), AC/CS(0.5-1).

Table 4: Constants parameters and regression coefficient for Langmuir, Freundlich and (D–R) models for adsorption of methylene blue dye.

adsorbent	Langmuir			Freundlich			D–R			
	R^2	q_{max}(mg/g)	K_L (l/mg)	R^2	K_f($mg^{1-(1/n)}L^{1/n}/g$	n	R^2	ß (mol^2/J^2)	Qm (mol/g)	E (kJ/mol)
AC (0.25-.5)	0.91	7.27	0.28	0.95	2.37	0.97	0.93	7.00E-09	0.00539	8.45
AC/CS (0.25-0.5)	0.92	41.84	0.06	0.96	2.18	0.98	0.98	6.00E-09	0.00278	9.13
AC (0.5-1)	0.98	6.97	0.55	1.00	1.00	1.00	0.98	5.00E-09	0.00134	10
AC/CS (0.5-1)	0.92	18.83	0.09	0.87	1.56	0.83	0.91	9.00E-09	0.02459	7.45

From table 4, the adsorption of methylene blue dye onto granular activated carbon and activated carbon/chitosan composite fitted the three equilibrium models due to the high values of R^2 and the q_{max} calculated by Langmuir model were higher for the composite than the activated carbon in two granular sizes , that means the coating improve the ability of the activated carbon to adsorbe methylene blue dye. The mean free energy (KJ/mol) calculated from D-R model were 8.45, 9.13, 10 and 7.45 Kj/mol for AC(0.25-.5), AC/CS(0.25-0.5),AC(0.5-1)and AC/CS(0.5-1) respectively. These E values confirm the chemical nature of the adsorption.

Conclusions:

Two granular sizes of activated carbon and two composites of activated carbon/chitosan were used as an adsorbent for methylene blue dye removal from dilute solution. The ANOVA table indicate that the initial concentration of the dye in the solution plays a significant role in the adsorption and so , it affect the solid phase concentration .The maximum qt value was 7.78mg/g at initial concentration of methylene blue 10ppm .The data of adsorption fitted Langmuir and Pseudo-second-order, this results confirm the chemical nature of the adsorption.

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