Removal of Methylene Blue from Aqueous Solution Using Untreated Palm Seeds Powder

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ABSTRACT

This research aimed to investigate the potential of untreated palm seeds powder (PSP as an alternative and environmental friendly adsorbent for the treatment of dye-containing wastewater.

PSP was applied to treat methylene blue (MB) simulated solutions, and various operation parameters were investigated under batch system. Kinetic and thermodynamic studies were investigated, pseudo second-order was observed to be the most suitable to describe the adsorption process. Values obtained from thermodynamic analysis show that the adsorption process is endothermic, spontaneous and chemisorptions in nature.

Keywords: Dye Removal, Dye Adsorption, Biomass, Palm Seed, Methylene Blue

ÖZ

Bu araştırmada, boya içeren atıksuların arıtılması için bir alternatif ve çevre dostu adsorban olarak işlenmemiş palmiye tohumu tozu (PSP) potansiyelinin araştırılması amaçlanmıştır.

PSP yapay metilen mavisi (MB) çözetisinin iylestirilmesi uygulaması, farklı uygulama sartlarında batch sistem altında incelenmistir. Kinetik ve termodinamik çalısma incelemeleri, yalancı ikinci-derecenin, adsorpsiyon prosesini tanımlayan en uygun gözlem olduğunu göstermistir. Termodinamik değerlerin analizi sonucu adsorpsiyon prosesinin endotermik, kendiliğinden ve doğal kimyasalsorpsiyon olduğunu göstermektedir.

Anahtar Kelimeler: Boya Giderimi, Boya Adsorpsiyonu, Biyokütle, Palmiye Tohumu, Metilen Mavisi

My Research is Dedicate to My Mother & Father

And also

Dedicate to my Brothers & Sisters

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I would like to thank the Almighty God who gave me this golden opportunity to do these studies. And great appreciation to Assoc. Prof. Dr. Mustafa Gazi my research supervisor for his valuable and constructive suggestions during the planning and development of this research work.

I would also like to take this opportunity to express a deep sense of gratitude to my great Father (Rest in Peace), my sweaty Mom and all my brothers and sisters for their valuable guidance and co-operation during the period of this study. The blessing help and guidance was a deep inspiration to me.

I am very thankful to all my friends who all supported me, for I have completed my project effectively and moreover, on time.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS ABBREVIATIONS

MB	Methylene Blue
PSP	Palm Seeds Powder
ppm	Part per million
ppb	Part per billion
FT-IR	Fourier transform infrared
UV/VIS	Ultraviolet visible
ΔG^o	The Gibbs free energy change (kJ $mole^{-1}$)
ΔH^o	The Enthalpy change (kJ $mole^{-1}$)
ΔS^o	The Entropy change (J mole-1 K^{-1})
K_1	The Pseudo-first-order rate constant (min^{-1})
K_2	The Pseudo-second-order rate constant ($mg.g^{-1}.min^{-1}$)
q	The Amount of Adsorbate per gram of adsorbent ($mg.g^{-1}$)
q_e	The Amount of Adsorbate per gram adsorbent at equilibrium ($mg.g^{-1}$)
q_t	The Amount of Adsorbate per gram of adsorbent at any time
q_m	Equilibrium adsorption capacity using model
q_{max}	Maximum adsorption capacity (mg/g)
R^2	Linear correlation coefficient
R_L	Separation factor
t	Time (min)
T	Temperature (K)
COD	Chemical oxygen Demands
C_e	Amount of MB in solution, ppm (mg/L)
C_{ads}	Amount of MB adsorbed ppm (mg/L)
C_0	Initial concentration of MB, ppm (mg/L)

Chapter 1

INTRODUCTION

Wastewater containing dyes is undesirable since tiny amount of dye material destroy the aesthetic values of the water. It is necessary to effectively treat effluent containing dyes due to the environmental and toxicology threats posed to human and aquatics. Many process have been used for removing dyes from wastewater however, some of these techniques are inefficient or expensive to treat both diluted and concentrated pollutants (Vadivelan et al. 2005).

Various alternative methods including adsorption, ion exchange, coagulation and flocculation, precipitation and chemical oxidation had been used for the treatment of dye-contaminated wastewaters. Adsorption technique has been found to be a superior separation and purification method to other methods due to its easy-nature, low cost, high selectivity, and high efficiency (Ozdes et al. 2014).

Many low-cost adsorbents have been used for this purpose such as bentonite, fruit peel, papaya seeds, orange peels, saw dust, walnut shells, zeolites synthesized from fly ash, swelling clay, cedar saw dust and crushed bricks, but there is still a need for adsorbents which are cheap, easily available and efficient (Ashiq et al. 2012).In this study, PSP was applied to remove methylene blue from wastewater. The adsorption capacity was estimated as a function of contact time, different initial dye concentrations, initial pH and biosorbent dosage.

1.1 Palm Seeds

Palm tree are regarded as international socio-economic plants (Dewir et al. 2011). The palms belong to the Arecaceae sub-group, which are a botanical family of perennial shrubs, and trees commonly known as palm trees. They are flowering plants, the only family in the monocot order Arecaceae and mostly restricted to tropical and warm temperate climates. Most palms are distinguished by their large, compound, evergreen leaves arranged at the top of an un branched stem.

However, many palms are exceptions, and in fact exhibit an enormous diversity in physical and morphological characteristics (Rafatullah et al., 2013). Many common products and foods are derived from palms, and palms are also widely used in landscaping for their exotic appearance, making them one of the most economically important plants. However, little information has been documented on the utilization of the palm seeds for water treatment. This prompted us to evaluate the potential of palm seeds as alternative adsorbent.

Figure 1.1: palm tree plant

1.2 Methylene Blue in the Environment

Methylene blue (MB) is a cationic dye and regarded as significant threat to human and biota due to its carcinogenic and mutagenic properties. Methylene blue has been widely used in coloring paper, wools, as biological stains and dying cottons (Sarici-Ozdemir et al. 2014). Therefore, it of environmental concern to treat MB-containing effluent before been discharged into fresh streams. The properties of MB are presented in Table 1.1.

Table 1.1: Methylene blue structure

Molecular weight (M.W)	319.85222 g/mol
Molecular formula	$C_{16}H_{18}N_3SCl$
Solubility	Slightly soluble
Melting point	100-110 °C (with decomposition)
Appearance	Dark green
Systematic name	3, 7-Bis (dimethylamino) phenothiazin-5-ium

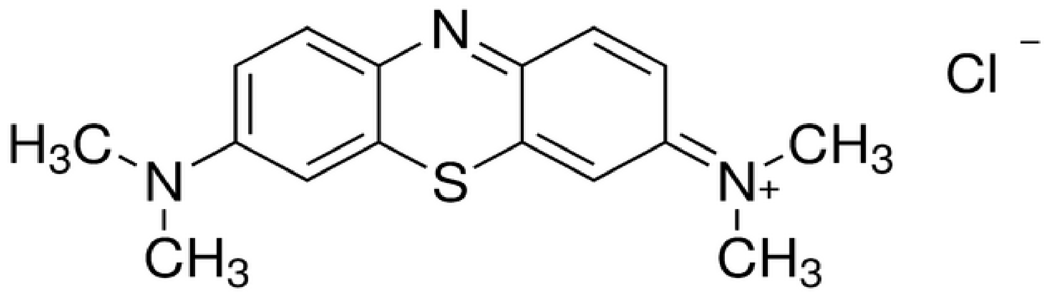

Figure 1.2: Chemical structure of Methylene Blue

1.3 Dye Contaminated Wastewater

Wastewater containing dyes can be described to possess low chemical oxygen demand (COD) and high alkalinity. The treatment of this effluent may be difficult due to the complex aromatic structures of dyes. Dyes can be categorized as:

- Anionic (direct, acid and reactive dyes)
- Cationic (basic dyes)
- Nonionic (disperse dyes)

Figure 1.3: Dye Contamination

1.4 Dye Treatment Process

Several treatment techniques have been utilized for removing dyes from aqueous solution such as: photocatalytic degradation, sonochemical degradation, electrochemical degradation, ultra-filtration, adsorption/precipitation processes, integrated chemical–biological degradation etc. As the artificial dyes in aqueous solution cannot be decolorized by conventional methods effectively, the adsorption of artificial dyes on cheap and effective solid supports has been reported to be suitable and promising (Rafatullah et al. 2013).

Activated carbons have been reported to be remarkable to treat contaminated wastewater due to their large surface areas and porosity, however its regeneration and desorption kinetics is questionable (Ahmad et al. 2012). Therefore, our focus is to develop low cost adsorbent that can effectively remove acidic and basic dyes from aqueous solutions.

1.5 Aim and Objective of the Research

1.5.1 Aim of the Research

The aim of this research is to use the palm seeds powder (PSP) as adsorbent for removing methylene blue (MB) from aqueous solution using the adsorption process.

1.5.2 Objective

- To examine the removal of methylene blue (MB) from aqueous solution by using palm seeds powder (PSP) as adsorbent.
- To investigate the adsorptive capacity of the adsorbent.
- To examine the influence of different parameters on the adsorption process.
- To study the kinetics and thermodynamics properties for the adsorption process.

Chapter 2

EXPERIMENTAL

2.1 Materials and Methods

Table 2.1: Materials and manufactures

Chemicals	Company
Hydrochloric acid	Riedal-deHean /Germany
Sodium hydroxide	Aldrich-Germany
Ethanol	Sema-North Cyprus
Potassium hydrogen phthalate	Analar-UK
Sodium tetra borate	Aldrich-Germany
Sodium dihydrogen phosphate	Analar-UK
Potassium chloride	Aldrich-Germany

2.2 Stock Solution Preparations

Preparations of stock solution of methylene blue was carried out by dissolving 1 g of methylene blue (MB) in 1000 ml of distilled water in order to get 1000 ppm concentration, while the working concentrations are prepared by using the equation

$$N_1 V_1 = N_2 V_2 \qquad (1)$$

The concentration of MB was measured using UV-visible spectrometer. A calibration curve was plotted between absorbance and concentration of dye solution to obtain absorbance-concentration profile as shown below.

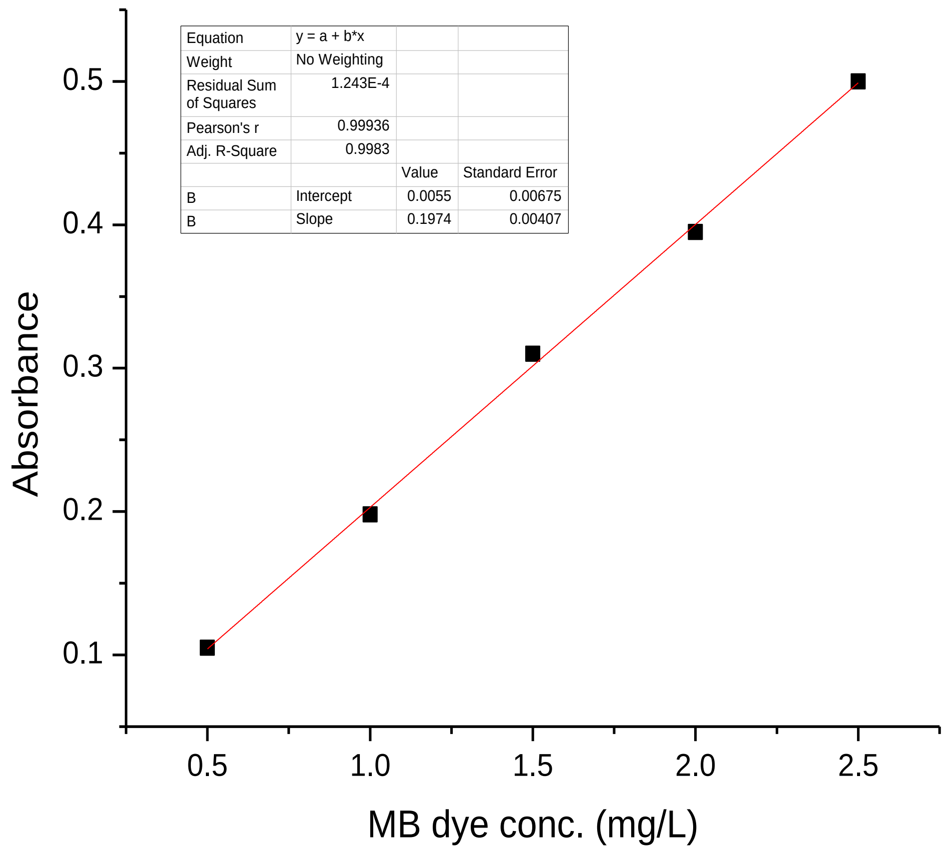

Figure 2.1: Calibration curve for MB

2.3 Adsorbent Preparation

The starting material palm seeds were collected from EMU campus, washed severally with distilled water and ethanol to remove color, dirt and organic materials such as (protein, fat and soluble carbohydrate), the remaining plant used as adsorbent should be insoluble fiber or cellulose origin as illustrated in (Figure 3.1). Then the washed seeds were dried in a convection oven at 65˚C for 24 h, then sieved using standard sieve to size within 75-300 µm. The material is then stored in desiccators for later use.

Figure 2.2: Adsorbent preparation process

2.4 Adsorption Studies

2.4.1 Effect of Initial Dye Concentration

In order to examine the effect of initial dye concentration, various dye concentrations (25, 50, 75 and 100ppm) were prepared from the dye stock solution. 50 ml of the solution is mixed with 300 mg of PSP in a flask and agitated under mechanical shaker. 5 ml was withdrawn from the flask after pre-set period and the absorbance was taking using UV-VIS (T80+, Beijing) at 664 nm.

2.4.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage was investigated using 100ppm dye at various doses (50, 100, 200 and 300 mg). 50 ml of the solution is mixed with PSP in a flask and agitated under mechanical shaker. 5 ml was withdrawn from the flask after pre-set period and the absorbance was taking using UV-VIS (T80+, Beijing) at 664 nm.

Figure 2.3: Palm seeds before and after MB adsorption.

2.4.3 Effect of Solution pH

The influence of solution pH (2-10) was also examined to understand the adsorption mechanism. 50 ml of the dye solution is mixed with 200 mg of PSP at constant concentration of 100pm in a flask and agitated under mechanical shaker. 5 ml was withdrawn from the flask after pre-set period and the absorbance was taking using UV-VIS (T80+, Beijing) at 664 nm.

2.4.4 Effect of Ionic Strength and Temperature

The effect of ionic strength was tested on the potential of PSP by preparing various concentrations of KCl (0.01, 0.05, 0.075, and 1 M). The effect of temperature was also conducted under mechanical shaker at varying temperature (25, 45, 65 and 85C^0).

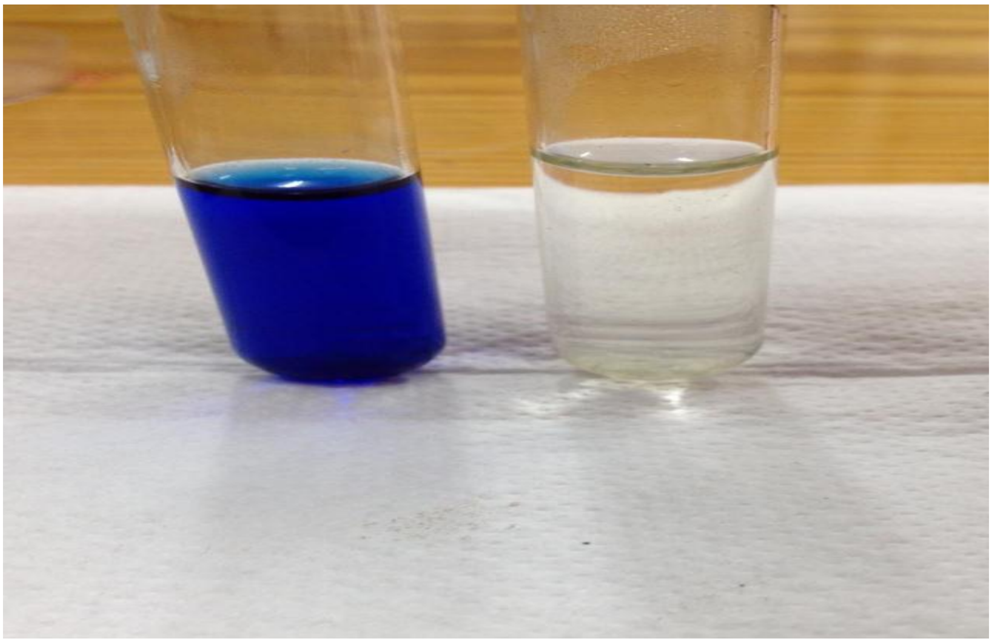

Figure 2.4: Dye solution before and after adsorption process with MB: 10 ppm, adsorbent dosage: 0.3 g, volume of MB dye solution: 50 ml

Chapter 3

RESULT AND DISCUSION

3.1 FT-IR Analysis

FT-IR analysis was conducted to detect the functional groups and investigate the surface characteristics of PSP in the range of 450-4000 cm^{-1} before and after treatment with methylene blue dye.

The spectrum before treatment with MB shows peaks at 3356.8$cm^{-1}$and 2924.1cm^{-1}which are attributed to O–H stretching and C-H stretching bond of alkyl group respectively. A small peak was noticed at about 2853.5$cm^{-1}$and assigned to the C–H stretching vibration of alkyl group, and the band at 1746.7cm^{-1} is related to the C=O stretching carbonyl group, Another band was found at about 1640.7 cm^{-1}, which is ascribed to C=C stretching alkenes group.

All the peaks were observed in both spectra before and after treated with MB with some changes in the wave number, showing that MB might have interacted chemically with PSP.

The peak that appears at about 3356.8cm^{-1}was seen to increase to 3368.6cm^{-1} and the peak of C-H stretching alkyl group was decreased from 1746.7cm^{-1} to 1743.3 cm^{-1}.Also the C=C band was decreased from 1640.7cm^{-1} to 1599.5cm^{-1} which is an indication that a new peak has been formed, which is related to N-H bending of amide group and this is predicting that the functional groups has responsibility for the electrostatic attraction of MB cations onto PSP.

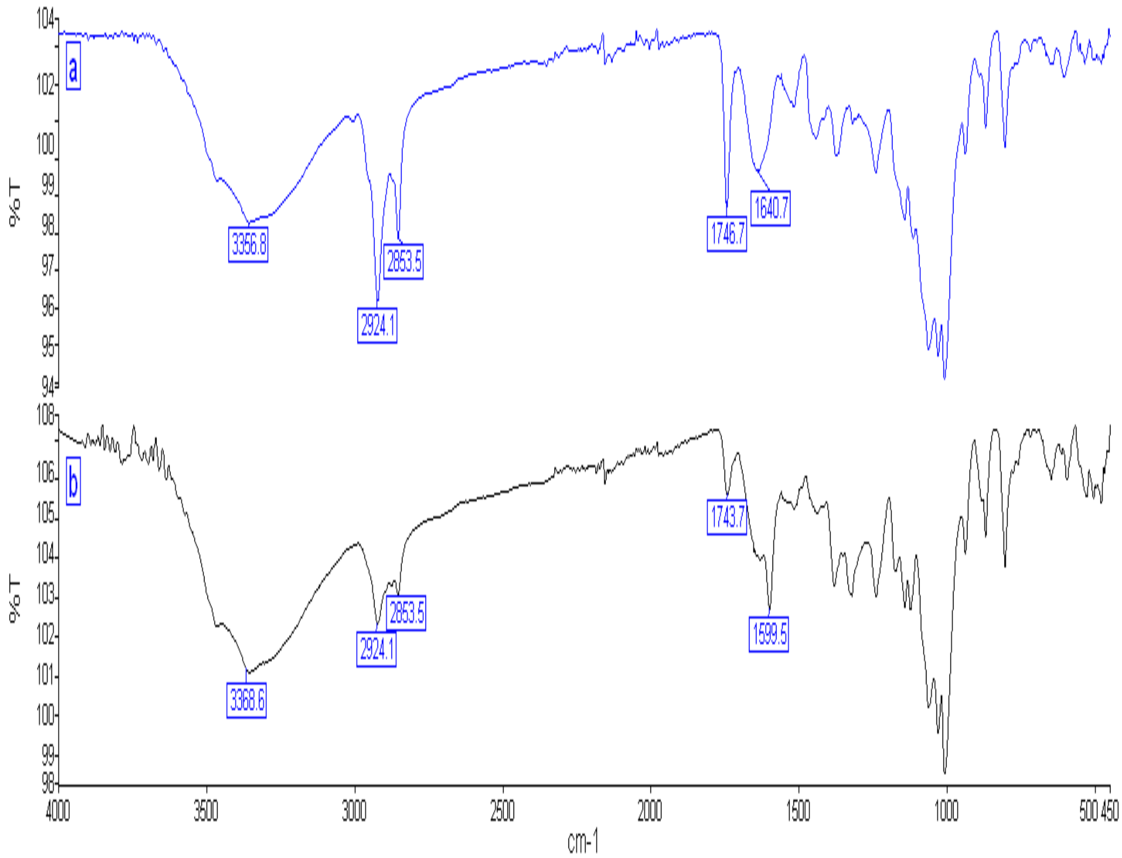

Figure 3.1: FT-IR Analysis of palm seeds powder (PSP) (a) before treatment with MB (b) after treatment with MB.

3.2 Adsorption Studies

3.2.1 The Effect of the Contact Time on MB Adsorption

The removal of MB was investigated at varying contact time. The adsorption of MB onto PSP was noted to occurred within 10 h and reached equilibrium at about 15 h. MB removal by PSP from aqueous solution proceeds in a rapid manner at the early stage (1-10 h) of adsorption due to high number of free available adsorption sites and after about 13 h, a decreasing removal percent was noted due to the saturation of the active sites until equilibrium was attained at 15 h as shown in (Figure3.2). After equilibrium achieved no feasible uptake was observed (Baek et al. (2010).

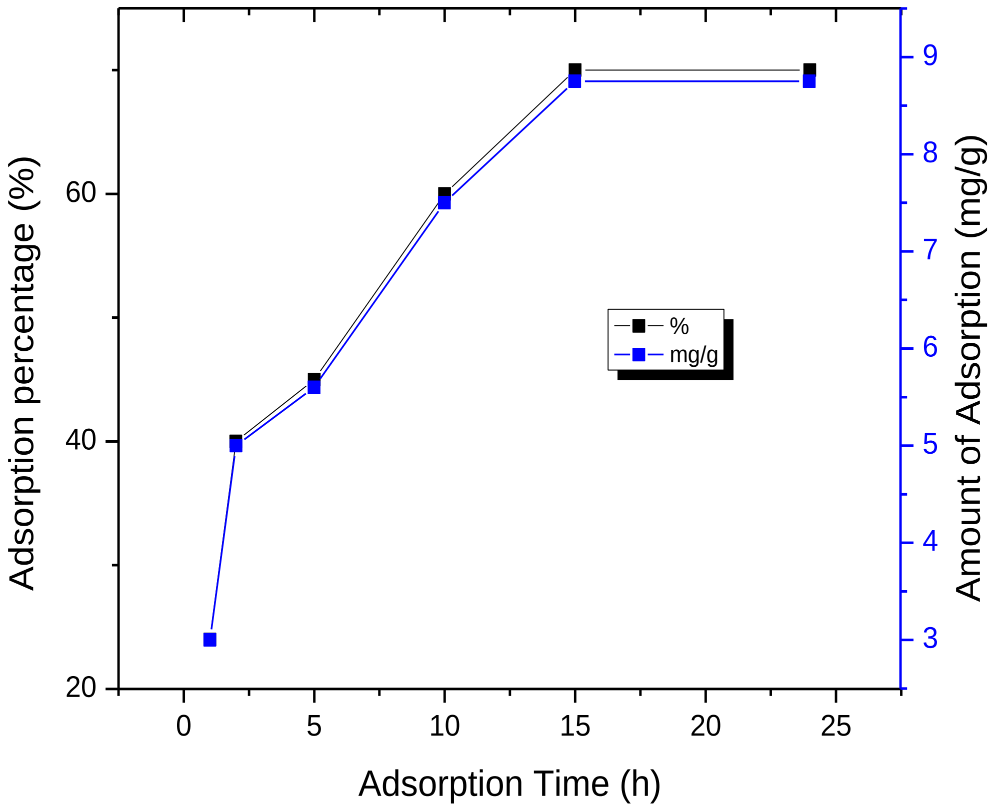

Figure 3.2: Effect of contact time on the adsorption (Adsorbent dosage: 0.3g, volume of the MB dye solution: 50 ml, initial concentration of MB 25 ppm, pH: 6.9, temperature: 298 K, particle size: 75-300 µm).

3.2.2 The Effect of PSP Dosage on MB Adsorption

The removal percent was observed to increase with increasing PSP dosage due increased surface area and active functional groups, resulting in increased removal efficiency. Meanwhile, an opposite trend was observed with the uptake capacities shown in (Figure 3.3). A decreasing uptake capacity with increasing PSP dosage could be as a result of rapid saturation of the total adsorption sites as the treatment process proceed and similar observation have been reported elsewhere (Baek et al. (2010).

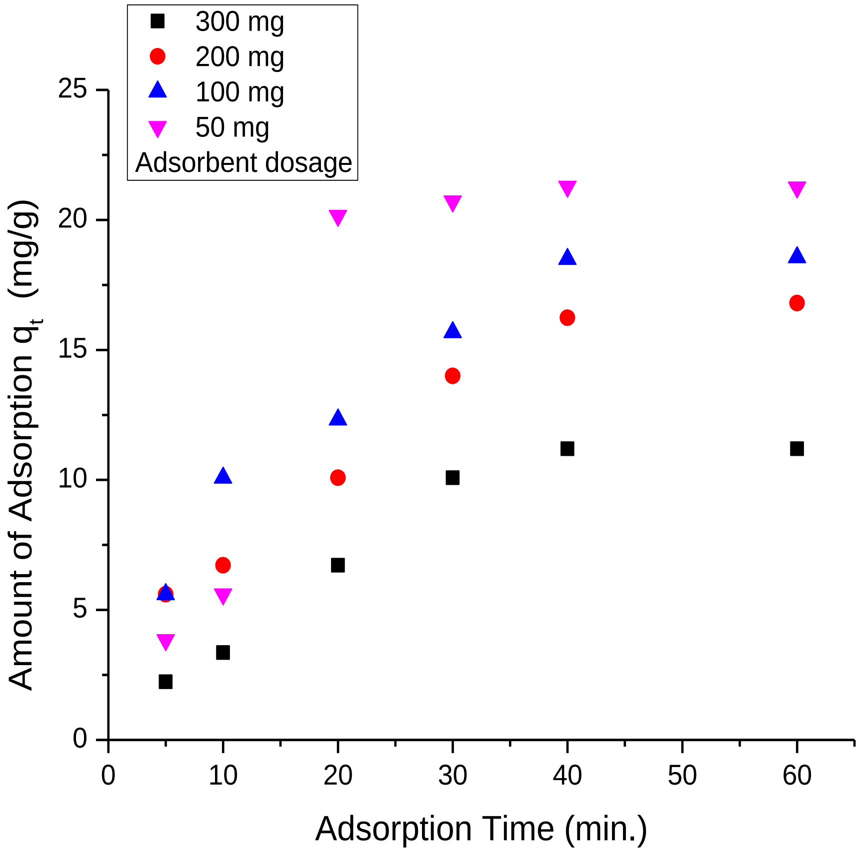

Figure 3.3: Effect of the adsorbent dose on the sorption capacity of MB onto PSP (volume of the MB dye solution: 50 ml, initial concentration of MB 100 ppm, pH: 6.9, temperature: 298 K, particle size: 75-300 µm).

3.2.3 Effect of Initial Concentration on MB Adsorption

The effect of initial concentration as a function of contact time is shown in (Figure 3.4). The amount of MB adsorbed decreases with increasing initial concentration, while maximum adsorption was obtained at the lower concentration. The greatest amount of methylene blue adsorbed onto PSP was attained at about 30 min, which is an indication that the adsorption is relatively fast due to the presence of more adsorption sites. Lower uptake capacity at higher dye concentration could be as a result of high ratio of dye molecules to available sites and subsequently the fractional adsorption becomes dependent of initial concentration. In the case of lower concentrations, the ratio of initial number of MB moles to the free available binding sites is low, and the fractional adsorption becomes independent of the initial concentration (Ayla et al. 2013).

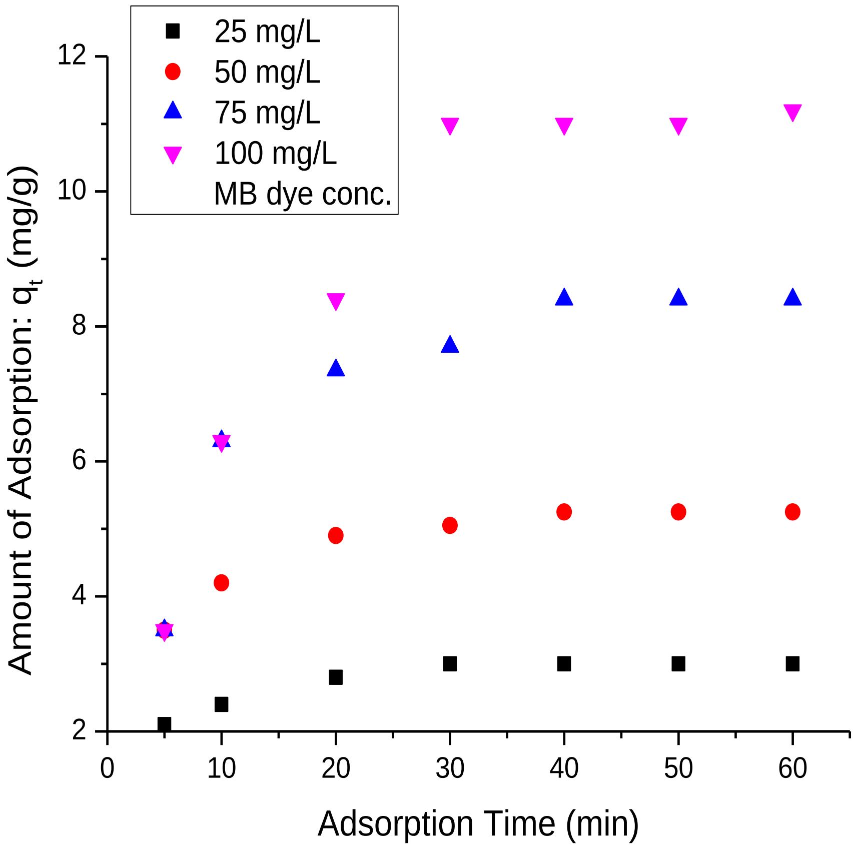

Figure 3.4: The effect of the initial dye concentration on the sorption of MB onto PSP (Adsorbent dosage: 0.3g, volume of the MB dye solution: 50 ml, pH: 6.9, temperature: 298 K, particle size: 75-300 µm, agitation speeds: 200 rpm).

3.2.4 Effect of pH on the Adsorption of MB Dye

The pH is a significant factor affecting adsorption of pollutants from wastewater. The adsorption of MB onto PSP increased with increasing pH from 2-6, and the maximum uptake capacity was attained at pH 7. This phenomenon may be ascribed to electrostatic interaction between cationic MB ions and the negative surface of the PSP. At low pH range the surfaces of PSP are protonated and competition set in between the PSP surfaces and MB ions resulting in low uptake capacity as shown in (Figure 3.5).

As the solution pH increases a decreasing charge density on the PSP surfaces was obtained, which is favorable for electrostatic interaction with cationic pollutants. At pH above 7.0, no substantial uptake was observed and this could as a result of saturation of the actives site or low stability of the dye molecules at higher pH as reported elsewhere (Gecgel et al. 2013).

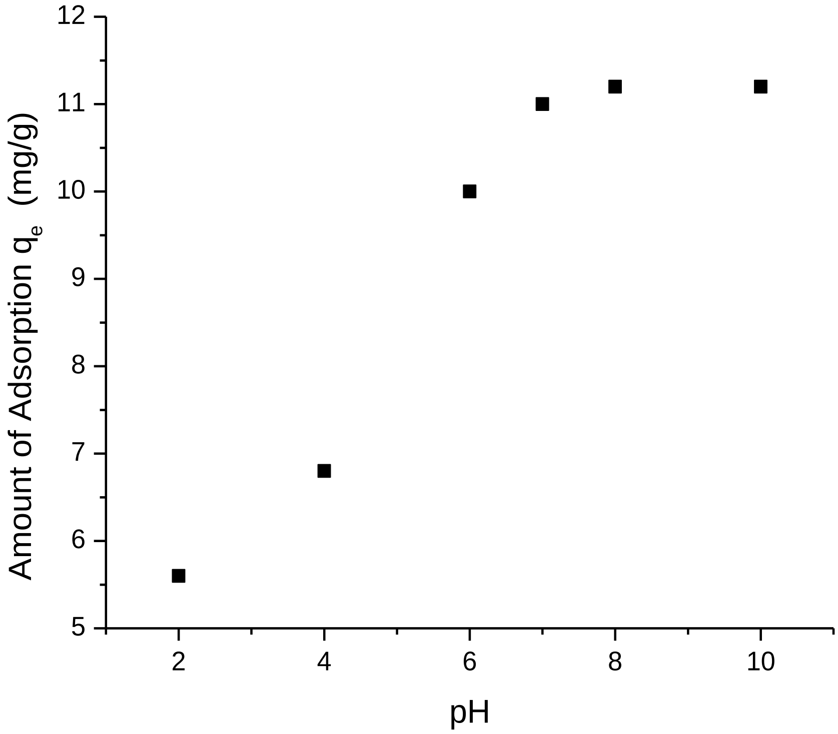

Figure 3.5: Effect of initial dye solution pH on the sorption of methylene blue capacity onto untreated palm seeds powder (Adsorbent dosage: 0.3g, Volume of the MB dye solution: 50 ml, Temperature: 298 K, Initial concentration of MB100 ppm, pH: 2, 4, 6, 7, 8 and 10, Particle size: 75-300 µm, Agitation speed: 200 rpm).

3.2.5 Effect of Inorganic Salt Concentration on the Adsorption of MB

The effect of salt concentration (KCl) on the removal of MB was studied at different KCl concentrations of 10, 50, 75 and100 mg/L with a fixed adsorbent dosage of 0.3 g as shown in (Figure 3.5). It was observed that the amount of dye adsorption by PSP decreased with increasing ionic strength. This result may be because of competition for adsorption sites between K^+ ions and MB, similar observation has been reported (Ghosh et al. 2013).

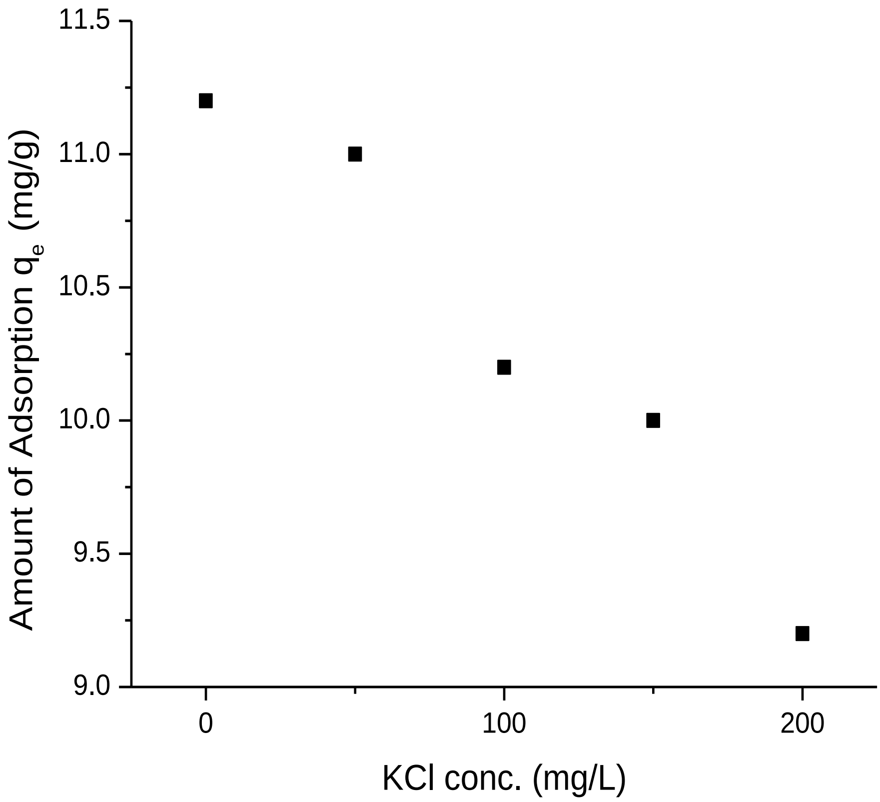

Figure 3.6: The effect of KCl salts concentration on the sorption of methylene blue dye onto untreated PSP (volume of dye solution = 50 mL; temperature = 25 ^{0}C, PSP dosage 0.3 g, pH = 6.9, and initial dye concentration 100 mg/L, agitation speed: 200 rpm)

3.3 Kinetics of the Adsorption

The two common kinetic models were applied to fit the experimental results of MB adsorption by PSP as represented below.

Lagergren equation for pseudo first order:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (2)$$

Where K_1 is the rate constant of the pseudo first-order adsorption (min^{-1}), At different times the amount of MB adsorbed onto PSP is the q_t (mg/g), and at the equilibrium the amount of methylene blue adsorbed onto palm seeds powder is q_e (mg/g) then after taking integral for above equation it becomes:

$$In(q_e - q_t) = Inq_e - K_1 t \qquad (3)$$

The intercepts and the slope of the plots of $\log(q_e - q_t)$ versus t were used to determine k_1 and q_e. The values obtained for k_1 and q_e are presented in (Table 3.1). The experimental data were noticed not to match with the pseudo-first order kinetics with lower R^2values obtained at various concentrations investigated as shown in (Table 3.1). It is concluded that the adsorption process cannot be explained by this model (Baekn et al. 2010).

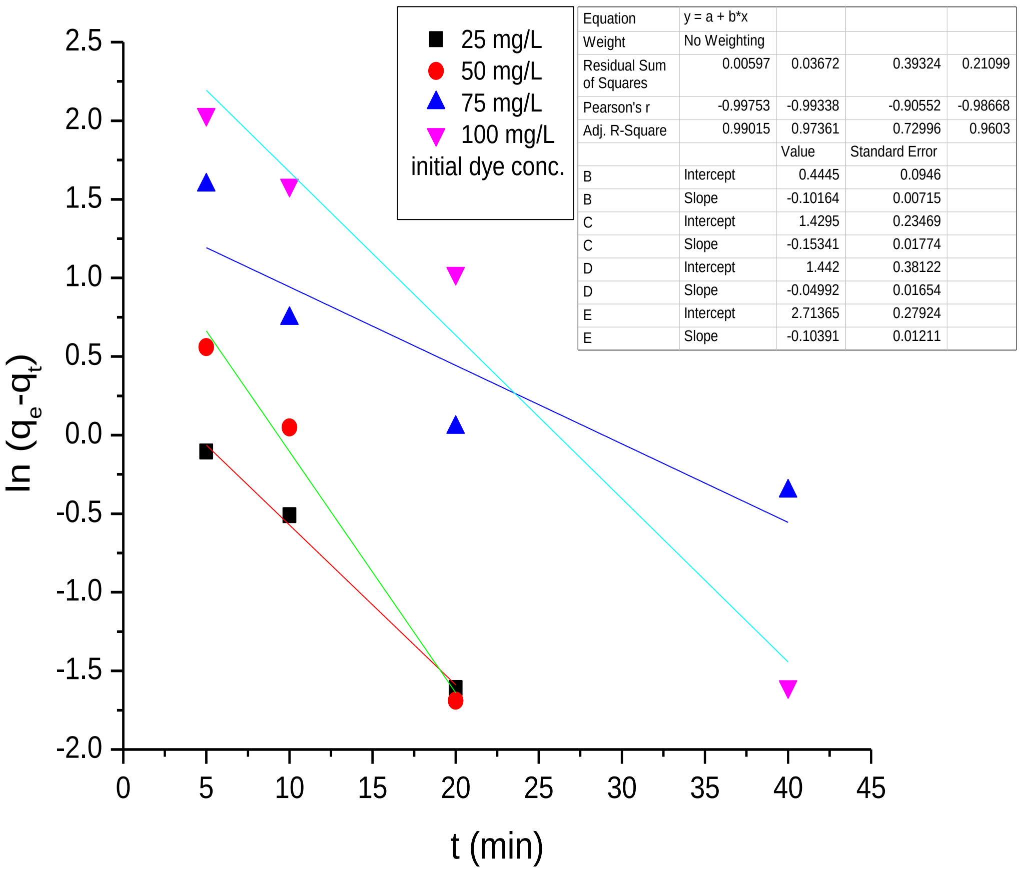

Figure 3.7: The Pseudo first-order kinetics plot for the sorption of methylene blue dye on to the palm seeds powder PSP.

Table 3.1: Kinetic parameters for adsorption of MB on to PSP

Initial concentration (mg/L)	Pseudo first-order kinetics			
	q_e (exp.)	K_1 min^{-1}	q_e (cal) mg/g	R^2
25	3.00	0.10164	1.5597	0.99015
50	5.25	0.15341	4.1766	0.97361
75	8.34	0.04992	4.2291	0.72996
100	11.2	0.10391	15.0842	0.9603

The pseudo second order model can be expressed as:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \qquad (4)$$

Where the pseudo second order kinetics rate constant is K_2 (g/mg.min) then the above equation (3) after taking integral becomes:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \qquad (5)$$

The value of correlation coefficient R^2 at various MB concentration were more than 0.991 and the experimental value were close to q_e calculated as shown in (Table 3.2).It is concluded that pseudo-second order model may is the most suitable to describe the adsorption of MB onto PSP.

Table 3.2: Kinetic parameters for adsorption of methylene blue on to PSP

Initial concentration (mg/L)	Pseudo-second order kinetics			
	q_e (exp.)	K_2 min^{-1}	q_e (cal) mg/g	R^2
25	3	0.1279	3.1534	0.99912
50	5.25	0.3515	5.5398	0.94033
75	8.34	0.01644	9.4589	0.99512
100	11.2	0.00581	13.9159	0.98362

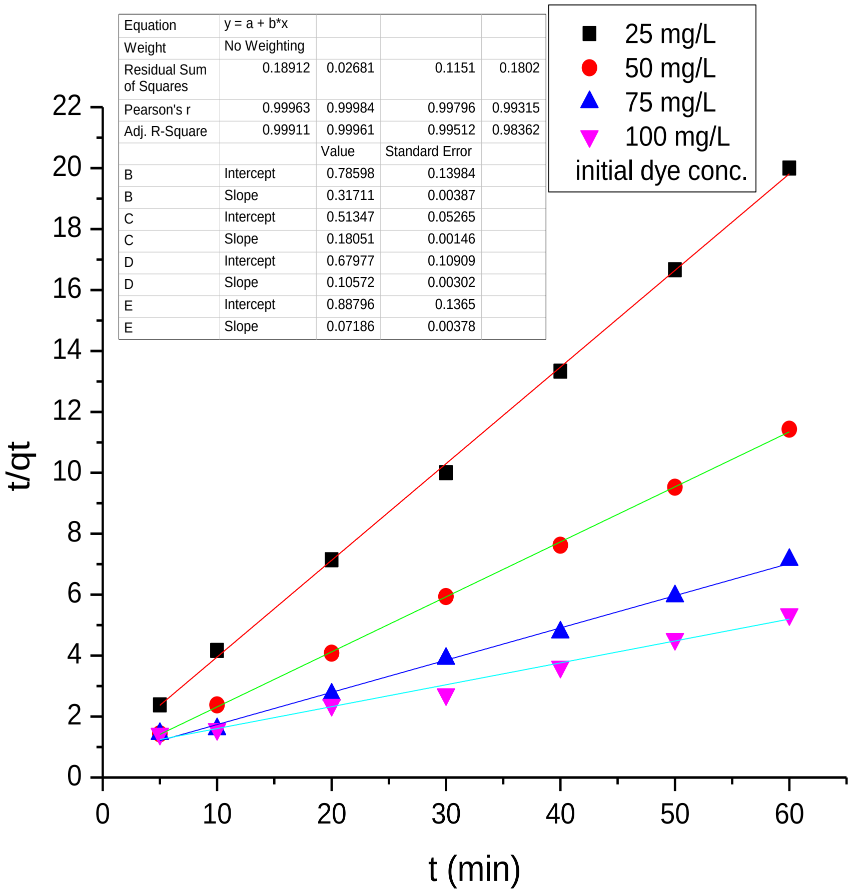

Figure 3.8: The pseudo second-order kinetics plot for the sorption of methylene blue dye on to the palm seeds powder PSP.

3.4 Thermodynamic Properties

The thermodynamic properties of PSP for MB adsorption were investigated at varying reaction temperature. The following were employed to elucidate the mechanism of MB removal by PSP:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \qquad (6)$$

$$InK = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (7)$$

Where, T, R, K are represented as the temperature (K), gas constant (8.314 J/mol K), and equilibrium constant respectively. Where K can be obtained from:

$$K = \frac{C_{ads}}{C_e} \qquad (8)$$

$$\Delta G\circ = -RT \ln K \qquad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (10)$$

Table 3.3: Thermodynamic parameters for the adsorption of MB onto PSP

				ΔGº (kj/mol)	
C^0 (mg/L)	ΔSº (kJ/mol)	Δ*H*º (kj/mol.K)	25 ^{0}C	35 ^{0}C	45 ^{0}C
100	0.0268	9.786	-1.776	-1.581	-1.237

The evaluated thermodynamic parameters (ΔGº, ΔHº, ΔSº) are outlined in (Table 3.3) The enthalpy change ΔHº for the adsorption of MB onto the PSP indicates that the adsorption processes endothermic, negative value of ΔGº indicates spontaneity and the positive ΔSº is an indication of increased randomness at the solute-PSP interface (Vadivelanet al. 2005).

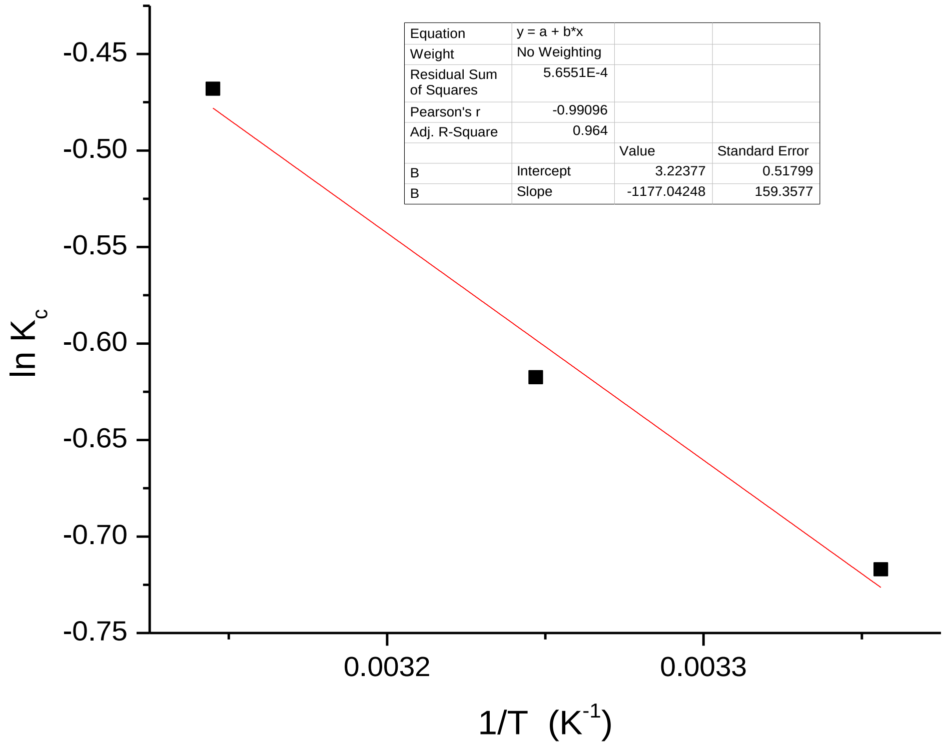

Figure 3.9: Temperature effect on the adsorption of methylene blue on to untreated palm seeds Powder (Volume of the MB dye solution: 50 ml, Adsorbent dosage: 0.3g, Temperature: 298 K, 308 K, 318 K, Initial concentration of MB 100 ppm, pH: 6.9, Particle size: 75-300

Chapter 4

CONCLUSION

The study indicates that the palm seeds powder might be used as an adsorbent for adsorption of methylene blue from aqueous solution. The adsorption potential of methylene blue from aqueous solution was noted to be affected by various independent variables. The adsorption process was strongly based upon reaction temperature, pH and initial dye concentration. The adsorption process followed pseudo-second order kinetics, the removal processes was endothermic and spontaneous in nature.

Finally, PSP has proved to be remarkable adsorbent for treatment of dye-polluted effluent and its efficiency is comparable to expensive or chemically modified adsorbent used by other researchers.

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