Adsorption of Methylene Blue from Solution Using Anionic Surfactant Modified Palm Seed Powder

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ABSTRACT

Cationic dyes are widely utilized in plastic, textile, leather and tanning industries. High concentrations of these dyes in aquatic environments pose serious threat to human health and the environment due to their toxic profile. Therefore, various environmental protection agencies and governments have established standard control limits to the quality of domestic and industrial effluents before being discharged to water bodies. Among the various treatment processes, adsorption technique was employed in this study for the treatment of methylene blue (MB) simulated effluents under various operational conditions.

Here, palm seed powder (PS) was employed as adsorbent for removal of MB from laboratory simulated colored effluent. The sorption capacity of the PS was improved through surface modification by anionic surfactant (sodium dodecyl sulfate). Comparatively, the modified palm seed powder (MPS) efficiently removed 93% of MB while only 57% removal was recorded by PS after 720 min treatment time. The MPS sorption capacity was affected by the presence of interfering ions (Na^+ and Mg^{2+}); however, about 18 mg/g of MB was removed even at salt concentration of 100 mg/L.

Freundlich isotherm fits suitably the MPS experimental data more than Langmuir isotherm, indicating multilayer sorption process of MB on the heterogeneous MPS surface. The Weber–Morris models confirmed that intraparticle transport played a significant role in the sorption process. **Keywords**: Adsorption; modified palm seed powder, cationic dyes removal

ÖZ

Katyonikboyalar genellik'le pilastik, tekstil, deri ve solaryum endüstürilerinde kullanılır. Bu boyaların yüksek konsantreli olanları akuatik çevrelerde, toksik kimliklerine bağlı, isnsan sağlığı ve çevresi için ciddi bir tehdit oluşturmaktadır. Bu yüzden çeşitli çevre koruma kurumları ve devletler, yerel ve endüstriyel akıntıların kalitesi ile ilgili su kaynaklarına dökülmeden önce standart kontrol limitleri belirlemiştir. Çeşitli tehdit süreçlerinin yanısıra, adsorpsiyon (emme) teknikleri, çeşitli mavi metilen tehditleri similasyonunun,türlü kondisyonlar, araştırmasında kullanılmıştır.

Burda, palmiye ağacı tohumunun pudrası laboratuvardadaki mavi metileni renk içeren akıntıdan ayırmak icin emici işlemini yapmakta. Palmiye tohumunun soğurma kapasitesi, anyonik yüzeyin(sodyum dodesil sülfat) yüzeysel değişiklikleri ile kanıtlanmıştır. Orantılı olarak, değişmiş olan palmiye tohumu pudrası etkili biçimde mavi metilenin 93% ortadan kaldırmasına karşı, normal palmiye tohumu sadece 57% mavi metileni 720 dakika işlemden sonra yok etmiştir. Modifiye edilmiş palmiye tohumunun soğurma kapasitesi bazı anyonik etkenlerin (Na+ ve Mg2+) varlığının tesiri altında değişmiştir. Ancak mavi metilenin yaklaşik 18mg/g, 100mg/L konsantredeki tuzda bile ortadan kaldırılmıştır.

Mavi metilenin farklı yapıdaki modifiyeli palmiye tohumu yüzeyinden soğurma sürecindeki değişkenlerinde, Freundlich izotermi, Langmuir izotermine göremodifiye edilmiş palmiye tohumu araştırması verilerine daha uygun. Weber-Morris modelleri kanıtlamıştır ki intraparticle arası ulaşım soğurma sürecinde önemli role sahiptir.

Anahtar Kelimeler: Emme; Modifiye edilmis palmiye tohumu pudrası; Katyonik boya çözücü

DEDICATION

I am dedicating this research for all the people who supported me, to god, to my family, for all their love, patience, kindness, and also to myself, for accomplishing another milestone in my life.

ACKNOWLEDGMENT

I am deeply thankful for my supervisor Assoc. Prof. Dr. Mustafa Gazi , whose stimulating, motivation and valuable ideas helped me to complete this work.

Special thanks to my dear wife Nasima A. Hwaileh for her moral support and endless love, who was always standing by me in my hard times during this work.

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Chapter 1

INTRODUCTION

1.1 Overview of Dye Pollution

Environmental pollution is currently attracting serious concern due to the continuous discharge of toxic pollutants such as pigments and dyes into the aquatic environments. The growing health hazards are attributed to the rapid development of plastic, leather tanning, pigment and textile industries dye (Yang et al. 2014). The color is one of the visible characteristics of the textile effluents; it disrupts the aesthetic nature of the water, obstructs sunlight penetration into the aquatic bodies and impedes photosynthetic mechanism (Oladipo et al. 2015). Most of these dyes are reported to be mutagenic, carcinogenic and stable to bio-degradation due to their complex aromatic structures (Khan et al., 2008; Janaki et al. 2012; Fernandez et al. 2010; Yu et al. 2015).

Approximately over 12,000 various dyes are utilisedindustrially, and more than 700,000 tonnes of synthetic dyes are produced worldwide yearly (Zollinger, 1987; Robinson et al. 2001; Yang et al. 2014). The textile materials can be dyed via a semi-continuous, continuous, batch processes depending on many characteristics such as the type of materials, property of dye and quality assessment in the dyed fabrics (Chequer et al. 2013). The most common process is the batch system due to its simplicity and cost. During the dyeing and finishing processes, approximately 200 000 tonnes of dyes are lost to the effluents annually due to the inefficiency of the processes (Ogugbue and Sawidis, 2011). However, the common conventional wastewater treatment processes are unable to eliminate these dyes due to their high stability to temperature, light, detergents and bleach (Couto, 2009).

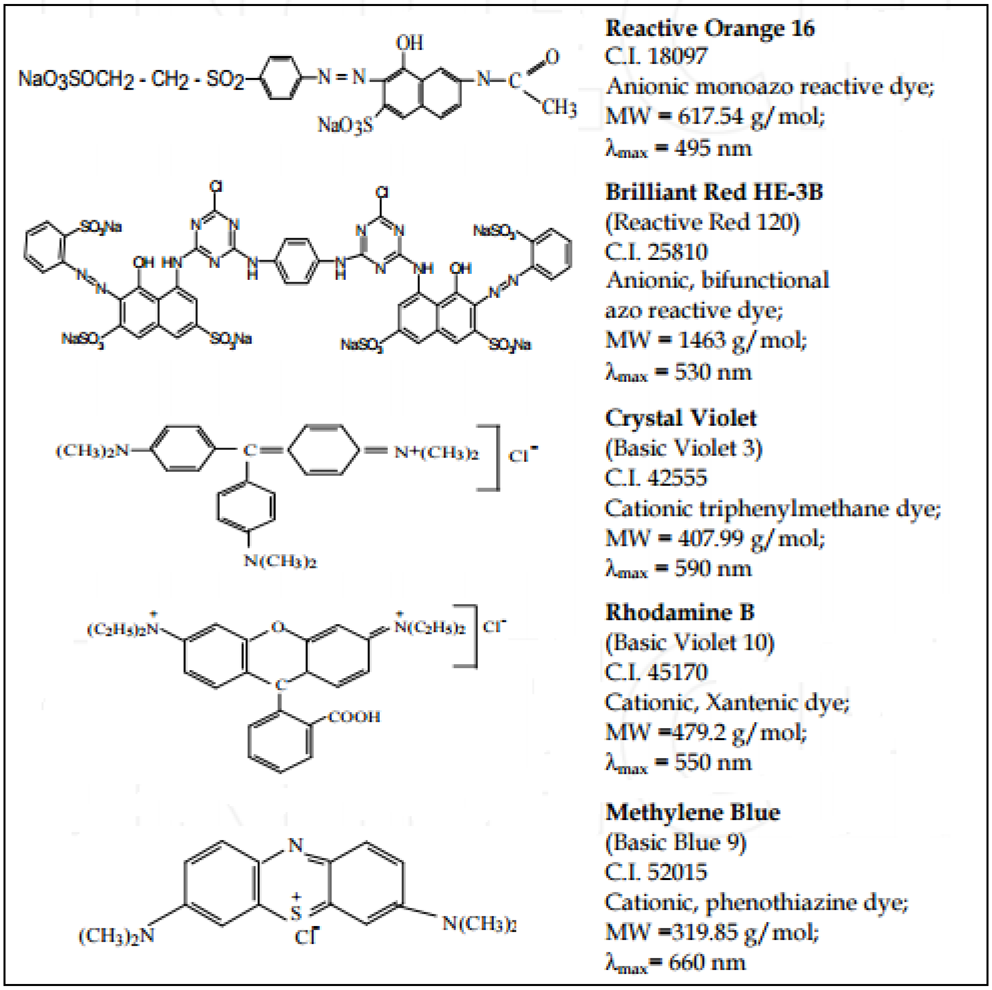
Figure 1: Direct discharge of textile effluents from dyeing industries

1.2 Classification and Characteristics of Textile Dyes

Dyes are classified as natural, and synthetic compounds based on origin and colorify the universe through various products. The origin and nature of dyes are primary criteria for their classification. Natural dyes extracted from animal and vegetable resources were majorly used in textile industries until 1856 (Carmen and Daniela, 2012). For instance, dyes extracted from madder plants were applied for dyeing and wrapping of Egyptian mummies accessories during the ancient period. Just after 1856, the synthetic dyes such as mauve (aniline) dye, brilliant fuchsia and some azo dyes were synthesised by W.H. Perkin (UK) and P. Gries (Germany) in 1858 (Welham, 2000).

These synthetic dyes have aromatic rings within their structure and various functional groups. Their colour is characteristic of the chromogen–chromophore structure and their dyeing capacity is attributed to the auxochromes electron donor groups (Carmen and Daniela, 2012). The chromogen unit is constituted from the aromatic rings of anthracene, benzene, or naphthalene. While the chromophore is represented by the ethylene group (=C=C=), carbon-sulphur groups (≡CS-S-C≡; =C=S), nitro (–NO-OH–;–NO_2), azo group (–N=N–), etc. The binding capacity of the dyes are characteristics of the auxochrome (ionizable) groups such as the amino group (–NH_2), carboxyl groups (–COOH) and sulphonic (–SO_3H) groups (Welham, 2000; Suteu et al. 2011).

Textile dyes are classified into two groups based on (a) its application (such as disperse, azo, acid, sulphur dye, basic, direct, reactive), and (2) its chemical structure (such as anthraquinone, azo, xanthene, quinolone, carotenoid, nitro). Some of these dyes are depicted structure and property-wise in figure 2.



Reactive Orange 16
C.I. 18097
Anionic monoazo reactive dye;
MW = 617.54 g/mol;
λ_{max} = 495 nm

Brilliant Red HE-3B
(Reactive Red 120)
C.I. 25810
Anionic, bifunctional
azo reactive dye;
MW = 1463 g/mol;
λ_{max} = 530 nm

Crystal Violet
(Basic Violet 3)
C.I. 42555
Cationic triphenylmethane dye;
MW = 407.99 g/mol;
λ_{max} = 590 nm

Rhodamine B
(Basic Violet 10)
C.I. 45170
Cationic, Xantenic dye;
MW =479.2 g/mol;
λ_{max} = 550 nm

Methylene Blue
(Basic Blue 9)
C.I. 52015
Cationic, phenothiazine dye;
MW =319.85 g/mol;
λ_{max}= 660 nm

Figure 2: Various types of dyes based on classification
Table, p.3+36+55 Macoveanu et al (2002)

On production quantities, azo dyes constitute the largest group of organic colourants (60-70%) produced worldwide (Carliell et al. 1998). The wide range of application of azo dyes is attributed to their cost effectiveness, ease of synthesis, high molar extinction coefficient, suitable structural diversity and medium-to-high fastness properties as compared to other organic and natural dyes (Bafana et al. 2011; Seesuriyachan et al. 2007). The toxic impacts of the azo dyes are mainly due to the generation of aryl amine derivatives during the bio-reduction of the azo bond (Rajaguru et al. 1999). Azo dyes are metabolised by azo-reductases or nitro-reductases to toxic aromatic amines after ingestion in the intestinal microorganisms (Umbuzeiro et al. 2005).

The main anionic dyes are the water-soluble, reactive, brightly colored direct and acid dyes (Robinson et al. 2001). The non-ionic dyes such as disperse dyes do not ionise in the aquatic environment and have a high rate of bioaccumulation and the common cationic dyes are the azo and anthraquinone dyes, and these types of dyes are resistant to degradation because of their clustered aromatic structure.

1.3 Polluting Effects and Environmental Problems of Textile Dyes

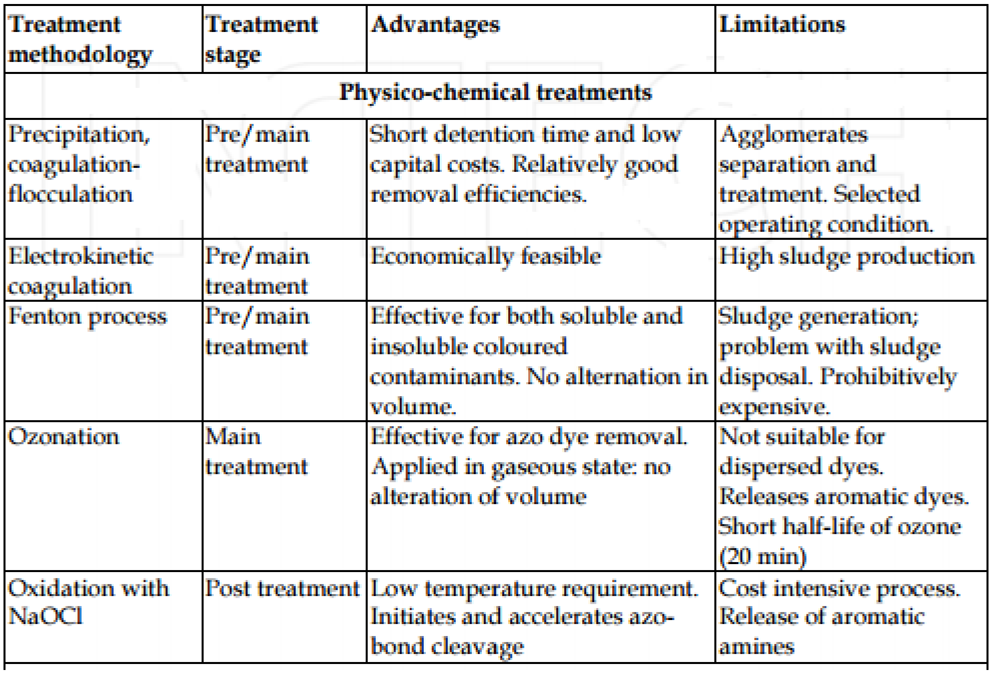
Various environmental and eco-toxicological problems are associated with residual textile effluents. Re-oxygenation capacity of water bodies and light penetration are inhibited by the high concentrations of dyes, thus upsetting the biological activity of aquatic species (Zaharia et al. 2009). Toxic effects are one of the polluting issues generated from dye-containing wastewaters. Due to their complex aromatic configurations, most of the dyes cause allergies, skin irritation or different tissue damages when exposed to an overdose of even trace concentration. Various azo dyes electron-donating substituents can disrupt the DNA leading to the formation of malignant tumours (Bafana et al. 2011; Seesuriyachan et al. 2007; Oladipo et al. 2014).

1.4 Elimination and Separation of Dyes from Industrial Wastewater

Organic dyes must be eliminated from industrial wastewater through efficient and viable treatment process before releasing the effluents to water streams. The common separation techniques include filtration, centrifugation, reverse osmosis and flotation. Also, various physico-chemical techniques (such as chemical precipitation, ionic exchange, adsorption and coagulation-flocculation) have been applied to separate or eliminate dissolved pollutants from effluents (RameshBabu et al. 2007; Zaharia, 2006; Robinson et al. 2001; Suteu et al., 2009).

Similarly, partial or complete elimination of pollutants has been reported by biological and advanced oxidation processes (Dos-Santos et al. 2004; Wiesmann et al. 2007). Chemical oxidation involves the transformation of pollutants by chemical oxidising agents to less harmful compounds and/or easily biodegradable by-products. However, recent synthetic dyes are resistant to mild oxidation conditions. Thus, efficient treatment technique must be achieved by powerful oxidising agents such as Fenton reagents, ozone/UV, chlorines, peroxide/UV, or combinations. The UV/H_2O_2 treatment can mineralize dye molecules to less hazardous organic compounds, H_2O, CO_2 or inorganic oxides, etc (Carmen and Daniela, 2012).

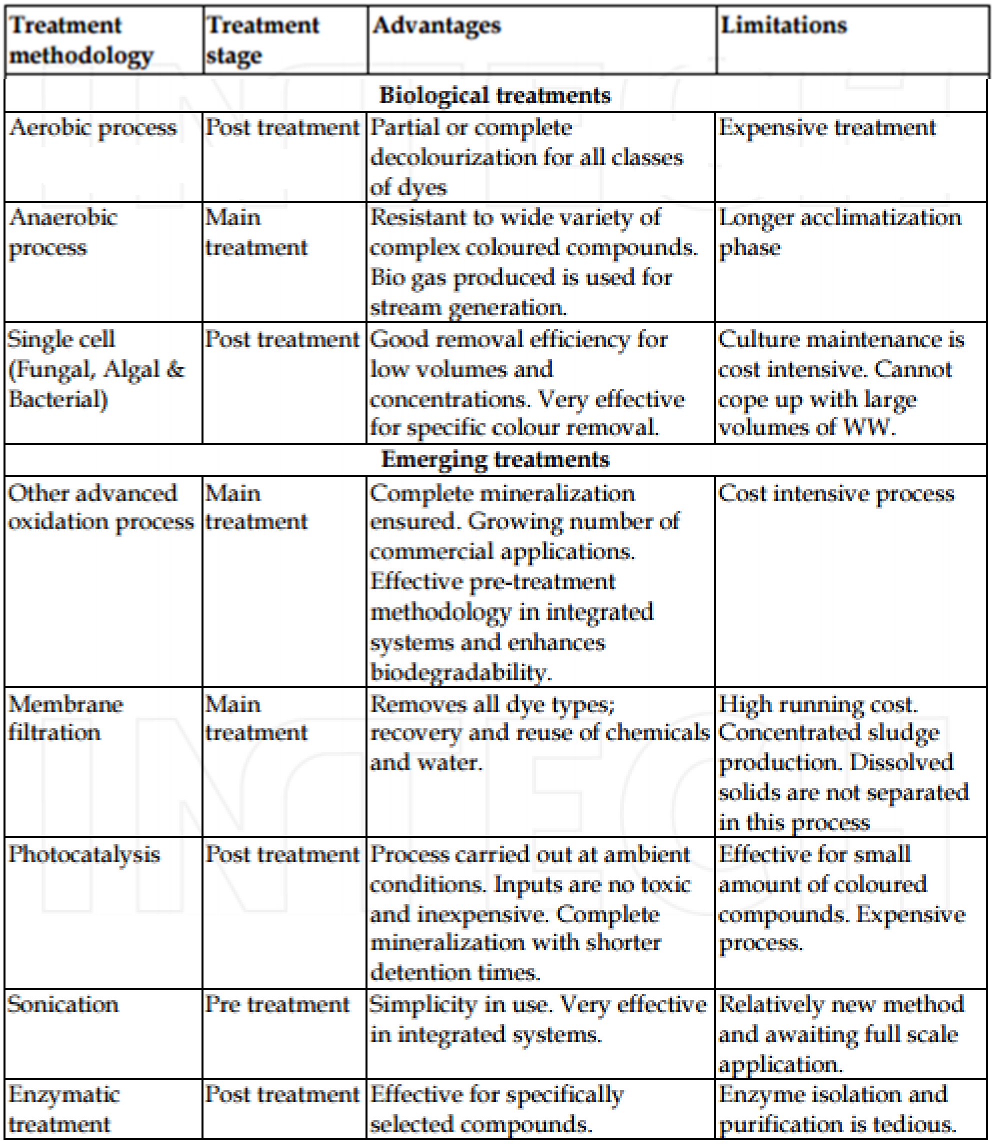
Ion exchange technique has not been applied widely for treatment of dye-laden effluents due to the general perception that ion exchangers cannot accommodate varieties of dyes (Slokar and Le Marechal, 1997; Carmen and Daniela, 2012). The ion-exchange process involves the interaction of ionic species within the wastewater and the adsorptive material. Ion exchange process is different from the adsorption process by morphology and nature of adsorbents (Macoveanu et al. 2002). The advantages and limitations of some of the mentioned treatment methodologies are depicted in Figure 3 and 4.



Treatment methodology	Treatment stage	Advantages	Limitations
Physico-chemical treatments			
Precipitation, coagulation-flocculation	Pre/main treatment	Short detention time and low capital costs. Relatively good removal efficiencies.	Agglomerates separation and treatment. Selected operating condition.
Electrokinetic coagulation	Pre/main treatment	Economically feasible	High sludge production
Fenton process	Pre/main treatment	Effective for both soluble and insoluble coloured contaminants. No alternation in volume.	Sludge generation; problem with sludge disposal. Prohibitively expensive.
Ozonation	Main treatment	Effective for azo dye removal. Applied in gaseous state: no alteration of volume	Not suitable for dispersed dyes. Releases aromatic dyes. Short half-life of ozone (20 min)
Oxidation with NaOCl	Post treatment	Low temperature requirement. Initiates and accelerates azo-bond cleavage	Cost intensive process. Release of aromatic amines

Figure 3: Advantages and limitations of various treatment technologies; **Table p.18,** Robinson et al (2001)

Biological treatments can be performed under anaerobic, aerobic or combined aerobic-anaerobic conditions. Aerobic microorganisms are currently being applied in biodegradation process by utilising molecular oxygen. Under aerobic conditions, most azo dyes are rapidly degraded by oxidation of the substituent's groups. The main advantage of biological treatment as compared with certain physico-chemical techniques is that more than 70% of organic pollutants may be transformed into bio-solids (Anjaneyulu et al. 2005). The advantages of each biological treatment process and emerging techniques as well as their limitations are listed in Figure 4.

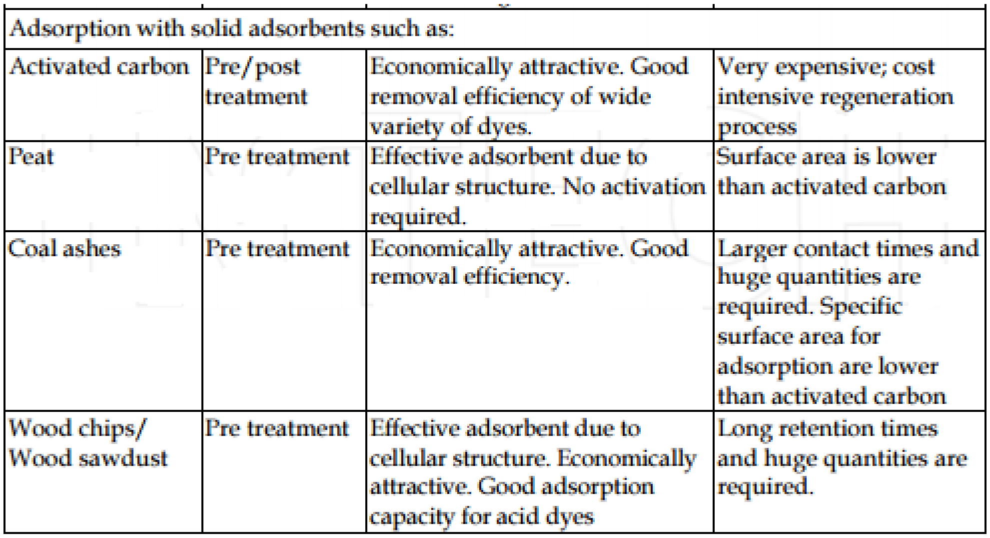


Treatment methodology	Treatment stage	Advantages	Limitations
Biological treatments			
Aerobic process	Post treatment	Partial or complete decolourization for all classes of dyes	Expensive treatment
Anaerobic process	Main treatment	Resistant to wide variety of complex coloured compounds. Bio gas produced is used for stream generation.	Longer acclimatization phase
Single cell (Fungal, Algal & Bacterial)	Post treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific colour removal.	Culture maintenance is cost intensive. Cannot cope up with large volumes of WW.
Emerging treatments			
Other advanced oxidation process	Main treatment	Complete mineralization ensured. Growing number of commercial applications. Effective pre-treatment methodology in integrated systems and enhances biodegradability.	Cost intensive process
Membrane filtration	Main treatment	Removes all dye types; recovery and reuse of chemicals and water.	High running cost. Concentrated sludge production. Dissolved solids are not separated in this process
Photocatalysis	Post treatment	Process carried out at ambient conditions. Inputs are no toxic and inexpensive. Complete mineralization with shorter detention times.	Effective for small amount of coloured compounds. Expensive process.
Sonication	Pre treatment	Simplicity in use. Very effective in integrated systems.	Relatively new method and awaiting full scale application.
Enzymatic treatment	Post treatment	Effective for specifically selected compounds.	Enzyme isolation and purification is tedious.

Figure 4: Advantages and limitations of biological and other emerging treatments
Table p. 18, Robinson et al (2001)

1.5 Adsorption Process

The adsorption process is an effective, economically feasible and proven treatment process with potential application in heavy metal and dye-laden wastewater (Oladipo and Gazi, 2016). It involves the transfer of soluble pollutants (adsorbates) from aqueous solution to the surface of solid materials (adsorbents). The adsorbent possesses finite capacity and surface functional groups for trapping and interacting with various compounds to be eliminated. In most cases, the 'spent' adsorbents are regenerated and reused, making the process cost effective. The major factors influencing adsorption process include adsorbent surface area, solution pH, adsorbate/adsorbent interaction, contact time, adsorbent size, presence of interfering ions and temperature (Lafi and Hafiane, 2016; Zhao et al. 2014). Activated carbon is the most commonly used adsorbent because it is effective and possesses high sorption capacity. However, its high cost, low desorption kinetics, and poor regeneration after use, limits its industrial use. Hence, increasing attentions are directed to the development of low-cost, highly sorptive and effective materials for wastewater treatment (Chen et al. 2011; Gupta et al. 2011; Das et al. 2012).



Adsorption with solid adsorbents such as:			
Activated carbon	Pre/post treatment	Economically attractive. Good removal efficiency of wide variety of dyes.	Very expensive; cost intensive regeneration process
Peat	Pre treatment	Effective adsorbent due to cellular structure. No activation required.	Surface area is lower than activated carbon
Coal ashes	Pre treatment	Economically attractive. Good removal efficiency.	Larger contact times and huge quantities are required. Specific surface area for adsorption are lower than activated carbon
Wood chips/ Wood sawdust	Pre treatment	Effective adsorbent due to cellular structure. Economically attractive. Good adsorption capacity for acid dyes	Long retention times and huge quantities are required.

Figure 5: Advantages and drawbacks of selected adsorbents; Comparison between solid adsorbents,p.16, Makoveanu et al (2002)

Various low-cost agricultural or industrial wastes have been used recently as adsorbents materials (such as clay, rice husk, neem leaf powder, coal ash, biochar and other cellulosic wastes, etc.). The use of these low-cost adsorbents is advantageous because of their cheapness and bio-availability, and some detailed information has been provided in Figure 5 regarding selected adsorbents. However, the low sorption capacity of most of the low-cost adsorbents can be enhanced via surface modification since the sorption takes place primarily on the adsorbent surface. Agricultural waste like a palm seed is capable of adsorbing varieties of pollutants as a readily available inexpensive bio-waste. The palm seed powder is polysaccharide in nature and contains various functional groups that can interact with dyes, heavy metals and other pollutants. Therefore, the palm seed powder is considered as alternative biosorbent for treatment of dye-laden wastewater.

1.6 Research Objectives

The dye-laden wastewaters are continuously discharged into water bodies without proper treatment, hence resulting in environmental threats to both aquatic species and human beings. The objectives of the current work are:

a. To examine the adsorption efficiency of waste palm seed powders towards dye-laden industrial and domestic wastewaters.
b. To enhance the sorption capacity and stability of palm seed powder for wastewater treatment.
c. To study the effect of various parameters like pH, contact time, adsorbant dosage, ionic strenght and initial dye concentration, affecting the treatment of cationic dyes.
d. To establish the sorption mechanisms of non-modified and surfactant modified palm seed powders.

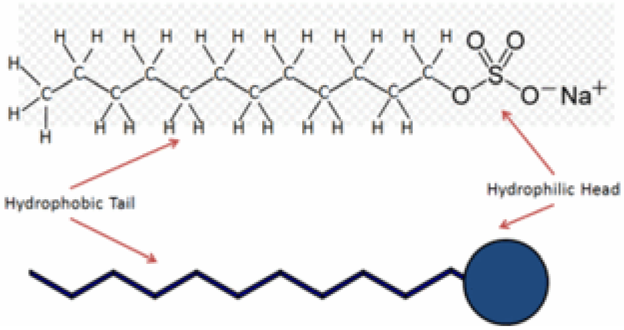
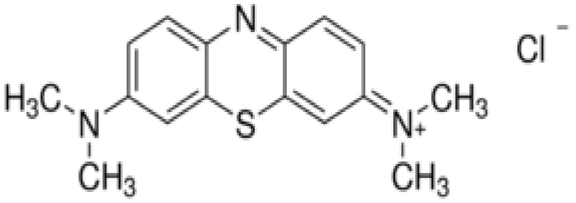
Chapter 2

EXPERIMENTAL

2.1 Materials and Reagents

All the reagents used in this research is of analytical grade and were applied without purification.

Table 1: Chemical structure and properties of SDS and MB

	Chemical Structures of SDS and MB	Properties
SDS		**Molar mass**: 288.372 g/mol **Density**: 1.01 g/mL **Water Solubility**: 40 g/L **Odor**: Odorless **Type**: Anionic surfactant
MB		**Molar mass**: 319.85 g/mol **Density**: 0.98 g/mL **Water Solubility**: 2.5 g/100 mL **Absorption**: λ_{max} 665 nm **Type**: Cationic dye

Methylene blue (MB) dye, sodium hydroxide and hydrochloric acid were purchased from Sigma–Aldrich (Germany). The sodium dodecyl sulphate(SDS) is the anionic surfactant used to modify the surface of the biomass and was purchased from Riedel-de Haën (Germany). The structure and chemical properties of the SDS and (MB) dye are shownin Table 1. Distilled water was utilised for preparation of all the solutions in this study. The solution pH was moderatedwith 0.1 mol/L NaOH and HCl solutions.

2.2 Sample Collection and Pre-treatment

Palm seeds with fruity shell were collected from Eastern Mediterranean University campus, North Cyprus. The collected palm seeds were washed with tap water to remove adhered soil particles and then soaked in boiled tap water for 15 min. The hot water removed the colouring matter, outer shell and organic materials from the fruity palm seeds (PS) as shown in Fig. 1. Then, the PS was dried in an oven at 70 °C for 24 h. The PS was milled into powder, sieved using standard meshes into 125–250 µm and preserved in the ambient condition for later use.

Figure 6: Fleshy and non-fleshy palm seeds

2.3 Preparation of Surfactant Modified Palm Seed Powder (MPS)

The palm seed powder was modified through impregnation method following a modified procedure described elsewhere (Das et al. 2012). Specifically, 5.0 g of PS was mixed with 50 mL of freshly prepared 0.6 mol/L SDS solution in a conical flask. The flask containing the mixture was agitated at 40 ± 2.5 °C for 24 h. The modified PS was filtered, washed three times with distilled water to eliminate unreacted surfactant and then dried at 40 °C overnight. The resulting adsorbent was designated as MPS as shown in Fig.7, characterised and used for sorption experiments.

Figure 7: Non-modified and surfactant-modified palm seed powders

2.4 Characterization of PS and MPS

The PS and MPS were characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and pH point zero charge (pH_{pzc}) as described elsewhere (Oladipo et al., 2015).

2.5 Batch Sorption Studies

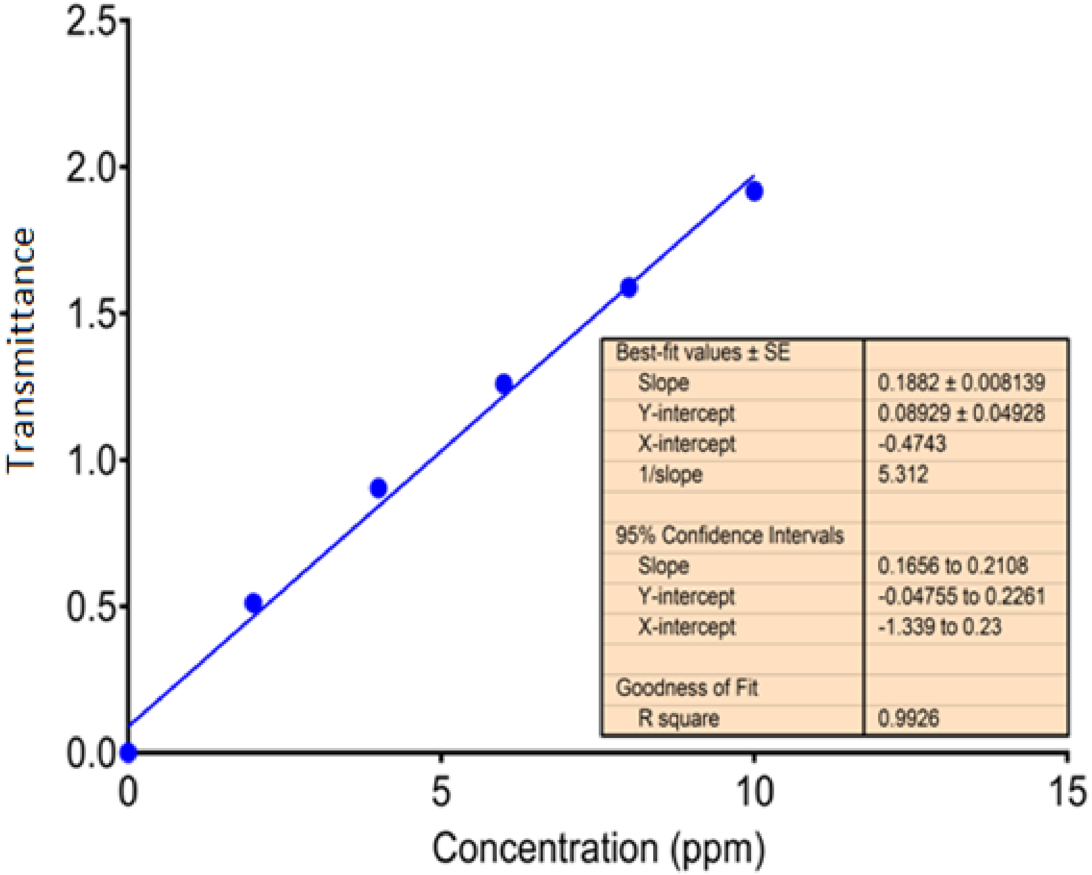
Stock solution (100 ppm) of MB was prepared by dissolving an appropriate amount of MB in distilled water and diluted to get the desired working concentrations. The calibration curve was prepared by measuring the absorbance of pre-selected concentration (2–10 ppm) of the MB. The concentration of MB in the solution was measured using the UV–vis spectrophotometer (T80+PG Instruments Ltd., Leicestershire, UK) at 665nm. In this research, 50 mL of MB solution was introduced into 100 mL flasks containing 50 mg adsorbents (MPS and PS).

The flasks were agitated on a rotatory shaker at 200 rpm, and 12 samples were withdrawn periodically during 24 hours for analyses. The isotherm studies were performed by varying the MB initial concentration (10–50 ppm) at a constant pH. The kinetic data were obtained from the periodical assessment of the sample solution. The effect of salt concentrations (NaCl and $MgCl_2$) was evaluated on the sorption efficiency of PS and MPS. Effect of solution pH, reaction time and temperature on the adsorption capacities of the adsorbents was checked. For reproducibility, duplicate experiments were performed under identical conditions, and the average values reported. The amounts of adsorption and removal efficiency were calculated according to equations (1) and (2), respectively:

$$\mathrm{q_e} = V\frac{\mathrm{C_0 - C_e}}{\mathrm{m}} \qquad (1)$$

$$\mathrm{R(\%)} = 100 \times \frac{\mathrm{C_0 - C_e}}{\mathrm{C_0}} \qquad (2)$$

where q_e is the amount of dye adsorbed per unit gram of the adsorbent (mg/g), V (L) is the solution volume, R(%) is the percentage removal, C_o (mg/L)is the initial concentration of MB, and C_e (mg/L) is the equilibrium concentration.



Best-fit values ± SE	
Slope	0.1882 ± 0.008139
Y-intercept	0.08929 ± 0.04928
X-intercept	-0.4743
1/slope	5.312
95% Confidence Intervals	
Slope	0.1656 to 0.2108
Y-intercept	-0.04755 to 0.2261
X-intercept	-1.339 to 0.23
Goodness of Fit	
R square	0.9926

Figure 8: Calibration curve for MB adsorption

Chapter 3

RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The point of zero charge (pHpzc) of PS and MPS occurred at pH 6.0 and 5.0, respectively. The adsorbents were positively charged below this pH and negatively charged above it (Ngwabebhoh et al. 2016).

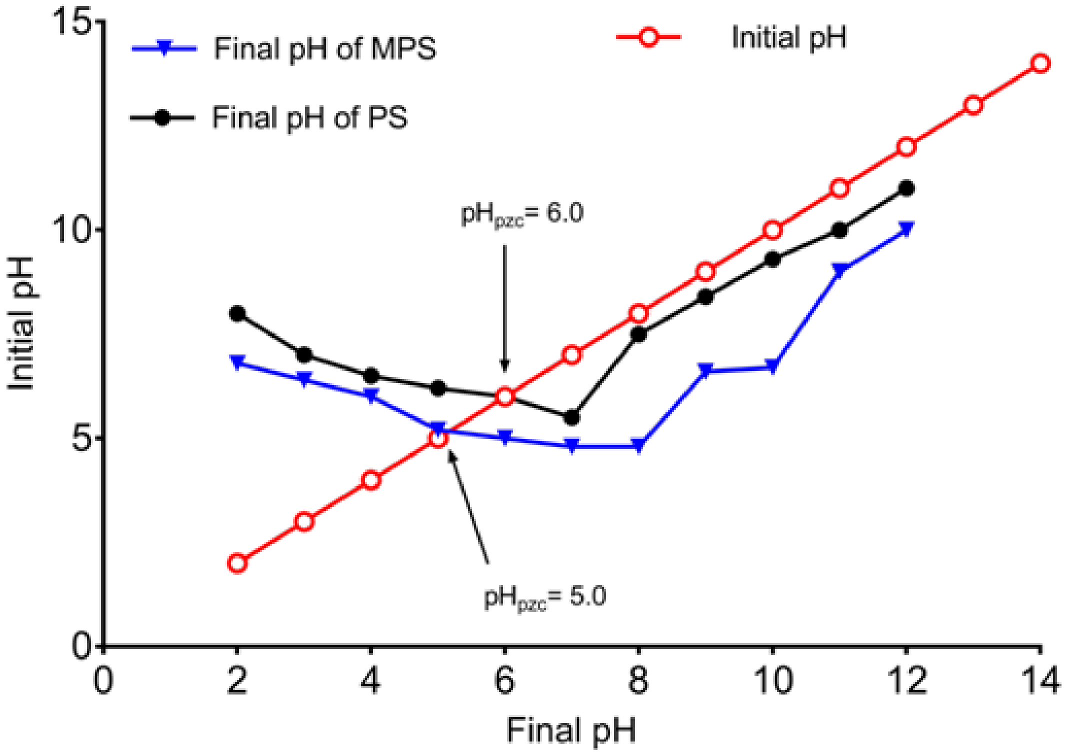


Figure 9: pH point zero charge for PS and MPS

The surface charges of the PS impregnated with anionic surfactant was probably negative above pH 5 because the hydrophilic negatively charged head groups of the surfactants are arranged toward the aqueous phase. For this reason, the capacity of MPS to adsorb cationic dye (MB) increases in proportion to the quantity of MPS present in the reaction flasks.

The SEM images of PS and MPS are shown in Fig. 10. The micrographs of PS and MPS exhibited rough surfaces and pores of various dimensions. Both PS and MPS showed flattened large walls and irregular intercellular spaces. The surface had an undulating, wrinkle and depressed appearance. The provided pores and rough surface areas indicate that there was a good possibility for the MB molecules to be trapped and adsorbed onto the surface of the adsorbents. The MB molecules can penetrate into the adsorbents structure and interact therein with the surface functional groups.

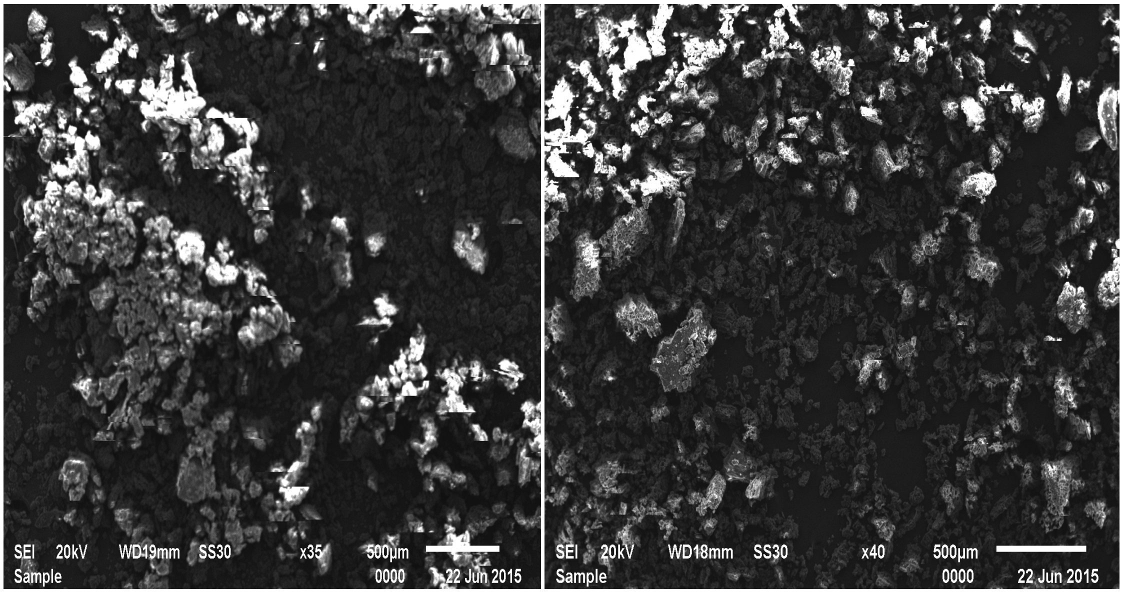


Figure 10: SEM images of PS and MPS

3.2 Effect of Parameters Affecting Adsorption Process

3.2.1 Effect of pH on MB Sorption

It is a known fact that the solution pH of the system is a significant parameter in the adsorption process. The surface chemistry of the adsorbent and the charged adsorbate often depends on the pH of the solution. Fig.11 and 12 show the variation of MB adsorption on MPS and PS at varying solution pH. From Fig. 11, removal efficiency increases at solution pH 3–4 and the adsorption quantity equally increased from 16 mg/g to 26 mg/g. Then removal efficiency rapidly increased from 25% to 87% when solution pH was adjusted from 4 to 6. The maximum removal was recorded at pH 7, where 96.4 mg/g MB was adsorbed by MPS.

Apparently, the adsorption of MB prefers a neutral to higher solution pH. At lower solution pH ($pH < pH_{pzc}$), the more the positive charges on the MPS surface, the less attractive to the cationic MB. However, at pH greater than the pH_{pzc}, the more the negative charges on the MPS surface, the greater the electrostatic attraction while MB existed as positively charged ions. It is interesting to note that even at pH 3–5, the adsorption quantity was over 50 mg/g. This suggested that other actions, such as ion exchange or π–π dispersion interactions existed at lower solution pH between MPS and MB (Zhao et al. 2014).

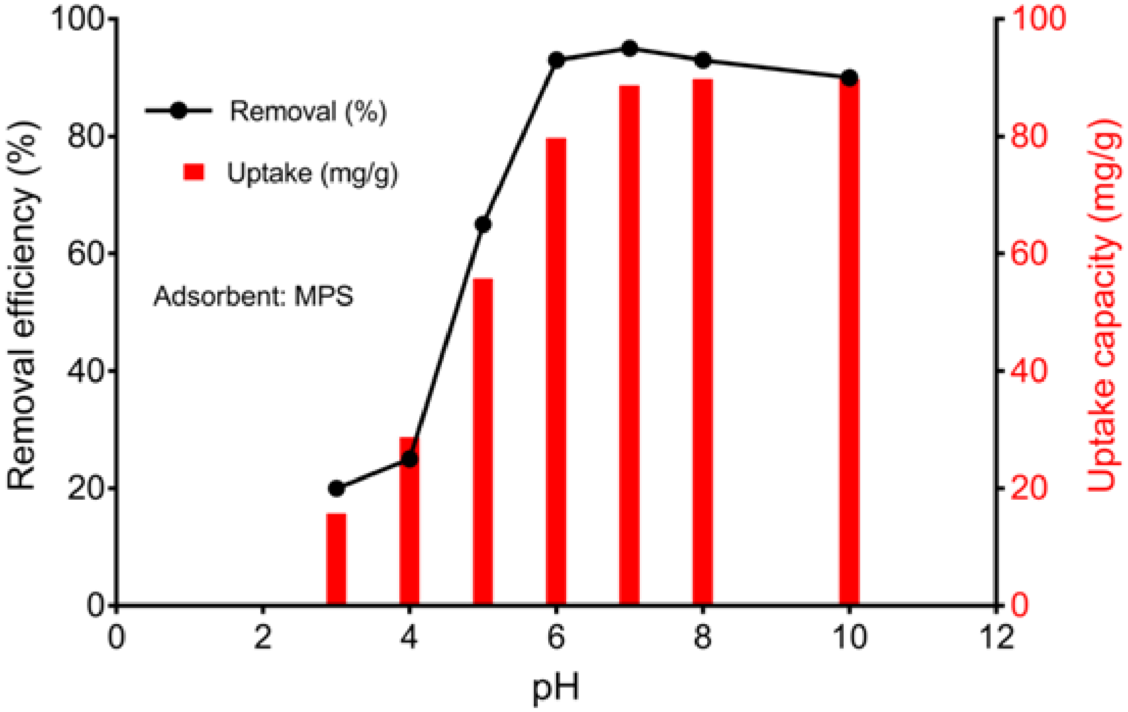


Figure 11: Effect of solution pH for removal of MB by MPS

A similar trend was noticed in the presence of PS and MB (Fig.12). The maximum uptake of 83 mg/g was observed at pH 7 which was lower than that observed for MPS (95 mg/g). Beyond pH 7, a slight decrease in the removal efficiency was observed with PS. The results could be explained by the different interaction between MB and PS in terms of surface charge and degree of aggregation of MB (Lafi and Hafiane, 2016).

At pH beyond the pHpzc of PS (6.0), the strong electrostatic attraction between the negatively charged adsorption site and the cationic MB molecule results in high adsorption of MB dye. The slight reduction observed beyond pH 7, may be attributed to aggregation of MB molecules to form a larger molecular form (dimer). The dimer becomes unable to enter into the pore of the PS and caused the decline of adsorption of

MB. A similar behaviour has been reported in the literature (Gad and El-Sayed, 2009; Ghanadzadeh et al. 2002).

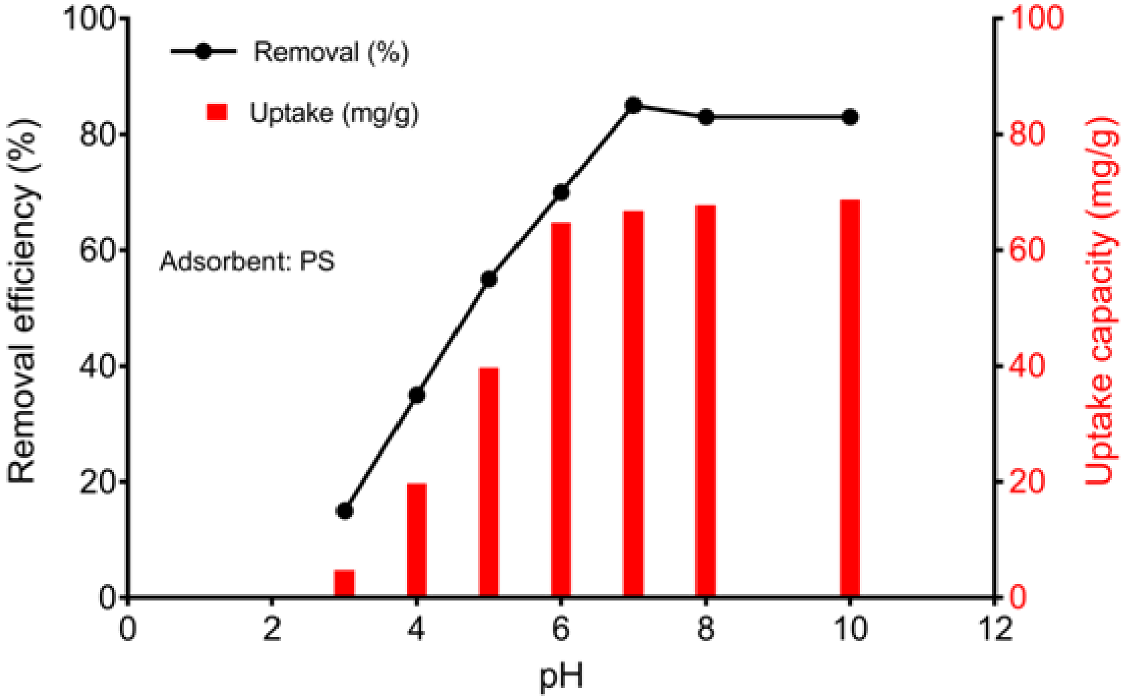


Figure 12: Effect pH on the removal of MB by PS

3.2.2 Effect of Contact Time and MB Removal Kinetics

The effects of contact time on MB adsorption by PS and MPS are shown in Fig. 13 and 14, respectively. It was observed from Fig.13–14, that a three-stage kinetic behaviour was evident in the adsorption of MB. For PS, a rapid initial adsorption within the first 90 minwas observed, followed by a slower uptake until 180 min and gradual decrease after equilibrium at 200 min. A similar trend was observed in the presence of MPS (Fig.14), however, beyond 200 min, equilibrium was established for a longer period. Four adsorption kinetics models (Elovich, pseudo-first-order, pseudo-second-order, intraparticle diffusion) were used to explain the adsorption mechanism and adsorption characteristics.

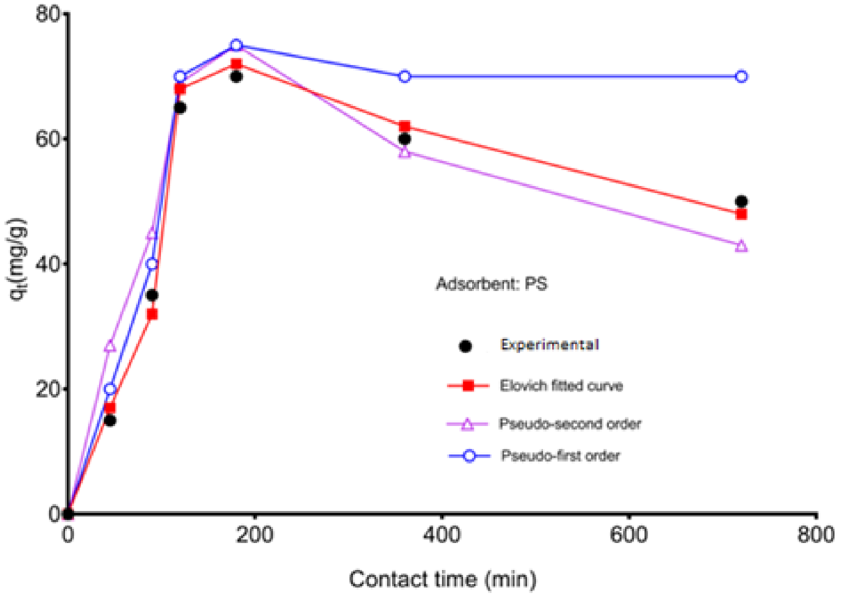


Figure 13: Effect of contact time for MB removal by PS

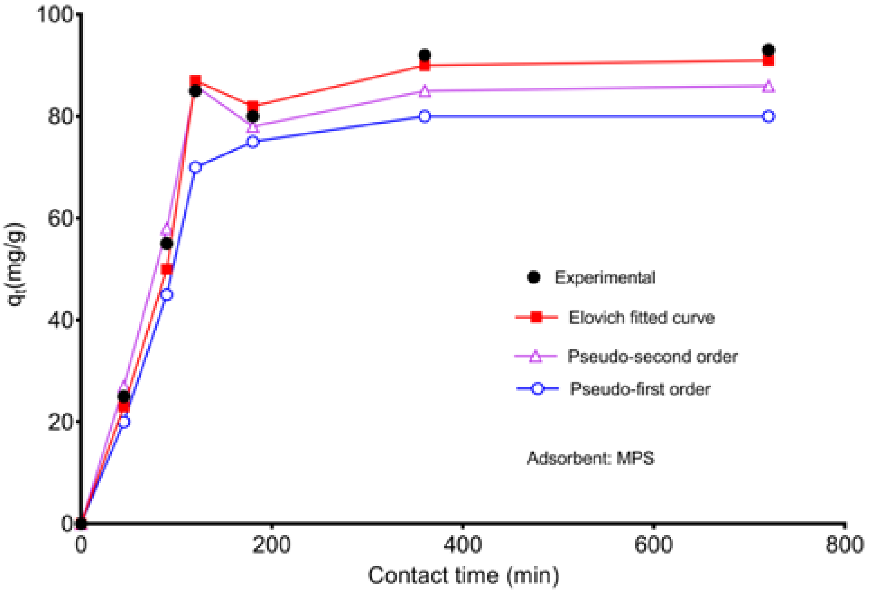


Figure 14: Effect of contact time for MB removal by MPS

The kinetic equations are expressed by Eqs. (3)–(6), respectively (Cheung et al., 2000):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta t) \tag{3}$$

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

$$q_t = k_i t^{0.5} + C \tag{6}$$

Where q_e and q_t represent the quantity of MB removed per MPS mass unit (mg/g) at equilibrium and time t, respectively. The rate constants arek_1 (1/min), k_i (mg/g min$^{0.5}$) and k_2 (g/mg min), for the pseudo-first order, intraparticle diffusion, pseudo-second order, respectively. The desorption constant and initial adsorption rate for the Elovich model are represented by α and β, respectively (Hossain et al., 2012; Pellera and Gidarakos, 2015).

The nonlinear regressive analysis was conducted using the Graphpad 7.0 software. The kinetic parameters obtained from the four models are presented in Table 2. The fitted curves from Elovich, pseudo-first order and pseudo-second-order kinetic equations are shown in Fig. 13–14. The intraparticle diffusion curve is shown in Fig. 15. From Table 2, the values of $R^2$and residual sum of squares (RSS) are used to predict the suitability of the models. The conformity between experimental data and the Elovich-predicted values was expressed by the high correlation coefficients (R^2= 0.995–0.998). However, the pseudo-second-order had the lowest RSS values (1.86–2.51).

Hence, it is concluded that both Elovich and pseudo-second order equations were suitable to predict the dynamic adsorption of MB adsorption on MPS. The Elovich model describes the adsorption kinetics in terms of ion exchange systems while pseudo-second order assumes that the adsorption system is based on chemical process (Cheung et al., 2000).

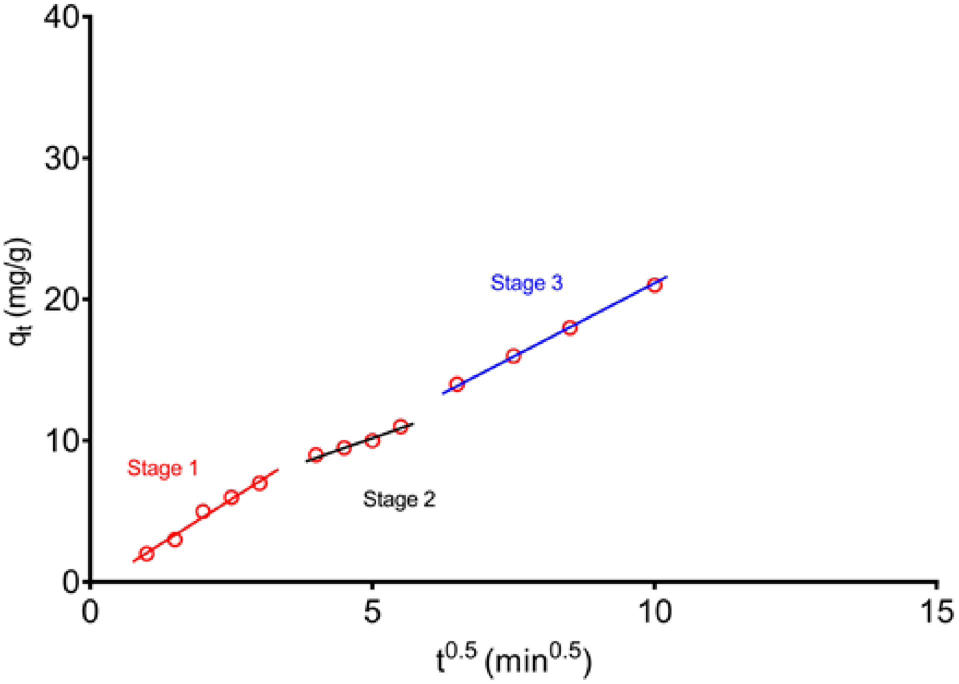


Figure 15: Intraparticle diffusion model for MB adsorption by MPS

To further understand the transport mechanism of the MB molecules, the experimental data were fitted to the Webber Morris equation (6). In the first rapid stage 1, the MB molecules were adsorbed on the external surfaces and large pores of the MPS (Muthusamy et al., 2013). Progressively, the second slow stage 2 involves gradual transport of the MB molecules into the smaller micropores of the MPS due to diffusional influences (Stasinakis et al., 2008) and the third stage 3 is the slowest and involves the final uptake of the MB molecules.

Table 2: Kinetic parameters for MB adsorption by MPS

Kinetic models	**Parameters**	**10 ppm**	**30 ppm**
Pseudo-first order	q_e	34.8	89.9
	k_1	0.011	0.0133
	R^2	0.808	0.523
	RSS	6.89	7.89
Elovich	α	1.37.E + 14	1.11.E + 13
	β	0.908	0.996
	R^2	**0.995**	**0.998**
	RSS	1.99	2.99
Pseudo-second order	q_e	40.6	72.8
	k_2	0.0062	0.0069
	R^2	0.993	0.994
	RSS	**1.86**	**2.51**
Intraparticle diffusion	k_i	0.1161	0.1213
	C	11.11	18.22
	R^2	0.984	0.996
	RSS	3.15	4.89
Experimental	$q_{e,exp}$(mg/g)	45.9	69.6

3.2.3 Effect of MPS Dosage on MB Sorption

Adsorbent dosage has a significant impact regarding performance and economics of the treatment technology. Hence, the effect of MPS dosage on the removal efficiency of MB is depicted in Figure 16. Here, the pH of the solution was not adjusted, and initial MB concentration of 30 mg/L was used. Based on the experimental observation, the MB removal efficiency increased with increasing MPS dosage from 10 to 50 mg. About 80% MB was removed within 200 min when 20 mg of MPS was used. A slight increment to 93% was recorded when the MPS dosage increased to 30 mg. The increasing trend in the removal efficiency is attributed to increases in the specific surface area of MPS and availability of more sorption sites (Anandkumar and Mandal, 2012; Nassar et al., 2014).

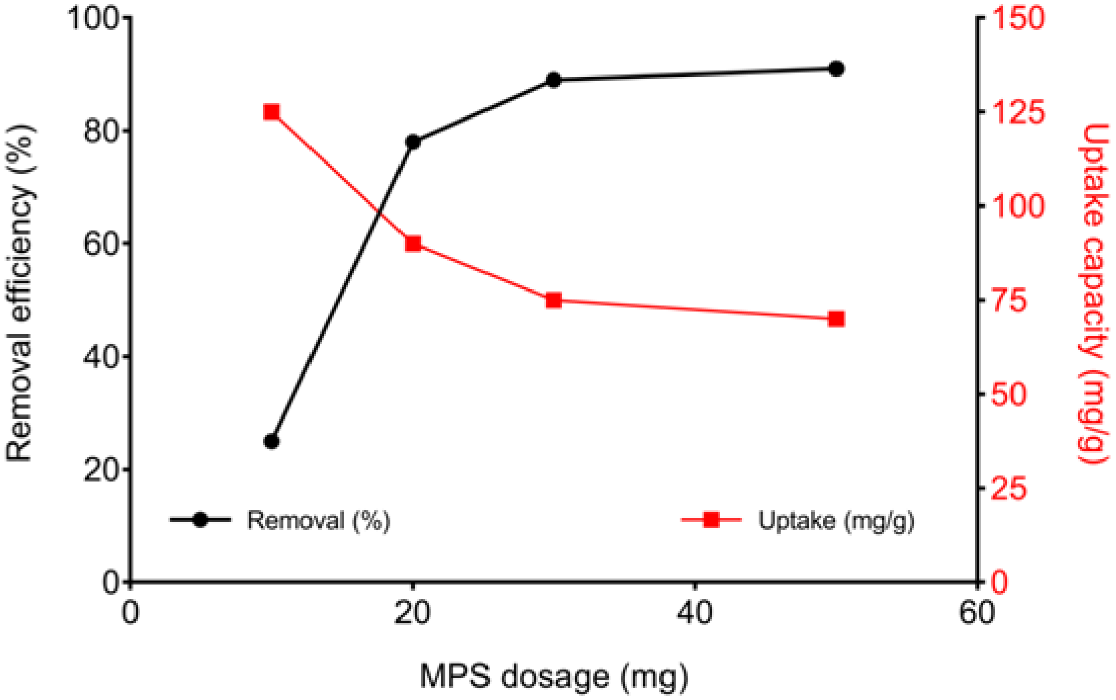


Figure 16: Effect of MPS dosage on MB adsorption

The amount of MB adsorbed per unit mass of MPS (q_e, mg/g) decreased with increasing dosage, which was an expected result, so the decrease in adsorption density may be due to: when the MPS amount is small, the MB can easily access the adsorption sites and the uptake capacity q_e (mg/g) is high. With increasing MPS content, the corresponding increase in sorption per unit mass is less because of increase of the surface area of MPS.

3.2.4 Effect of Ionic Strength on MB Adsorption

The dye-laden wastewaters commonly contain high salt concentration, and ionic strength effect is of importance in the treatment of dye-containing wastewaters. The effect of ionic strength (salt concentration) on MB adsorption by MPS is shown in Fig. 17. As shown, the NaCl and $MgCl_2$ existing in the reaction solution affected MB adsorption onto MPS. The increase in the salt concentration resulted in a decrease of MB uptake. This trend showed that the adsorbing efficiency of MPS decreased with the increase of salt concentration, and attributed to the competitive effect between MB ions and metal ions (Na^+ or Mg^{2+}) for the sites available for the adsorption process (Zhao et al. 2014; Oladipo and Gazi, 2016).

Also, the $MgCl_2$ has more contribution to ionic strength at the same concentration as compared with NaCl. This may be attributed to the higher surface charges on Mg^{2+} than Na^+ which resulted in more competition on the adsorption sites of MPS. However, even at 100 mg/L $MgCl_2$ salt, there was still adsorption capacity of 18 mg/g. So MPS can still remove MB from aqueous solution with salt presence. These results also implied that the main mechanism between MPS and MB might be an electrostatic attraction.

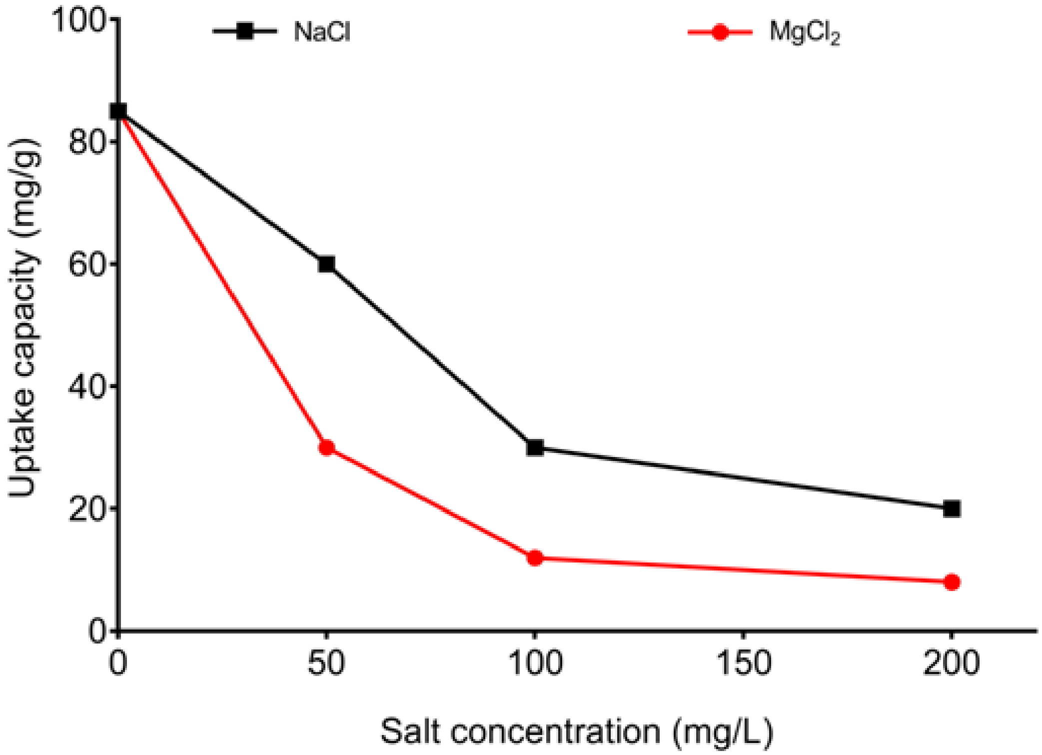


Figure 17: Effect of ionic strength on MB adsorption by MPS

3.2.5 Effect of Initial MB Concentration

The effect of the initial MB concentration on the MPS removal efficiency was investigated at pH 7 using 30mg MPS. The MB removal efficiency increases steadily as the initial concentration increases as seen in Figure 18. About 50% MB was removed when the concentration was 5 mg/L, and it increased beyond 80% when the concentration was increased to 25 mg/L. The increasing trend could be as a result of driving force provided by the higher initial MB concentration to overcome the mass transfer flux (Ngwabebhoh et al., 2016). Similarly, the MB uptake capacity increased with increasing MB initial concentration due to partition or distribution equilibrium.

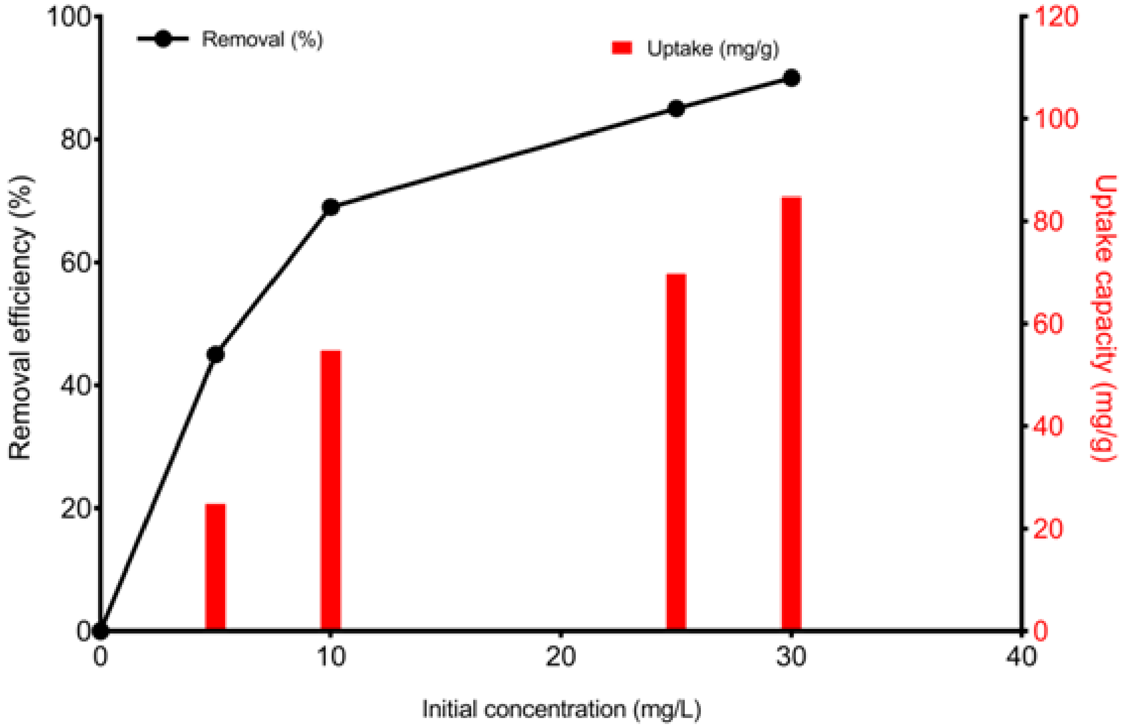


Figure 18: Effect of initial MB concentration

3.3 Isotherm Analyses

In order to design an effective treatment system, it is important to find the most appropriate correlation of the equilibrium data. Two common adsorption isotherm models, Langmuir and Freundlich,were selected to fit equilibrium data. The isotherm equations are expressed as follows, respectively (Song et al., 2016):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (7)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (8)$$

Where C_e (mg/L) and q_e (mg/g) are the equilibrium total MB concentration and amount of total MB removed at equilibrium time, respectively. The q_m (mg/g) represent the maximum amount of total MB removed. The Langmuir and Freundlich constants are denoted by K_L (L/mg) and n respectively.

The Langmuir model is based on the assumption that monolayer reactions take place at the interphase of the adsorbent and the adsorbate by uniform energy levels. The isotherm equally assumes the lack of interactions or transmigration of the adsorbed molecules on the adsorbent surface. Contrastingly, the Freundlich model describes multilayer (heterogeneous) interactions between the adsorbate and the adsorption sites occurring at different energy levels (Fayazi et al., 2015; Oladipo and Gazi, 2014).

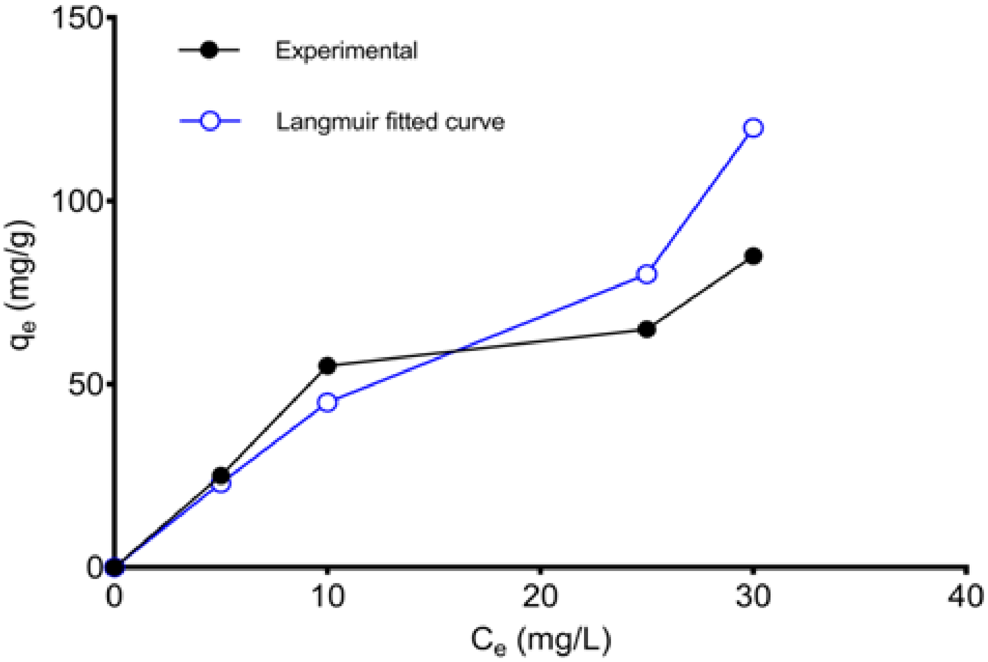


Figure 19: Langmuir isotherm for MB removal by MPS

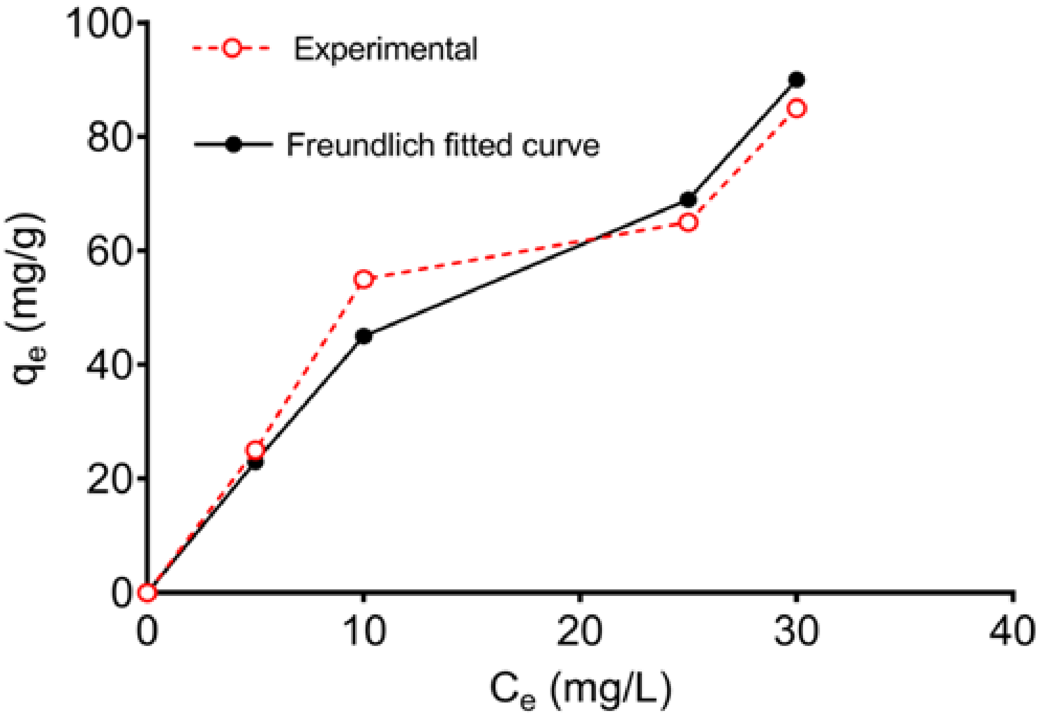


Figure 20:Freundlich isotherm for MB removal by MPS

The respective parameters obtained from Langmuir and Freundlich isotherms are presented in Table 3. According to the values of R^2 and RSS, the MB removal by MPS was well fitted to the Freundlich model. The lower the RSS values, the more suitable is the model, on the other hand, R^2 values near the value of one indicate a good fit of the experimental data with the model. As a result of the Freundlich fitness, it is concluded that the removal mechanisms occur at heterogeneous adsorption sites on MPS, hence, forming multilayer coverage of MB on the entire surface of the MPS. The values of the *n* constant of the Freundlich isotherm are also greater than 1, confirming a favourable process (Song et al., 2016) and the maximum MB removal under optimum conditions was 97.7 mg/g.

Table 3: Isotherm parameters for MB adsorption

Model	**MPS dosage (mg)**			**Solution pH**		
	10	**25**	**30**	**3**	**7**	**10**
Langmuir						
q_m (mg/g)	47.5	86.5	97.7	15.9	96.4	69.3
K_L (L/mg)	0.54	0.14	2.15	2.78	3.88	4.11
R^2	0.887	0.679	0.789	0.991	0.923	0.959
RSS	3.23	3.11	2.98	2.89	3.67	4.78
Freundlich						
K_F (mg/g)	33.8	45.6	88.3	26.3	83.9	63.9
N	1.94	1.22	3.76	5.11	2.51	3.75
R^2	0.996	0.997	0.999	0.999	1.000	0.999
RSS	1.45	1.32	1.27	1.39	2.01	1.11

3.3 Thermodynamic Data for MB Adsorption

To further evaluate the effect of temperature on the MB adsorption and investigate the possible mechanism involved in the adsorption process, standard free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined. They can be determined using adsorption isotherm by following equation (Zhao et al. 2014):

$$\Delta G^{0} = -RT \ln K_{L} (9)$$

$$\ln K_{L} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT} (10)$$

where K_L is the Langmuir constant that is relatedto the energy of adsorption; R is the gas constant (8.314 J/(mol·K)), and T is the temperature (K).

The values of ΔH^0 and ΔS^0were obtained from the slope and intercept of the plot of K_L versus 1/T, which gave a straight line (graph not shown).The values of ΔG^0were obtained according to Eq. (9) as -16.95, -12.03, -10.22 kJ/mol at 303, 318, 333 K, respectively. The negative values of ΔG^0 are due to the fact that the adsorption processes were spontaneous. The decrease of the absolute value of ΔG^0as temperature rises indicated that the affinity of MB on MPS decreased at a higher temperature. The negative value of ΔH^0 indicated that the adsorption process was exothermic in nature while the positiveΔS^0 value confirmed the increased randomness at the solid–solute interface during adsorption (Wang et al.2016).

Table 4: Thermodynamic parameters for MB adsorption by MPS

Temperature (K)	**ln K_L**	**ΔG^0 (kJ/mol)**	**ΔH^0 (kJ/mol)**	**ΔS^0 (J/(mol·K))**
303	6.73	-16.95	-30.115	48.288
318	4.55	-12.03		
333	3.69	-10.22		

Chapter 4

CONCLUSION

In this research, palm seed powder (PS) and anionic surfactant modified palm seed powder (MPS) were utilised as adsorbents for the treatment of methylene blue (MB) simulated effluent. The adsorbents were characterised by SEM, and their surface chemistry investigated by pH points zero charges (pHpzc). Several factors including solution pH, contact time, salt concentration and equilibrium dye concentration, were investigated during the adsorption process.

The adsorption was favoured at a pH values higher than pH 5.0 for MPS (pH>pHpzc) and maximum removal efficiencies were recorded at pH 7.0. The coexisted salt in the solution was not in favour of the adsorption capacity, though the high salt concentration attributed to a competitive effect between MB and metal ions, which decreased the adsorbing efficiency of MPS. From the effect of contact time and MB removal kinetics, both pseudo-second-order equation and Elovich equation could predict the kinetic process. Freundlich model better fitted the equilibrium data, and the adsorption capacity was up to 96.4 mg/g at pH 7. The process was spontaneous and exothermic in nature from thermodynamic perspectives. Further study should be about practical wastewater's treatment and regeneration of the spent adsorbents.

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