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Raw and surfactant-modified pineapple leaf as adsorbent for removal of methylene blue and methyl orange from aqueous solution

Auni Afiqah Kamaru, Nor Suriani Sani, Nik Ahmad Nizam Nik Malek*

Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia, Tel. +60 75533547; Fax: +60 75536062; email: niknizam@fbb.utm.my (N.A.N.N. Malek)

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ABSTRACT

Adsorption capacity of pineapple leaf powder (PLP) and surfactant-modified pineapple leaf powder (SMPLP) in removing cationic dye, methylene blue (MB) and anionic dye, methyl orange (MO) from aqueous solution was investigated. SMPLP was prepared by reacting PLP with different concentrations of cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br). Batch mode experiments were conducted at room temperature to study the effects of initial dye and surfactant concentrations on the adsorption capacity of PLP and SMPLP towards cationic (MB) and anionic (MO) dye. The experimental adsorption isotherm data for both MB and MO fitted well with Langmuir in comparison to the Freundlich model. The maximum monolayer adsorption capacity for MB and MO were 52.6 and 47.6 mg/g, respectively. The highest adsorption for MB and MO were achieved by PLP and PLP treated with 4.0 mM HDTMA-Br, respectively. It was found that PLP and SMPLP showed different adsorption behaviour towards cationic and anionic dye. The MO adsorption was dramatically increased with PLP treated with 4.0 mM HDTMA-Br in comparison to PLP treated with 1.0 and 2.5 mM HDTMA-Br. Thus, the concentration of HDTMA-Br affects the adsorption capacity of SMPLP towards MO. The overall result implied that PLP can be applied as an effective adsorbent material to remove different types and classes of dyes from aqueous solution.

Keywords: Adsorption; Pineapple leaf; Cationic surfactant; Cationic dye; Anionic dye

1. Introduction

Synthetic dye used in diverse industries is highly soluble in water and the direct discharge of dye bearing effluent into receiving water bodies without adequate treatment creates point source of serious environmental pollution. Due to adverse harmful effects of synthetic dyes and their metabolites towards aquatic life and human beings, removal of dyestuffs from wastewater prior to discharge has received considerable concern over the past decades. There are various physical, chemical and biological methods that are available to treat wastewater containing dye including membrane filtration, chemical precipitation, microbial degradation, Fenton's reaction [1], Fenton-like process, photo Fenton process and ultrasonic irradiation [2]. However, the aforementioned conventional methods are inefficient to treat various classes of dyes, ineffective in completely removing coloured material from aqueous phase [3], do not effectively oxidize complex dye molecules [1], completely

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*Corresponding author.

mineralize dye, produce secondary waste and require optimization of main operational conditions [2]. Conversely, adsorption defined as rapid separation process involves the transfer of adsorbate from liquid or gaseous phases onto solid and porous adsorbent through specific binding affinities between adsorbent and adsorbate [3] has emerged as a noteworthy, effective and low-cost treatment process.

Activated carbon is extensively employed as versatile and efficient adsorbent to remove dye from wastewater, yet higher operating cost, difficult to separate from wastewater after treatment, decrease in adsorption capacity after regeneration and disposal issues [4,5] hamper its large scale application. The abundance of agricultural wastes such as green tea leaves [6], potato peel [7] and yam peel [8] has attracted interest of researchers in utilizing these natural materials as alternative adsorbent to overcome the limitation of activated carbon. This is because agricultural wastes offer lower treatment cost and capability to regenerate after multiple treatment processes. Hence, in this paper, pineapple leaf, one of the agricultural wastes being produced, up to 255,000 tonnes annually in Malaysia, was selected as studied adsorbent to replace the use of activated carbon in removing dyes from aqueous solution.

The major compositions of pineapple leaf are cellulose (70–80%), lignin (5–12%) and hemicelluloses [9]. In aqueous solution, cellulose and lignin in pineapple leaf tend to release hydrogen ions which result in the formation of negatively charged surface area [10]. The direct use of raw pineapple leaf as adsorbent is only beneficial to remove cationic dye but not its counterpart. Therefore, it is necessary to modify the raw pineapple leaf prior to removal process in order to increase its adsorption capacity towards anionic dye. Bhatnagar and Sillanpa [11] suggested that surface modification process is able to enhance the affinity of raw agricultural wastes towards anionic dye, while Namasivayam and Sureshkumar [12] proposed that cationic surfactant is the best modifying agent for the aforesaid purpose. Several researchers have implemented the use of cationic surfactant to modify the surface of agricultural wastes for the removal of dyes from aqueous solution [10,13–19].

Although many surfactant-modified agricultural wastes have been reported for decontamination of wastewater containing dyes, studies on surfactant-modified pineapple leaf as adsorbent in removing dyes from aqueous solution have not entered the scientific literature yet. Therefore, the aim of this paper is to report the modification of pineapple leaf with cationic surfactant quaternary ammonium compound, hexadecyltrimethylammonium bromide (HDTMA-Br) and to evaluate the potential of this modified agricultural waste to adsorb methylene blue (MB) and methyl orange (MO) which are cationic and anionic dyes, respectively. The selection of HDTMA-Br as surface modifying agent is due to the presence of hydrophilic head group containing tetra-substituted ammonium cation, with permanent +1 charge pentavalent nitrogen that is able to convert the surface charge of pineapple leaf from positive to negative potential [10]. We investigated parameters that may affect the adsorption process including initial dye concentration, different types of dyes and different surfactant concentration. Models to fit the adsorption equilibrium data were also formulated.

2. Materials and methods

2.1. Preparation of adsorbent

Pineapple leaves (PL) from Josapine type of pineapple was provided by Malaysian Agricultural Research and Development Institute (MARDI), Pontian, Johor, Malaysia. The pineapple leaves were washed under running tap water several times, sun-dried for a week and subsequently oven dried at 90˚C for 24 h. The dried leaves were cut into small pieces, crushed and ground into powder form. The resulting powder was abbreviated as raw pineapple leaf powder (PLPR) and subjected to pretreatment process by repeatedly washing with boiled, distilled water until the filtrate produced was free of colour and turbidity. The washed powder was oven dried at 90˚C for 24 h and abbreviated as pretreated pineapple leaf powder (PLP).

2.2. Preparation of surfactant solution

Cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) used in the present work was purchased from Merck, Germany. Three different concentrations of HDTMA-Br solution (1.0, 2.5 and 4.0 mM) were prepared by dissolving the appropriate amount of HDTMA-Br in distilled water.

2.3. Preparation of surfactant-modified adsorbent

Three series of surfactant-modified pineapple leaf powder (SMPLP) were prepared by reacting PLP with HDTMA-Br solution in the ratio of 10:1 (PLP: HDTMA-Br solution, w/v) under constant stirring for 15 min at room temperature. The resulting SMPLP was filtered and oven dried at 90˚C for 24 h. The filtrate was kept for the determination of the amount of surfactant adsorbed onto PLP. The dried SMPLP was ground into fine powder and sieved to constant size using #40 American Society for Testing and Materials sieve. SMPLP less than 425 µm was used as adsorbent in adsorption study. The resulting SMPLPs modified using 1.0, 2.5 and 4.0 mM of HDTMA-Br solution were abbreviated as PLPH 1.0, PLPH 2.5 and PLPH 4.0, respectively.

2.4. Determination of surfactant adsorbed

The procedure for determination of surfactant adsorbed onto SMPLP was performed as described by Scott [20]. Sulfuric acid, chloroform and acid orange II were purchased from RCI Lab Scan, Thailand, *QRëC*, New Zealand and Sigma-Aldrich, USA, respectively. Initially, 25 mL distilled water, 5 mL sulfuric acid (2 M), 10 mL chloroform and 2 mL acid orange 7 (1 mM) were mixed and shaken in a separating funnel. Then, 1 mL HDTMA-Br filtrate was added to the previous mixture and shaken vigorously. The chloroform layer was extracted and analysed using a visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at $\lambda_{487\ \mathrm{nm}}$. The amount of HDTMA-Br adsorbed onto SMPLP, q_{ads} (mmol/kg) was calculated using the following equation:

$$q_{\mathrm{ads}} = \frac{(q_{\mathrm{i}} - q_{\mathrm{e}})V}{w} \tag{1}$$

where q_{i} and q_{e} (mmol/L) are the concentration of HDTMA-Br before and after adsorption, respectively. V (L) is the volume of HDTMA-Br solution and w (kg) is the weight of SMPLP sample.

2.5. Characterization of adsorbent

The samples of PL, PLPR, PLP and SMPLP were characterized by Fourier transform infrared (FTIR) spectrometer (model Nicolet iS5, Thermo Fisher Scientific, USA) using attenuated total reflectance method. The FTIR spectrum was recorded using OMNIC software at spectral range of 400–4000 cm^{-1}.

The samples of PLP and PLPH 4.0 were characterized using a scanning electron microscope (SEM) (model JSM-6390 LV, JOEL, Malaysia) at an electron acceleration voltage of 10 kV in order to observe the surface texture change before and after the modification process. Prior to scanning, PLP and PLPH 4.0 were coated with a thin layer of platinum using an autofine coater to make the samples electrically conductive.

2.6. Preparation of adsorbate solution

MB and MO were purchased from Sigma-Aldrich, USA and AJAX Chemicals, Australia, respectively. The stock solutions were prepared by dissolving 1,000 mg of MB or MO in 1,000 mL of distilled water. All working solutions were prepared by diluting the stock solutions with distilled water to the desired concentration.

2.7. Adsorption studies

Batch mode experiments were conducted at room temperature where 250 mg of PLP and SMPLP were added to 25 mL of each dye solution and shaken at 250 rpm for 2 h.

The effect of initial dye concentration on the adsorption of MB and MO onto PLP and SMPLP was determined at different dye concentration ranging from 5 to 1,000 mg/L.

The effect of initial pH of dye on the adsorption of MB and MO onto PLP and SMPLP was carried out at constant dye concentration of 100 mg/L with different initial pH ranging from 3.00 to 11.00. The dye pH was adjusted using 0.1 M NaOH and HCl. The pH of dye solution before and after adsorption was recorded.

The effect of temperature on the adsorption of MB and MO onto PLP and PLPH 4.0, respectively was determined at constant initial dye concentrations ranging from 100 to 1,000 mg/L with different working temperatures of 308.15, 313.15 and 333.15 K.

The concentration of MB and MO before and after adsorption was determined using visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at $\lambda_{661\ \mathrm{nm}}$ and $\lambda_{460\ \mathrm{nm}}$ for MB and MO, respectively. The amount of MB and MO adsorption at equilibrium, q_{e} (mg/g) was calculated using the following equation:

$$q_{\mathrm{e}} = \frac{(C_{\mathrm{i}} - C_{\mathrm{e}})V}{w} \tag{2}$$

where C_{i} and C_{e} (mg/L) are the initial and equilibrium concentrations of MB and MO, respectively. V (L) is the volume of dye solution and w (g) is the weight of PLP or SMPLP sample.

2.8. Desorption studies

Desorption of surfactant and dye from PLP and SMPLP was performed as a function of desorbing solution pH.

The desorption of HDTMA-Br from SMPLP was carried out by adding 250 mg of PLPH 1.0, PLPH 2.5 and PLPH 4.0 to 25 mL of distilled water with the pH ranging from 3.00 to 9.00. The pH of distilled water was adjusted using 0.1 M NaOH and HCl. The solution was shaken at 250 rpm for 2 h. The pH of distilled water before and after desorption was recorded.

The PLP and PLPH 4.0 used for the adsorption of 100 mg/L MB and MO, respectively were further subjected to desorption of respected dyes. The MB-loaded PLP and MO-loaded PLPH 4.0 were filtered and washed with distilled water to remove the superficially adsorbed dye. The washed spent adsorbent was oven dried at 90°C overnight. The dried spent adsorbent was added to 25 mL of distilled water with the pH ranging from 3.00 to 11.00. The pH of distilled water was adjusted using 0.1 M NaOH and HCl. The solution was shaken at 250 rpm for 2 h. The pH of distilled water before and after desorption was recorded. The amount of desorbed surfactant and dye was estimated as before.

3. Results and discussions

3.1. Amount of surfactant adsorbed

The amount of HDTMA-Br adsorbed onto SMPLP at different initial concentrations of HDTMA-Br is presented in Fig. 1. It can be observed from Fig. 1 that the amount of HDTMA-Br adsorbed onto SMPLP increased with the increase in the initial concentration of HDTMA-Br solution. As the initial concentration of the HDTMA-Br solution increased from 1.0 to 4.0 mM, which was a fourfold increment, the amount of HDTMA-Br adsorbed onto SMPLP showed only a threefold increment, which was from 138.61 to 381.67 mmol/kg. Therefore, it can be concluded that the amount of HDTMA-Br adsorbed onto the sample was not in the same proportion and independent of the initial concentration of HDTMA-Br solution.

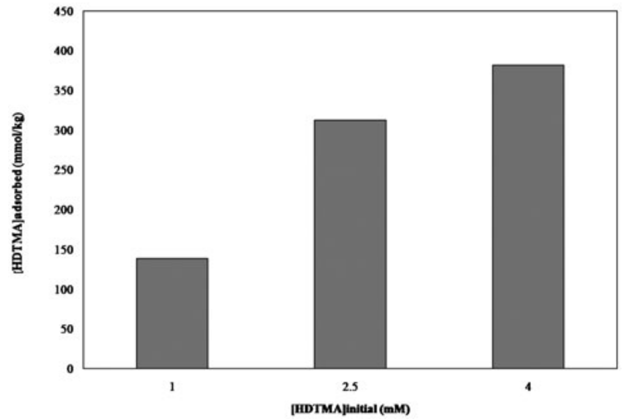


Fig. 1. Amount of HDTMA-Br adsorbed onto SMPLP at three different initial concentrations.

3.2. Characterization of adsorbent

FTIR spectroscopy was performed as a preliminary qualitative analysis of surface chemical groups present in the sample [13,17,18] and to determine the properties of functional groups involved in the adsorption process [3]. The FTIR spectra of PL, PLPR, PLP and SMPLP are presented in Fig. 2. From Fig. 2, the broad and intense band ranging from 3,333 to 3,345 cm^{-1} was due to –OH vibration in cellulose and lignin [3,9]. The peaks in the range of 1,731–1,732 cm^{-1} in all samples corresponded to C–O stretching of carbonyl groups in hemicelluloses [21] and ester linkage in lignin [22]. The weak peaks which appeared around 1,621–1,652 cm^{-1} were due to the C–O–O bond in lignin aromatic structure [9]. The peaks centered at 1,423–1,456 cm^{-1} were ascribed to the asymmetric $–CH_2$ deformation in methyl and methylene group of lignin and hemicelluloses, respectively and the stretching of benzene ring in lignin structure [21]. The bands ranging from 1,371 to 1,372 cm^{-1} were attributed to C–H deformation of cellulose and xylan. The peaks which appeared at 1,239–1,243 cm^{-1} were assigned as C–O–C bond of cellulose chain and stretching of lignin aryl group [22]. The prominent peaks at 1,158–1,159 cm^{-1} can be ascribed to the antisymmetric C–O–C bridge in the pyranose ring of cellulose [9,21]. The existence of weak band in the region of 528–605 cm^{-1} indicates the torsional vibration of cellulose pyranose ring. The appearance of strong, sharp peaks ranging from 2,917 to 2,921 cm^{-1} can be ascribed to the –CH stretching vibration in cellulose and hemicelluloses [9,21]. However, the intensity of –CH vibration peaks increased from PLP to PLPH 4.0. This might be due to the increase in aliphatic carbon content in SMLP, reflecting that cationic surfactant, HDTMA-Br was successfully introduced into the structure of pineapple leaves. This observation is in line with FTIR spectra of hexadecyltrimethylammonium bromide-modified coir pith [12], cetylpyridinum chloride-modified barley straw [15], cetyltrimethylammonium bromide-modified wheat straw and hexadceylpyridinum bromide-modified wheat straw [18].

The overall FTIR spectra revealed a diverse, important chemical nature and properties of pineapple leaves due to the presence of cellulose, hemicelluloses and lignin. The result from FTIR spectroscopy demonstrated that the chemical structure of pineapple leaves remain unchanged after pretreatment and surface

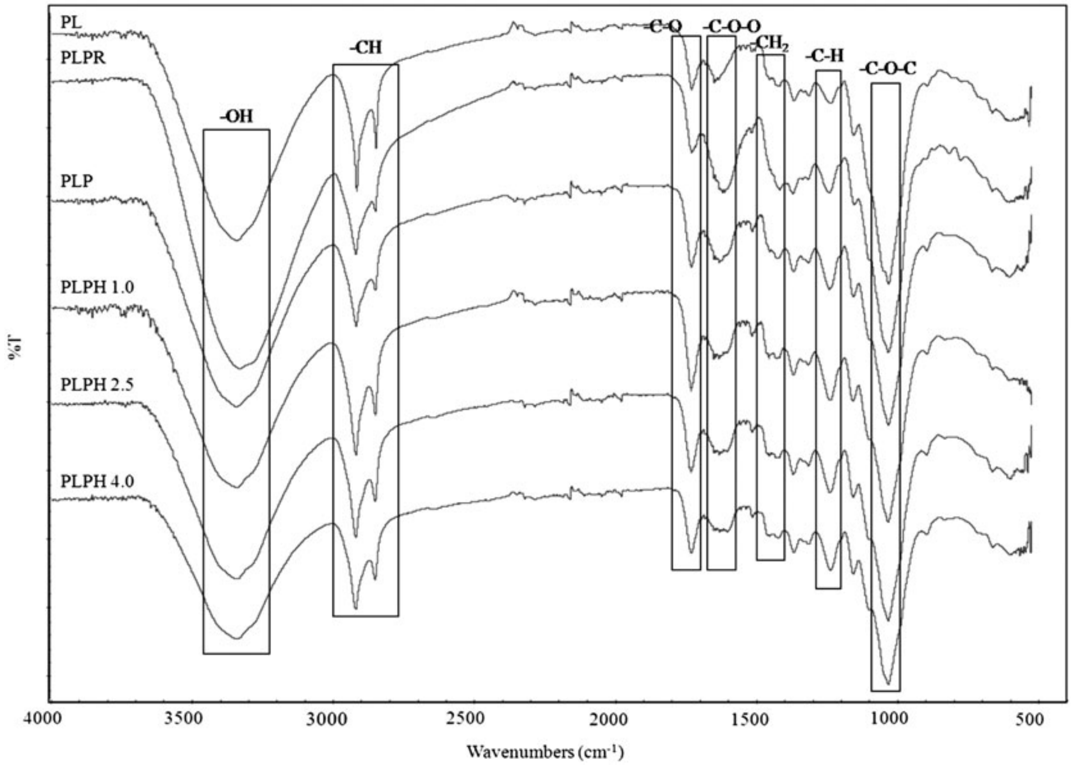


Fig. 2. FTIR spectra of PL, PLPR, PLP and SMPLP.

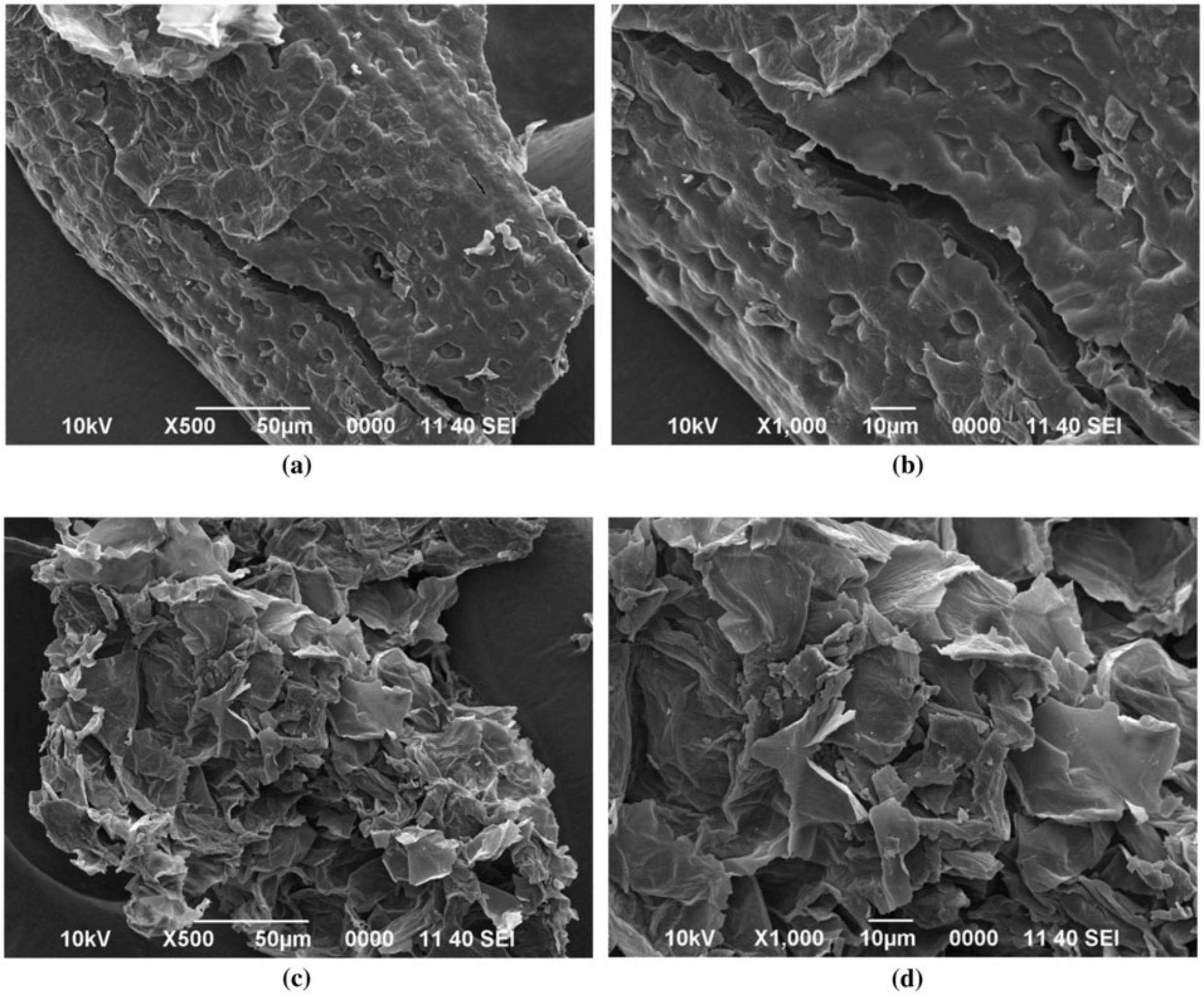
modification, suggesting that the treatment processes did not change the structure of pineapple leaves substantially.

SEM analysis was performed to study the surface morphology of pineapple leaves before and after surface modification. The SEM micrographs of PLP and PLPH 4.0 are presented in Fig. 3. From Fig. 3(a) and (b), the PLP exhibits a rough surface with porous structure. The presence of pores provides larger surface area that facilitates the adsorption of surfactant and dye onto PLP. However, in Fig. 3(c) and (d), it is clearly observed that the surface of PLPH 4.0 was covered with layers of smooth texture, indicating that HDTMA-Br was successfully adsorbed onto the surface of PLP. The similar observation was reported for the modification of tea waste with cetyltrimethylammonium bromide [19].

3.3. *Effect of pH*

pH is one of the important factors that governs the adsorption of adsorbate onto adsorbent. The pH of the solution influences the surface charge of adsorbent and ionization state of adsorbate. The effect of pH on the adsorption of MB and MO are presented in Figs. 4 and 5, respectively. From Fig. 4, it is observed that the adsorption of MB onto PLP and SMPLP was lower at pH 3.00 and started to increase at pH 4.00. The adsorption was almost constant at pH 4.00–10.00 and increased slightly at pH 11.00. The low adsorption rate at acidic pH was due to the repulsion between MB and the net positive surface charge of PLP and SMPLP [4]. Besides, the presence of H^+ ions surrounding the surface of PLP and SMPLP [27] results in competition with MB^- ions for binding sites causing a decrease in the amount of MB adsorbed [24]. Nevertheless, at higher pH, the surface of PLP and SMPLP become negatively charged which enhances the adsorption of MB through electrostatic attraction [25]. Similar observations have been reported for the adsorption of MB onto hazelnut shell [26] and garlic peel [27].

However, the trend of MO adsorption by PLP and SMPLP contradicted that of MB. From Fig. 5, it is observed that the adsorption of MO was higher at pH 3.00 and exhibited a sharp decrease at pH 4.00. The adsorption rate was constant at pH ranging from 4.00 to 10.00 and decreased further at pH 11.00. The higher removal at acidic pH was due to the abundance of H^+ ions which attracted the adsorption of MO onto PLP and SMPLP. In contrast, as the pH increased, the OH^- ions available in the solution caused repulsion



(a) (b) (c) (d)

Fig. 3. SEM micrographs of (a) PLP at 500× magnification, (b) PLP at 1,000× magnification, (c) PLPH 4.0 at 500× magnification and (d) PLPH 4.0 at 1,000× magnification.

between MO^- ions and the negatively charged surface of PLP and SMPLP which results in the decrease in MO adsorption [28]. This is in line with the previous study reported on the removal of MO by cationic surfactant-modified wheat straw [17].

The pH changes before and after the adsorption of MB and MO are presented in Figs. 6 and 7, respectively. It was observed that the pH of both dye solutions after the adsorption fall in the range of 5.00–6.00. This is due to the liberation of H^+ ions during the adsorption process which results in the change of pH to acidic condition.

3.4. Effect of initial adsorbate concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of adsorbate between aqueous solution and solid phase. The effect of MB and MO initial concentration on the adsorption onto PLP and SMPLP are presented in Figs. 3 and 4. From Figs. 3 and 4, it was observed that the adsorption capacity of PLP and SMPLP towards MB and MO increased with the increase in initial MB and MO concentration. The adsorption was rapid at an early stage (lower initial concentration) due to the interaction of single dye molecules with functional groups in PLP and SMPLP binding sites. The dye uptake further increased as the initial concentration increased. This is because the higher the concentration, the stronger the driving force to overcome all mass transfer resistance of dye molecules between aqueous and solid phase, facilitating an increase in dye adsorption [3]. However, PLP and SMPLP have limited number of binding sites, which become

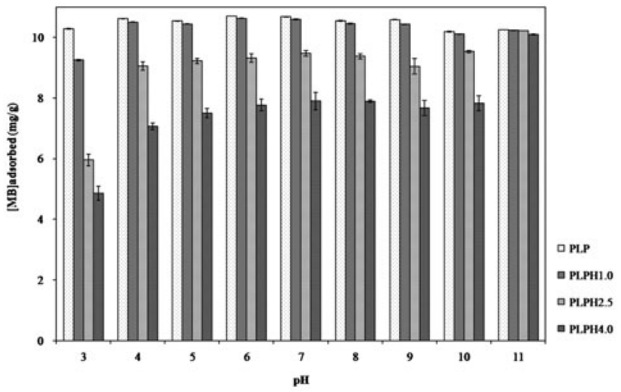


Fig. 4. Effect of pH on MB adsorption onto PLP and SMPLP.

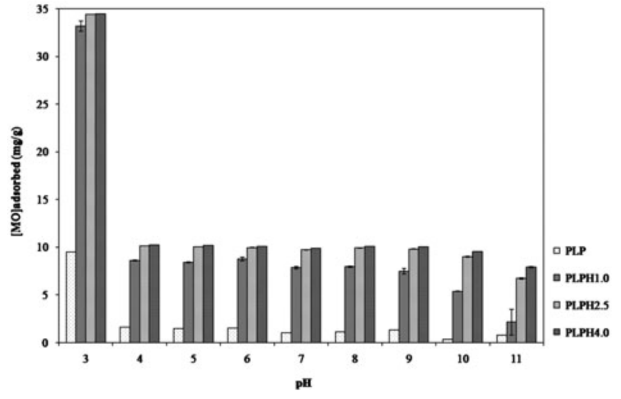


Fig. 5. Effect of pH on MO adsorption onto PLP and SMPLP.

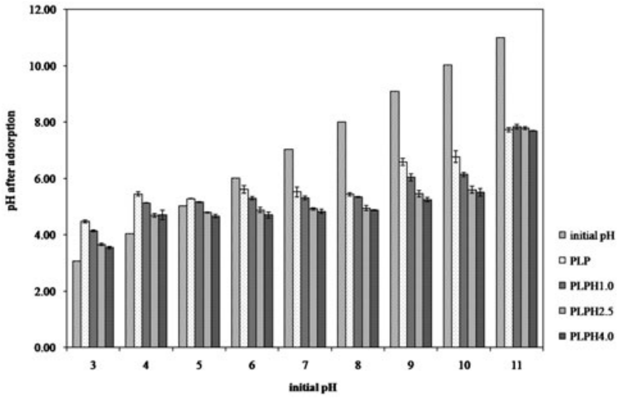


Fig. 6. Changes in pH before and after MB adsorption onto PLP and SMPLP.

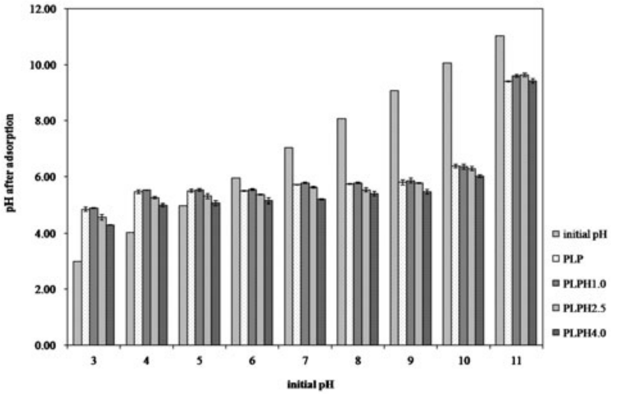


Fig. 7. Changes in pH before and after MO adsorption onto PLP and SMPLP.

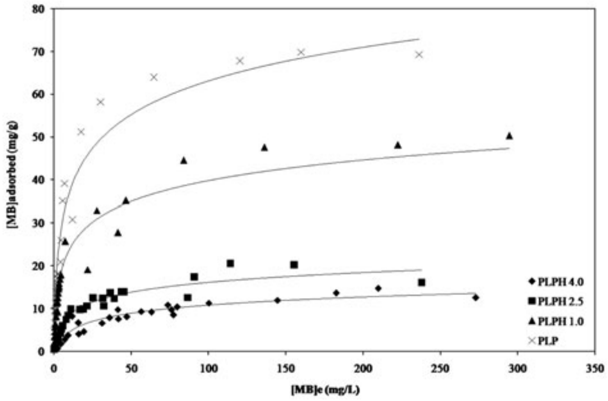


Fig. 8. Effect of initial concentration on MB adsorption onto PLP and SMPLP.

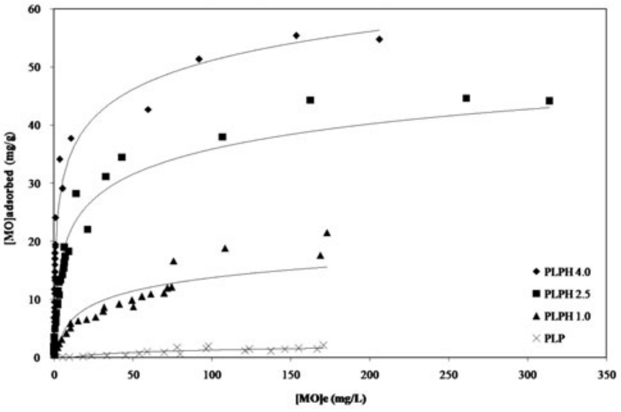


Fig. 9. Effect of initial concentration on MO adsorption onto PLP and SMPLP.

saturated at a certain concentration. At such concentrations, more dye molecules are left unadsorbed in the solution due to the saturation of binding sites, resulting in the constant removal rate. At this stage, the adsorption process reached equilibrium and the amount of dye adsorbed onto PLP and SMPLP was equal to the amount desorbed. Similar results have been reported for the adsorption of MB onto hazelnut shell [26] and the removal of MO by surfactant-modified wheat straw [17].

3.5. Effect of temperature

Temperature is an important parameter for the adsorption process. The adsorption studies were performed at different temperatures over a range of initial dye concentrations. The effect of temperature on the adsorption of MB onto PLP and MO onto PLPH 4.0 are presented in Figs. 10 and 11, respectively. It can be observed that the equilibrium adsorption capacity of PLP and PLPH 4.0 decreased with the increase in temperature, indicating the exothermic nature of the adsorption reaction. This is due to the weakening of the physical bonding between dye molecules and the active sites of the adsorbent as temperature increases, whereas, the solubility of dyes increased, thus enhancing the interaction forces between solute and solvent. Similar observations have been reported for the adsorption of MB onto pomegranate pulp [29] and MO onto cationic surfactant-modified wheat straw [17].

3.6. Adsorption isotherm

The relationship between the concentration of adsorbed substance and adsorption capacity of adsorbing species is known as adsorption isotherm.

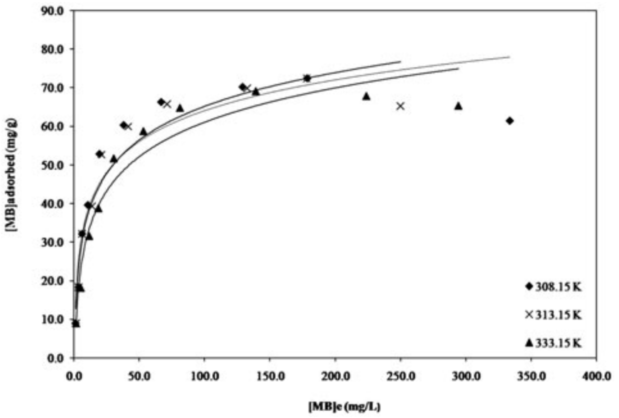


Fig. 10. Effect of temperature on MB adsorption onto PLP.

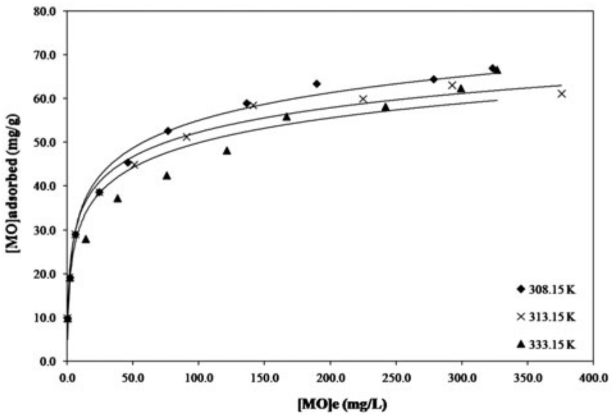


Fig. 11. Effect of temperature on MO adsorption onto PLPH 4.0.

The adsorption isotherm describes the distribution of adsorbate between liquid and solid phases and the behaviour of the adsorption system as adsorption process approaches equilibrium. In this study, the adsorption results were analysed using the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models.

The Langmuir isotherm model is based on the assumption that monolayer adsorption occurs on the homogenous surface of the adsorbent with constant adsorption energy and no transmigration or lateral interaction between the adsorbates in the surface of adsorbent [30]. The corresponding mathematical equation is given as:

$$q_e = \frac{bQ_oC_e}{1 + bC_e} \tag{3}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit of adsorbent and concentration of unadsorbed dye at equilibrium, respectively. Q_o (mg/g) is the maximum amount of dye per unit mass of adsorbent to form complete monolayer coverage on the surface of adsorbent and b is the Langmuir constant related to the affinity of binding site. The linear form of the Langmuir isotherm model is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{4}$$

The plot of $1/q_e$ against $1/C_e$ gives a straight line graph, where $1/bQ_o$ and $1/Q_o$ are the slope and Y intercept, respectively.

The Freundlich isotherm model is a non-linear empirical equation describing the multilayer adsorption on heterogeneous surface of adsorbent with inconsistent binding energy and unequal available active site on the surface of adsorbent [30]. The Freundlich mathematical expression is given as:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where K_F and n are the Freundlich constants with K_F (mg/g) denoting the maximum adsorption capacity of adsorbent and n indicator on the favourability of adsorption process. The linear form of the Freundlich isotherm model is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

The plot of $\log q_e$ against $\log C_e$ gives a straight line graph, where $1/n$ and $\log K_F$ are the slope and Y intercept, respectively.

The Dubinin–Radushkevich (D–R) is an isotherm model that does not assume the adsorption of adsorbate onto a homogenous surface of the adsorbent or a constant biosorption potential as the Langmuir isotherm. The Dubinin–Radushkevich mathematical expression is given as:

$$\ln q_e = \ln Q_o + \beta R^2 T^2 \ln^2\left(1 + \frac{1}{C_e}\right) \tag{7}$$

where β (mmol^2/J^2), R (8.314 J/mol/K) and T (K) are coefficients related to the mean free energy of adsorption, gas constant and temperature, respectively. The plot of $ln\, q_e$ against $\ln^2(1 + 1/C_e)$ gives a straight line, where β and Q_o are the slope and Y intercept, respectively.

The Temkin isotherm model is developed by taking into account the effect of indirect interaction between adsorbate–adsorbate on the adsorption process. The adsorption heat of all molecules decreases linearly with coverage due to the adsorbate–adsorbate interaction [24]. The linear form of the Temkin isotherm model is expressed as:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{8}$$

where B_T is the Temkin constant and K_T (L/g) is the Temkin adsorption potential. The plot of q_e against $\ln C_e$ gives a straight line, where B_T and $B_T \ln K_T$ are the slope and Y intercept, respectively. The values of adsorption isotherm parameters for all models are listed in Table 1.

The applicability of all isotherm models was compared based on the correlation coefficient (R^2). The experimental results indicate that the adsorption of MB and MO onto PLP and SMPLP followed the Langmuir isotherm model ($R^2 > 0.99$). The maximum monolayer adsorption of MB and MO according to this model was 52.6 and 47.6 mg/g, respectively. Conformation of adsorption data with the Langmuir isotherm model described the homogenous distribution of active sites on PLP and SMPLP surfaces with the formation of MB or MO monolayer coverage on the outer surface of both adsorbents. This finding was in line with previous studies reported on the suitability of the Langmuir isotherm model for the adsorption of MB by phoenix tree's leaves [23] and removal of MO by bottom ash and de-oiled soya [24]. The negative value of MO adsorption onto PLP for the Langmuir isotherm explained the inadequacy of this model to describe the adsorption process under certain conditions.

The comparison on adsorption capacity of PLP and SMPLP with other agricultural wastes obtained from the literature for adsorption of MB and MO are listed in Table 2. The maximum adsorption of MB by PLP was intermediate between various raw and modified agricultural wastes. However, the adsorption of MO by SMPLP was relatively high when compared to those in most of previous works. This suggests that PLP, a low-cost natural resource can be applied as an alternative adsorbent for cationic pollutants' adsorption and SMPLP provides an effective solution for the removal of anionic compounds from wastewater.

3.7. *Adsorption thermodynamic*

The thermodynamic study was carried out to understand the feasibility and spontaneity of the adsorption process. The thermodynamic parameters were calculated by vant't Hoff and Gibb's Helmholtz equation [17]:

$$\Delta G^\circ = -RT \ln K_C \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

where ΔG°, ΔH° and ΔS° are the Gibb's free energy change, enthalpy and entropy, respectively. T (K) is the solution temperature and R is the gas constant. K_C is the adsorption distribution coefficient and is determined as:

$$K_C = \frac{C_a}{C_e} \tag{11}$$

Table 1
Isotherm parameters for adsorption of MB and MO onto PLP and SMPLP

	Samples							
	MB				MO			
Isotherm	PLP	PLPH 1.0	PLPH 2.5	PLPH 4.0	PLP	PLPH 1.0	PLPH 2.5	PLPH 4.0
Langmuir								
Q_o (mg/g)	52.6	33.3	21.7	21.3	−1.2	19.2	26.3	47.6
b (1/g)	0.211	0.242	0.057	0.016	−0.005	0.035	0.369	0.677
R^2	0.994	0.971	0.998	0.987	0.823	0.994	0.990	0.991
Freundlich								
K_F (mg/g)	8.5	7.3	3.2	1.2	0.0	1.0	6.3	16.4
n (1/g)	1.325	2.331	2.717	2.058	0.905	1.637	2.410	3.717
R^2	0.990	0.913	0.871	0.922	0.805	0.958	0.931	0.876
Dubinin–Radushkevich								
Q_o (mg/g)	17.3	9.5	12.1	1.0	1.7	10.1	19.2	24.2
β (mmol^2/J^2)	−0.000000182	−0.000000117	−0.000004158	−0.000000087	−0.000371549	−0.000013664	−0.000001040	−0.000000088
R^2	0.925	0.970	0.918	0.939	0.755	0.714	0.894	0.926
Temkin								
K_T (L/g)	1.6	8.3	3.7	0.4	0.1	0.6	1.7	11.3
B_T	13.450	1.764	0.878	2.948	0.640	2.909	7.295	7.151
R^2	0.974	0.991	0.966	0.945	0.971	0.962	0.984	0.987

Table 2
Comparison of adsorption capacities of various agricultural wastes for MB and MO

Agricultural wastes	Maximum adsorption capacity (mg/g)	Refs.
Methylene blue		
Papaya seed	555.557	[31]
Succinylated sugarcane bagasse	478.50	[32]
Guava (*Psidium guajava*) leaf	295	[33]
Miswak (*Salvadora persica*) leaves	200.00	[24]
Hydrochloric acid modified *Calotropis procera* leaf	192.31	[4]
Garlic peel	142.86	[27]
Pumpkin seed hull	141.92	[34]
Pheonix's tree leaves	89.70	[23]
Pineapple leaf	52.632	Present study
Yellow passion fruit (*Passiflora edulis* Sims. f. *flavicarpa* Degener)	44.7	[35]
Rice husk	40.5833	[36]
Pomegranate (*Punica granatum*) pulp	36.36	[29]
Pineapple leaf	31.60	[37]
Wheat shells	21.50	[25]
Banana peel	20.80	[38]
Orange peel	18.60	[38]
Spent rice	8.13	[39]
Methyl orange		
Cetyltrimethylammonium bromide-modified wheat straw	50.4	[5]
Hexadecyltrimethylammonium-modified pineapple leaf	47.619	Present study
Banana peel	21.0	[38]
Orange peel	20.5	[38]
De-oiled soya	3.62	[28]

where C_a (mg/L) and C_e (mg/L) is the equilibrium dye concentration on the adsorbent and in the solution, respectively. The plot of ΔG° against T gives a straight line, where ΔH° and ΔS° are the slope and intercept-Y, respectively. The van't Hoff plots for the adsorption of MB onto PLP and MO onto PLPH 4.0 are presented in Figs. 12 and 13, respectively. The ΔG°, ΔH° and ΔS° are listed in Table 3.

The negative values of ΔG° at all temperatures indicate the spontaneous adsorption process, reflecting the affinity of PLP and PLPH 4.0 towards MB and MO, respectively. The negative value of ΔH° further confirms the exothermic nature of the adsorption process. The positive value of ΔS° for the adsorption of MB onto PLP indicates an increase in the randomness of the adsorption and affinity of PLP for MB, whereas, the negative value of ΔS° signifies the decrease in the randomness at the PLPH 4.0–MO interface and no significant change occurs in the internal structure of PLPH 4.0 during the adsorption process.

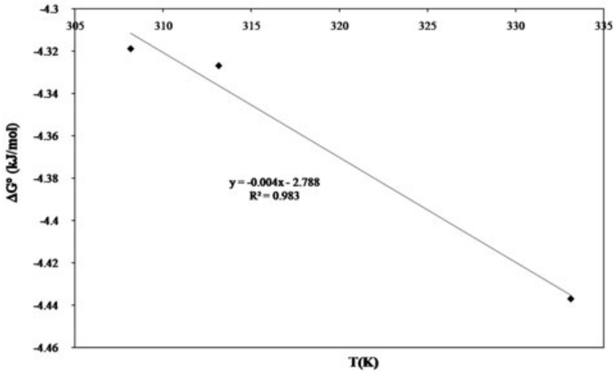


Fig. 12. Vant't Hoff plot for the adsorption of MB onto PLP.

3.8. Effect of surfactant concentration

The concentration of HDTMA-Br solution influenced the orientation of adsorbed HDTMA-Br molecules on SMPLP surface and the affinity of SMPLP towards dyes. The critical micelle concentration (CMC), defined as the minimum surfactant concentration above which micelle-like structure forms, determined the adsorption behaviour of HDTMA-Br molecules onto SMPLP. The CMC value of HDTMA-Br is 0.93 mM [40]. At a concentration below CMC, HDTMA-Br molecules exist as monomers in the

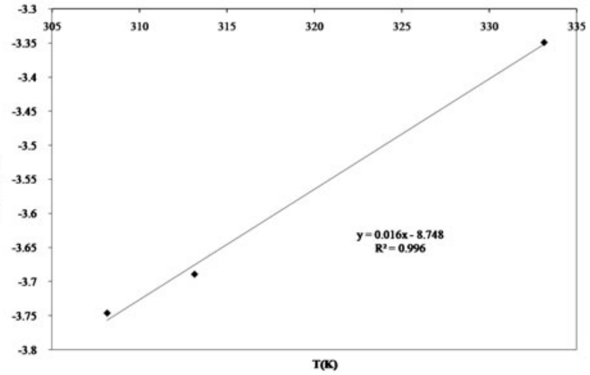


Fig. 13. Van't Hoff plot for the adsorption of MO onto PLPH 4.0.

Table 3
Thermodynamic parameters for adsorption of MB onto PLP and MO onto PLPH 4.0

T (K)	ΔG°	
	MB	MO
308.15	−4.319	−3.746
313.15	−4.327	−3.689
333.15	−4.437	−3.349
ΔH°	−2.788	−8.748
ΔS°	0.004	−0.016

solution and are adsorbed onto the SMPLP surface in a monolayer form. However, as the concentration increased above CMC, HDTMA-Br molecules rearranged on SMPLP surface to form a HDTMA-Br bilayer known as hemimicelle of admicelle. This results in surface charge reversal from negative to positive potential. Therefore, in this study, HDTMA-Br concentrations used to modify the surface of PLP were 1.0, 2.5 and 4.0 mM. This is in accordance, with the previous study reported on the modification of barley straw with hexadecylpyridinium chloride with the concentration above the CMC value of the corresponding surfactant [15,16].

The comparison of MB and MO adsorption by PLP and SMPLP is presented in Fig. 14. From Fig. 14, the highest and lowest adsorption of MB was by PLP and PLPH 4.0, respectively. The MB removal followed the trend of PLP > PLPH 1.0 > PLPH 2.5 > PLPH 4.0. However, for MO, the highest and lowest adsorption was by PLPH 4.0 and PLP, respectively. The trend of MO removal was PLPH 4.0 > PLPH 2.5 > PLPH 1.0 > PLP. It was observed that PLP and SMPLP showed different adsorption behaviour towards MB and MO. MB was strongly attracted to PLP, while MO was highly adsorbed by PLPH 4.0.

The major components of PLP are cellulose, hemicelluloses and lignin [9]. Cellulose and lignin consist of free hydroxyl groups which give the PLP surface its negative potential characteristic [29] and thus act as active sites to adsorb positively charged MB and repelled negatively charged MO. The MB molecules were retained on the surface of PLP through electrostatic forces.

The presence of HDTMA-Br bilayer on the outer surface of SMPLP results in the surface charge reversal from negative to positive potential since the positively charged head group of HDTMA-Br are pointed towards the bulk of dye solution [15,28]. Due to the difference in molecular potential, negatively charged MO was preferably adsorbed by positively charged head group of HDTMA-Br attached on the surface of SMPLP rather than by PLP. The interaction between HDTMA-Br and MO molecules occurred via the formation of electrostatic attraction. Similar results were reported for the adsorption of direct red 12 B, rhodamine B, acid brilliant blue and procion orange onto HDTMA-Br-modified coconut coir pith [10,14] and the adsorption of MO onto cetyltrimethylammonium-modified wheat straw [17]. However, surface modification using cationic surfactant did not affect the removal of cationic dyes to greater extent [14].

3.9. *Desorption of surfactant and dye*

The desorption study is important to understand the adsorption mechanism of adsorbate onto adsorbent and to regenerate the spent adsorbent for economical purpose [17]. The percentage of HDTMA-Br desorbed from PLPH 1.0, PLPH 2.5 and PLPH 4.0 are presented in Fig. 15. It was observed that the desorption capacity of SMPLP against HDTMA-Br decreased with the increase in the pH of distilled water. The presence of H^+ ions at acidic pH displaced the HDTMA-Br on the surface of SMPLP and this consequently promoted higher desorption rate. The highest and lowest desorption of HDTMA-Br were from PLPH 4.0 and PLPH 1.0, respectively. This is due to increase in the amount of HDTMA-Br adsorbed as the initial concentration of the respective surfactant increases. In addition, the HDTMA-Br adsorbed onto PLP at concentration above CMC was in the form of double layer or micelle. The weak hydrophobic interaction between hydrocarbon tail results in the release of HDTMA-Br throughout the desorption process.

The desorption capacity of PLP against MB and PLPH 4.0 against MO are presented in Figs. 16 and 17, respectively. From Fig. 16, desorption of MB was higher at pH 3.00, decreasing at pH 4.00 and remained constant at pH 4.00–11.00. This is because at acidic

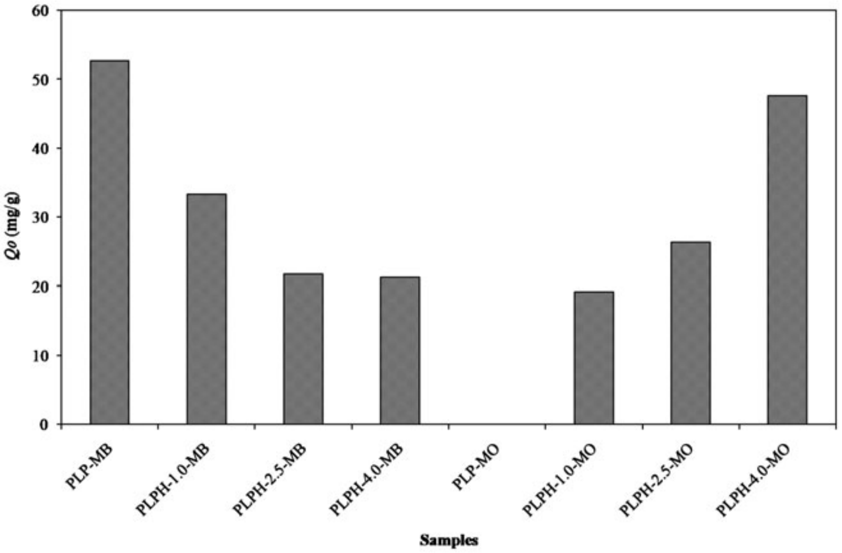


Fig. 14. Maximum adsorption capacity values of MB and MO adsorption by PLP and SMPLP.

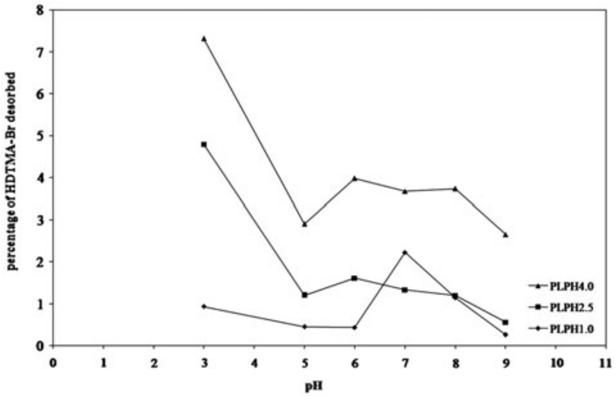


Fig. 15. Desorption of HDTMA-Br from SMPLP.

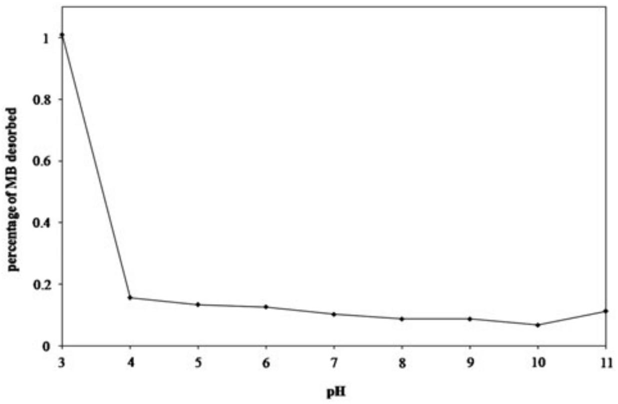


Fig. 16. Desorption of MB from PLP.

pH, the H$^+$ ions present competing for the adsorption sites favour the desorption of MB from PLP. The MO showed a different desorption trend from MB. From Fig. 17, the percentage of MO desorption was constant at pH 3.00–9.00 and exhibited a sharp decrease at pH 10.00–11.00. The reduction in positively charged adsorption sites as the pH increases has led to electrostatic repulsion of MO from PLPH 4.0 resulting in a higher desorption at alkaline pH [15]. This is in accordance with the previous study on desorption of procion orange from surfactant-modified coir pith [10].

The maximum desorption of HDTMA-Br, MB and MO were 7.32, 1.01 and 5.92%, respectively. The lower percentage of desorption suggests that HDTMA-Br, MB and MO have been chemisorbed onto the surface of adsorbent [14].

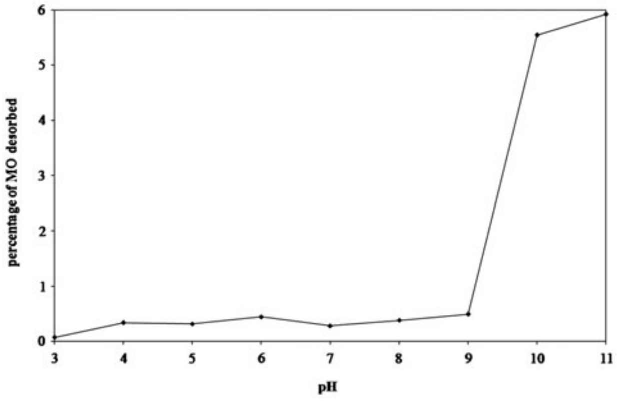


Fig. 17. Desorption of MO from PLPH 4.0.

4. Conclusion

The capability of raw and surfactant-modified pineapple leaves powder to adsorb cationic and anionic dyes was studied in batch mode at room temperature. The results from FTIR spectroscopy revealed that the functional groups and chemical characteristics of pineapple leaves remain unchanged after surface modification process. The SEM analysis before and after surface modification proved the adsorption of HDTMA-Br onto the surface of pineapple leaves. The determination of the amount of HDTMA-Br adsorbed onto PLP indicated that there was correlation between the amounts HDTMA-Br adsorbed onto pineapple leaves with the increase in the initial concentration of HDTMA-Br. The adsorption of MB and MO was favoured at pH 11.00 and 3.00, respectively. The adsorption of MB was rapid and efficient using raw PLP while PLP treated with the highest concentration of HDTMA-Br showed excellent adsorption capacity towards MO. The adsorption data were well fitted into the Langmuir isotherm model with maximum monolayer adsorption capacity for MB and MO being 52.6 and 47.6 mg/g, respectively. The high temperature was not beneficial for MB and MO adsorption. In addition, the thermodynamic parameters suggested the adsorption process for both dyes was spontaneous and exothermal. Therefore, the raw and surfactant-modified PLP are proven to be able to function as alternative adsorbents in treating wastewater containing diverse types of compounds. Furthermore, PLP treated with cationic surfactant, HDTMA-bromide could enhance the adsorption capacity of pineapple leaves towards anionic dye.

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