Chemical Modification of *Artocarpus odoratissimus* Skin for Enhancement of their Adsorption Capacities toward toxic Malachite Green Dye

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Abstract

Chemical modification of surfaces introduces new characteristics which would thereafter cause the adsorbent to behave as a new material. This aspect has become recently attractive to improve the performance of natural adsorbents toward environmental pollution control. The surface of *Artocarpus odoratissimus* skin (TS) modified by agents having high electron densities or negatively charged moieties acts more efficiently to attract malachite green (MG) dye molecules which bear positive charges. Among three modifies attempted; sodium dodecyl sulfate (SDS), ethylenediaminetetraacetic acid (EDTA) and sodium hydroxide (NaOH) in aqueous phase, the surface is more efficiently covered by SDS although the affinity of the modified surface toward MG was most significantly improved by NaOH treatment, owing to the acid-base type of reaction with surface carboxylic and phenolic acid moieties which would be converted to corresponding anions promoting sorption of MG. The maximum adsorption capacity (q_{max}) for TS and its SDS, EDTA and NaOH modified forms was 80.5 mg/g, 100.8 mg/g, 116.8 mg/g and 157.6 mg/g, respectively. TS and TS modified with SDS and EDTA followed the Redlich-Peterson (R-P) isotherm model while the Sips model best fitted the NaOH modified TS. The extent of adsorption of MG by the natural and modified TS is influenced by ionic constituents in the medium and the pH.

Keywords: Adsorption isotherm, malachite green dye, *Artocarpus odoratissimus* adsorbent, surface modification

1. Introduction

Many industries release wastes upon their preparation and manufacturing stages. These waste substances either pollute air or land, or find their ways to enter aquatic systems. Water pollution has thus become a major worldwide concern for many decades, and this problem is getting increasingly serious as it causes many adverse effects including health concerns. It is claimed that typical pollutants in water systems are organic substances, dyes, pesticides and heavy metals, which cause detrimental effects to natural aquatic systems through retardation and death of living organisms it holds. The greater environmental awareness in both the public and regulator sphere in recent years has necessitated for effective treatment of industrial effluent. As such, there has been a great deal of research in finding cost-effective methods for the removal of contaminants from wastewater [1-3].

Adsorption has shown exciting potential in removing pollutants, such as dyes and heavy metals. Adsorbents can be from wastes such as fruits [4-6], agricultural by-products [7], oil shales [8], peat [9, 10], and many others [11-14]. The reasons why adsorption has gained popularity in recent years lie in its having various attractive features such as abundance of materials which are low-cost, reusability, environmental friendliness, and low possibility of formation of harmful by-products as the pollutants are simply adsorbed onto the biomass in

contrast to other methods employed in pollution control to clean the environment such as chemical, biological, filtration and thermal treatments, which are associated with many undesirable aspects.

The area of chemical modification of natural adsorbents to enhance adsorption characteristics toward pollutant removal is relatively new. For example, peat has been reported to enhance its ability to adsorb Cu(II) through both acid and base modification [15]. An effective approach to enhance the removal of ionic species from solution would be to introduce opposite charges on the adsorbent surface so that the extent of adsorption, and hence, the extent of pollutant removal could be made more efficient through Coulombic attraction. Consequently, cationic pollutants, in particular, can be more efficiently removed by introducing negatively charges, or alternatively, increasing electron density on the adsorbent. Among few reports on this aspect, removal of crystal violet dye by NaOH modified *Artocarpus odoratissimus* skin [16], removal of humic acid by surfactant modified zeolite [17], magnetic EDTA-modified chitosan/SiO_2/Fe_3O_4 adsorbent for the removal of heavy metals [18], lauric acid modified oil palm leaves for removing crude oil from water [19] have taken recent attention in the field of environmental pollution control.

This paper focused on the removal of cationic malachite green (MG) dye using chemically modified skin of a tropical fruit, *Artocarpus odoratissimus*. *A. odoratissimus* belongs to the *Artocarpus spp.* of the Moreaceae family and is endogenous to the Borneo Island in South East Asia. In Brunei Darussalam, the locals call it "Tarap". This fruit was selected based on the report by Tang et al. [20] that the inedible Tarap skin (TS) accounts for almost 50% of the whole fruit. Being a popular fruit amongst the locals, there is a considerable amount of TS being discarded. Hence, utilizing TS will have a two-fold advantage – it not only helps to reduce discarded wastes but at the same time, converts TS which is normally of no economic value into a useful adsorbent for the removal of toxic environmental pollutant. Further this study utilizes TS and its modified forms as potential adsorbents for the removal of toxic MG dye and to the best of our knowledge this has never been previously reported. Chemical modification reagents used for this purpose are sodium dodecyl sulfate (SDS), [$CH_3(CH_2)_{11}SO_4^-Na^+$, an anionic surfactant], ethylenediaminetetraacetic acid (EDTA) (a chelating agent) and NaOH, all of which increase the electron density of the adsorbent, promoting the attraction of the cationic adsorbate. Performance of the natural skin was also investigated for comparison.MG was chosen in this study as it is a hazardous dye, known to bio-accumulate in fish and aquatic organisms resulting in transfer of pollutants higher up the food chain. It is also a suspected human reproductive toxicant. When tested on fish (*Ictalurus punctatus*), MG was reported to have LC_{50} of 0.14 mg/L.

2. **Experimental**

2.1. *Materials and sample preparation*

Artocarpus odoratissimus (Tarap) fruits were randomly purchased from the local open markets in Brunei Darussalam. The skin, which was separated from the rest of the fruit, was oven dried at 60 °C until a constant mass was obtained. Dried Tarap skin (TS) sample was then powdered, sieved using laboratory test sieve with stainless steel as the mesh material and the fraction of particle sizes ranging from 355 to 850 μm was obtained for experiments. Chemical treatment with NaOH was carried out by shaking TS (1.00 g) in 3.0 M NaOH (100 mL) overnight. The NaOH-treated TS (TS-NaOH) was then filtered and washed with double distilled water to remove excess NaOH until the filtrate reached neutral pH. TS-NaOH was then dried in an oven at 60 °C until a constant mass was obtained. Similar procedure was used to modify TS with SDS and EDTA to form TS-SDS and TS-EDTA, respectively.

Malachite green (MG)[Molecular formula = $C_{23}H_{25}ClN_2$ (chloride), Molar mass = 364.911 g/mol (chloride), λ_{max} = 618 nm] was purchased from Sigma Chemicals. All chemicals and reagents were used without prior purification. All experiments were carried out in triplicate unless otherwise stated. All shaking experiments were carried out on an orbital shaker set to 250 rpm at ambient temperature unless otherwise stated. The ratio of mass of adsorbent in gram: volume of dye solution in mL was kept at 1:500 throughout all experiments with adsorbent (0.050 g) in MG solution (25.0 mL). Percentage removal of MG dye in all the experiments was determined using initial dye concentration and its concentration established at adsorption equilibrium under the optimized experimental conditions.

2.2 *Instrumentation*

Quantification of MG present in filtrates was carried out by measuring absorbance at its λ_{max} of 618 nm using the Shimadzu UV-1601PC UV-Visible spectrophotometer (UV-Vis). Functional group characterization of the adsorbents was performed using Shimadzu Model IRPrestige-21 Fourier Transform Infra-Red (FTIR) spectrophotometer while elemental characterization of the surface of adsorbents was carried out on PANalytical Axios^{max} X-Ray Fluorescence (XRF) spectrophotometer. Morphological characteristics of the adsorbent's surface were investigated using TescanVega XMU Scanning Electron Microscope (SEM) while SPI-MODULE^{TM} sputter coater was used to gold coat the surface of adsorbents to brighten them before being observed by SEM. Thermoscientific orbital shaker set at 250 rpm was used in all experiments, which were conducted at ambient temperature unless otherwise stated.

2.3 *Effect of contact time*

Mixture of adsorbent (0.050 g) in 25.0 mL of 1000 mg/L MG was shaken for different shaking time periods up to 4.0 h with 15 minutes intervals for the first 1.0 h, followed by 30 minutes intervals for the next 3.0 h. After shaking, the suspension was filtered using a metal sieve to separate the filtrate for the determination of the concentration of MG. The extent of removal of MG was then monitored for each shaking time period to determine the optimum shaking time. Upon determining the optimum shaking time, the optimum settling time was determined with 30 minutes settling time intervals up to 4.0 h. After settling, the suspension was filtered as explained above, and the filtrate was analyzed.

2.4 *Effect of medium pH*

The extent of removal of MG at different medium pH was determined by shaking a mixture of 0.050 g of adsorbent and 25.0 mL of 100 mg/L MG solution with adjusted pH of 3.0, 4.0, 6.0, 8.0 and 10.0, followed by settling for pre-determined optimum time periods. Unadjusted ambient pH was also used for comparison. The solution was then filtered, and the filtrate was analyzed to determine the concentration of MG.

2.5 *Point of zero charge of adsorbents*

The investigation of the point of zero charge of TS and its modified forms was carried out following method by Lim et al. [21] with some slight modification. Briefly, solutions of 0.01 M KNO_3 of different pH (2.0, 3.0, 4.0, 6.0, 8.0 and 10.0) were prepared using 0.1 M NaOH and 0.1 M HCl, and the initial pH (pH_i) was recorded. An aliquot of 25.0 mL of 0.01 M KNO_3 was mixed with adsorbent (0.050 g), and the resulting suspension was shaken for 24 h at ambient temperature. The suspension was filtered and the final pH (pH_f) of the filtrate was recorded. The point of zero charge (pH_{PZC}) was determined by plotting a graph of difference in pH vs. pH_i. The point at which the difference in pH is zero corresponds to the zero charge of the sample.

2.6 *Effect of ionic strength*

The effect of ionic strength was done using method as reported by Lim et al. [22] with slight modification. Briefly, the adsorbent (0.050 g) was mixed with 100 mg/L MG dye (25.0 mL) that had been prepared in the various different concentrations of KNO_3 (0 M, 0.01 M, 0.1 M, 0.2 M, 0.4 M, 0.6 M and 0.8 M) and was shaken and settled at their optimum time. The mixtures were then filtered by using a metal sieve and the filtrates were diluted and analyzed by using UV-Visible spectrophotometer.

2.7 *Adsorption studies*

Adsorption studies were conducted by mixing TS (0.050 g) with 100 mg/L MG (25.0 mL) on an orbital shaker for optimized shaking and settling time periods. The solution was then filtered through a fine stainless steel sieve, and the concentration of MG in the filtrate was determined. Subsequent adsorption experiments were carried under the same conditions using MG solutions with different concentrations. The solution measurements were then used to determine the amount of MG adsorbed at different concentrations to test the validity of adsorption isotherms.

2.8 *Regeneration of spent adsorbent*
Investigation of the ability to reuse and regenerate spent adsorbent was carried out using method as reported by Chieng et al. [23], with slight modification. Briefly, the adsorbent (3.0 g) in 100 mg/L MG solution was shaken and settle at its optimum time. The MG-loaded adsorbent was washed with distilled water to remove excess dye and dried in an oven at 60 ˚C overnight after which different desorption treatments were done i.e. treatment with 1 M HCl, 1 M NaOH, rinsed by using small amount of water, shake with plenty of water and heat treatment at 200 ˚C. The desorbed samples were then shaken with a 100 mg/L MG at its optimum contact time. The filtrates were then analyzed. This procedure was repeated for five consecutive cycles. A control was kept for comparison.

3. **Results and discussion**
3.1. *Preliminary screening of adsorbents*
Prior to detailed investigation on adsorption of MG on TS modified with various chemical reagents, it is important to screen the performance of natural and chemically modified adsorbents for interaction with the MG. It has been observed, through comparison of the extent of removal of MG at 1000 mg/L concentration within a broad concentration range of each modifying agent, that the highest extent of removal of MG was obtained for 0.001 M SDS, 0.0001 M EDTA and 3.0 M NaOH, respectively. Hence, all subsequent modification of TS and adsorption experiments were carried out using these concentrations.

3.2. *Characterization of the adsorbents*
The point of zero charge (pH_{pzc}), the point where the ΔpH line intersects the x-axis at which the surface of the adsorbent will be zero charge, is an important property as it provides information on whether the surface charge is negative or positive at the desired pH .At pH lower than pH_{pzc}, the charge on the surface of the adsorbent will be predominantly positive while at $pH > pH_{pzc}$, the surface is predominantly negatively charged. Figure 1 shows that apart from TS-NaOH, which as expected, has a higher pH_{pzc} at pH 6.6, the other three adsorbents gave similar pH_{pzc} values of 4.9, 4.7 and 4.6 for TS, TS-SDS and TS-EDTA, respectively. This suggested that the adsorption processes for TS, TS-SDS and TS-EDTA are expected to be similar due to having similar charge environment. The higher pH_{PZC} observed for TS-NaOH is due to the deprotonation of the surface functional groups such as -COOH, -OH, $-NH_2$ by NaOH, thereby resulting in these functional groups becoming negatively charged. Therefore, the surface charge, and hence pH_{PZC}, is much affected with NaOH treatment.

Investigation of surface morphology of the adsorbents using SEM clearly shows that the surface of TS underwent significant changes upon various chemical treatments, indicating the efficiency of surface modification (Fig. 2). Prior to treatment, the surface of TS (Fig. 2A) was very uneven with holes and cavities being clearly visible. Among the three surface modifying agents, SDS results in a rather smooth and a flat surface (Fig. 2C), probably due to the surface coverage by bulky anionic tail component of the surfactant. Such a major surface change is not expected by NaOH treatment, as can be seen from Fig. 2B, although the chemical characteristics would have significantly changed. Treatment with EDTA also resulted in a visible change in the surface morphology of TS (Fig. 2D). The roughness of the surface of the adsorbent after treatment has been decreased, which is an important finding of the research, which would definitely improve the reproducibility of measurements. Such features would make it possible to extend the findings toward large-scale real applications. The observed change in decreased roughness is probably due to the chemical modification of the surface, which would also lead to filling some pores on the TS's surface.
Elemental characterization of TS using XRF spectroscopy showed that K (40.7%) is the major element present in TS followed by Fe (18.5%) and Ca (4.5%). Successful NaOH treatment of TS can be confirmed by a significant increase in the Na content in TS from 0% to 30.8% (Figure 3A). XRF spectra also showed that the sulfur content in TS has been increased by 1% after treatment with 0.001 M SDS, confirming that TS has been successfully modified. Further, K would have been replaced by Na when TS-NaOH is formed, where a decrease from 40.7% to 1.5% was observed, which is similar to report on NaOH modified breadnut peel [4]. Upon modification, TS-SDS and TS-EDTA also showed decreased K levels by 4.1% and 11.6%, respectively, indicating that K^+ were replaced by cationic constituents of modifying agents (Fig. 3B and 3C).
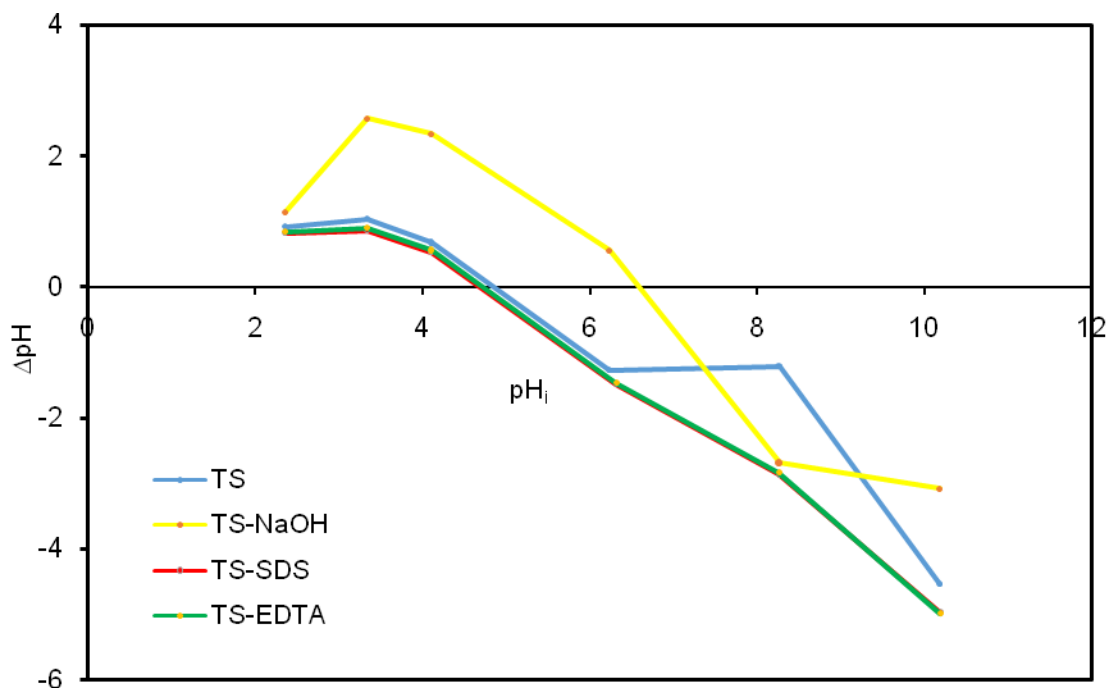
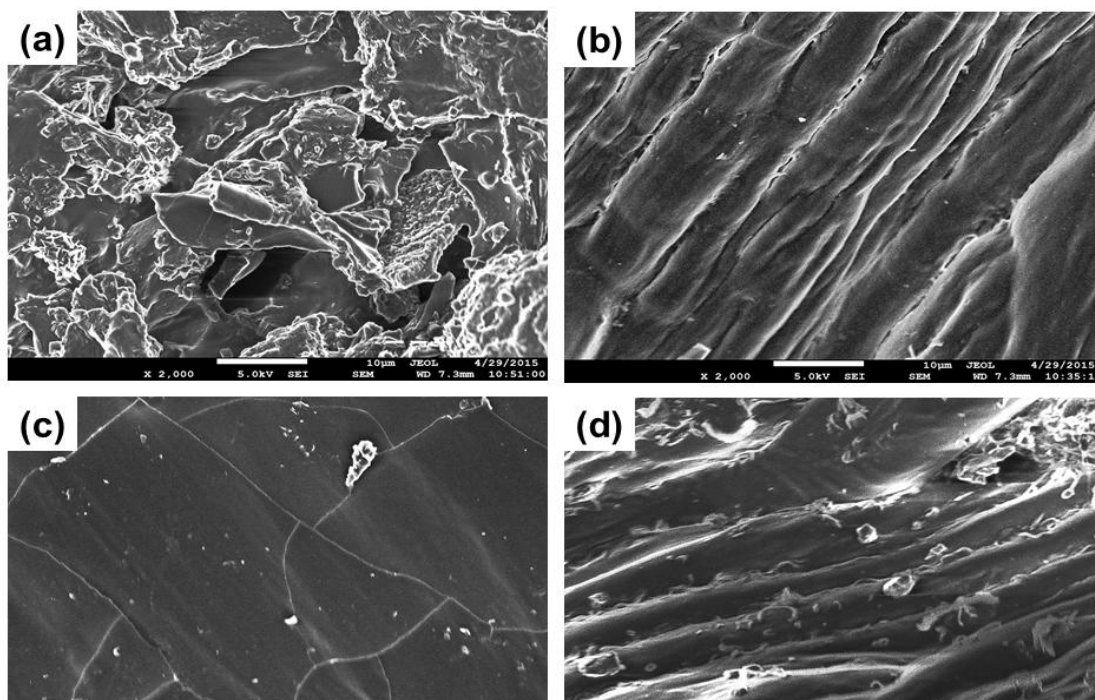**Figure 1:** Point of zero charge plots of all adsorbents

Figure 2: Surface morphology of (A) TS (B) TS-NaOH (C) TS-SDS and (D) TS-EDTA using SEM at 2000× magnification.
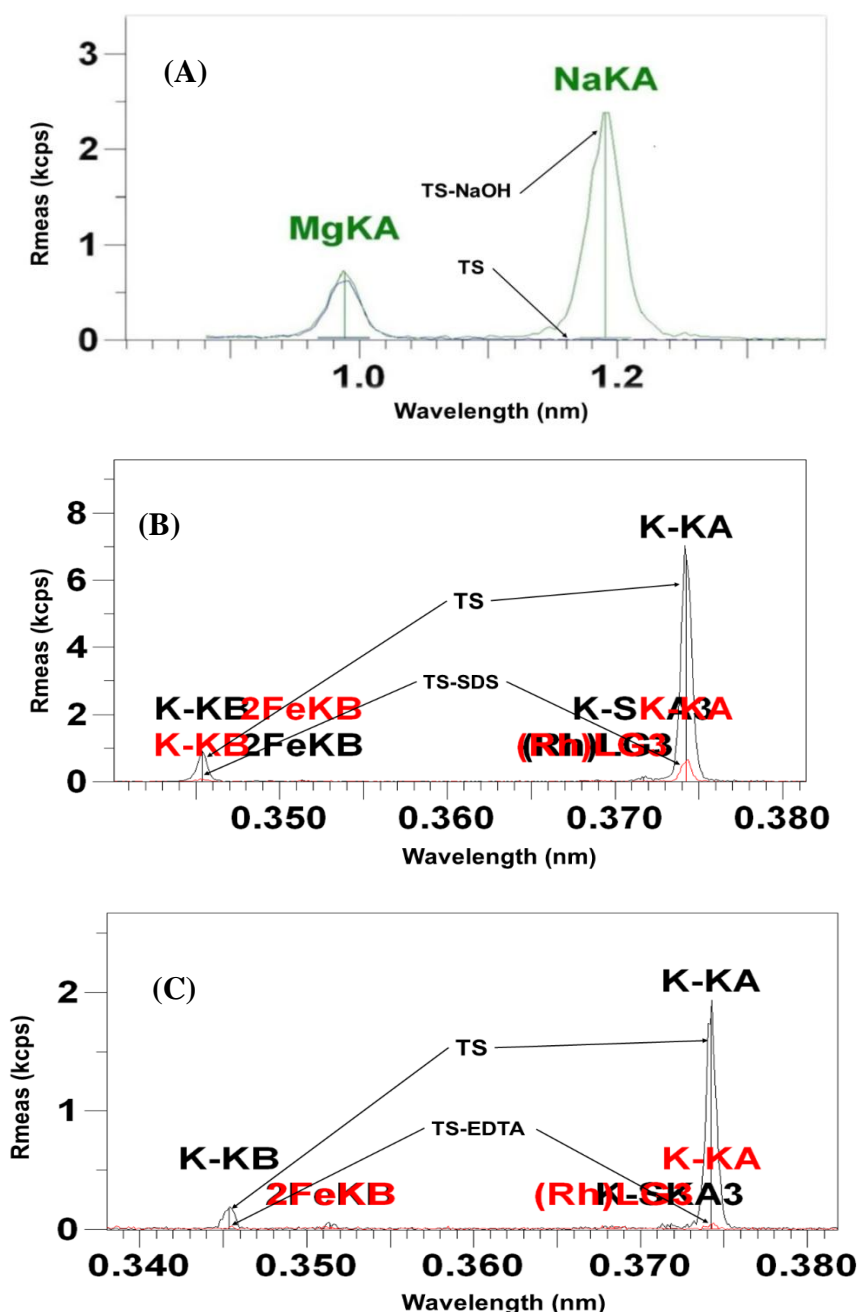
Figure 3: XRF results of the adsorbents comparing K before and after surface modification

Functional group characterization of TS, TS-NaOH, TS-SDS and TS-EDTA, before and after MG adsorption carried out using FTIR measurements, indicates that O-H stretching and amino N-H vibration that appeared in the range of 3320 to 3420 cm^{-1} were shifted upon adsorption with MG for all the samples, indicating that these functional groups could be involved in the adsorption process. Slight shifts in the wavelengths of peaks due to alkyl C-H, aromatic C=C stretching and amino N-H bending were also observed. Carboxyl C=O group at approximately wavelength 1734 cm^{-1} was found shifted to 1744 cm^{-1} and 1717 cm^{-1} for TS and TS-NaOH, respectively after adsorption with MG. However, no shift was observed for TS-SDS and TS-EDTA. For TS-NaOH, the broad peak given by O-H and N-H vibration was also found shifted to 3383 cm^{-1} after the adsorption process.

3.3. *Effect of contact time*

An important parameter that needs to be optimized is the effect of contact (shaking and settling) time required for the adsorbent-adsorbate system to reach equilibrium. Under the experimental conditions employed, untreated TS shows the slowest and least removal of 1000 mg/L MG while the rest of the three modified samples results in higher removal within the first hour, with TS-SDS reaching equilibrium in the shortest time frame, as shown in Fig. 4(A).
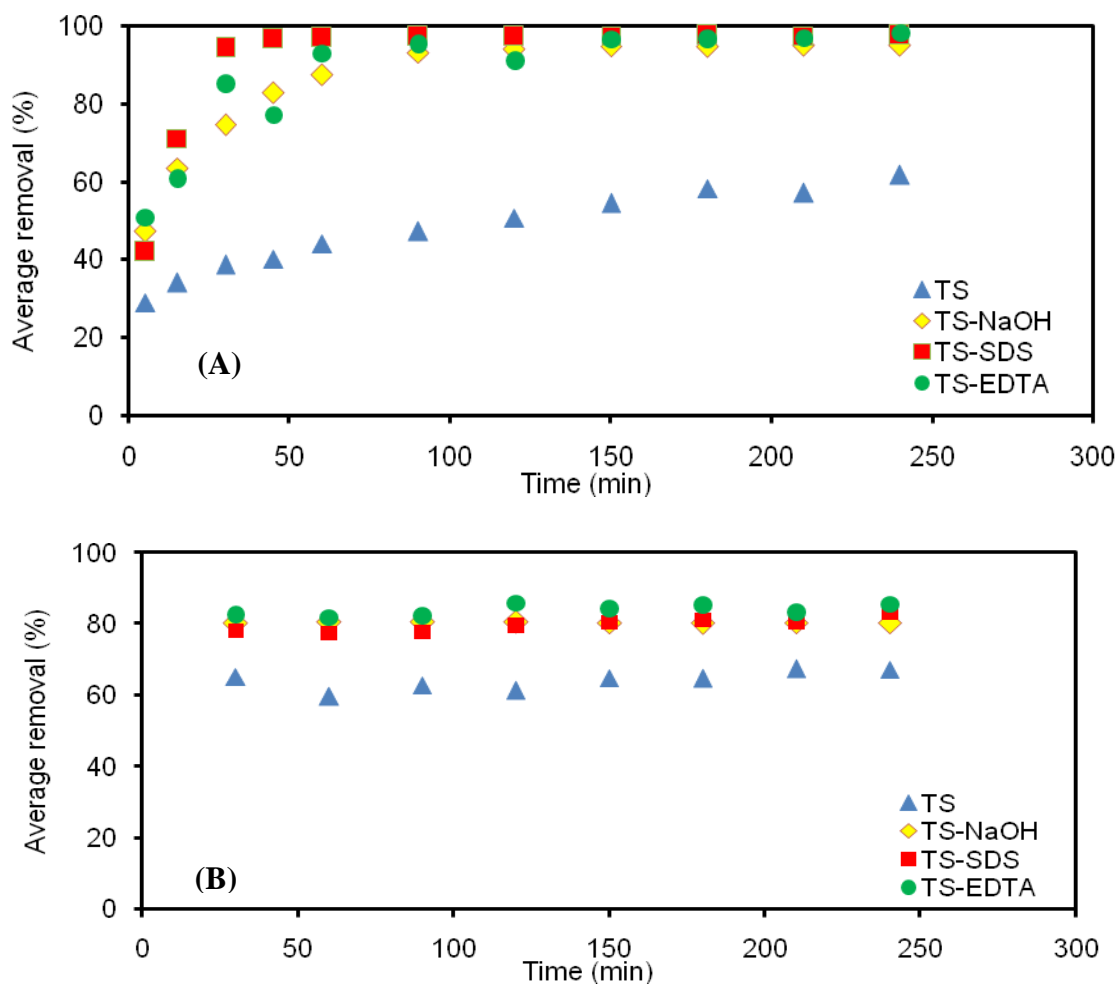

Figure 4: Effects of (A) shaking time and (B) settling time for TS, TS-NaOH, TS-SDS and TS-EDTA
(0.050 g TS, 25.0 mL of 1000 mg/L MG).

Fast initial dye update can be attributed to the availability of active vacant sites on the adsorbents' surfaces. Over time, the rate of adsorption decreases as these vacant sites are being filled and a saturation point is eventually reached. Based on the time taken to reach equilibrium, shaking times of 4.0 h, 3.0 h, 4.0 h, and 2.5 h were selected for TS, TS-SDS, TS-EDTA and TS-NaOH, respectively, as the optimum time period for each system. As for the settling time, it was observed in Fig. 4(B) that all four adsorbents were generally unaffected by the time required to settle. Hence, a 1.0 h was used to settle the adsorbate-adsorbent system after MG removal. Reports have shown that many adsorbents required considerably long shaking time even when much diluted concentration of MG was used. For example, breadfruit [22] and peat [24] required shaking time of 3.5 h and 4 h, respectively when 10 mg/L MG was used while *Azolla pinnata* [25], *Casaurina equisetifolia* needles [26] and base modified breadnut [4] took 3.0 h, 1.0 h and 2.0 h to reach equilibrium when the experiments were conducted using 100 mg/L MG dye solution.

3.4. *Effects of medium pH and ionic strength*

Regulating pH is one of the important factors that can affect adsorption as the medium pH can cause the surface of the adsorbent to be altered, thereby affecting the adsorption process. At the ambient pH of the dye, which is at pH = 4.0, the MG removal follows the order, TS (67.0%) < TS-SDS (82.3%) < TS-EDTA (82.8%) < TS-NaOH (94.1%). At pH 3.0, all the adsorbents exhibited reduction in adsorption ability toward MG with a decrease of approximately 26%, except for TS-NaOH (6%). The pKa of MG is 6.9 and therefore below this pH, MG is in cationic form. If the medium pH < pHpzc, the adsorbent's surface is expected to be predominantly positively charged. This will result in a decrease in MG dye being adsorbed since there will be an increase in electrostatic repulsion between the positively charged adsorbent and the cationic MG dye. Further, at low pH, there is also competition for the adsorption sites between H^+, which are present in large amount, and the cationic dye. Therefore, less dye would be expected to be removed under this condition. On the other hand, when the pH is increased, the surface of the adsorbents becomes less positive, resulting in more attraction between the adsorbents and MG. However, no adjustment of pH is necessary for this study, as there are no significant differences in the extent of MG removal beyond the ambient pH of 4.0, as shown in Fig. 5(A).
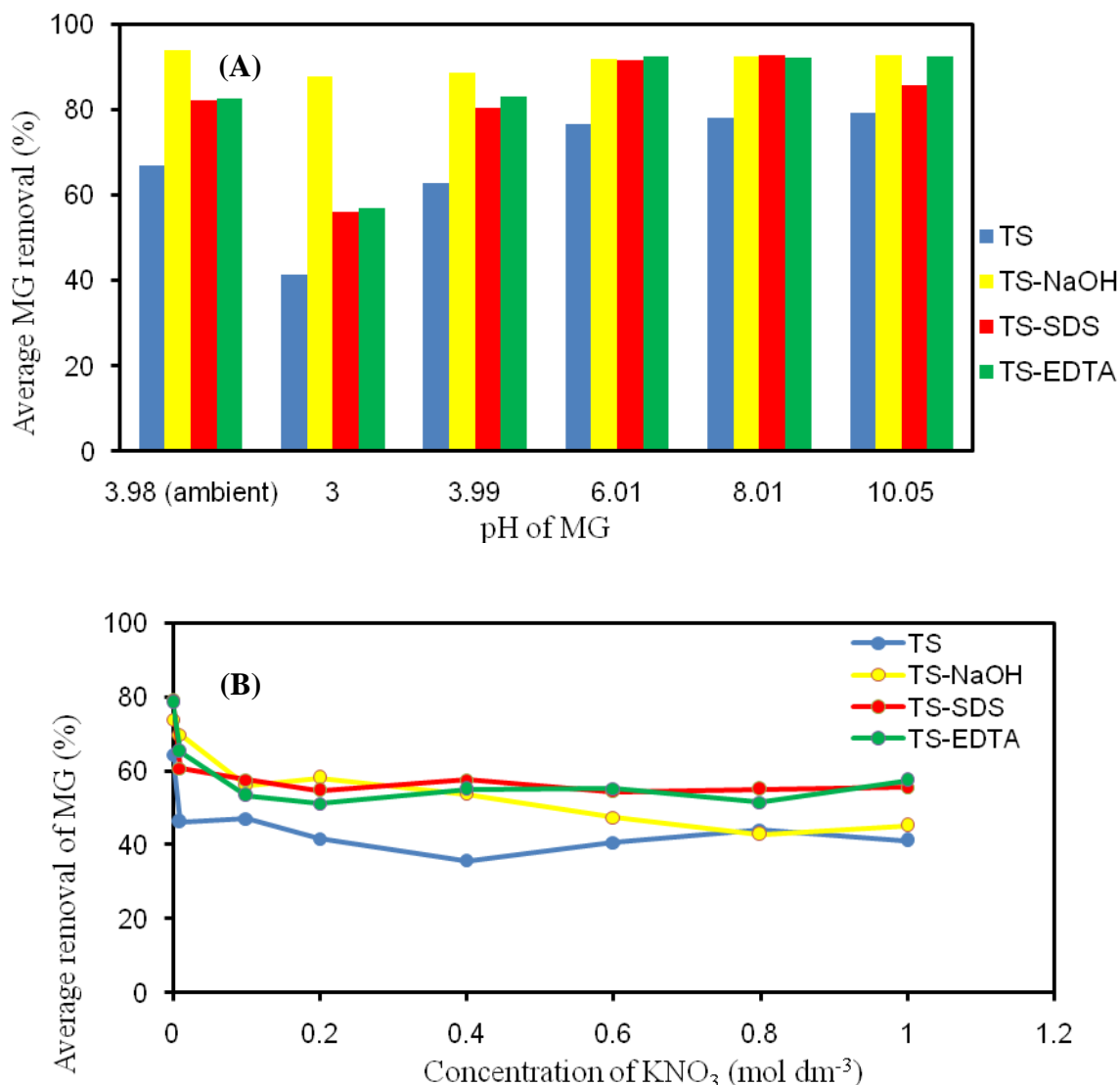

Figure 5: Effects of (A) medium pH and (B) ionic strength on the removal of MG

Real industrial effluents contain many different types of both inorganic and organic ions of varying concentrations, depending on the type of the industrial process. Consequently, there is a need to investigate the effect of ionic strength on the extent removal of MG. The influence of the presence of KNO_3 on the removal of MG is shown in Fig. 5(B). Increase in the concentration of KNO_3 resulted in decreased percentage removal of MG, probably due to the competition between K^+ ions and cationic MG for the limited number of sites available for sorption. All the four adsorbents investigated in this study, at 0.1 M KNO_3, showed more than 17% decrease in removal of MG, with TS-EDTA being the greatest (25%). However, from 0.2 M KNO_3 onwards, the ionic strength did not result in any further significant reduction for TS, TS-SDS and TS-EDTA, whereas TS-NaOH showed a further 10% decrease in the removal. Compared to breadnut, another *Artocarpus spp.*, which showed a drastic decrease of 17% and 65% for both breadnut skin and NaOH-breadnut skin, respectively [4] at lower concentration of 0.001M KNO_3, the adsorbents in this study are definitely more resilient to the effect of ionic strength. Hence, they would be more attractive as adsorbents in real wastewater treatment.

3.5. *Adsorption isotherms*

Experimentally obtained adsorption data of MG for each system (TS, TS-NaOH, TS-SDS and TS-EDTA), as shown in Fig. 6(A), were compared with simulated nonlinear isotherm equations as given in Equations (1) to (5) below:

Langmuir model: $\quad\quad\quad\quad\quad\quad\quad q_e = (K_L C_e q_{max})/(1 + K_L C_e)$ $\quad\quad\quad\quad$ (1)

Freundlich model: $\quad\quad\quad\quad\quad\quad q_e = K_F C_e^{1/n}$ $\quad\quad\quad\quad\quad\quad\quad\quad$ (2)

Dubinin-Radushkevich (D-R) model: $\quad q_e = q_s \exp(-\beta \varepsilon^2)$ $\quad\quad\quad\quad\quad\quad$ (3)

where $\varepsilon = RT \ln(1 + 1/C_e)$

Sips model: $\quad\quad\quad\quad\quad\quad\quad\quad q_e = (K_S q_{max} C_e^{1/n})/(1 + K_S C_e^{1/n})$ $\quad\quad$ (4)

Redlich-Peterson (R-P) model: $\quad\quad q_e = (K_R C_e)/(1 + a_R C_e^g)$ $\quad\quad\quad\quad$ (5)

K_L, K_F, K_S, K_R are the Langmuir, Freundlich, Sips and Redlich-Peterson constants, respectively. q_e and q_{max} are the adsorption capacity at equilibrium and maximum adsorption capacity, respectively. C_e is the concentration of dye at equilibrium, R is the universal gas constant, T is the temperature in Kelvin, a_R and g are the R-P constant and exponent which lies between 0 and 1, respectively.

All the simulated isotherm plots constructed were then used to determine the errors using six different functions, whose expressions are given below in Equations (6) to (11):

Average relative errors (ARE): $\quad\quad \dfrac{100}{n} \sum_{i=1}^{n} \left| \dfrac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right|_i$ $\quad\quad\quad\quad$ (6)

Sum square error (SSE): $\quad\quad\quad \sum_{i=1}^{n} (q_{e,calc} - q_{e,meas})_i^2$ $\quad\quad\quad\quad\quad$ (7)

Hybrid fractional error function (HYBRID): $\quad \dfrac{100}{n-p} \sum_{i=1}^{n} \left[\dfrac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right]_i$ $\quad\quad$ (8)

Sum of absolute errors (EABS): $\quad\quad \sum_{i=1}^{n} \left| q_{,meas} - q_{e,calc} \right|$ $\quad\quad\quad\quad$ (9)

x^2: $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \sum_{i=1}^{n} \dfrac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}$ $\quad\quad\quad\quad\quad$ (10)

Marquard's percent standard deviation (MPSD): $100 \sqrt{\dfrac{1}{n-p} \sum_{i}^{n} \dfrac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}}}$ $\quad$ (11)

where $q_{e,meas}$= experimental value, $q_{e,calc}$= calculated value, n = number of data points in the experiment and p = the number of parameters of the model.
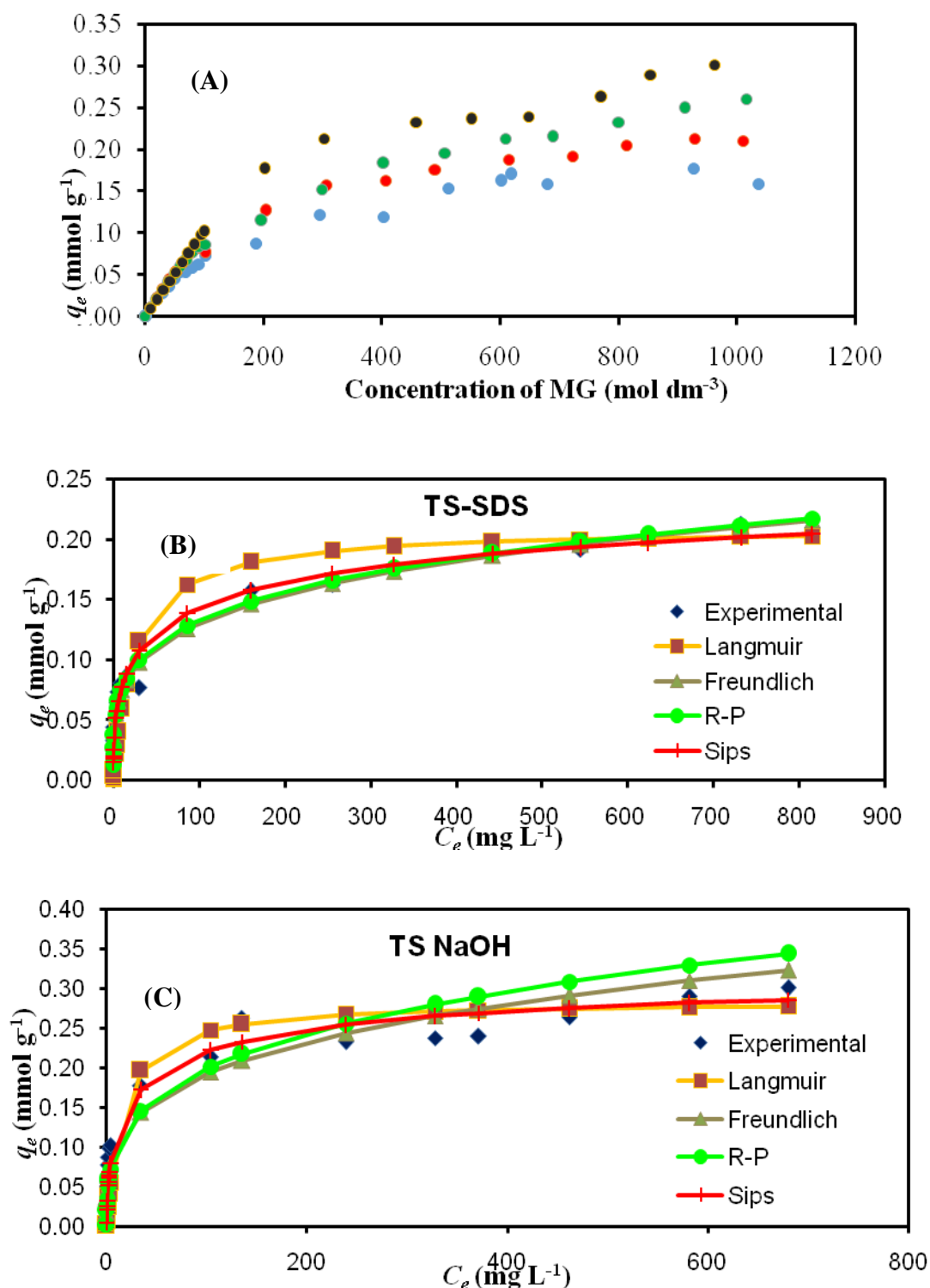
Figure 6: Adsorption isotherms of (A) all adsorbents and simulation isotherms of (B) TS-SDS and (C) TS-NaOH

ARE helps to minimize the fractional error distribution across the entire concentration range while SSE is the sum of squared differences between each observation and its group's mean and calculates the sum of the square errors of predicted function. HYBRID improves the fit of the sum of the squares of the errors at low concentrations by

dividing it by the measured value. Similar to SSE, EABS provides a better fit as the magnitude of the error increases, biasing the fit towards the high concentration data. MPSD is similar in some respects to a geometric mean error distribution modified according to the number of degrees of freedom of the system, while chi-squared (χ^2) test is a commonly used statistical test [27]. Simply basing experimental data on R^2 alone may not be accurate as there have been reports where even though an isotherm model may give higher R^2 value, however error analysis showed it was not the best fit model for the adsorption process [28, 29].

The adsorption parameters of the five isotherm models used are shown in Table 1. Based on R^2 and error values (Table 2), D-R isotherm model [30] gave the lowest R^2 and highest error values and is therefore not applicable to the adsorption of MG by TS and its modified forms. On the other hand, even though the Langmuir model [31], which predicts a monolayer adsorption on homogeneous adsorbent surface, gave generally good R^2 (> 0.97) for all the four adsorbents, nevertheless its relatively large error values ruled out its suitability in this study.

Table 1 Parameters of isotherm models:

Model	Tarap skin	TS-NaOH	TS-SDS	TS-EDTA
Langmuir				
q_{max} (mmol/g)	0.17	0.28	0.21	0.25
q_{max} (mg/g)	80.49	131.31	96.81	114.96
K_L (L/mmol)	0.02	0.07	0.04	0.03
R^2	0.9834	0.9867	0.9913	0.9777
Freundlich				
K_F (mmol/g)	0.02	0.06	0.04	0.04
K_F (mg/g)	10.09	25.77	20.06	18.74
n	3.16	3.71	4.17	3.66
R^2	0.9780	0.9177	0.9838	0.9904
Dubinin-Radushkevich				
q_{max} (mmol/g)	0.12	0.21	0.14	0.15
q_{max} (mg/g)	55.53	95.45	62.82	68.14
B (J/mol)	5.45E-07	1.51E-07	1.06E-07	1.24E-07
E (kJ/mol)	957.65	1818.97	2172.71	2011.42
R^2	0.7118	0.9067	0.8209	0.8128
Redlich Peterson				
K_R (L/g)	0.04	0.20	0.20	0.20
g	0.72	0.72	0.77	0.73
a_R (L/mmol)	1.48	3.61	4.32	4.82
R^2	0.9955	0.9733	0.9916	0.9911
Sips				
q_{max} (mmol/g)	1.00	0.34	0.29	0.40
q_{max} (mg/g)	463.50	157.59	134.42	185.40
K_S (L/mmol)	0.02	0.15	0.14	0.09
$1/n$	0.35	0.55	0.43	0.42
n	2.88	1.83	2.35	2.36
R^2	0.9779	0.9524	0.9710	0.9703

Multilayer adsorption onto heterogeneous surface as predicted by the Freundlich model [32] gave high R^2 (> 0.98) for all adsorbents except for TS-NaOH ($R^2 = 0.92$). All four adsorbents gave Freundlich n values > 1 (Table 2), suggesting a strong affinity between the adsorbents and MG dye [33]. The error functions, however, showed that this is not the best fit model as it still gave higher errors compared to the three parameter Sips [34] and R-P [35] models. Both these models are combination of the Langmuir and Freundlich models. In the case of the Sips model, adsorption follows the Langmuir at high concentration of adsorbate while at low concentration, it tends toward the Freundlich model and the reverse is true for the R-P model. Generally, it can be said that adsorption of MG onto TS, TS-SDS and TS-EDTA is best fitted to the R-P model which showed highest R^2 (> 0.99) and lowest errors. This is further supported by comparison of experimental data to the simulation of various

isotherm models. Since the simulation for TS and TS-EDTA are similar to that of TS-SDS (Fig. 6(B)), their simulation plots are not included for brevity.

On the other hand, even though adsorption of MG on TS-NaOH gave higher R^2 values for both the Langmuir (0.98) and R-P (0.97) models than the Sips (0.95), nevertheless the latter model has the overall lowest errors (Table 2). This can be reaffirmed from Fig. 6(C) where the Sips model fits better to the experimental data than the R-P model. The maximum adsorption capacity (q_{max}) of TS-NaOH based on the Sips models is 157.6 mg g^{-1}, compared to 80.5 mg g^{-1} for unmodified TS, thus showing a 96% enhancement in the adsorption capacity when TS is modified with NaOH. Similar effect was reported for NaOH modified breadnut skin where an increase of 99% was observed [4]. It has been suggested by Chowdhury et al. [36] that NaOH has the ability to remove fats and waxes on the surface of adsorbent thereby providing more active sites for the adsorption of MG. This is further supported by the significant change in the surface morphology as shown by SEM in Fig. 1.

Table 2: Regression coefficients and error values of different adsorption isotherms.

Adsorbent	Model	R^2	ARE	SSE	HYBRID	EABS	MPSD	χ^2
TS	Langmuir	0.9834	19.03	0.004	0.43	0.21	29.13	0.07
	Freundlich	0.9780	7.62	0.002	0.10	0.13	9.40	0.03
	D-R	0.7118	75.85	0.045	5.26	0.80	108.42	0.55
	R-P	0.9955	7.44	0.002	0.10	0.13	9.38	0.03
	Sips	0.9779	7.46	0.002	0.10	0.13	9.45	0.03
TS-NaOH	Langmuir	0.9867	33.87	0.019	1.17	0.52	44.13	0.33
	Freundlich	0.9177	34.31	0.012	0.92	0.42	69.88	0.14
	D-R	0.9067	76.26	0.103	7.74	1.20	113.84	0.86
	R-P	0.9733	21.45	0.017	0.63	0.48	31.19	0.17
	Sips	0.9524	17.55	0.006	0.34	0.29	30.15	0.12
TS-SDS	Langmuir	0.9913	35.83	0.011	1.07	0.41	50.57	0.21
	Freundlich	0.9838	15.34	0.001	0.25	0.10	42.32	0.03
	D-R	0.8209	50.53	0.051	3.16	0.87	67.05	0.39
	R-P	0.9916	8.99	0.001	0.09	0.09	17.07	0.04
	Sips	0.9710	11.44	0.002	0.15	0.13	21.34	0.04
TS-EDTA	Langmuir	0.9777	39.45	0.017	1.33	0.50	53.15	0.24
	Freundlich	0.9904	15.08	0.001	0.21	0.12	40.66	0.03
	D-R	0.8128	63.13	0.081	4.67	1.09	83.21	0.57
	R-P	0.9911	10.18	0.001	0.10	0.12	17.96	0.04
	Sips	0.9703	12.82	0.003	0.18	0.18	22.24	0.04

It is clear that the ability of TS towards adsorption of MG is greatly enhanced by surface modification. In order to further support this finding, maximum adsorption capacity (q_{max}) of TS and its modified surfaces were determined using the simulated adsorption isotherm which gives the smallest error (Table 3).

As compared to other *Artocarpus* wastes such as breadfruit, TS shows a better ability to adsorb MG. Although it is less superior when compared to breadnut, another fruit of the *Artocarpus spp.*, the most striking feature is that the adsorption capacity of TS toward MG has been increased by about 96% via NaOH treatment. This is probably due to the conversion of surface phenolic and carboxylic acid groups to corresponding anionic form, due to acid-base type of reaction, which would then be able to attract positively charged MG species more efficiently and strongly. This finding shows that TS-NaOH has a more superior adsorption capability to NaOH treated *Azolla pinnata* which showed an increase of only 26% removal toward MG [25]. Similar effect has already been observed for crystal violet cationic dye [16]. Further, TS and its modified forms all gave higher q_{max} than synthesized bimetallic Fe-Zn nanoparticles [42] for the removal of MG dye. Although compared to the synthesized tetraethylenepentamine-functionalized *Rosa canina*-L fruits activated carbon [43] which gave high q_{max} of 333.3 mg/g, nevertheless its synthesis involved microwave method which is far more complicated than the simple, fast and direct methods used in this study.

Table 3: Comparison of maximum adsorption capacity (q_{max}) of various adsorbents for the removal of MG

Adsorbent	q_{max}(mg/g)	Reference
Artocarpus odoratissimus skin (TS)	80.5	This work
TS-SDS	100.8	This work
TS-EDTA	116.8	This work
TS-NaOH	157.6	This work
Peat	143.7	[23]
Avena sativa (oat) hull	83.0	[37]
HCl modified Sphagnum peat moss	122.0	[38]
Pumice stone	22.6	[39]
Daucus carota - stem	43.4	[40]
- leaf	52.6	[40]
Walnut shell	90.8	[41]
Bimetallic Fe-Zn nanoparticle	21.7	[42]
Breadnut peel - untreated	177.4	[4]

3.6. Regeneration studies

All the four adsorbents were tested for their ability to be regenerated and reused. In real application for wastewater treatment, this is an important criterion in terms of the cost associated with. In this study, four different desorption methods *i.e.*, heat treatment, washing with 1.0 M HCl, 1.0 M NaOH and distilled water were carried out together with a control. Figure 7 shows that all, except washing with 1.0 M NaOH, result in a drastic decrease in the removal of MG throughout various cycles. Generally heat treatment is the worst and the ability for the adsorbents to remove MG fell below 10% after the second cycle. In all cases, washing with 1.0 M NaOH was the best method as all the adsorbents were able to retain high percentage removal of MG, close to 100%, even after 5 cycles.
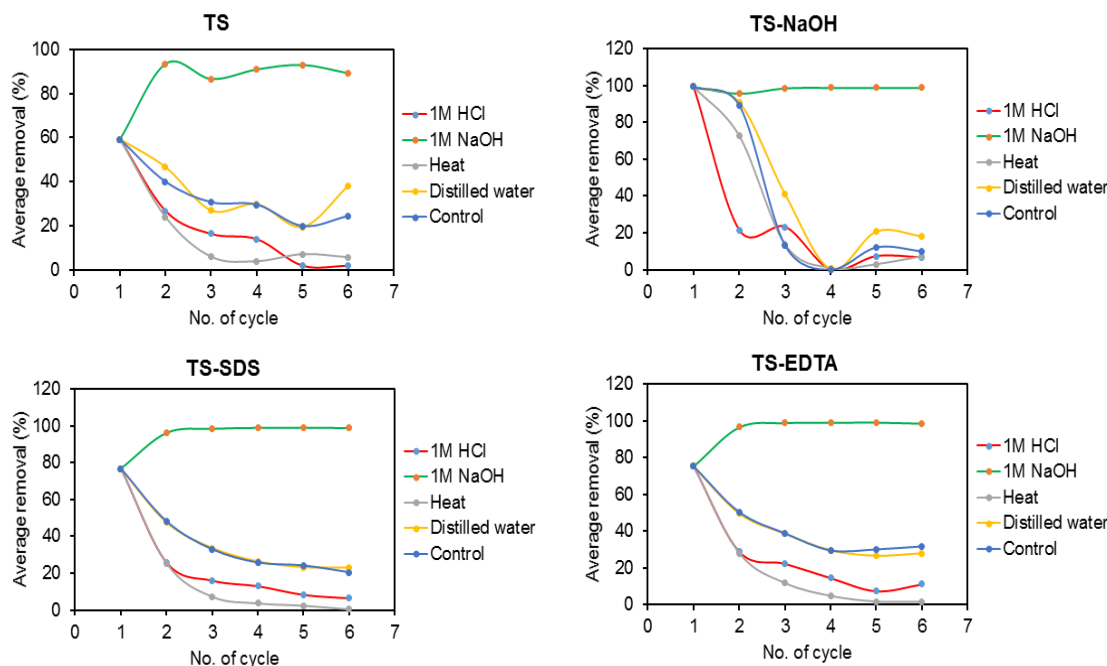

Figure 7: Regeneration studies

Conclusions

Artocarpus odoratissimus (Tarap) skin is able to adsorb Malachite Green (MG) dye with a capacity of 80.5 mg/g under optimized conditions of 4.0 h shaking time and 1.0 h settling time at the ambient pH of 4.0. The performance of Tarap skin (TS) can be significantly improved through chemical modification of its surface from aqueous solutions of sodium dodecyl sulfate (SDS), ethylenediaminetetraacetic acid (EDTA) and NaOH during a treatment period of 24 h. The optimum concentration for the most efficient removal by TS modified with the above reagents are determined to be 0.001 M, 0.0001 M and 3.0 M, respectively. According to adsorption isotherm modeling and error function analyses, natural TS, and TS modified with SDS and EDTA conform to the Redlich-Peterson (R-P) model, while TS modified by NaOH is compatible with the Sips model. The ionic constitutes present in the medium and the pH influence the extent of removal of MG. Moreover, the maximum adsorption capacity (q_{max}) of chemically modified TS when compared to untreated TS (80.5 mg/g) has been increased by 25%, 45% and 96% for SDS (100.8 mg/g), EDTA (116.8 mg/g) and NaOH (157.6 mg/g), respectively. Further research is needed to optimize the modification procedure and the modifier in order to improve adsorption characteristics of dyes on natural substances.

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