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# SYNTHETIC TEXTILE DYE REMOVAL FROM AQUEOUS SOLUTION USING MODIFIED LOCAL CLAY ADSORBENT

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## Abstract

Locally sourced clay from Kuala-Kangsar town in Perak state Malaysia was used in both its raw (RKKC) and modified (MKKC) form as adsorbents for the removal of methylene blue (MB) from synthetic textile wastewater in batch adsorption process. The raw clay was modified through $H_2SO_4$ acid treatment, $Al(OH)_3$ ion exchange, calcinations and then molded into beads before freeze drying. The BET surface areas of RKKC and MKKC were 11 and 100 $m^2/g$, respectively; their elemental analysis and surface morphology were determined using scanning electron spectroscopy (SEM). Adsorption isotherm studies of both adsorbents showed that the order of fitness in ascension was Langmuir, Freundlich and Redlich Peterson with their lowest correlation coefficient $R^2$ values of 0.883, 0.950 and 0.965, respectively; and the adsorption process obeyed pseudo-second-order reaction kinetic. Adsorption of MB on MKKC was spontaneous and endothermic as revealed by the thermodynamic studies of the process. The MKKC was good for adsorption of MB and found to be reusable.

*Key words:* adsorption, isotherm, kinetics, methylene blue, thermodynamics

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## 1. Introduction

Global population growth is having tremendous impact on our ecosystem since all waste materials generated are harbored by the environment (Mohapatra et al., 2010; Zaleschi et al., 2012). Depending on the nature of wastes (solid, liquid or gas) and sources of the wastes, pollution challenges can be tackled through separations techniques. Adsorption process-a unit operation mechanism has been applied in many environmental separations using the common adsorbent, activated carbon which has an annual worldwide sales estimated at $380 million (Keller, 1995; Ioannidou et al., 2010).

The expensive nature of activated carbon has prompted research into finding cheaper, renewable and efficacious alternatives of which agricultural wastes, clay, cellulose and other substances has come to lime light (Franca et al., 2014; Samarghandi et al., 2013).

Various types of clays such as montmorillonite/smectite, ball and kaolinite; have been found to be excellent in salvaging environmental pollution problems (Nogueira et al., 2009; Gupta and Suhas, 2009; Rafatullah et al., 2010). Locally sourced clays in either raw or modified form for adsorption purposes are coming to lime light for environmental pollution control with excellent results recorded. Adsorption of dyes using natural or raw clay nano-adsorbents depends largely on dye structure and geochemical features of the clay soil (Liu and Zhang, 2007). Some modifications have been done on clay to improve its adsorption capacity include acidification, calcinations, pillaring, use of some organic molecules and polymers (Vinod and Anirudhan, 2003; Weng and Pan, 2007; Yue et al., 2007).

Thus, this work was aimed at harnessing the potential of a large span of natural clay in Kuala-Kangsar town in Perak state of Malaysia and used in

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its raw and modified form for removal of cationic dye Methylene blue from synthetic textile wastewaters. Methylene blue is the most important basic dye discovered by Caro in 1878. It has wide applications in various fields which include biology, chemistry, medicine, and so on (El Qada et al., 2006). Even though it is less harmful, it can have adverse effect on breath when inhaled and can cause diarrhea, mental disorder, headache, vomiting, and nausea when orally ingested (Ahmad et al., 2009). The modification involved $H_2SO_4$ acid treatment, $Al(OH)_3$ ion-exchange, calcinations and characterization of the raw and modified adsorbent for determination of pore size and surface area, structural morphology and constituent elements. Effects of pH on the adsorption process, equilibrium, kinetic and thermodynamic studies were carried out; and, reusability of the modified Kuala-Kangsar clay (MKKC) was investigated.

## 2. Materials and methods

### 2.1. Materials

Raw clay from Kuala-Kangsar town in Perak state of Malaysia was crushed, ground, and sieved into 20-45 μm particle sizes and dried in an oven overnight at 100 $^o$C. Analytical grade chemicals such as $Al(OH)_3$ (aluminum hydroxide), $H_2SO_4$ (sulphuric acid) and $C_{16}H_{18}SCl$ (methylene blue) were purchased from R & M marketing Essex, U.K., Merck chemical company and Sigma-Aldrich chemicals, respectively.

### 2.2. Preparation of clay adsorbents

The dried Kuala-Kangsar clay (KKC) was transformed into beads with the addition of sodium alginate and then freeze dried for 8 h and labeled RKKC. A sample of KKC was treated with 2 M $H_2SO_4$ using wet process at 90 $^o$C for 3 h in a ratio of 0.2 g clay/ mL (clay/acid). Thereafter, it was washed with distilled water to remove the excess acid; this was done until neutrality (pH 6.8-7) was attained in the activated clay solution and then dried in an oven for 6 h at 100 $^o$C. A mixture of 100 mL of 0.5 M $Al(OH)_3$ and the dried acid treated KKC were refluxed for 2 h at 90 $^o$C, left overnight after reflux and washed with distilled water. After washing, it was dried in an oven at 110 $^o$C and then calcined for 3 h at 500 $^o$C. The calcined treated KKC was molded into beads (1-2 mm) using sodium alginate as binder; freeze dried for 8 h and then labeled modified Kuala-Kangsar clay (MKKC). The RKKC and MKKC adsorbents are shown in Fig. 1.

### 2.3. Characterization of the clay adsorbents

Chemical composition of the raw clay was done using X-ray fluorescence spectrometer (XRF-Philips PW2400).The two adsorbents RKKC and MKKC surface area, elemental analysis and morphological structure were analysed using Brunauer Emmett Teller (BET) and scanning electron microscope.
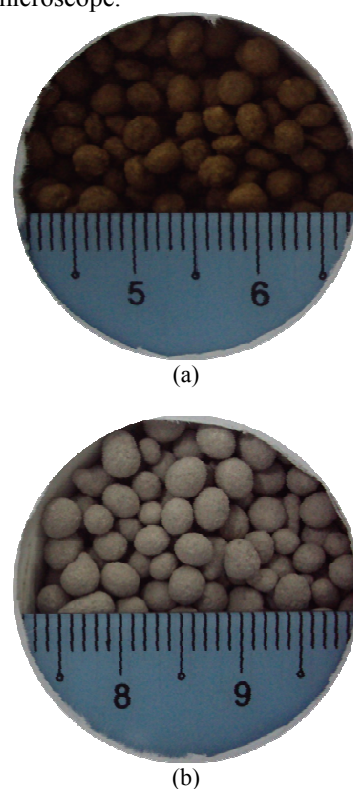




**Fig. 1.** Structural view of the adsorbents (a) RKKC and (b) MKKC

The BET was carried out by nitrogen adsorption-desorption method using nitrogen temperature (-196 $^o$C) with an autosorb BET apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer. The analysis procedure was automated and operated with static volumetric techniques. The samples were first degassed at 200$^o$C for 2 h before each measurement was recorded.

Energy-dispersive X-ray spectroscopy (EDS or EDX) for elemental analysis and morphological structure of both RKKC and MKKC were carried out using scanning electron microscope (Model EMJEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system.

### 2.4. Batch equilibrium studies

Batch equilibrium adsorption study, a requirement for design of adsorption column was performed in a set of Erlenmeyer flasks (250 mL) containing 200 mL of dye solutions at different initial concentrations (30-300 mg/L). To each flask, about 0.2 g (1-2 mm) of RKKC adsorbents was added and placed in water bath isothermal shaker at 30 $^o$C for 12 h, at 140 rpm shaker speed to attain equilibrium. The residual concentration of MB in the flask was determined with the aid of UV-Vis spectrophotometer (Shimadzu UV/Vis 1601 spectrophotometer, Japan) at maximum wavelength of 668 for MB. The procedure was repeated at

adjusted water-bath shaker temperature of 40 and 50°C. Similarly, the entire process was repeated using MKKC adsorbent.

The amount of the dye adsorbed at time *t*, at equilibrium $Q_e$ (mg/g) was calculated using Eq. (1) where $C_o$ and $C_e$ (mg/L) are the liquid-phase concentration of the dye at the initial and equilibrium, respectively; V (L) is the volume of the solution; and *W* (g) is the mass of the dry adsorbent used.

$$Q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

## 2.5. Effect of solution pH on adsorption

An important parameter, pH which plays a significant role in influencing the adsorbent chemistry, was studied to find its effect on MB molecules adsorption on both RKKC and MKKC. A range of pH 3-12 using 0.1 M HCl or 0.1 M NaOH for adjustment was investigated. Effective solution pH was ascertained using pH meter (Model Delta 320, Mettler Toledo, China). The study was conducted in a set of 250 mL Erlenmeyer flasks charged with 100 mg/L (200 mL) and 0.20 g of MB and adsorbent (RKKC or MKKC), respectively at a temperature of 30 °C for 12 h.

## 2.6. Batch kinetic studies

The experimental set up for the kinetic study was similar to equilibrium studies of section 2.4, but before dynamic equilibrium was attained, the residual concentration of the adsorbate in solution was determined at intervals of time. The amount of the dye adsorbed at time *t*, $Q_t$ (mg/g) was calculated using Eq. (2), where $C_o$ and $C_t$ (mg/L) are the liquid-phase concentration of the dye at the initial and any time *t*, respectively; $V$ (mL) is the volume of the solution; and W (g) is the mass of adsorbent (RKKC or MKKC) used.

$$Q_t = \frac{(C_0 - C_t)V}{W} \qquad (2)$$

## 2.7. Desorption studies

Desorption capability of MKKC was investigated by carrying out important adsorption studies components, desorption and regeneration operations. The MB adsorbed on 0.2 g of MKKC was recovered from initial 100 mL of 100 mg/L dye solution and rinsed slightly with distilled water to remove un-adsorbed dye on the surface before air drying.
The air dried MKKC was placed in 100 mL distilled water of pH 4 and then shaken in isothermal water-bath shaker at 30 °C with shaker speed of 140 rpm for the predetermined equilibrium time of the adsorption process. Desorption efficiency was

calculated with Eq. (3), where: $M_d$ (mg/L) is the concentration of MB desorbed from pre-adsorbed MKKC adsorbent, $V_d$ (mL) is the volume of the solution used for desorption, w (g) is the mass of the pre-adsorbed adsorbent, $Q_e$ (mg/g) is the amount of the adsorbate pre-adsorbed on the adsorbent. The procedure was repeated until there was significant difference in desorption efficiency.

$$Desorption\ efficiency\ (\%) = \frac{M_d V_d}{w \times Q_e 100} \times 100 \qquad (3)$$

## 3. Results and discussion

### 3.1. Characterization of the adsorbents

The chemical analysis of Kuala-Kangsar clay using X-ray fluorescence spectrometer is summarized in Table 1. Fig. 2 shows the BET $N_2$ adsorption/desorption isotherms at 77 K isotherms for the RKKC and MKKC. The BET surface areas for RKKC and MKKC were 11 and 100 m²/g, respectively. Mesopores and micropores were the preponderating pore sizes found in MKKC.

The graph of pore size against pore width showed that the highest pore width peak was about 13 nm. Cation exchanged activities which was undertaken by addition of Al(OH)₃ and subsequent stabilization by calcinations may have contributed to increase in the surface area; it has been reported that intercalation of polycations between basal spaces increased porosity when cation treatment was accompanied by heating (Hymore, 1996). The high surface area could also be attributed to latent conversion of residual Al(OH)₃ to gamma-alumina during calcinations of the MKKC at 500 °C even though the modified clay was thoroughly washed. It is common for alumina to get transformed on heating at 500 °C to gamma-alumina which has high surface area (Chuah et al., 2000).

The elemental and morphological features of RKKC and MKKC using Energy-dispersive X-ray spectroscopy were determined. The spectrum of the MKKC revealed massive disappearance of some cations as compared with the RKKC spectrum; the RKKC had 36.73 wt% of O, 0.12 wt % of Mg, 13.16 wt % of Al, 30.74 wt % of Si, 14.81 wt % of K, 0.89 wt % of Ca, 0.53 wt % of Ti, 3.02 wt % of Fe and the MKKC had 45.86 wt% of O, 25.47 wt % of Al, 25.61 wt % of Si, 3.05 wt % of K. It was attributed to reaction of $H_2SO_4$ with some cations to form oxides and sulfates which reduces the percentage of such products in the activated clay (Tiwain et al., 1996).

The spectra and micrographs of the RKKC and MKKC are illustrated in Fig. 3. It was observed from the micrographs that MKKC particle were dispersed after treatment compared with the congregated nature of particles of the RKKC. The loss of volatile organic components after calcination, the cation ion exchange activities and leaching of

some cations contributed to the dispersed MKKC particles. In a study reported on reactive adsorption of methylene blue on montmorillonite via ESI-MS, the raw, pillared and calcined montmorillonite clay, exhibited similar trend of morphological settings (Nogueira et al., 2009).

### 3.2. Effect of solution pH on adsorption

The effect of pH on adsorption of MB on both RKKC and MKKC was studied and results of MB percentage removal against pH were plotted (Figure not shown). Sorption of particles on surfaces contributes to removal of certain substances from wastewaters, and this can be influenced by the type of charges of the pollutant and the surfaces to be attached (Giora et al., 2011; Hua-Yue et al., 2010). The pH study results revealed that the percentage of MB adsorbed by either RKKC or MKKC increased with increasing pH and vice versa.

The maximum percentage adsorption of MB was at pH 11 while the minimum was from pH 4 and below; similar result was obtained with high adsorption capacity of 580 mg/g of methylene blue at pH 11 (El Qada et al., 2006). The adsorbents surfaces became more negatively charged as the pH was increasing, promoting electrostatic attraction due to coulombic forces between the positive MB molecules and the negatively charged adsorbents surfaces. The protonated $H^+$ formed as the pH was decreasing the occupied surfaces of either RKKC or MKKC thereby repelling the cationic MB molecules from attaching, and resulting to poor adsorption.

### 3.3. Effect of initial dye concentration

The percentage adsorption of MB was found to decrease with increase in concentration of the solution. At lower concentration of the solution, fewer molecules present were adequately adsorbed while larger molecules of MB at higher solution concentration were hampered by limited active pores of MKKC. The higher percentage adsorption at lower concentration also enhanced faster attainment of equilibrium condition than at higher solution concentration. The MB adsorption by MKKC was found to increase significantly with increase in the initial dye concentration; at 30 $^oC$ the experimental adsorption capacity was found to increase from 24.20 to 151.37 mg/g when the initial concentration was changed from 30 to 300 mg/g.

The increase in adsorption may be attributed to increase in the mass transfer to the vacant pore sites of the adsorbents. Similar observation was made in a study of aromatic organic contaminant removal from an aqueous environment by p(4-vinylpyridine)-based material (Sahiner et al., 2011). The graph on the effect of initial concentration on MB adsorption is illustrated in Fig. 4.

### 3.4. Adsorption isotherm

Langmuir, Freundlich and Redlich-Peterson isotherm models were used to study the isotherm behavior of the adsorption process of MB on both RKKC and MKKC.

**Table 1.** Chemical analysis of Kuala-Kangsar clay

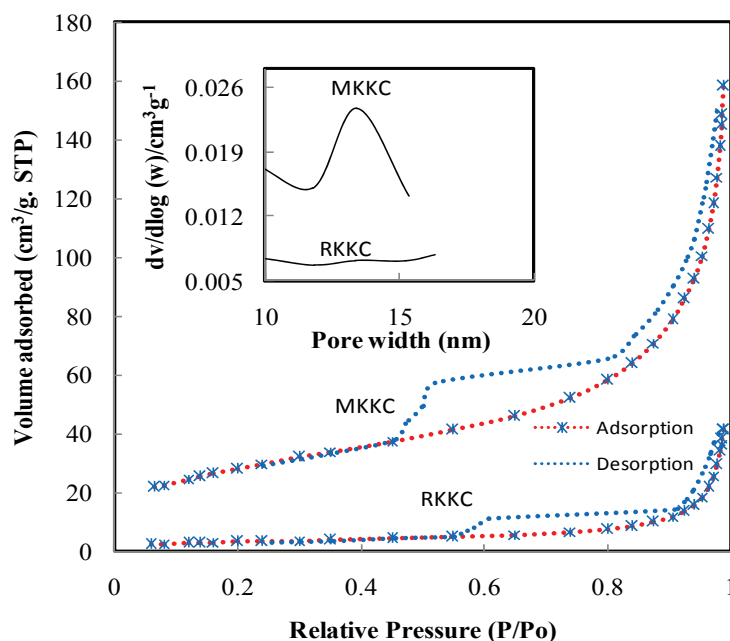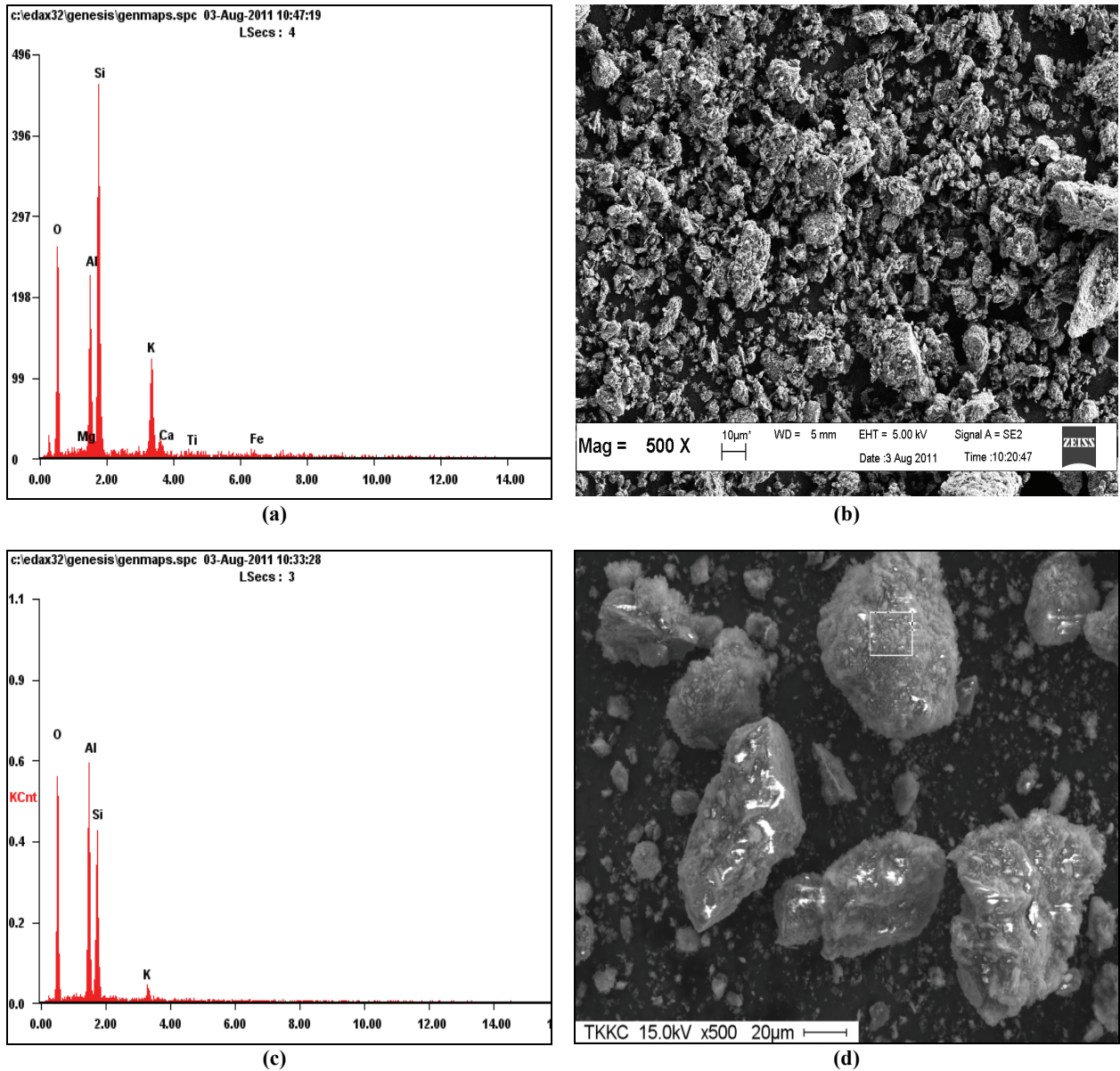| *SiO₂* | *Al₂O₃* | *Fe₂O₃* | *CaO* | *MgO* | *Na₂O* | *K₂O* | *MnO* | *TiO₂* | *P₂O₅* | *Others* | *LOI* | *Total* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 50.50 | 34.97 | 2.99 | 0.08 | 0.20 | 0.04 | 2.65 | 0.01 | 0.37 | 0.02 | 0.18 | 7.99 | 100 |



**Fig. 2.** BET plot of RKKC and MKKC

**Fig. 3.** EDX analysis: (a) RKKC spectrum, (b) RKKC micrograph, (c) MKKC spectrum and (d) MKKC micrograph
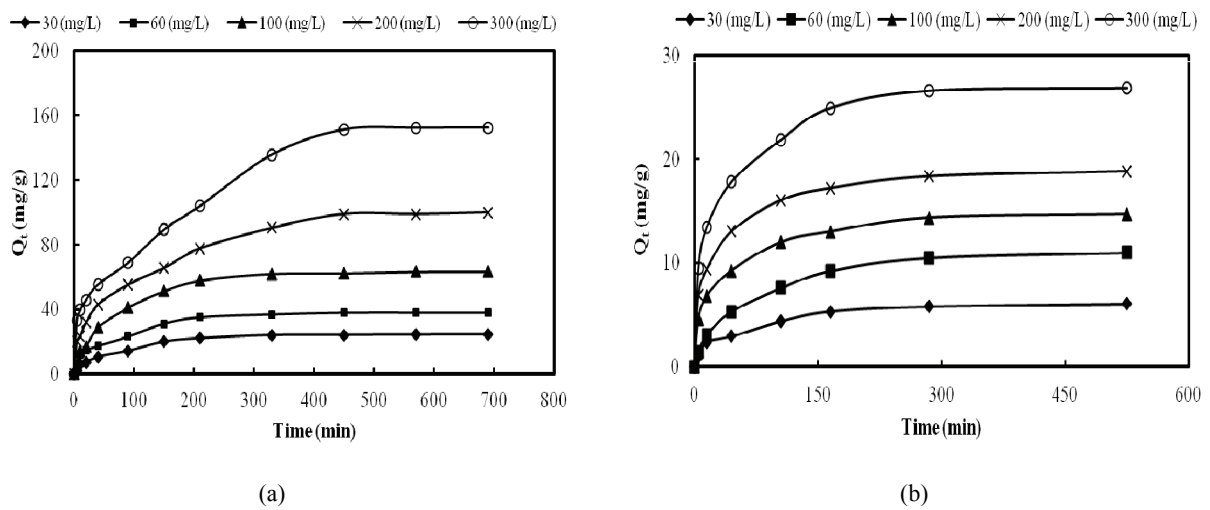


**Fig. 4.** Adsorption of MB at different initial concentrations (a) RKKC (b) MKKC at 30 ºC

The non-linear form of the Langmuir isotherm model (Langmuir, 1916) is given by Eq. (4), where: $C_e$ (mg/L) is the equilibrium concentration of MB adsorbed, $Q_e$ (mg/g ), is the amount of MB adsorbed, $Q_m$ and $b$ (Langmuir constants), the monolayer adsorption capacity and affinity of adsorbent towards adsorbate respectively.

$$Q_e = \frac{Q_m C_e b}{\left(1 + b C_e\right)} \qquad (4)$$

A plot of $Q_e$ against $C_e$ gave a fitted curve (Figure not shown), and the Langmuir constants were generated from the plot of sorption data; the parameters evaluated for MB adsorption on the adsorbents are shown in Table 2.

The non-linear form of the Freundlich model was used to investigate the adsorption process adherence to the model, the equation (Freundlich, 1906) is given by Eq. (5), where $Q_e$ (mg/g) is the amount of dye adsorbed at equilibrium; $C_e$ (mg/L) is the equilibrium concentration of the adsorbate; $k_F$ and $n$ are the Freundlich equilibrium coefficients. The value of n gives information on favourability of adsorption process and $k_f$ is the adsorption capacity of the adsorbate.

$$Q_e = k_F C_e^{1/n} \qquad (5)$$

The Redlich-Peterson isotherm model (Redlich and Peterson, 1959) is given by Eq. (6).

$$Q_e = \frac{A C_e}{1 + B C_e^g} \qquad (6)$$

Taking the natural logarithm gives the Eq. (7), where A, B and g are the model's constants. The challenge posed by involvement of the three parameters in resolving the model equation linearly lead to the development of a trial and error procedure. The method helps to obtain optimal value of the constant $A$ from the best coefficient of determination $R^2$ through the linear regression of $ln(C_e)$ on $ln[A(C_e/Q_e)-1]$ (Ho et al., 2005).

$$ln\left(A\frac{C_e}{Q_e} - 1\right) = g\,ln(C_e) + ln\,B \qquad (7)$$

Based on the values obtained from the three isotherm models as presented in Table 1; the three models investigated all described the adsorption process very well due to their high correlation coefficient values $R^2 > 0.8$ although variation of fitness was observed with the poorest and best fit models as Langmuir and Redlich-Peterson isotherms, respectively. The fitness of the isotherm models was selected based on the highest $R^2$ values of a model;

that is closest to unity implied the goodness of fitness of the experimental data to the isotherm model. The adsorption of MB on both RKKC and MKKC were more of heterogeneous process as the first and second best fit isotherms were Redlich-Peterson and Freundlich models, respectively. This is because the Freundlich model constants values obtained as seen in Table 2, (n>1 and 0<1/n<1) were within favourable limit to heterogeneity and; the Redlich-Peterson model's g-values obtained were far from unity signifying high tendency to Freundlich model and not Langmuir model which is approached when g=1.

The Redlich Peterson model's constants helps in describing the interaction between the adsorbate and adsorbent which are contained in the model's equation that is linearly and exponentially dependent on the concentration at the numerator and denominator, respectively. The model's constants values increased with increase in temperature of the process for the RKKC and MKKC. However, at 50 °C the model's constant values for RKKC did not follow the trend; this may be attributed to un-aligned nature of the adsorbent as compared with the stable MKKC. Similarly, Redlich Peterson isotherm emerged the best fit out of Langmuir-Freundlich, Temkin, Langmuir, Freundlich models tested for the study of methylene blue removal by walnut shells activated carbon (Yang and Qiu, 2010). The monolayer coverage of this work at 50 °C can be compared with those from literature as shown in Table 3.

*3.5. Adsorption kinetic models*

The non-linear pseudo-first order equation (Lagergren and Svenska, 1898) is given as Eq. (8), where $Q_e$ and $Q_t$ (mg/g), are the adsorption capacities at equilibrium and at time $t$ (h), respectively; $K_1$ (h$^{-1}$), is the rate constant for pseudo-first-order adsorption.

$$Q_t = Q_e\left(1 - e^{-K_1 t}\right) \qquad (8)$$

A plot of $Q_t$ against $t$, at various temperatures and concentrations studied resulted in non-linear graphs (Figure not shown) and the model's parameters $K_1$ and $Q_e$ were obtained as presented in Table 4. The pseudo-second order equilibrium adsorption model (Ho and McKay, 1999) is given by Eq. (9), where $k_2$ (g/mgh) is the rate constant of second order adsorption. The pseudo-second-order parameters obtained from the plots of $Q_t$ against $t$ (Figure not shown), for adsorption of MB on MKKC are presented in Table 4.

$$Q_t = \frac{K_2 Q_e^2 t}{\left(1 + K_2 Q_e t\right)} \qquad (9)$$

Pseudo-second-order model's correlation coefficient $R^2$ values were in the range of 0.951-

0.988 while 0.897-0.985 was the range of $R^2$ values for pseudo-first-order kinetic model. Although the highest $R^2$ values for the two models were close in value to each other, on the overall the pseudo-second-order $R^2$ values were higher. This distinction shows that pseudo-second-order model fitted the adsorption data better than pseudo-first-order model equation. Hence, the adsorption of MB on MKKC follows the pseudo-second-order kinetics. Similar results have been reported in the literature (Auta and Hameed, 2011; Bi et al., 2011).

### 3.6. Adsorption thermodynamics

Three thermodynamic parameters that give information on how a mole of solute moves from the bulk of solution onto the solid-liquid interface are enthalpy ($\Delta H$), Gibbs free energy ($\Delta G$) and entropy ($\Delta S$). The parameters were obtained at various temperatures of 30, 40 and 50 $^{o}$C. Gibbs free energy which provides information on the spontaneity of adsorption process was calculated using Eq. (10), where $R$ (8.314 J/Kmol), is the universal gas constant; $T$ (K), the absolute temperature; $K_o$ is the

distribution coefficient expressed as $K_o = Q_e/C_e$; and $\Delta G$ is the Gibbs free energy.

$$\Delta G = -RT \ln K_0 \qquad (10)$$

Van't Hoff equation was used to determine the average standard enthalpy change (Eq. 11).

$$\ln K_0 = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} = \frac{\Delta H}{RT} \qquad (11)$$

A plot of lnKo against 1/T gives a graph (Fig. not shown) where we can obtain $\Delta S$ from the intercept and $\Delta H$ from the slope. Enthalpy is an important thermodynamic function useful when a differential change occurs in a system. The positive value of it obtained ($\Delta H$= 24.260 kJ/mol) indicates that the adsorption process was endothermic. The endothermic nature of MB adsorption on MKKC which was observed as temperature of the process was varied, could be attributed to increased rate of adsorbate diffusion across the external boundary layer and internal pores of MKKC (Li et al., 2010).

**Table 2.** Langmuir, Freundlich and Redlich-Peterson isotherm models parameters for MB adsorption on both RKKC and MKKC at different temperatures

| Isotherms | Parameters | RKKC | | | MKKC | | |
|---|---|---|---|---|---|---|---|
| | | 30 $^{o}$C | 40 $^{o}$C | 50 $^{o}$C | 30 $^{o}$C | 40 $^{o}$C | 50 $^{o}$C |
| | $Q_m$ (mg/g) | 41.77 | 47.05 | 53.26 | 100.44 | 125.18 | 200.23 |
| Langmuir | $b$ (L/mg) | 0.0074 | 0.0094 | 0.0185 | 0.0613 | 0.125 | 0.0543 |
| | $R^2$ | 0.882 | 0.931 | 0.827 | 0.883 | 0.932 | 0.971 |
| | $K_F$ | 1.115 | 1.962 | 3.875 | 8.851 | 19.187 | 19.861 |
| Freundlich | $1/n$ | 0.566 | 0.518 | 0.436 | 0.549 | 0.462 | 0.453 |
| | $R^2$ | 0.986 | 0.918 | 0.971 | 0.966 | 0.969 | 0.950 |
| | $g$ | 0.497 | 0.462 | 0.565 | 0.385 | 0.637 | 0.624 |
| Redlich-Peterson | $B$ (L/mg)$^g$ | 2.269 | 9.863 | 4.280 | 0.550 | 0.845 | 0.861 |
| | $A$ (L/g) | 3.707 | 17.205 | 16.807 | 19.908 | 24.672 | 27.732 |
| | $R^2$ | 0.996 | 0.968 | 0.989 | 0.988 | 0.965 | 0.978 |

**Table 3.** Comparison of monolayer adsorption of MB onto various adsorbents

| Adsorbent | Adsorption capacity (mg/g) | Reference |
|---|---|---|
| Raw Kuala-Kangsar clay (RKKC) | 53.26 | This work |
| Modified Kuala-Kangsar clay (MKKC) | 200.23 | This work |
| Montmorillonite clay | 289.12 | Almeida et al. (2009) |
| ZnAl–PW$_{10}$Mo$_2$ | 30.87 | Bi et al. (2011) |
| Natural palygorskite clay | 48.39 | Chen et al. (2011) |
| Heat-treated palygorskite clay | 78.11 | Chen et al. (2011) |
| Calcined pure kaolin | 8.88 | Gosh and Bhattacharyya (2002) |
| Calcined raw kaolin | 7.59 | Gosh and Bhattacharyya (2002) |
| Bentonite | 151-175 | Hong et al. (2009) |
| Persian kaolin | 29.85 | Tehrani-Bagha et al. (2011) |

**Table 4.** Pseudo-first and Pseudo-second-order kinetic models parameters for MB adsorption on MKKC

| Dye concentration (mg/L) | $Q_{exp}$ (mg/g) | Pseudo-first-order parameters | | | Pseudo-second-order parameters | | |
|---|---|---|---|---|---|---|---|
| | | $K_1$ (h$^{-1}$) | $Q_{cal}$ | $R^2$ | $K_2$ (10$^4$) | $Q_{cal}$ | $R^2$ |
| 30 | 24.195 | 0.013 | 24.064 | 0.977 | 6.34 | 27.150 | 0.987 |
| 60 | 38.227 | 0.023 | 36.323 | 0.947 | 7.92 | 39.831 | 0.984 |
| 100 | 62.417 | 0.019 | 61.570 | 0.985 | 3.58 | 68.761 | 0.988 |
| 200 | 99.008 | 0.014 | 92.898 | 0.897 | 2.05 | 102.727 | 0.951 |
| 300 | 151.374 | 0.006 | 154.492 | 0.953 | 0.387 | 186.777 | 0.964 |

The adsorption process was found to be spontaneous and the mechanism was physisorption; this was due to the negative values of $\Delta G$ (-3.981 kJ/mol at 303K, -6.558 kJ/mol at 313K, -5.811 kJ/mol at 323K) obtained and their low nature (<20 kJ/mol), respectively.

The level of dispersion of the MB adsorption on MKKC was found to increase with temperature, signifying good affinity between the adorbate and adsorbent; the intimation to this fact was the positive value of $\Delta S$ ($\Delta S > 0$), obtained. Similar result has been reported by Khalid et al. (2011) indicating that the positive values of entropy showed affinity between Ghassoul clay and methyl violet and the increasing randomness at the solid-solution interface during the adsorption process.

### 3.7. Desorption studies

Maximum desorption efficiency test result for the three feasible runs were carried out at solution pH 4. The results obtained were 63.40, 52.33 and 39.26 % for first, second and third runs, respectively. The effect of pH on adsorption of this work revealed that at lower solution of pH 4 and below, electrostatic repulsion activities dominated the adsorption operation.

This was due to increased positive charge sites of the MKKC at lower pH promoting repulsion between the positively charge adsorbent and the cationic MB adsorbate; that lead to release of MB adsorbate into the desorbing aqueous solution. Similar method of desorption analysis has been reported (Mahmoodi et al., 2011; Yang and Qiu, 2010).

### 4. Conclusions

Adsorption of MB on KKC was found to be endothermic, spontaneous and physical. It was also found to be dependent on initial MB concentration, contact time, temperature and solution pH. In order of least to the highest, the isotherm studies revealed that Langmuir, Freundlich and Redlich-Peterson models were the order of fitness to the adsorption process.

The adsorption process which followed pseudo-second-order kinetics was aided by the porous and larger surface area of the adsorbent revealed from characterization results. The study demonstrated that KKC is a good adsorbent that can be used for adsorption of MB from wastewaters.

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