Characterization of modified mineral waste material adsorbent as affected by thermal treatment for optimizing its adsorption of lead and methyl orange

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Abstract

Thermal treatment is one of the most common processes in mineral modification and this process has been applied to the modification of mineral waste material to improve its adsorption ability of methyl orange (MO) and lead (Pb) in this study. The properties of modified mineral waste material (MMWM) before and after thermal modification were characterized by using the Brunauer–Emmett–Teller (BET) N₂ adsorption/desorption measurement, field emission scanning electron microscope (FESEM) coupled with energy dispersive X-ray (EDX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Phase transformation related to the change in surface morphology and dehydroxylation that occurred in MMWM samples during the process of thermal treatment were investigated. To study adsorption performances of Pb and MO onto the newly modified MMWM, a number of experiments were carried out under different adsorption conditions and the results were determined using inductively coupled plasma optical emission spectrometry.
(ICP-OES) and UV-Vis spectrophotometry. The thermally treated MMWM samples showed morphological transformation, and an increasing trend in BET specific surface area (SSA) up to 500 °C followed by a decreasing trend till 1000 °C. Thermal modification of MMWM had successfully improved Pb adsorption from 349 to 515 mg/g, corresponding to the MMWM modified at 600 °C, and the methyl orange (MO) adsorption from 68 to 87.6 mg/g at 400 °C. The adsorptions of Pb and MO were mainly chemisorption and monolayer coverage, as the pseudo-second-order model and the Langmuir equation displayed good correlations for Pb and MO adsorption data.

**Keywords:** Adsorption, dehydroxylation, lead (Pb), methyl orange (MO), modified mineral waste material (MMWM)

**Introduction**

The modified mineral waste material (MMWM) is a mixed clay mineral type of adsorbent that was originally derived from industrial mineral waste after physical and chemical modifications (Jiang et al. 2013a). It can be used as a low-cost, environmentally safe adsorbent and found to have strong adsorption abilities (Jiang et al. 2013b). Consisting primarily of smectite and illite, MMWM shows great ability in adsorbing pollutants from water, soil and air which have been applied in our previous experiments for removing environmental pollutants (Jiang et al. 2014; Lu et al. 2016). These investigations have confirmed that the MMWM has better adsorption abilities...
of heavy metals (lead (Pb), copper (Cu) and cadmium (Cd)) in solution than activated
carbon (AC) (Lu et al. 2016). MMWM was also found to have the ability to adsorb
organic compounds from wastewater such as organic phosphate (Jiang et al. 2014).
The adsorptive efficiency of some organic pollutants is found to be even better than
AC.

As one of the main components in MMWM, the smectite group of clays (e.g.
montmorillonite) is normally abundant and has extraordinary properties which make it
a compelling and reasonable precedent for a low cost and effective adsorbent
(Rathnayake et al. 2017). Smectite is comprised of a number of clay minerals
consisting of tetrahedral-octahedral-tetrahedral (t-o-t) layers of both dioctahedral and
trioctahedral types (Hurlbut and Klein 1977; Bhattacharyya and Gupta 2008). Similar
to smectite (e.g. montmorillonite), illite is another kind of clay mineral in MMWM. It
can be defined as the mineral occurring in the clay fraction with Al–K, is non-
expanding, di-octahedral with mica-type properties, and is a mineral that is commonly
used in the traditional ceramic industry and can be applied in the removal of heavy
metals in solution (Srodon and Eberl 1984; Ozdes et al. 2011; Csáki et al. 2017;
Húlan et al. 2017). On the other hand, the swelling properties of the 2:1-layer silicates
(e.g. montmorillonite) result in an increased water and contaminants retention ability,
which is dependent on the interlayer spacing upon the charge of layer, hydration
energy, chemical potential and relative humidity (Tambach et al. 2004; Fonseca et al.
2017).
Investigations pertaining to the use of mineral related adsorbents have a long history, and the high adsorption capabilities of clay minerals are the result of the net negative charges on the lattice of minerals. These negative charges will be neutralized by the adsorption of positively charged contaminants, providing clay adsorbents the ability to attract and hold cations such as heavy metals (Bailey et al. 1999). The maximum adsorption capacity of Pb for natural goethite is observed to be 109.2 mg/g (Lounis et al. 2012). The maximum adsorption capacities of kaolinite (Cd 11.4 mg/g, Cr (VI) 13.9 mg/g, Pb 82.65 mg/g) and montmorillonite (Cd 33.2 mg/g, Pb 31.3 mg/g) are achieved after activation of these minerals (Alvarez-ayuso and Garcia-Sanchez 2003; Adebowale et al. 2008; Sen and Bhattacharyya 2008). Ozdes et al. (2011) reported that the maximum adsorption capacity of illite towards Pb (239 mg/g) can be achieved when the adsorption is conducted at pH = 4 and room temperature for 240 mins. A group of modified mineral adsorbents has been used in removing Pb from aqueous solution and the adsorption capacities of the clays for Pb are 22.7 mg/g and 6.3 mg/g for acid-activated montmorillonite and kaolinite respectively (Bhattacharyya and Gupta 2008). Bhatnagar et al. (2006) reported that the adsorption of Pb on adsorbents prepared from industrial wastes (blast furnace sludge) is as high as 227 mg/g. The maximum adsorption capacity of beidellite for Pb is 86.9 mg/g, and the polymer/montmorillonite clay nanocomposite, imprinted by zinc ion, can adsorb a maximum of 301 mg/g Pb (Etcı et al. 2010; Msaadi et al. 2017). The adsorption of Pb on rectorite is mainly dominated by surface complexation and cation exchange, with
the equilibrium adsorption capacity being 17.9 mg/g (Msaadi et al. 2017). Beside metal pollutants, mineral adsorbents are also applied for removal of organic contaminants such as dyes. Methyl orange (MO) is a kind of anionic dye that has been widely applied in the printing industry, but it is unfortunately toxic and carcinogenic (Eljiedi et al. 2017). One new material, uncalcined glycerol-modified nanocrystallined Mg/Al layered double hydroxides, is applied as a good adsorbent for MO removal (Yao et al. 2017). Habiba et al. (2017) suggested that the removal of MO in wastewater could be predominated by adsorption at low initial concentrations, whereas flocculation was observed at high concentrations.

A number of methods have been developed for the modification of clay mineral adsorbents. Mechanochemical activation such as the grinding treatment is used for kaolinite modification. The process can be identified as the creation of a new amorphous material with the destruction of kaolinite, and then an agglomerated material is produced by the aggregation of the ground particles (Kelley 1957; Takahashi 1959; Frost et al. 2004). Dehydroxylation, which results in the release of physically and chemically bounded water, is one of the most significant phenomena occurring during thermal treatment of clay mineral. By investigating the kinetic of dehydroxylation in clay mineral, the dehydroxylation concept of kaolinite can be expressed as a result of the interaction between two hydroxyl groups to form a water molecule by proton transfer, leaving chemically bonded oxygens (oxide anion) in the
lattice (Miller and Oulton 1970). The reactions are shown as the following (Frost et al. 2004):

\[ -\text{OH}^- \Leftrightarrow \text{H}^+ + -\text{O}^{2-} \]
\[ \text{H}^+ + -\text{OH}^- \Leftrightarrow -\text{H}_2\text{O} \]

The hysteresis occurred during the hydroxylation and dehydroxylation processes of intercalated cations. Some studies conclude that the transition from two- to one-layer hydroxylated montmorillonite is harder than that from one water layer to completely dehydroxylate, which is joined by a diminishing of the basal spacing and a change in the contrary ion and the water atoms, other than the arrangement of hydrogen bonds being obviously weak (Fonseca et al. 2017). The transition of montmorillonite is temperature dependent. Dehydroxylation and desorption of physically adsorbed water molecules occur between 30 and 150 °C, decomposition of ammonium cations and dehydroxylation of structural water between 400 and 600 °C, and transformation of intercalated hydroxylated species to metal oxides at above 750 °C (Ruan and Gilkes 1996; Elkhalifah et al. 2013; Martinez et al. 2017). GuccnNnnrtr et al. (1978) reported that the dehydroxylation of dioctahedral 2:1-layer silicates (e.g. muscovite) is not a homogeneous process, the strength of the Al-OH bond can be greatly affected by the coordination number of neighbouring polyhedra. This can be classified by using a muscovite dehydroxylation model, the loss of hydroxyl groups of neighbouring polyhedra in octahedral coordination occurs more than five-fold at lower temperatures, which results in the distribution of oversaturated apical oxygens that also affect the
proton position and the Al-OH bond strength (GuccnNmrtr et al. 1978). For
dehydroxylation of illite at temperature intervals from 450 to 700 °C, the initial step
can be comprised of the condensation of OH- groups inside the octahedral layer and a
resulting 1-D dispersion of the simply framed water atoms through tetrahedral rings
into an interlayer region; and the second step can be represented by a 2-D dispersion
of water particles far from the interlayer space (Csáki et al. 2017; Húlan et al. 2017).
The aims of this research are to figure out the most suitable conditions for thermal
modification of MMWM to improve its adsorption ability, and the characterization of
physicochemical and mineralogical properties of MMWM before and after thermal
treatment in relation to the dehydroxylation process and phase transformation; and to
investigate the abilities and kinetics of adsorptions of Pb and MO, which are the
representatives of metals and organic compounds, onto this newly modified MMWM.

Experimental and analytical methods

Mineral waste material collection and modification

The modified mineral waste material (MMWM) was obtained from a commercial
company in Hong Kong after an initial physical and chemical treatment (Jiang et al.
2013a; Lu et al. 2016). The sample was ground with an agate mortar and sieved to
0.015 mm, packaged in air-tight polyethylene (PE) bags and reserved in a vacuumed
desiccator.
For thermal treatment, MMWM sub-samples were heated at temperatures from 300 to 1000 °C with a 100 °C increment between samples for 120 mins in a vacuumed tube oven. To prevent reintroducing moisture, once the samples were cooled down to 200 °C inside the oven they were immediately transferred into a desiccator for further cooling down to room temperature. These samples were kept in polyethylene (PE) bags and reserved in a vacuumed desiccator before analysis. The un-heated MMWM sample was labelled as “MM un-heated” and the heated MMWM samples were labelled as MM 300, MM 400, etc., where the MM denoted MMWM and the number denoted the thermal treatment temperature.

**Analysis of chemical composition of MMWM**

A homogenized sample (approximately 200 mg) was first mixed with 10 ml of strong acid (4:1 concentrated 65% HNO₃ and 40% HF (v/v)) in an airtight Teflon tank (effective volume 50 mL) and was then heated at 180 °C in the microwave digester (Sineo, MDS-10, Shanghai, China) for 20 mins. After cooling down to room temperature, the supernatant was separated from the solid particles by vacuum filtration through a 0.22 μm filter and diluted to 100 mL with deionized (DI) water. The concentrations of metals (calcium (Ca), iron (Fe), aluminum (Al), magnesium (Mg), titanium (Ti), manganese (Mn), strontium (Sr), zinc (Zn), rubidium (Rb), barium (Ba), copper (Cu), etc.) in the digested solutions were determined using
inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 2100 DV, USA).

Investigation of the properties of MMWM

**Burnauer, Emmett, and Teller (BET) specific surface area**

The specific surface area (SSA) of MMWM was determined by the BET method (thirteen-point liner plot) using nitrogen adsorption. Prior to measurements, samples were outgassed at 120 °C for 12 hrs. The SSA was detected and calculated by using Beckman Coulter, SA3100 surface area analyzer; the adsorption isotherms achieved a \( p/p_0 \) range of 0.009-0.25.

**Fourier transform infrared (FTIR) spectroscopy**

Fourier transform infrared absorption spectra of samples were obtained by using a PerkinElmer Frontier FT-IR/NIR spectrometer. The MMWM samples were dispersed in potassium bromide (KBr) with a KBr:MMWM ratio of 100:1. The mixtures were ground to fine powder and pressed into lamellar forms to make disks. A wavenumber range between 4000 and 450 cm\(^{-1}\) was recorded at a resolution of 4.0 cm\(^{-1}\) and 32 scans. The spectral manipulation including baseline adjustment, smoothing and normalization was performed using Origin Pro 2017 (OrginLab Corporation, Northampton, MA 01060 USA)
Field emission scanning electron microscopy (FESEM)

A representative portion of MMWM sample was sprinkled onto a double-sided carbon tape mounted on a SEM stub. All the samples were sprayed with a coat of gold before analysis. The FESEM measurements were performed on a high-resolution LEO 1530 field emission scanning electron microscope coupled with an energy dispersive X-ray detector from OXFORD.

X-ray diffraction (XRD) analysis

Sub-samples of un-heated and heated MMWM were prepared for XRD by grinding 500 mg of each sample and back filling in a quartz plate holder. Analysis was conducted via XRD by using non-monochromatic Cu $K\alpha$ radiation on a computer-controlled Bruker AXS D8 advanced X-Ray diffractometer. The step time of scans was 53.1 s and the step size was 0.02 ° 20. Patterns were recorded from 10 to 75 ° 20.

Adsorption experiments

Methyl orange adsorption

Batch experiments were carried out to determine the adsorption ability of MMWM towards MO. An initial experiment was conducted to determine the maximum adsorbent dosage of MO per unit of MMWM. For this purpose, 0.01, 0.02, 0.03, 0.04 and 0.05 g of adsorbents were dispersed in 50 ml of 100 mg/L MO solutions. The mixture in the flask was agitated on a shaker at room temperature (25 °C) for 480, 540,
600, 660 and 720 mins and filtered with a 0.22 μm filter. The solution was analyzed using a UV-Vis spectrophotometer (Thermo, Evolution 220, USA) coupled with an auto sampler with the detector being operated at 465 nm.

After the initial experiment, the adsorption capacity of MMWM was calculated, and the MMWM with the highest MO adsorption ability (0.04 g) was selected and categorized according to the design of intercalation method and kinetic and isothermal experiments. Adsorption kinetic experiment performed at room temperature (25 °C) and at pH = 7 was conducted by dispersing 0.04 g of the adsorbent in 50 ml of 100 mg/L MO solution in a flask. The amount of adsorbent selected was based on approximately 80% of MO being removed from solution at the equilibrium point. Then all the flasks were capped and placed in a shaker bath maintained at 25 °C and shaken at a speed of 300 rpm. The samples after MO adsorption were collected at different time intervals (1, 2, 3, 5, 15, 20, 30, 60, 120, 180, 240, 300, 360, 420, 480 and 540 mins) and filtered with a 0.22 μm filter to collect the supernatants. Adsorption isotherm studies were carried out by placing 0.04 g of MMWM in various volumes (15, 20, 25, 30, 35, 40, 45, and 50 mL) of 100 mg/L MO solutions under the same temperature and shaking speed as for the kinetic experiment. The samples after MO adsorption were collected at 540 mins and filtered with a 0.22 μm filter to collect the supernatants. The collected supernatants of both kinetic and isotherm experiments were analyzed using a UV-Vis spectrophotometer (Thermo, Evolution 220, USA) coupled with an auto sampler with the detector being operated at 465 nm.
Lead adsorption

Similar to the MO adsorption, an initial experiment of Pb adsorption was undertaken to find out the optimal adsorbent dosage of Pb per unit of MMWM. For this purpose, 0.01, 0.02, 0.03, 0.04 and 0.05 g of adsorbents were dispersed in 50 ml of 350 mg/L Pb solutions. The mixture in the flask was agitated on a shaker with a shaking speed of 300 rpm for 840 mins at room temperature (25 °C), and then filtered with a 0.22 μm filter. The solution after filtration was analyzed using ICP-OES (Perkin Elmer Optima 2100DV, USA).

After the initial experiment, the MMWM with the highest Pb adsorption ability (0.02 g) was selected and categorized according to the design of intercalation method and kinetic and isothermal experiments. Adsorption kinetic experiment performed at room temperature (25 °C) and at pH = 7 was conducted by dispersing 0.02 g of the selected adsorbent in 50 ml of 350 mg/L Pb solution. Then all the flasks were capped and placed in a shaker bath with the temperature set at 25 °C and shaken at a speed of 300 rpm. The samples after Pb adsorption were collected at different time intervals (5, 10, 20, 30, 60, 120, 180, 240, 300, 360, 420, 480, 560 and 840 mins) and filtered with a 0.22 μm filter to collect the supernatants. Adsorption isotherm studies were carried out by placing 0.02 g of MMWM in various volumes (5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 mL) of 350 mg/L Pb solutions. The mixture in the flask was agitated on a shaker with a shaking speed of 300 rmp for 840 mins at room temperature (25 °C). The samples after Pb adsorption were collected at 840 mins and filtered with a 0.22
μm filter to collect the supernatants. The Pb concentrations in the collected supernatants of both kinetic and isotherm experiments were determined using ICP-OES.

**Analysis of adsorption kinetics**

The amount of Pb and MO adsorbed onto the sample at different periods \( q_t \) can be calculated by the equation (1);

\[
q_t = \frac{(C_0 - C_t) \times V_0}{m}
\]  

(1)

where \( C_0 \) and \( C_t \) are the concentrations of Pb or MO at initial and different time intervals (mg/L), respectively; \( V_0 \) is the volume of Pb or MO solution (L) added, and \( m \) is the amount of adsorbent (g) added.

To model the kinetic of Pb and MO adsorptions, the adsorption data were fitted to the pseudo-second-order model, which can be described using equations (2) and (3) (Frost et al. 2004)

\[
\frac{t}{q} = \frac{1}{kq_e^2} + \frac{1}{q_e} t
\]  

(2)

which can be rewritten as:

\[
q = \frac{kq_e^2 t}{1 + kq_e t}
\]  

(3)

Where \( q_e \) and \( q \) are the amounts of Pb or MO adsorbed by adsorbent at initial and different time \( t \) (min) intervals (mg/g), respectively; \( k \) is the adsorption rate constant of the pseudo-second-order model.
For the isotherm study, the equilibrium adsorption capacity \( q_e \) can be calculated by the equation (4);

\[
q_e = \frac{(C_0 - C_e) \times V_0}{m}
\]  

(4)

Where \( C_0 \) and \( C_e \) are the initial and equilibrium Pb or MO concentration in solution (mg/L); \( V_0 \) is the volume of Pb or MO solution (L) added and \( m \) is the mass of adsorbent (g) added.

The Langmuir equation models the monolayer adsorption on the adsorbent surface (Langmuir 1917). Freundlich equation is based on the assumption that the adsorbent has a heterogeneous surface composed of different adsorption sites (Freundlich 1907). The equilibrium data were fitted to the Langmuir and Freundlich isotherm models shown in equations (5) and (6), respectively.

\[
\text{Langmuir equation: } q_e = q_m K_l \frac{c_e}{1 + K_l c_e}
\]  

(5)

\[
\text{Freundlich equation: } q_e = K_f c_e^{\frac{1}{n}}
\]  

(6)

where \( c_e \) (mg/L) is the Pb or MO concentration of solution at equilibrium point, \( q_e \) (mg/g) is the adsorption capacity of adsorbent at equilibrium point, \( q_m \) (mg/g) is the maximum adsorption capacity and \( K_l \) is the Langmuir adsorption equilibrium constant related to adsorption capacity and energy or net enthalpy of adsorption. \( K_f \) and \( n \) are the constants in the Freundlich isotherm model, which measure the adsorption capacity and intensity, respectively.
Results and discussion

Chemical composition of MMWM

The metal concentrations of MMWM determined by ICP-OES after microwave assisted digestion are shown in Table 1. Calcium, Fe, Al and Mg were the four most abundant metals. As expected, these four important metals in MMWM were present in over 98.7% of the total metal content. These results are similar to that of Jiang et al. (2013a), who reported that calcium silicate hydrate (Ca$_6$Si$_6$O$_{17}$ (OH)$_{17}$) and calcium aluminum silicate hydrate (CaAl$_2$Si$_2$O$_8$$\cdot$H$_2$O) were the two most abundant chemical compounds in MMWM, and Ca, Fe, Al and Mg were also the major metal compositions of montmorillonite, illite and chlorite. Krupskaya (2017) characterized the chemical composition of acid modified montmorillonite and found that Ca, Mg, Fe, and Al were the four most abundant metals. Aluminum is the main constituent of the octahedral layer [AlO$_3$ (OH)$_3$]$^{6-}$, and Ca, Mg are the compositions of the exchangeable interlayer. The remaining metals, such as Ti, Mn, Sr, Zn, Rb, Ba and Cu that were detected at very low or trace concentrations, were present in less than 1.2% of the total metal content.
Change in property after thermal modification

Change in Burnauer, Emmett, and Teller (BET) specific surface area (SSA)

To investigate the variation of SSA of MMWM as affected by thermal treatment, N$_2$-adsorption /desorption was carried out for each sample. Figure 1 demonstrates the variation of SSA of MMWM before and after thermal treatment at different temperatures. The appearance of thermally treated MMWM samples that were changing corresponded to the variations in temperature. The color of samples turned from white grey into pink grey and more obvious changes in color was observed at higher temperatures. It was clearly demonstrated that the SSA of thermally treated samples increased from 4.070 to 6.496 m$^2$/g when the temperature was increased to 500 °C (Fig. 1). This could be attributed to the loss of water molecules and the change in mineral layer structures, e.g. amorphous and/or meta-phases formed during thermal transformation of minerals (Ruan and Gilkes 1996; Martinez et al. 2017). The SSA then decreased to 0.874 m$^2$/g after heating to 1000 °C, where the reformation of crystal structures occurred. The MMWM samples used in this study consisted mainly of clay minerals. Hydroxylation and dehydroxylation may occur easily in these typical mineral structures, particularly on the surface structures. It is expected that the changes in mineral surface structure can greatly enhance its adsorption ability.

Although the SSA of MMWM was much smaller than that of a typical activated carbon (AC), the adsorption of metal pollutants per unit amount was always much higher than that of AC (Lu et al. 2016). This study suggests that the greater adsorption
ability of MMWM could be contributed by the hydroxyls on the mineral surface. The
chemical bonding of adsorption formed by the release of loosely bonded water
molecules and the enlargement of surface area during thermal treatment at 500 °C and
lower temperatures also contributed to elevate the absorption ability of MMWM. It is
believed that such changes in structure, including the creation of defects in mineral
surface, may provide more adsorption sites and further increase its affinity for
adsorption (Ruan and Gilkes 1996).

**Fourier transform infrared (FTIR) analysis for chemical bonding**

Infrared spectra are plotted to characterize the surface properties of MMWM, the
changes in bonded water molecules on the surface, and in the interlayer and mineral
structure during thermal modification. The infrared spectra of MMWM in the
vibrational range of 4000-450 cm$^{-1}$ are displayed in Fig. 2. The changes in infrared
spectra are obviously observed from MM un-heated to MM 1000. The disappearance
of a band at 1639 cm$^{-1}$ first occurs in the spectrum of MM 300, and the intensity of
the band at 1428-1415 cm$^{-1}$ decreases with increasing temperatures (MM 300, MM
400, MM 500, MM 600, and MM 700 of Fig. 2) and completely disappears in the
spectrum of MM 700. Another broad band can be observed at 3448-3442 cm$^{-1}$ from
the spectra of MM un-heated and MM 300, but it disappears when the thermal
treatment temperature reaches higher than 400 °C. This can be attributed to the release
of absorbed or loosely bonded surface water. One intense water bending band at 1639
and three intense hydroxyl deformation bands at 875-726 cm\(^{-1}\) are observed and assigned to different OH modes. Two fundamental vibrational modes of adsorbed water molecules on MMWM are observed in FTIR spectra: a group of symmetric O-H stretching vibrations in the spectral regions of 3448-3442 cm\(^{-1}\), and another group of H-O-H bending vibrations at the range of wavenumber 1428-1415 cm\(^{-1}\).

**O-H stretching vibration of MMWM.**

It is noted that the sharp intense band at 3643 cm\(^{-1}\) was overlapped with the broad band of vibrations of water (Fig. 3a). This is attributed to O-H stretching vibrations for the structural hydroxyl groups of MMWM (MM un-heated, MM 300, MM 400 and MM 500), which appeared at 3643 cm\(^{-1}\). However, such O-H stretching vibrations disappeared in the spectra of MMWM being thermal treated at temperatures higher than 600 °C (MM 600, MM 700, MM 800, MM 900, and MM 1000). This suggests that the structural O-H groups were retained in clay interlayers when thermal treatment temperature was increased up to 600 °C, but they were removed when the temperatures of thermal treatment were higher than 600 °C. A prominent broad band of vibration of water could only be observed in MM un-heated and MM 300 with the center at 3448-3442 cm\(^{-1}\) while the intensity of this band decreased significantly with increasing temperatures. The loosely bonded water molecules in MMWM were removed when heated to 400 °C, and then the structural hydroxyl groups were
removed when temperatures rose above 600 °C. These findings are consistent with those reported by Elkhalifah et al. (2013) and Martinez et al. (2017).

H-O-H bending vibration of MMWM

When considering vibrations of water molecules (Fig. 3b), the changes of FTIR spectra in both regions of O-H stretching and H-O-H bending were due to the reduction of hydrogen bonded water molecules with increasing temperature during thermal treatment, changing the surface properties from hydrophilic to hydrophobic. This phenomenon was due to the reduction of water content in MMWM by losing hydroxyl groups of hydrated interlayers. The FTIR spectrum of MMWM dehydroxylated at the highest temperature (i.e. 1000 °C) in this study exhibits the lowest band intensity in terms of more water molecules being released (see MM 1000 of Fig. 2).

In summary, the O-H stretching and H-O-H bending vibrations of hydrogen bonded water in MMWM provide evidence for the change in surface affinity from hydrophilic to hydrophobic (Rathnayake et al. 2017). This phenomenon of surface variation from the dehydroxylation of MMWM could correspond to the increase in adsorption capacity. We assume that the absence of infrared bands represents the process in which MMWM performed partial to total loss of hydroxylation water due to heating at different temperatures. This change in property of the MMWM as a result of losses in water molecules, in particular those on the mineral surface, is an
important process to make the dehydroxylated MMWM a superior adsorbent over the non-dehydroxylated MMWM. Calcination of MMWM at suitable temperatures can certainly improve its adsorption capacity by removing the physically and chemically bonded water molecules and turning the surface properties from hydrophilic into hydrophobic. However, metal oxides that formed on the mineral surface at high temperatures that were observed in this study, may reduce the adsorption capacity of MMWM.

Morphological change observed by field emission scanning electron microscopy (FESEM)

Figure 4 shows the FESEM images of MMWM before and after thermal treatment, as well as the EDX results of MMWM prior to dehydroxylation. The bulk of the material consists mainly of schistose substances with various particle sizes being observed from Fig. 4(a & c) which are associated with blurry and lamellar layers being found at a high amplification. Moreover these small schistose substances also congregate into a rough surface as shown in Fig. 4(d). In addition, the area scanning results of EDX displayed in Fig. 4(b) indicate that the MMWM sample shown in Fig. 4(a) (mainly containing Ca, Si, Al and Fe, apart from the organic components O and C) are consistent with the results of ICP-OES. The MMWM used in this study is mainly composed of clay minerals and its shape primarily presents a schistose appearance. The images shown in Fig. 4(e-i) reflect the effects of thermal treatment on the morphological changes of MMWM. The images in Fig. 4(e, f & g) show the
increases in amorphous particles that corresponded to thermal treatment temperatures at 300, 400, and 500 °C. Blurry edges and some cloud-like particles are also observed. Meanwhile a number of crystals were separated into several pieces, like the amorphous substances forming the poorly crystalline minerals in MMWM. When MMWM was heated to 500 °C, the MMWM mass clearly revealed small pieces of schistose layers (less than 100 nm), composed mainly of granular and schistose crystals. When the thermal treatment temperature was increased to 600 °C as seen in Fig. 4(h), the surface morphology differed slightly as some crystalline particles were forming due to recrystallization during phase transformation. The schistose appearances became increasingly evident when the temperature was increased from 700 to 1000 °C, and the schistose layers increased to larger than 500 nm (Fig. 4(i-l)). This is probably due to the formation of new phases during transformation. It is consistent with the results reported by Kremer et al. (2008). The external appearances of the thermally treated MMWM samples heated at 600 °C and higher (Fig. 4 (h-l)) were different from those of non-dehydroxylated MMWM samples (Fig. 4 (a, c-d)) and dehydroxylated MMWM at lower temperatures (Fig. 4 (e-g)). The thermal modification at the appropriate temperatures (e.g. 300-700 °C) may provide a mass of layers, rough surface and large surface area which would improve the adsorption ability of MMWM.
Change in X-Ray diffraction (XRD) pattern

Figure 5 displays the XRD patterns of MMWM before and after thermal treatment. The reflections at 20.71° and 26.45° correspond to quartz detected in MMWM samples (Fig. 5) and it can be used as an internal standard for d-spacing manipulation. The peaks observed in the XRD patterns of MMWM were identified as a series of minerals compared to the standard patterns. The mineral compositions of MMWM used in this study include montmorillonite (Clay) (ICSD (00-002-0239)), illite (ICSD (00-002-0056)), kaolinite (ICSD 01-078-2110), muscovite (ICSD (00-002-0056)), mica (ICSD (00-002-0051), feldspar (ICSD (01-08908575)), quartz (ICSD (00-046-1045)), calcite (ICSD (00-005-0586)) and rectorite (allevardite) (ICSD (00-029-1495)). The MMWM samples that consisted of a series of clay minerals reveal their great potential ability in contaminant adsorption, most of which can be further modified by sintering to achieve better adsorption capacity (Alvarez-ayuso and Garcia-Sanchez 2003; Adebowale et al. 2008; Sen and Bhattacharyya 2008; Etcı et al. 2010; Msaadi et al. 2017). All the peaks showed decreases in intensity with increasing temperature, and then some small peaks disappeared as the temperature reached 900 °C. Reflection of microcline (ICSD (00-019-0926)) at 27.08° was observed for MM un-heated, MM 300, MM 400, MM 500, and MM 600 samples, but it disappeared as temperatures reached 700 °C. The reformation of mineral structures during thermal treatment might contribute to the fading away of microcline. Two new reflections at 30.02° and 31.33° with low intensity were observed in the spectrum of
MM 1000, which were attributed to the generation of magnesian gehlenite after comparing with the standard pattern (ICSD (01-079-2422)). According to Traoré et al. (2008), micro-composite microstructure at the micron scale is obtained by sintering clay (kaolinite) and calcite at 1100 °C, where the formation of gehlenite occurs. The sintering modification of MMWM resulted in the formation of new minerals at a high temperature (1000 °C) but contributed less to adsorption ability. The study therefore suggests that the improvement of adsorption ability of MMWM after thermal treatment is seldom contributed by the crystal reformation.

**Improvement of adsorption ability after modification**

**Adsorption capacity of methyl orange**

The maximum amounts of MO adsorbed by MMWM samples heated at different temperatures are plotted in Fig. 6. These MMWM samples showed various adsorption abilities towards MO, changing from 24.9 to 87.6 mg/g, which minimized in the MM 1000 sample and maximized in the MM 400. The MMWM sample heated at 400 °C showed a better MO adsorption capacity than those of bottom ash and de-oiled soya from the soya oil industry with the adsorption capacity of each adsorbent being 3.61 and 16.66 mg/g, respectively (Mittal et al. 2007). According to Liu et al. (2011), organic-montmorillonite adsorbent treated by microwave irradiation reaches a maximum value of MO adsorption of approximately 50 mg/g. Our results indicated that the adsorption capacity of MMWM on MO was increased by 28.43% from 68.21
to 87.60 mg/g with the increase in temperatures up to 400 °C during thermal treatment, corresponded to a 59.61% enlargement of SSA at this temperature (Fig. 1). When the thermal treatment temperature was increased to higher than 400 °C, the adsorption capacity showed a decreasing trend and minimized at 1000 °C with a value of 24.96 mg/L, which was only 28.5% of the value at 400 °C. The MO adsorption capacity followed a similar trend with the loss of structural O-H groups and the change in SSA, suggesting that the adsorption of MO was mainly attributed to the functional groups performing affinity of adsorption in the interlayers of dehydroxylated MMWM in conjunction with the increase in SSA. The FTIR spectra of MM 400 before and after MO adsorption were selected to be demonstrated in Fig. 7. Two new bands at 1633 and 3432 cm\(^{-1}\) were observed in the MO adsorbed MM 400, but the band at 3643 cm\(^{-1}\) was overlapping and shifting to 3623 cm\(^{-1}\). Referring to the band fitting for spectra of Fig. 8 (a & b), the band at 3643 cm\(^{-1}\) cannot be found in the MO adsorbed MM 400, whereas absorbance bands are found at 3623 and 3232-3230 cm\(^{-1}\). Meanwhile, the intensity of the band at 3435 cm\(^{-1}\) increases conspicuously after MO absorption. Fig. 8(d & e) demonstrates band fitting spectra of MM 400 before and after MO adsorption in the range of 1750-1350 cm\(^{-1}\). Three hidden bands are found in each spectrum, bands at 1634 and 1462/1464 cm\(^{-1}\) remain unchanged but the band at 1434 cm\(^{-1}\) shifts to 1420 cm\(^{-1}\) after MO adsorption. The shift of vibrational frequency is believed to be due to the change in surface property from hydrophobic to hydrophilic after MO adsorption (Rathnayake et al. 2016). The disappearance of O-H stretching
vibration at 3643 cm\(^{-1}\) for the structural hydroxyl groups of MM 400 after MO absorption is observed and comes with the appearance of a new vibration at 3435 cm\(^{-1}\). This phenomenon was caused by MO molecules bonded to the \(-\text{OH}\) group on the interlayer of MM 400 surface, and the newly appeared vibration was contributed by the MO molecule. Thus, adsorption of MO by dehydroxylated MMWM was mainly contributed by combining MO molecules with the functional groups on mineral surface, where more affinity sites were created during phase transformation resulting from the dehydroxylation process. According to Chen et al. (2012), the adsorption of MO onto heat-treated clay mineral is controlled by two mechanisms: hydrogen bonding between oxygen groups of \(-\text{SO}_3^\text{−}\) (anionic head of MO) and \(\text{H}^+\) of coordinated water (<300 °C), and electrostatic interaction between dye and negatively charged surface of heat-treated clay (>400 °C). In conclusion, the enhancement of MO adsorption capacity of thermally treated MMWM (e.g. MM 400) is caused by the appearance of O-H groups after losing loosely bond water molecules and the increasing surface area of dehydroxylated MMWM, during which the process of hydrogen bonding is dominant (Chen et al. 2012). The gradual loss of structural hydroxyl groups of dehydroxylated MMWM resulted in the decline of MO adsorption ability from 65.24 to 24.96 mg/g when thermal treatment temperature was increased from 500 to 1000 °C, during which the process of electrostatic interaction was dominant associated with the decrease in SSA of MMWM, showing a similar trend identical to the variation of temperature (Chen et al. 2012). In addition, the SEM (Fig.
4) results show that the structure of MM 400 is looser, which could facilitate the adsorption of MO onto surface (Liu et al. 2011). Hence, the increase or decrease in MO adsorption capacity of dehydroxylated MMWM are contributed by both the changes in surface properties such as SSA and morphology and phase transformation during dehydroxylation at different stages of thermal treatment corresponding to heating temperature.

The amounts of MO adsorbed by the MMWM heated at 400 °C as a function of adsorption time is shown in Fig. 9. The MO adsorption onto MM 400 increased rapidly during the first 100 minutes and then slowed down until MO adsorption reached 87.6 mg/g after 420 mins, where the adsorption equilibrium point was achieved. The equilibrium uptake per unit mass of the adsorbent was higher than bentonite (6.7 mg/g) but lower than palygorskite (95.9 mg/g) (Chen et al. 2012; Leodopoulos et al. 2012). Compared with the organic-montmorillonite (49.8 mg/g) pre-treated by microwave irradiation, MM 400 showed a shorter equilibrium time and doubled the adsorption capacity (Liu et al. 2011). The adsorption curve was fitted by using the pseudo-second-order model. The corresponding parameters and correlation coefficient \( R^2 \) showed that the experimental data were well fitted to the pseudo-second-order kinetic model with \( R^2 = 0.994 \), suggesting that the MO adsorption onto MM 400 is chemisorption dominated. According to Chen et al. (2012), a pseudo-second-order model provided the best correlation of the experimental kinetic data to
the MO adsorption of clay mineral. This is also consistent with the previous results from FTIR spectra of MMWM in this study.

Figure 10 shows the Langmuir and Freundlich adsorption isotherms of MM 400 in the solution with various initial MO concentrations at room temperature (25 °C). A high correlation coefficient ($R^2 = 0.964$) was derived from the fitting data of adsorption experiment into the Langmuir isotherm model, as well as the comparison with that of the Freundlich isotherm model ($R^2 = 0.724$). This suggests that the observed feature of adsorption onto MM 400 can be assigned to monolayer coverage.

Similar results for heat-treated clay minerals were reported by Chen et al. (2012) and Luo et al. (2015), in which the adsorption isotherms of MO onto clays could be best described by the Langmuir equation.

Adsorption capacity of Lead

The amounts of Pb adsorbed by MMWM samples at 25 °C before and after thermal treatment at different temperatures are plotted in Fig. 11. The MMWM samples showed various adsorption abilities towards Pb adsorption, increasing from 349.3 (un-heated) to 518.9 mg/g when the treatment temperature was increased to 600 °C. However, the adsorption capacity then decreased to 45.5 mg/g when heating temperature was increased up to 1000 °C, where the reformation of crystal structures occurred. The MMWM sample heated at 600 °C (MM 600) showed much better Pb adsorption capacity than those of the adsorbents prepared from industrial wastes (blast
furnace sludge, 227 mg/g) and clay minerals (acid-activated kaolinite (6.3 mg/g) and acid-activated montmorillonite (22.7 mg/g)) (Bhatnagar et al. 2006; Gupta and Bhattacharyya 2005). In addition, the MM 600 showed greater adsorption capacity than those of natural goethite (109.2 mg/g), modified illite (239 mg/g), kaolinite (82.65 mg/g) and activated-montmorillonite (31.3 mg/g) (Alvarez-ayuso and Garcia-Sanchez 2003; Ozdes et al. 2011; Lounis et al. 2012). The EDX results of MM 600 after Pb adsorption is exhibited in Fig. 12, where Pb is observed as the second most abundant element (W: 37.4%) on the MMWM surface. The study suggests that the adsorption of Pb on MMWM was mainly performed by surface adsorption, and the variations in Pb adsorption capacity can be attributed to the enlarged surface area where more adsorption sites could have been provided. This is associated with the changes in surface property where variations in bonding were due to the performance of functional groups and to the alteration in surface charges and porosity related to phase transformation of minerals during the process of dehydroxylation.

The Pb adsorption capacity of the heated MMWM sample (MM 600) as a function of adsorption time is shown in Fig. 13. The Pb adsorption onto MM 600 increased rapidly during the first 80 minutes and then changed gradually until the amount of Pb adsorbed reached 510 mg/g after 420 mins, where the adsorption equilibrium was attained. As the adsorption kinetics were described using the pseudo-second-order model, the corresponding parameters and correlation coefficient ($R^2$) showed that the experimental data were well fitted to the pseudo-second-order kinetic
model with $R^2 = 0.941$, suggesting that the Pb adsorption onto MM 600 was chemisorption. This is consistent with the previous results in this study that MM 600 can adsorb a large amount of Pb onto its surface although the surface area of MMWM is rather small. This could be attributed to the increase in negative charges on the lattice of the mineral surface, especially during the process of dehydroxylation, dominating the adsorption. Moreover, the rate constant $k$ of the pseudo-second-order fitting plot of MM 600 was 0.0375 g mg$^{-1}$ min$^{-1}$, which is close to that of kaolinite (0.035 g mg$^{-1}$ min$^{-1}$) but smaller than that of montmorillonite (0.084 g mg$^{-1}$ min$^{-1}$) (Naseem and Tahir 2001). Therefore, MM 600 exhibited a dramatically enhanced Pb removal performance, including much higher Pb adsorption capacity and faster adsorption with a high adsorption rate. Herein, MM 600 was chosen for further Pb adsorption isotherm study.

Figure 14 shows the Langmuir and Freundlich Pb adsorption isotherms of MM 600 in various initial concentrations in solution at room temperature (25 °C). A high correlation coefficient ($R^2 = 0.971$) was derived from fitting the experimental adsorption data into the Langmuir isotherm model, as well as a comparison with the Freundlich isotherm model ($R^2 = 0.881$). This suggests that the observed feature of adsorption onto MM 600 can be assigned to monolayer coverage, which is in agreement with the previous findings that the interaction between Pb and the schistose adsorbent is endothermic in nature (Frost et al. 2004). Moreover, MM 600 possessed a considerable adsorption capacity compared to other clay minerals (acid-activated
montmorillonite, 22.7 mg/g; beidellite, 86.9 mg/g) or mixed metal-modified clay mineral adsorbents (Zn-imprinted polymer/montmorillonite, 301 mg/g) (Etcı et al. 2010; Msaadi et al. 2017).

Implications

Modification on the properties of MMWM to increase its adsorption capacity can be achieved by thermal treatment. Property characterization revealed that the changes in surface morphology of MMWM can be clearly observed at different stages of the thermal process. Different levels of phase transformation are related to the variations in mineral properties of MMWM as affected by dehydroxylation. The capacities of MMWM on adsorption of MO (MM 400, 87.60 mg/g) and Pb (MM 600, 514 mg/g) have been successfully optimized after thermal modification. The increase in adsorption capacity is attributed to the enlarged SSA where more adsorption sites were generated, to the change in surface property where variation of bonding is due to the performance of functional groups, and to the alteration of surface charge. The MO and Pb adsorption curves of MMWM can be well fitted to the pseudo-second-order kinetic model, to which the MO and Pb adsorptions by MMWM are mainly chemisorption. Adsorption isotherms are better fitted to the Langmuir model than to the Freundlich one, suggesting that adsorptions of MO and Pb onto MMWM could be assigned to monolayer coverage. Thus, thermally treated MMWM is confirmed to be a good adsorbent for the removal of contaminants, especially for Pb in solution. The
results of this study may provide information for the production of adsorbent derived
from mineral waste material that can be applied to environmental remediation and
useful to the integrated management of solid waste materials.

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### Table

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Figures

Figure 1 BET SSA of MMWM heated at different temperatures.

Figure 2 FTIR spectra of thermally treated MMWM at different temperatures in the vibrational range of 4000-450 cm$^{-1}$
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Figure 9 Pseudo-second-order fitting plot of MO adsorption onto MM 400 at room temperature (25 °C)

Figure 10 Langmuir and Freundlich fitting plots of MO adsorption isotherms of MM 400 at room temperature (25 °C)
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Figure 12 The EDX results of MM 600, (a) spectrum after Pb adsorption, (b) element content and (c) SEM image (amplification 6.0K) used for EDX analysis.
Figure 13 Pseudo-second-order fitting plot of Pb adsorption onto MM 600 at room temperature (25 °C)

Figure 14 Langmuir and Freundlich fitting plots of Pb adsorption isotherms of MM 600 at room temperature