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Studying competitive sorption behavior of methylene blue and malachite green using multivariate calibration

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HIGHLIGHTS

- Competitive sorption of two cationic dyes of significant spectral overlapping is studied using MVC.
- Simultaneous determination of two dyes (spectral overlap 96.4%) is achieved using PLS1.
- Irregular L2-isotherm shape was observed for dyes sorption in binary systems.
- Langmuir model was found applicable for presenting competitive sorption of cationic dyes.
- Competitive sorption process of cationic dyes was found exothermic and spontaneous.

GRAPHICAL ABSTRACT

Adsorption isotherms of methylene blue MB and malachite green by clay from bi-solute solution. Irregular L2-isotherm shapes are obtained.

ABSTRACT

Sorption of methylene blue MB and malachite green MG (with 96.4% spectral overlap) from bi-solute solution by natural kaolinitic-clay and philipsite-rich-zeolite tuff was addressed where solutes simply quantified using multivariate calibration MVC. For simultaneous quantification of dyes in solution, partial least squares PLS1 (a powerful MVC tool) was found satisfactory with high recovery (98.7–103.2%) and precision (RSD 9.2–11.7%). In MVC, the spectral range 409–700 nm is used and 43 spectral points where taken for each sample. Natural clay (80% kaolinite) and zeolite tuff (95% philipsite) showed a high uptake for dyes with maximum capacities of 0.77 mmol MB/gclay and 0.64 mmol MG/gclay, 0.66 mmol MB/zeolite and 1.22 mmol MG/zeolite reported at 1.0 g/L, particle diameter <45 μm, 20.0 °C and pH 7.0. Due to competition between dyes for active sites, the sorption capacities were reduced and the highest reduction was 30% which observed for MG sorption by clay. The competition between dyes was higher in clay as indicated from competition factors CFs. Sorption isotherms of bi-solute systems have irregular L2 isotherm shape and the data were fairly correlated to Langmuir and competitive Langmuir models. The contribution of ion-exchange mechanism in dyes removal was found significant, 61% and 79% of MB were removed via ion-exchange by clay and zeolite, respectively. Using MVC, studying competitive sorption of MB and MG without the need for chromatographic separation is accomplished. Studying competitive sorption of more than two solutes using PLS1 is also possible indicating the high resolution power of this technique.

1. Introduction

Large amounts of dyes are heavily applied in textile, pharmaceutical, paper, foodstuff and leather industries [1]. The direct
discharge of dyes into the aquatic environment is presenting a real risk and should be handled with great care [1]. For example, textile wastewaters that remain after dyeing process contain large amounts of un-reacted dyes beside auxiliary chemicals [2]. Commercially, there are many kinds of dyes of variable chemistries including acidic, basic disperse, azo, diazo, anthraquinone based and metal complex dyes [3]. Basic dyes (also known as cationic dyes) are applied in acrylic, nylon, silk, and wool dyeing [4]. Cationic dyes are positively charged heterocyclic aromatic compounds with high stability and more toxic by-products would produce upon their degradation [5]. Cationic dyes are toxic materials even at trace levels [6], for example, the concentration of malachite green (a cationic dye) should not exceed 1.0 μg L⁻¹ in drinking water and 100 μg L⁻¹ in potable waters [6]. Adsorption using activated carbon, natural adsorbents and bioadsorbents is widely employed for safe removal of wide ranges cationic dyes [7–9].

Sorption tests are often carried out using single-solute solution where measuring two or more solutes requires a separation step before quantification. Within literature, most of studies discussed single-solute systems and much less attention is given for multi-solute sorption systems. For multi-solute systems, more attention is needed for accurate solute quantification. For dyes, few studies have been reported which extend from simple spectrophotometric procedures [10,11] to more advance spectrophotometric ones [12,13]. The selection of the analytical method is dependent on the extent of spectral overlap between solutes or presence of a complex matrix. Due to complexity of real matrices or high spectral/chromatographic overlap, chromatographic methods are needed in certain systems [14].

The most adopted analytical procedures for dyes quantification are high performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry (LCMS), capillary electrophoresis, gas chromatography and mass spectrometry, electrochemical methods [15,16]. In fact, dyes quantification based on chromatographic procedures is a laborious work and takes much more time where solutes separation is necessary before detection [15]. In absence of peaks overlapping or even small peaks overlapping, simple spectrophotometric determination is also recommended because it is possible to obtain high accuracy, precision, and reproducibility using inexpensive procedures compared to chromatography. In the case of intense spectral overlap or complex matrices, MVC methods including multilinear regression MLR principal component regression PCR and partial least squares PLS have been effectively applied for dyes quantification [1,6,13,15,16]. The main advantages of MVC methods are to minimize/eliminate sample preparation and to avoid applying tedious chromatographic or electrochemical methods [6,15].

In multi-dye sorption, evaluating the competition of dyes for active sites is very important. The prediction and modeling of multi-component sorption equilibrium is also an important issue and very helpful for understanding sorption in multi-solute systems. In fact, limited studies have studied the application of MVC for studying competitive sorption of dyes [13]. To the best of our knowledge, using MVC for studying competitive sorption of MB and MG by aluminosilicates is not reported yet. In this work, competitive sorption of MB and MG (of intense spectral overlapping) is studied with the aid of MVC. Two natural aluminosilicates (clay and zeolite) are used as solid media for dyes removal from solution. Multivariate calibration tools including MLR, PCR and PLS-1 are applied for dyes quantification. For better understanding sorption of dyes by aluminosilicates, detailed chemical and physical characterization studies were carried out. Specific surface area and cation exchange capacity of adsorbents were computed form dyes sorption data and compared with those obtained from standard tests. Sorption data are modeling using different models to get a better idea regarding competitive sorption of dyes and the nature of solute-adsorbents interactions. Thermodynamics of dyes competitive sorption is also addressed.

2. Experimental procedures

2.1. Physical and chemical properties of aluminosilicate adsorbents

Two natural aluminosilicates were used for dyes sorption. The adsorbents were donated by the Royal Scientific Society–Industrial Chemistry Center (Amman, Jordan). Grounding and sieving of adsorbents were carried out at the department of Environment and Earth Sciences–The Hashemite University (Jordan). Initially, 0.5 kg of each sample was crushed and sieved to particle size less than 45 μm. The natural clay and zeolite tuff samples were washed several times with distilled water with constant stirring to remove any soluble or adhering materials. Na-form of the adsorbents was made by shaking adsorbents in 1.0 M NaCl for 24 h. The adsorbents were washed with distilled water to remove excess NaCl and then dried at 105 °C for 24 h. Sorption tests were conducted on particle size less than 45 μm. Mineral constitution of adsorbents was studied using X-ray powder diffraction XRD technique (Shimadzu X-ray Diffractometer XRD-6000, Japan). However, chemical compositions of adsorbents were determined using X-ray fluorescence (Shimadzu XRF-1800 Sequential X-ray Fluorescence Spectrometer, Japan). Total acidity and basicity of adsorbents were determined using standard Boehm titrations [17]. To 50.0 cm³ solution of 0.01 M NaOH or HCl, 0.50 g of dried adsorbent was added and the solution was agitated form 24 h. The resulting solution was carefully filtered and centrifuged to get clean supernatant. The final solution was titrated with 0.01 M NaOH or 0.01 M HCl using phenolphthalein as an indicator. Surface basicity or acidity was quantified from the consumed acid or base. For accurate determination of cation exchange capacity CEC for silicates, ammonium displacement method was adopted [18]. pHpc (pH at zero point of change) was estimated using pH-drift method [19]. In this method, six solutions of different pHs (2)–(12) were prepared using 0.05 M HCl or 0.05 M NaOH in 0.1 M NaCl solution. To each solution, 0.5 gram of dried adsorbent is added and the solutions were agitated for 24 h. The solutions were filtered and the final pH was measured. pHpc is estimated from the plot between pHlim = VS pHmax. The pHpc is the point where the curve pHlim = VS pHmax intersects the line pHlim = pHmax [19]. The textural characteristics of both adsorbents including surface area, pore volume, pore size distribution were determined using standard N2–adsorption techniques (Nova 2400E, Surface Area and Pore Size Analyzer). Specific surface and external surface areas were estimated using multipoint BET method [20] and t-plot method [20], respectively. Total pore volume was calculated from amount of adsorbed N2 at P/P0 = 0.95 [21]. Micropore volume was estimated from Dubinin–Radushkevich method [21,22]. Mesopore volume was calculated from the amount of N2 adsorbed between relative pressure P/P0 = 0.40–0.95 assuming that the molar volume of liquid nitrogen is 35.0 cm³/mol [23]. Average pore diameter was of adsorbents obtained from Barrett–Joyner–Halenda (BJH) method [20].

2.2. Cationic dyes

Two common cationic dyes that have a wide industrial application were selected, namely, methylene blue (C.I. 52015) and malachite green (C.I. 42000). The dyes were purchased from Aldrich® Company with purity higher than 99%. The chemical structures of dyes were illustrated in Fig. 1. Both dyes have high solubility in water at 20 °C and often used for estimation of cation exchange capacity and specific surface area of different adsorbents [24,25].
As indicated in Fig 1, MB has a positive charge on S atom while MG has a positive charge on N atom. Molecular dimensions, as reported in the literature [24,25], are also provided in Fig 1. Standard dyes solutions of 1000 mg L\(^{-1}\) were prepared individually by dissolving 1.000 g in double-distilled water in a 1.0 liter volumetric flask using sodium acetate buffer at pH 7.0. Diluted solutions were prepared from standard solutions using acetate buffer. All sorption tests were carried out at pH 7.0.

2.3. Sorption of dyes from single and bi-solute solutions

Removal performance of clay and zeolite for cationic dyes were studied using concentration variation procedure for single and bi-solute systems. Experimental conditions of sorption tests were set as follows: initial concentration range of dyes: 0.0–1.56 mM MB and 0.0–1.37 mM MG; mass of adsorbent: 100 mg; particle diameter: <450 \(\mu\)m; pH: 7.0; volume of solution: 100 mL; temperature 20 °C and agitation time: 1.0 day. In competitive sorption tests, equal concentration of solutes was used and the concentration ranges were 0.0–1.56 and 0.0–1.37 mM for MB and MG, respectively. The concentration range of both dyes is equivalent to 0.0–500 mg/L. In all experiments, 100 mg of dry adsorbent is added to 100 mL dye solution and the mixture is closed and placed in a thermostated shaker (20 °C) for 1.0 day (this time was estimated from earlier kinetic studies) which is necessary to attain equilibrium. At the end of shaking period, the solutions were removed, filtered and centrifuged to get clean solution in preparation for spectral measurements. The content of dyes in single and bi-solute systems was determined using multivariate calibration as will be shown later. Influence of temperature on dyes removal was studied at the same experimental conditions but at 30.0 and 40.0 °C.

2.4. Collection of spectral data and multivariate calibration

The spectral data of dyes were recorded using a double beam Unicam spectrophotometer (Cary 50 UV–Vis spectrophotometer). The instrument is interfaced with a computer for displaying results and the data were collected as \(x, y\) pairs. For standards and sorption solutions of dyes, 4.0 mL solution is placed in glass cell and the spectrum was recorded over the region 490–700 nm with 5 nm resolution (i.e., 43 spectral points taken for the sample). The cell was rinsed with distilled water before the next measurement. Data treatment and multivariate calculations were carried out using MATLAB® (version 7.0). The adopted algorithms of multilinear regression MLR, principal component regression PCR, and partial least squares PLS1 are easily accessed in the literature [26]. For MLR, the regression coefficients needed for dyes quantification were estimated from the calibration matrix: \(K = (C'C)^{-1}C'X\), where prediction of dyes concentrations from spectral data is obtained as: \(C_{\text{un}} = (KK')^{-1}KX_{\text{un}}\), where \(C, C_{\text{un}}, X, \) and \(X_{\text{un}}\) are true concentrations, predicted concentrations, calibration matrix containing spectral data, and spectral data of unknown/validation samples. For PCR, the matrix of calibration coefficients is found as: \(P = (U'U)^{-1}U'X\) and dyes predicted in sorption/validation solutions as: \(C_{\text{un}} = X_{\text{un}}P\) where score matrix \(U\) and loading matrix \(V\) were estimated using PCR algorithm using the optimum number of factors [26]. For PLS1, the calibration sensitivity vector was estimated as: \(b = WPW'q\), where \(W, P, \) and \(q\) were estimated using PLS1 algorithm using the optimum number of latent variables [26]. Prediction of MB and MG contents in single and bi-solute solutions was carried out for each dye using the corresponding \(b\) vector as: \(C_{\text{un}} = X_{\text{un}}b\). For PCR and PLS1 the optimum number of factors and latent variables were estimated using cross-validation procedure [1,26]. The calibration and validation sets for dyes were 16 and 9, respectively. The earlier sets were used to build the optimum multivariate calibration model that used to find dyes levels in solutions. In the earlier equations, bolded capital letters are used for presenting matrices and bolded small letters for presenting vectors. \(T\) stands for transpose operation. Multivariate calculations by MLR, PCR, and PLS-1 were carried out using MVC1 program which is available on the Internet and performs under MATLAB environment [27]. Before running MVC1, the spectral data for calibration, validation and sorption solutions were saved in special format that is suitable for MVC1.

2.5. Analyzing sorption data

Equilibrium concentrations of dyes \(C_{\text{eq}}\) (mol/L) that left after sorption were estimated using MVC and then used to find the corresponding surface concentrations \(C_s\) (mol/g). Two common isotherms were used to correlate sorption data of single and bi-solute systems, Langmuir and Freundlich equations: Langmuir equation could be presented as [28]:

\[
\frac{C_s}{C_{\text{eq}}} = \frac{K_L C_{\text{im}}}{1 + K_L C_{\text{im}}}
\]

where \(C_s\) (mol/g), \(C_{\text{eq}}\) (mol/L), \(K_L\) (L/mol) and \(C_{\text{im}}\) (mol/g) are surface concentration of MB/MG, concentration of MB/MG remaining in solution, binding or equilibrium constant, and the maximum adsorbed quantity of dye, respectively. Freundlich equation could be presented as [29]:

\[
C_s = K_F C_{\text{eq}}^n
\]

\(C_s\) and \(C_{\text{eq}}\) have the same meaning as in Langmuir equation. \(K_F\) and \(n\) are Freundlich constant (L/g) and a dimensionless number, respectively. Sorption data of bi-solute systems were also modeled using Competitive Langmuir model which is suggested for multi-solute sorption systems as following [28,30]:

\[
\frac{C_{\text{eq}}}{C_s} = \frac{K_{11} C_{\text{m1}} C_{\text{q1}}}{1 + K_{11} C_{\text{q1}} + K_{12} C_{\text{q2}}}
\]

and,

\[
\frac{C_{\text{eq}}}{C_s} = \frac{K_{12} C_{\text{m2}} C_{\text{q2}}}{1 + K_{12} C_{\text{q1}} + K_{12} C_{\text{q2}}}
\]

where \(C_{\text{m1}}, C_{\text{m2}}, C_{\text{q1}}, C_{\text{q2}}, K_{11},\) and \(K_{12}\) are the surface concentration of solute 1 and 2, the maximum sorption values for solute 1 and solute 2, the aqueous concentration of solute 1 and solute 2, and equilibrium constants for solute 1 and solute as obtained from Langmuir equation. In our case, solute 1 and solute 2 may...
presenting MB and MG, respectively. From theoretical point of view, the equilibrium constants ($K_1$ and $K_2$) are identical to those obtained from single-solute systems as equilibrium constant is a temperature dependant parameter and related to enthalpy of sorption process \cite{28}. Enthalpy $\Delta H$ and entropy $\Delta S$ of dyes sorption process are estimated from Langmuir equilibrium constant using linearized van't Hoff equation as following \cite{12,29}:

$$
\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
$$

(5)

where $R$ and $T$ are the gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and solution temperature, respectively. The values of $\Delta H$ and $\Delta S$ are obtained from the slope and y-intercept linear plot between $\ln K_L$ vs $1/T$. Spontaneity of sorption process $\Delta G$ is estimated from the earlier parameters as following \cite{12,25,29}:

$$
\Delta G = RT \ln K_L
$$

(6)

Another important parameter that often estimated to evaluate extent of competition between solutes is competition factor $CF$ \cite{28}:

$$
CF = \frac{C_{\text{im(bi-solute)}}}{C_{\text{im(single-solute)}}}
$$

(7)

where $C_{\text{im}}$ (bi-solute) and $C_{\text{im}}$ (single-solute) are the maximum sorption values obtained from single and bi-solute solutions, respectively. Positive competition is encountered if $CF$ is more than unity and sorption is enhanced by other competing solutes. Sorption of no competition is encountered if $CF = 1.0$. The common case is $CF < 1$ which indicates that sorption of the solute is reduced due to competition with other solute(s) \cite{28}.

As already known, CEC and SSA of ionic surfaces like clays and zeolites could be simply estimated from cationic dyes adsorption \cite{25,31,32}. Cation exchange capacity CEC and specific surface area SSA of both adsorbents were estimated from MB and MG sorption data as outlined in the work of Yener and co-workers \cite{32}. Initially, $C_{(ex)}$ and $C_{(ad)}$ were obtained from isotherms where $C_{(ex)}$ and $C_{(ad)}$ are the amount of cationic dye adsorbed via ion–exchange pathway and the amount of cationic dye adsorbed via other physical forces \cite{32}.

CEC and SSA were estimated as \cite{32}:

$$
\text{CEC} = 10^3 \left( \frac{C_{(ex)}}{M^+} \right)
$$

(8)

and,

$$
\text{SSA} = \left( \frac{C_{(ad)}}{1000 M^+} \right) LA
$$

(9)

where $M^+$, $L$ and $A$ are molar mass of cationic dye (MB or MG), Avogadro’s number $(6.022 \times 10^{23}$ mol$^{-1}$), and the largest perpendicular area for the cationic dye assumed to lie flat on the surface \cite{32}. The values of $A$ are 134 and 65 Å$^2$ for MB and MG, respectively \cite{25,32}.

3. Results and discussions

In fact, few studies have used advanced spectrophotometric methods like multivariate calibration \cite{13} and derivative spectrophotometry \cite{12} for analyzing dyes mixture in sorption systems. Moreover, some researchers have applied simple spectrophotometry for dyes analysis due to the lower spectral overlap between solutes \cite{11,28}. In the current system, an intense spectral overlap is encountered between dyes and this necessitates application of MVC or liquid chromatography for accurate dyes quantification. Moreover, application of MVC will be necessary not only for dyes quantification but also for handling the negative influence of unex-pected interferences that may involve in sorption systems. Application of MVC is applied for reactive dyes removal from solution \cite{13} but no is reported on cationic dyes sorption.

3.1. Intense spectral overlapping and importance of multivariate calibration

The spectral overlap between MB and MG is extreme and this shall retard their direct quantification by simple spectrophotometry and separation of solutes becomes necessary. Fig. 2 depicted the absorption spectra of both dyes $(11.0 \mu\text{mol}/\text{L})$ at pH 7.

As shown in Fig 2, a significant spectral overlap occurs in the band of dyes. Using the method of Goicocchea and Olivieri \cite{33}, the extent of spectral overlap (estimated at pH 7) between dyes were 96.4%. The wavelengths of maximum absorption ($\lambda_{\text{max}}$) were 610 and 670 nm for MB and MG, respectively. Therefore, this would limit the application of univariate calibration (i.e., running analysis at $\lambda_{\text{max}}$) for dyes quantification in their mixtures. To show the poor performance of univariate calibration for the current system, analysis was carried out using calibration equations derived based on Beer’s law. The outputs of univariate analysis are not acceptable as will be shown next. Relatively speaking, univariate analysis predicted MB concentration even in the presence of MG while, prediction of MG is not possible in the presence of MB. Accordingly, univariate calibration is not applicable for the current sorption system and more accurate analytical method is needed. At this stage, for accurate determination of MG in the mixtures, the application of chromatographic procedures or MVC is necessary. Compared to chromatographic procedures, MVC is simpler to implement so we can avoid using expensive instruments and toxic organic solvents. Unlike univariate calibration, MVC needs a spectrum per sample and not only a single measurement per sample. Before running multivariate calibration, absorbance values are collected in matrix $X$ and the true concentrations of dyes are collected in matrix $C$. The main goal in this case is to get a calibration vector for each solute that will be used for predicting dyes concentration in solution. As mentioned earlier, there are number of multivariate calibration tools to be applied including MLR, PCR, PLS-1 and the application of these methods depends on the complexity of the matrix to be analyzed and number of solutes. MLR and PCR are applied in cases of high spectral overlap and matrices of low complexity, however, PLS1 could be applied even in the presence of un-modeled chemical interferences and matrices of high complexity \cite{16,26}. In the current case, we do not expect negative influence of clay/zeolite on sorption solution as dyes are colored materials and the leachate of adsorbents is colorless and hence there is no spectral interferences.

As a demonstration, the application of MLR on spectral data will be presented. The original dimensions of the data matrices are high $(16 \times 43$ and $9 \times 43$ for calibration and validation sets, respectively) and for simplicity we use only 8 spectral points. MLR could

![Fig. 2. Absorbance spectra of MB and MG (11.0 μmol/L) at pH 7.0.](image-url)
be used for handling overlapping signals and in the presence of unexpected interferences [26].

In MLR, \( K \) matrix is computed from \( X \) and \( C \) matrices as follow [26]:

\[
K = (C' C)^{-1} C' X
\]

Prediction of dye concentration in new samples is carried out as following [26]:

\[
C_{un} = (KK^T)^{-1}KX_{un}
\]

where \( X_{un} \) is the absorbance matrix for unknown samples.

The components of calibration and validation matrices/ssets are presented in Table 1.

Absorbance matrix \( X_{16-8} \) and concentration matrix \( C_{16-2} \) were collected from the data given in Table 1. For validation, a set of 9 synthetic mixtures of MB and MG were prepared as mentioned earlier. The validation set was used to test the workability of the selected MVC method. In fact, calibration was carried out on different number of spectral points and earlier analysis indicated that 43 point/sample is reasonable. Therefore, MVC was carried out using 43 spectral points/sample. As mentioned earlier, the numerical analysis started by finding the regression coefficients (or absorbivities matrix) \( (K_{8-2}) \) as following [1,26]:

\[
K_{8-2} = (C' C)^{-1} C' X
\]

The components of matrix \( K \) is shown below

\[
K_{8-2} = \begin{bmatrix}
0.0103 & 0.0065 \\
0.0127 & 0.009 \\
0.0235 & 0.0222 \\
0.0412 & 0.0565 \\
0.0732 & 0.1264 \\
0.0279 & 0.1615 \\
-0.0176 & 0.2111 \\
0.0035 & 0.0165
\end{bmatrix}
\]

Now, \( K \) matrix is used for dyes prediction in any solution mixture using the following equation [26]:

\[
C_{un} = (KK^T)^{-1}KX_{un}
\]

To assess the calibration power of MLR, PCR, and PLS-1 for the current overlapping system, %recovery and RSD were estimated for dyes quantification in both sets. Univariate analysis are also included for comparison purposes as shown in Table 2.

As can be seen from Table 2, MVC outperformed univariate calibration and predicted dyes concentrations with high accuracy and precision. Form the results in Table 3, the following main conclusions would be deduced: (a) For MB, both MLR and univariate analyses give a reasonable recoveries and precisions. However, for MG the prediction power of univariate analysis was not acceptable with recovery and precision of 298.2 and 117.0 (for calibration set) and 260.1 and 145.0 (for validation set), (b) MLR and PCR gave acceptable results for dyes quantification as indicated from recovery and precision magnitudes, and (c) Due to its high calibration power and handling intense overlapping, PLS-1 was managed to predict dyes contents with reasonable accuracy and precision. Based on the earlier discussion, the competitive removal of both dyes by clay and zeolite would be safely studied with the aid of PLS1 for accurate estimation of both dyes in adsorption solutions. The concentration levels of dyes that used in sorption tests were 10 times higher than that employed in MVC, therefore, in most cases dilution by distilled water was made before spectral measurements/MVC.

3.2. Characterization of aluminosilicates adsorbents

The selected aluminosilicate minerals were characterize for their textural properties, chemistries, and mineralogical constitutions using different techniques including X-ray diffraction (XRD) and X-ray fluorescence spectrometers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. µm</th>
<th>Absorbance values</th>
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<tr>
<td></td>
<td>MB</td>
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<td>1</td>
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</table>

Wavelengths in nm.

* The original spectral data containing 43 point per sample, however, 8 spectral points were presented for simplicity.
3.2.1. XRD and XRF techniques

Types of minerals in the adsorbents were identified from XRD scans which are given in Fig. 3. As indicated in Fig. 3A, six peaks with reasonable intensities were observed at: 8°, 13°, 21°, 25°, 27°, and 30°. The earlier peaks are characteristics for kaolinite mineral (13° and 21°), quartz (25° and 27°) and smectite (8° and 21°) [34]. The high intensities of kaolinite peaks reflected its higher concentration in clay sample which is essential for dyes uptake from solution [31,32]. XRD analysis confirmed the presence of philipsite as a major mineral in zeolite tuff as indicated in Fig. 3B [6]. Based on the provided XRD analysis, kaolinite and philipsite minerals are making about 80% and 95% of clay and zeolite tuff samples. It is important to mention that the types and contents of minerals were identified using a special software that connected with XRD instrument. Table 3 shows the chemical compositions of the tested adsorbents.

As indicated in Table 3, Si and Al oxides are making large fractions of the adsorbents with a total mass percentage more than 50%. The large abundance of Si and Al is expected because they are making the main structure of aluminosilicate adsorbents [34]. Si/Al ratio is a good indicator for predicting uptake of cationic solutes. Adsorbents of high Si/Al ratios were found effective for attracting positively charged solutes [34]. The Si/Al ratios were 2.76 and 1.65 for zeolite and clay, respectively. As both ratios were higher than unity then the tested adsorbents would have a high affinity for cationic dyes in solution [34,35]. In addition to the high Si/Al ratio, the tested adsorbents are expected to show high cation-exchange capacity due to the high contents of Na, K, Mg, and Ca as indicated in Table 3.

3.2.2. Chemical and physical properties and relationships with dyes sorption from solution

For better understanding dyestuffs sorption process by aluminosilicates, some important physical and chemical properties were provided and the results are summarized in Table 4. N₂ adsorption/desorption isotherms are also provided in Fig 4.

Chemical properties of adsorbents indicated that a high content of active surface functional groups, mainly siloxane group Si–OH, which is the most common in aluminosilicates adsorbents [35]. Kaolinitic-clay has higher density of surface groups with a value of 7.0 group/nm² while the corresponding value of philipsite–zeolite is 3.0 group/nm². As pH of sorption tests was 7.0 then the net surface charge of clay (pHₚₑₒₑ = 6.2) is negative due to presence of –Si–O⁻ groups while the net surface charge of zeolite (pHₚₑₒₑ = 9.5) is positive due to formation of protonated siloxane groups –Si–OH⁺. Based on that, clay would show a better performance than zeolite for removing cationic dyes from solution. Dyes
N₂ adsorption–desorption isotherms were summarized in Table 4. Adsorption isotherms were of type II, in accordance with the IUPAC classification [22]. The isotherm (Fig 4) features a combination of type I and type II isotherms indicating L2 isotherm according to Giles classification [36]. This indicated that dyes sorption by aluminosilicates was accomplished by forming one monolayer layer on the surface [36]. L2 isotherm is also indicated a high affinity between solute and adsorbent at lower concentration then the surface become saturated at higher concentrations. L2-isotherm is also observed in metals and ionic dyes sorption with a weak competition with solvent molecules [28]. In fact, the majority of reported isotherms of MB and MG from single-solute solutions by different sorbents have L2 isotherm shape [32]. It is interesting to notice the instability of dyes isotherms in bi-solute systems for both sorbents. As shown in Fig 5C and D, the shapes are not similar to single-solute isotherm where obtained isotherms become scatter especially at higher solute concentration and this is clear in the case of MB and MG sorption by clay (Fig. 5C). The most stable isotherm was observed in MB sorption by zeolite and this would be attributed to lower competition with MG molecules which have a higher affinity for zeolite (Fig. 5D). The obtained irregular L2 isotherms is attributed to the high competition between MB and MG at higher concentrations as shown in Fig 5C. Similar shapes of isotherms was reported for competitive sorption of anionic dyes [11,28]. We believed that the extent of competition is increased at higher concentrations and this is reflected on the shapes of isotherms. Equilibrium sorption data of single and bi-solute systems were modeled by Langmuir, Freundlich, and Competitive Langmuir equations. The extent of competition between dyes – were obtained using non-linear regression protocol with the aid of Microsoft Excel [25]. The results of modeling and SSE values are presented in Table 5. As indicated in Table 5, LM model was the most suitable for presenting MB and MG sorption data in single and bi-solute systems.

### Table 4

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
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<tbody>
<tr>
<td>Adsorbent</td>
<td>Acidity (mmol/g)</td>
</tr>
<tr>
<td>Clay</td>
<td>0.846</td>
</tr>
<tr>
<td>Zeolite</td>
<td>0.081</td>
</tr>
</tbody>
</table>

where mesopore volumes making 96% and 89% of total pore volume for clay and zeolite, respectively. Migration of both solutes (molecular dimensions 1.2–1.7 nm) inside microporous adsorbents is highly possible where the average pore diameter is significantly higher than the dimensions of both solutes, 1.9 and 2.1 nm for clay and zeolite, respectively. It is highly possible that zeolite would exhibit a better sorption than clay due its higher SSA where of a value of 172.8 m²/g was estimated using N₂-adsorption method. From physical and chemical point of view, both adsorbents are liable for dyes sorption from solution.

3.3. Competitive sorption of MB and MG and mechanism of sorption from solution

Adsorption isotherms of dyes from single and bi-solute solutions are shown in Fig 5.

For single-solute systems (Fig 5A and B), the shapes of isotherms indicating L2-isotherm according to Giles classification for isotherms [36]. This indicated that dyes sorption by aluminosilicates was accomplished by forming one monolayer layer on the surface [36]. L2 isotherm is also indicated a high affinity between solute and adsorbent at lower concentration then the surface become saturated at higher concentrations. L2-isotherm is also observed in metals and ionic dyes sorption with a weak competition with solvent molecules [28]. In fact, the majority of reported isotherms of MB and MG from single-solute solutions by different sorbents have L2 isotherm shape [32]. It is interesting to notice the instability of dyes isotherms in bi-solute systems for both sorbents. As shown in Fig 5C and D, the shapes are not similar to single-solute isotherm where obtained isotherms become scatter especially at higher solute concentration and this is clear in the case of MB and MG sorption by clay (Fig. 5C). The most stable isotherm was observed in MB sorption by zeolite and this would be attributed to lower competition with MG molecules which have a higher affinity for zeolite (Fig. 5D). The obtained irregular L2 isotherms is attributed to the high competition between MB and MG at higher concentrations as shown in Fig 5C. Similar shapes of isotherms was reported for competitive sorption of anionic dyes [11,28]. We believed that the extent of competition is increased at higher concentrations and this is reflected on the shapes of isotherms.

Equilibrium sorption data of single and bi-solute systems were modeled by Langmuir, Freundlich, and Competitive Langmuir equations. The extent of competition between dyes – were obtained using non-linear regression protocol with the aid of Microsoft Excel [25]. The assessment of modeling by different isotherms was made by calculating sum of square errors squared SSE where lower values of SSE indicating better performance for the model [34]. SSE is simply estimated from the formula: \( \sum_{i=1}^{n} (C_{i,calc} - C_{i,prod})^2 \), where \( C_{i,calc} \), \( C_{i,prod} \), and \( n \) represent the calculated sorption values, model-predicted sorption values and the number of sorption points/experiments, respectively. The results of modeling and SSE values are presented in Table 5.

As indicated in Table 5, LM model was the most suitable for presenting MB and MG sorption data in single and bi-solute systems.

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<td>0.081</td>
</tr>
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</table>
The earlier model was more applicable for single-solute compare to bi-solute systems as indicated from SSE values. For single dye system, SSE values were fall within 0.01–0.05 while higher values were obtained for bi-solute systems 0.10–0.30. The applicability of LM for presenting sorption data indicated that, (a) a limited number of active sites are available, (b) sorption of dye molecules continues until surface saturation and, (c) interaction between sorbed molecules is neglected. LM model was reasonably predicted $C_{sm}$ for MB and MG in single and bi-solute systems. Analysis of single-solute data indicated that MB and MG are almost of comparable affinities (0.77 and 0.64 mmol/g for MB and MG, respectively) while MG is preferably removed by zeolite with $C_{sm}$ of 1.22 mmol/g compare to 0.66 mmol/g for MB. The favorable uptake of MG by zeolite is also indicated from the high $K_f$ value (77.4). Generally speaking, zeolite had a better performance for MB and MG uptake in single and bi-solute solutions and this is highly attributed to the higher CEC and SSA as shown in Table 4. It is interested to notice that $K_f$ values of MB and MG are comparable for single and bi-solute systems and this was expected as $K_f$ is a temperature dependent parameter. On the other hand, FM showed a high applicability for modeling MB and MG sorption by both sorbents with lower SSE values 0.005–0.01. The lower values of $n$ (<1.0) indicated the favorable uptake of both dyes by both sorbents at the studied concentration range and the high heterogeneity of the silicate surfaces [34]. On the other hand, higher $K_f$ indicated higher sorption intensity which is observed for MG sorption by zeolite with a value of 1.57 and this trend was also predicted from LM. Unfortunately, the model was not applicable for modeling bi-solute systems with high SSE values 0.42–0.62. FM model was only applicable for MB sorption (in the presence of MG) with SSE value of 0.06. It seems that FM cannot handle bi-solute sorption data in the case of high competition between solutes. The degree of competition between dyes was evaluated form CF. As shown in Table 5, a negative competition between dyes is involved as the values of CF for both dyes are always less than unity. The competition between dyes was higher in clay compare to zeolite as indicated from the corresponding CL values. The highest CL value was observed for MG sorption by zeolite and this would be attributed to its high affinity for zeolite compare to MB. For better modeling competitive sorption data, Competitive Langmuir model CLM was applied. Competitive Langmuir model has been applied for modeling mixture of cationic dyes by peat [30]. The earlier model assumes a homogenous surface with respect to the energy of adsorption, no interaction between solutes, and no competition between active sites [28,30]. As indicated in Table 6, CLM outperformed Freundlich model for presenting competitive adsorption data with reasonable SSE values 0.05–0.28. Moreover, CLM was more applicable for presenting sorption data for both dyes in the case of zeolite. For clay, LM and CLM have comparable applicability for modeling dyes sorption as indicated from SSE values. Even though the SSE values may indicate the applicability of CLM, the obtained $C_{sm}$ values do not represent the actual sorption values in bi-solute systems. For example, in MB-clay system the SSE value was 0.05 while the predicted $C_{sm}$ value is 0.75 mol/g and this value is higher than $C_{sm}$ obtained in single-solute system 0.66 mmol/g. Furthermore, the CLM predicted a value of 2.01 mmol/g for MG sorption by zeolite which is almost two-fold higher than the one reported in single-solute system. In a similar study, Gao and co-workers have been studied sorption of two anionic dyes (acid red 14 and reactive red 15) by acid treated natural biomass (okara) where single and bi-solute systems were considered [13]. Analysis of bi-solute sorption data indicated that partial competitive Langmuir, competitive Langmuir–Freundlich isotherms were effective for modeling sorption data [13]. On the other hand, Noroozi and co-workers reported that competitive sorption of two cationic dyes (basic blue 41 and basic red 18) could be reasonably modeled using

---

**Fig. 5.** Adsorption isotherms of single and bi-solute solutions at 20 °C and pH 7.0. A and B sorption of MB and MG from single-solute solution C and D sorption of MB and MG from bi-solute solution. MB: 0.0–1.56 mM MG: 0.0–1.37 mM.
ideal adsorbed solution theory extended Langmuir equation [10]. In the current case, the correlation between theoretical and experimental data had only limited success due to competitive and interactive effects between the dyes and the dye–surface interactions.

The reduction in dyes removal observed in bi-solute systems (as a result for competition) indicated that number of active sites is limited and ion-exchange mechanism has a significant role for dyes removal. The contribution of ion-exchange mechanism would be assessed by comparing the magnitude of CEC with the maximum dye sorption capacity. As both dyes have one positive charge, then sorption by ion exchange will proceed with 1:1 ratio in which the maximum dye sorption capacity. As both dyes have one positive charge, then sorption by ion exchange will proceed with 1:1 ratio in which the maximum dye sorption capacity.

Bi-solute systems

Table 6

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>MB C(ads)</th>
<th>MB SSA</th>
<th>MG C(ads)</th>
<th>MG SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>100.0</td>
<td>50.0</td>
<td>112.0</td>
<td>31.3</td>
</tr>
<tr>
<td>Zeolite</td>
<td>108.0</td>
<td>112.0</td>
<td>33.8</td>
<td>31.3</td>
</tr>
</tbody>
</table>

(a) Values of C(ex) and C(ad) are in mg/g and obtained from single-solute isotherms (Fig. 5A and B) as outlined in the literature [32].
(b) CEC (cmol(+)/kg) and SSA (m²/g) were estimated from C(ex) and C(ad) as outlined Section 2.4.

Table 5

<table>
<thead>
<tr>
<th>Dye</th>
<th>Clay</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LM</td>
<td>CF</td>
</tr>
<tr>
<td></td>
<td>C(sm) mmol/g</td>
<td>Kt</td>
</tr>
<tr>
<td>MB</td>
<td>0.77</td>
<td>33.8</td>
</tr>
<tr>
<td>MG</td>
<td>0.64</td>
<td>23.2</td>
</tr>
</tbody>
</table>

The values of SSA and CEC of both adsorbents were estimated using popular N₂-adsorption and ammonium displacement methods, respectively. Relatively speaking, the results of MB are reasonable for both adsorbents when compared with standard values. For clay, the predicted values of CEC and SSA estimated from MB were comparable to those estimated from standard procedures. However, SSA was fairly predicted using MG sorption for clay while the predicted CEC (28.3 cmol(+)/kg) was lower than the value obtained from ammonium displacement method. For zeolite, CEC was reasonably predicted by MG sorption (41.2 vs 51.8), however, the predicted SSA by MG (301.0) is significantly higher than N₂-adsorption value (172.8). In fact the high C(ad) (280 mg/g) value of MG that reported for zeolite may explain the high SSA value that estimated by Eq. (9). In summary, it is highly recommended to use MB for determination SSA and CEC of aluminosilicate adsorbents.

3.5. Thermodynamics of competitive sorption of dyes from solution

Thermodynamics of MB and MG sorption by kaolinitic clay were studied by running sorption tests at different temperatures (20.0, 30.0, 40.0 °C) and at pH 7.0. Usually, thermodynamic parameters (ΔΗ, ΔS, and ΔG) of MB and MG were estimated from single-solute solution. In this work, the estimation of the earlier parameters was based on bi-solute sorption data which obtained with the aid MVC. Single-solute sorption isotherms of both solutes were conducted side by side at the selected temperatures to assess the competition between solutes at higher temperatures. It is important to mention that effect of temperature on dyes sorption was studied only for clay. Thermodynamic parameters are presented in Table 7 which estimated from Kt as outlined earlier.

The following main conclusions would be drawn from Table 7, (a) Extent of sorption of both dyes was decreased by temperature and this evident from the values of C(sm) or Kt. For both dyes, Kt values have been reduced by 60% and 40% for MB and MG, respectively after increasing solution temperature by 20.0 °C. This experimental observation indicated that sorption of both dyes is sensitive to temperature and the process is physically controlled.
(b) Sorption data at 30 and 40 °C and for both solutes were satisfactorily modeled by Langmuir equation with reasonable SSE values (0.10–0.16) and the predicted Kt and C(sm) values were also meaningful.
(c) vant Hoff equation was found applicable for sorption data with high correlation coefficients r² > 0.99. Sorption process of dyes by clay was found exothermic with ΔΗ values of −26.0 and −25.1 kJ/mol for MB and MG, respectively. Moreover, sorption of dyes from solution was established with a net reduction in the entropy of the entire system. Sorption processes are spontaneous.

3.4. Estimation of CEC and SSA of aluminosilicates using MB and MG sorption

As already known, MB and MG are often used for estimating CEC and SSA for aluminosilicates and other sorbents [24,25,31,31]. For more details on experimental procedures and theoretical background on this subject we recommend the recent work of Yener and co-workers [32]. The aim of this section is to find the proper dye (MB or MG) that can predict CEC and SSA for both adsorbents. The values of C(ex) and C(ad) which are necessary in calculations were summarized along with CEC and SSA values in Table 6.
at the studied temperatures (20–40 °C) and this is a good advantage from industrial point of view, (d) The type of sorption process (either physical or chemical-controlled process) would be figured out from the magnitude of ΔH; sorption process of ΔH less than 84 kJ/mol is controlled by physical forces while chemically-controlled process have ΔH 84–420 kJ/mol [37]. Based on the earlier classification, sorption of both dyes is controlled by physical forces which would be varied from ion-exchange to weak van der waals' forces. There is a conflicting picture regarding the sorption enthalpies of MB and MG in the literature. In agreement with our results, exothermic sorption processes of MG by kaolinite [25] and MB by cobalt–hectorite composite [38] were reported in the literature. On the other hand, endothermic sorption processes of MB by wheat shells [39] and MG by activated carbon [40] were noted in the literature. It seems that the extent of competition between MB and MG did not considerably changed by temperature. For example, CF observed for MG were 0.7, 0.7, and 0.68 at 20, 30, and 40 °C.

4. Conclusions

With the aid of MVC, studying competitive sorption behavior of MB and MG without the need for solutes separation is accomplished. Natural aluminosilicates minerals were found effective for cationic dyes removal and ion-exchange mechanism has a significant role in dyes removal. Due to high competition between dyes at higher concentrations, irregular L2 isotherm shapes were observed. Among the tested models, Langmuir and competitive Langmuir isotherms were found effective for presenting dyes isotherms. Relatively speaking, CEC and SSA would be correctly obtained from MB sorption rather than MG sorption. The estimated CF indicated that competition between dyes was higher in clay compare to zeolite. Sorption process of both dyes was found exothermic and spontaneous at the studied temperatures. Using PLS1, competitive sorption of more than two dyes seems to possible based on the results reported in this research.

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References


