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.
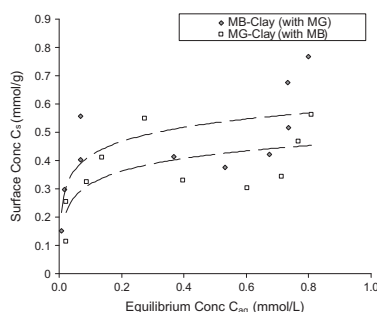
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ABSTRACT

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/g_{clay} and 0.64 mmol MG/g_{clay}, 0.66 mmol $MB/g_{zeolite}$ and 1.22 mmol $MG/g_{zeolite}$ 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.

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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 $1.0 \, \mu g \, L^{-1}$ in drinking water and $100 \, \mu g \, L^{-1}$ 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, liquid chromatography and 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 studied 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 $50.0 \, cm^3$ 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]. pH_{zpc} (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. pH_{zpc} is estimated from the plot between $pH_{initial}$ vs pH_{final}. The pH_{zpc} is the point where the curve pH_{final} vs $pH_{initial}$ intersects the line $pH_{initial} = pH_{final}$ [19]. The textural characteristics of both adsorbents including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques (Nova 4200e, 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 N_2 at P/P_o 0.95 [21]. Micropore volume was estimated from Dubinine–Radushkevich method [21,22]. Mesopore volume was calculated from the amount of N_2 adsorbed between relative pressure P/P_o 0.40–0.95 assuming that the molar volume of liquid nitrogen is $35.0 \, cm^3/mol$ [23]. Average pore diameter was of adsorbents obtained from Barrette–Joynere–Hanlenda (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].