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Research Paper

# Insights on the role of organic matters of some Egyptian clays in methyl orange adsorption: Isotherm and kinetic studies

Ahmed M. Zayed[a,*], Mahmoud S.M. Abdel Wahed[a,c], Essam A. Mohamed[b], Mika Sillanpää[c]

[a] Department of Geology, Faculty of Science, Beni-Suef University, Egypt
[b] Faculty of Earth Sciences, Beni-Suef University, Egypt
[c] Department of Green Chemistry, Faculty of Engineering Science, Lappeenranta University of Technology, Finland

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ABSTRACT

The role of organic matters (OM) of some Egyptian clay in Methyl Orange (MO) adsorption from aqueous solutions was tested for the first time. To elaborate this role, the raw Organic Matters-Rich Clays (OMRC) was calcinated at 500 °C/4 h to remove their associated OM by oxidation. Then the MO removal efficiency by both OMRC and its calcinated derivative (COMRC) was tested at different experimental parameters. The adsorption of MO by the studied adsorbents was pH- and time-dependent process and the equilibrium was attained after 60 min. The pseudo-second-order model with high determination coefficients ($R^2 > 0.999$) fitted well the adsorption kinetics, while the intra-particle diffusion was not the rate governing step in MO adsorption by both adsorbents. The MO adsorption characteristics revealed that equilibrium data of OMRC and COMRC fitted well to the Freundlich and Langmuir models, respectively. Electrostatic interaction was the primary but not the only governing mechanism for MO adsorption by the investigated adsorbents; participation from hydrogen bonding mechanism was involved, with some preference for COMRC. The superiority of OMRC over COMRC in MO adsorption can be attributed to the involvement of oxygen- and nitrogen-bearing groups of both OM and clay minerals in the adsorption process on the contrary of COMRC in which only oxygen-bearing groups of the clay minerals were incorporated.

## 1. Introduction

The discharge of organic dyes into aquatic environments can damage water quality in several ways such as dissolved oxygen depletion and prevention of sunlight penetration (Jalil et al., 2010; Mohammadi et al., 2011). The methyl orange (MO) is a typical anionic azo dye that is released into the aquatic environments through several industrial activities such as plastic, paper, textiles and cosmetic industry. Thus, the discharge of this anionic dye into the aquatic system without proper treatment can cause serious problems not only due to its mutagenic and carcinogenic effect on human health (Su et al., 2014), but aesthetically due to the visibility of its color in water even at low concentration. Accordingly, the removal of MO from solutions is a vital requirement.

There are some difficulties in the remediation of MO from solutions by chemical and biological methods owing to the high thermal and chemical stability of such dye (Deligeer et al., 2011). It is therefore preferable to remove MO from solutions by adsorption process as it can produce uncontaminated water effluent of high quality (Mokhtari et al., 2016).

Several natural, modified and synthetic materials such as bentonite (Leodopoulos et al., 2012), kaolinite (Gaston et al., 2014), mesoporous $TiO_2$ (Asuha et al., 2010), bentonite-supported zero-valent iron (Chen et al., 2011), calcined - layered double hydroxides (Ni et al., 2007), calcium aluminate hydrates (Ni et al., 2007), aminated pumpkin seed powder (Subbaiah and Kim, 2016), calcined volcanic mud (Jalil et al., 2010), mesoporous carbon (Mohammadi et al., 2011), modified coffee waste (Lafi and Hafiane, 2016), modified waste tires (Saleh et al., 2014), modified wheat straw (Su et al., 2014), carbon-coated monolith (Hosseini et al., 2011), activated carbon/$Fe_3O_4$ nanoparticle composite (Do et al., 2011), modified mesoporous carbons (Goscianska et al., 2014), multiwalled carbon nanotubes (Yao et al., 2011), modified carbon coated monolith (Cheah et al., 2013), sliver nanoparticles coated activated carbon (Pal et al., 2013), chitosan/MgO composite (Haldorai and Shim, 2014), chitosan/$Al_2O_3$/magnetite nanoparticles composite (Tanhaei et al., 2015), surfactant/nanoclay systems (Cavallaro et al., 2016) and composite of biopolymer/nanoclay beads (Cavallaro et al., 2013; Belhouchat et al., 2017), showed excellent removal capacity toward colorant dyes, especially MO anionic dye.

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* Corresponding author.
*E-mail address:* ahmed.zayed@science.bsu.edu.eg (A.M. Zayed).

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Clays and clay minerals are classified as good adsorbents for various pollutants due to their noticeable efficiency, wide availability, low costs and their safe use in wastewater remediation. Some of these clays are marked with high content of organic matters (OM) that gives them their black and/or grayish black color (the color reflects the intensity of OM concentration). The bridging of iron and aluminum hydroxyl of clays for the hydroxyl and carboxyl function of the humic substance played the major role in binding the majority of these OM with their host clays (Cheshire et al., 2000) to finally produce strongly interacted interlayer clay-organic complexes (organo-mineral complexes) (Liu et al., 2018). The intercalation of nano-sized OM into the interlayer of swelling clay minerals (i.e. interlayer expansion) has a positive impact on the total surface area of these clays and hence their cation exchange capacity (Liu et al., 2018).

Although the great responsibility of the OM on a large proportion of the cation exchange capacity of clays, no special attention was paid for the role of these matters (even in indirect way) in the adsorption process of different contaminants by OMRC. From this point of view, this work was dedicated to: 1) investigate the use of some Egyptian OMRC and their calcinated derivative (COMRC) in the adsorption process of MO from aqueous solution at different experimental conditions, 2) highlight the possible catalytic role of the OM in upgrading the adsorption properties of the hosting clays, 3) evaluate the influence of the applied experimental parameters such as contact time, initial MO concentration, solution pH, adsorbent mass on the adsorption process, 4) analyze the adsorption behavior and the mechanism of MO uptake by fitting the experimental data to different isotherm and kinetics models, 5) examine the impact of interaction between the MO ions and the functional groups of the studied adsorbents during the adsorption process and 6) elaborate the involved mechanisms in the adsorption process of MO ions by the addressed adsorbents.

## 2. Materials and methods

### 2.1. Materials

Organic matters-rich clays (OMRC) collected from the Western Desert in Egypt, methyl orange dye (MO) imported from Fluka, Switzerland, distilled water (DW), 0.01 M hydrochloric acid and sodium hydroxide delivered from Alfa Aesar with 97% purity (for initial pH adjustment), are the materials that were used in this study.

### 2.2. Calcination of organic matters rich clay

The most commonly applied protocols in removing OM from their host clays are wet-oxidation via oxidizing reagent (e.g. sodium hypochlorite and hydrogen peroxide) and calcination by heating at 300–600 °C (Rihs et al., 2017). Both protocols have some concerns and undesirable effects. For example, oxidation of OM by hydrogen peroxide not only cannot remove OM completely (Max. 60%) but also can cause the dissolution of Al- and Fe-bearing fractions, as well as calcite (Mikutta et al., 2005). Also OM destruction by heating at high temperature can cause a change in the mineralogical characteristics of clayey and non-clayey constituents, due to the removal of their structural water and hydroxyl groups during the calcination process (Hoogsteen et al., 2015). In the contrary of wet oxidation treatment by $H_2O_2$, minor destruction $_{of}$ $CaCO_3$ is anticipated at 500 °C, since calcite decarbonation to CaO usually take place at temperature higher than 500 °C (Salehi et al., 2011).

In the light of these great uncertainties, the current study favored calcination protocol (the more effective approach) to assure that the pristine OMRC (owning to its OM content) still can compete with the COMRC in MO removal although the enhancement in adsorption properties of the latter by calcination. So, the calcination protocol was executed as follow:-.

Grounded and quartered sample of the OMRC was washed several times with distilled water to remove any adhering impurities such as NaCl. It was then oven dried at 65 °C for 24 h to a constant weight. The dried sample was grounded and sieved to obtain < 100 μm size fraction.

About 20 g of the sieved OMRC was calcinated at 500 °C for 4 h in a programmable furnace with a 20 °C/min heating rate to remove the associated impurities and oxidize their organic matters content. The calcinated sample was gently grounded and sieved to < 100 μm mesh fraction. The produced powder was named as COMRC.

### 2.3. Sample characterization

The raw OMRC were investigated by the XRF technique (Philips X-ray fluorescence analyzer model PW/2404) to get its chemical composition. While the diffraction patterns of the raw OMRC and the calcinated one (COMRC) were obtained using a Philips APD-3720 diffractometer with Cu Kα radiation that worked at 20 mA and 40 kV with a 5°/ min scanning speed in the 2θ range of 5°-80°. The morphological characteristics and the functional groups of the OMRC and the COMRC before and after MO uptake were determined by SEM (JSM-6700F, JEOL, Tokyo, Japan, beam energy: 20–30 kV, working distance: 11.1–12.2 mm) and FT-IR spectroscopy (Bruker FTIR-2000 Spectrometer with mode of reflection at a 4 $cm^{-1}$ resolution) in the range of 400–4000 $cm^{-1}$, respectively. For SEM investigation, the adsorbents powder (< 100 mμ) was mounted on stubs and coated with gold by a gold-coating device (JEOL-JSM-420, Japan). Whereas, for FT-IR study, the adsorbents powder was mixed with KBr (Merck) in a 1:10 ratio to get translucent pellets used for identifying the functional groups of the addressed adsorbents.

In association with SEM scanning, the EDX (Energy Dispersive X-Ray Spectroscopy) was measured for the applied adsorbents after MO uptake. The Total Organic Carbon (TOC) of the OMRC before and after calcination was determined using Leco Sc 623 device after digestion with hot HCL (10%) to get rid of the carbonate impurities.

The surface area, pore volume and pore size of the OMRC and COMRC were determined by Surface Area Analyzer (Nova 2000 Quantachrome) after degassing the samples in a vacuum at 100 °C for 2 h to remove the adsorbed contaminants from the samples surfaces and pores. The BET surface area was estimated by Brunauer-Emmet and Teller model (Brauner et al., 1938), while the pore volume and size were measured using the Barrett-Joyner-Halenda (BJH) formula (Barrett et al., 1951).

### 2.4. Adsorption experiments

A stock solution (1.0 g/L) of methyl orange was prepared by dissolving 1 g of MO in one litter of distilled water (DW). The initial concentrations of MO for the kinetic and equilibrium studies were prepared by diluting the MO stock solution with DW to the desired concentration.

To conduct equilibrium experiments, a fixed mass (0.1 g) of both OMRC and COMRC were separately added to 25 mL of methyl orange solution with variable initial concentrations ranging from 60 to 140 mg/L with intensive shaking (200 rpm) for 1 h. After shaking, the liquid-solid phases were separated by centrifuging. A double beam UV–visible spectrophotometer (Shimadzu, Model UV 1601, Japan) was used to measure the remaining MO in the liquid phase at $\lambda_{max} = 468$ nm (Subbaiah and Kim, 2016). Other $\lambda_{max}$ (463 nm) was used to determine MO concentration in solution (Alqaragully, 2014).

The adsorbed MO ($q_e$, mg/g) at equilibrium was calculated by this equation:

$$qe = \frac{V(Ci - Cf)}{m} \tag{1}$$

where $C_i$: the initial MO concentration (mg/L), $C_f$: the concentration of the remediated MO at equilibrium, V: the volume of solution (L) and m: