**Development and characterization of organically grafted clay minerals for the removal of methylene blue from water**

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**Supplemental Material**

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**Figure S1.** Number of publications: (a) related to clay modification and application in adsorption processes (Research was conducted using Clarivate’s *Web of Science* on January 15th, 2024 using the keywords ‘clay AND organic grafting AND methylene blue,’ ‘clay AND organic grafting AND adsorption,’ ‘clay AND pillared AND methylene blue,’ ‘clay AND pillared AND adsorption,’ ‘clay AND magnetic AND methylene blue,’ ‘clay AND magnetic AND adsorption,’ ‘clay AND activated AND methylene blue,’ and ‘clay AND activated AND adsorption’); and (b) related to organoclays and the type of clay used (Research was conducted on July 11th, 2024 using Clarivate’s *Web of Science* with the keywords ‘organoclay,’ ‘montmorillonite,’ ‘bentonite,’ and ‘kaolin\*’).

(b)

(a)

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**Figure S2.** Thermogravimetric analysis of: (a) Shymkent natural clay and (b) Shymkent-TEAO.

**Text S1. Calculation to determine surface areas**

The Langmuir method is given in eqn 1 (Diaz de Tuesta et al., 2022; Lowell et al., 2004) and was calculated in the *P*/*P*0 range of 0.05–0.35:

|  |  |
| --- | --- |
| $$\frac{q\_{e}}{q\_{m}}= \frac{K∙P}{1+K∙P}$$ | (1) |

Where qe refers to the adsorbate (in this case, N2) adsorbed per mass of adsorbent at equilibria stage, qm and K are constants, and *P* is the pressure. The Langmuir equation can be rewritten as eqn 2:

|  |  |
| --- | --- |
| $$\frac{P}{q\_{e}}=P∙\frac{1}{q\_{m}}+\frac{1}{K∙q\_{m}}$$ | (2) |

By plotting *P/q*e versus *P*, the parameters K and qm can be obtained. The surface area can then be derived from eqn 3 (Lowell et al., 2004):

|  |  |
| --- | --- |
| $$S\_{Langmuir}= \frac{q\_{m}∙A∙ N}{M}$$ | (3) |

where *A* is the cross-sectional area of the adsorbate (in this case, N2 and equals 0.162 nm2 (Bardestani et al., 2019)), N is Avogrado’s number and *M* is the adsorbate molar mass (Bardestani et al., 2019).

The value of *S*BET was calculated using eqn 4 (Bardestani et al., 2019) in the *P*/*P*0 range of 0.05–0.35:

|  |  |
| --- | --- |
| $$\frac{^{P}/\_{P\_{0}}}{W(1-^{P}/\_{P\_{0}})}=\frac{1}{C∙W\_{ml}}+\frac{C-1}{C∙W\_{ml}}∙^{P}/\_{P\_{0}}$$ | (4) |

where *W* is the mass adsorbed at relative vapour pressure, *P* and *P0* are the actual and saturated vapor pressures of the adsorbate, *W*ml is the mass of adsorbate that forms a complete monolayer, and C is a constant. Plotting $\frac{^{P}/\_{P\_{0}}}{W(1-^{P}/\_{P\_{0}})}$ versus $^{P}/\_{P\_{0}}$ allows us to obtain values for β0 (intercept) and β1 (slope). The mass of adsorbate that forms a monolayer, *W*ml*,* is obtained from the sum of β0 and β1, as shown in eqn 5, and *S*BET can be calculated from eqn 6:

|  |  |
| --- | --- |
| $$\frac{1}{W\_{ml}}= β\_{0}+β\_{1}$$ | (5) |
| $$S\_{BET}=\frac{W\_{ml}}{M∙m}∙N∙A $$ | (6) |

where *M* is adsorbate molar mass, m is the sample mass, *A* is the adsorbate cross-sectional area (for N2 it equals 0.162 nm2) and N is Avogadro’s number (Bardestani et al., 2019).

**Table S1**. Literature reporting adsorption of dyes with organoclays.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Clay | Grafted molecule | Pollutant | Conditions | Results | References |
| Bentonite | Silylating agents (chlorotrimethylsilane, n-octyltrichlorosilane, n-octadecyltrichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, triphenylchlorosilane) | Sudan (II) | pH = 4.0, [adsorbent] = 0.4 g/L, [adsorbate] = 50 mg/L | 60-80% of Sudan removal depending on grafted molecule (Q = 73-95 mg/g) | [Saeed](https://doi.org/10.1016/j.micromeso.2019.109697%22%20%5Ct%20%22_blank%22%20%5Co%20%22Persistent%20link%20using%20digital%20object%20identifier) et al. (2019) |
| Commercial Vermiculite | 3-aminopropyltriethoxysilane | Alizarin Red S | pH = 2.0, [adsorbent] = 0.8 g/L, [adsorbate] =400 mg/L | Q = 18.2 mg/g (max. removal of 90%) | [Ali](https://doi.org/10.1016/j.eti.2020.101001). et al. (2020) |
| Natural clay [(Na,Ca)0.3(Al,Mg)2Si4O10(OH)2.nH2O)] from Cameroon | N1-(3-trimethoxysilylpropyl)diethylenetriamine | Reactive Blue 19 and Reactive Green 19 | [adsorbent] = 1.5 g/L, [adsorbate] = 300 mg/L, pH = 2.0. | Q = 200 mg/g for both pollutants | Teixeira et al. (2023) |
| Montmorillonite from industrial facility | N-methylimidazolium tetrafluoroborate or N-butylimidazolium tetrafluoroborate | Orange-II | [adsorbate] = 10 mg/L, pH 2.0. | Q = 2.29 mg/g (90% removal) | Yilmazoğlu et al. (2022) |
| Commercial bentonite | Silica-polyethylene glycol | Methylene Blue | [adsorbate] = 100 mg/L, pH 6.0, [adsorbent] = 2 g/L, 2 h | Q = 50 mg/g | Suchithra et al. (2012) |
| Kaolin from São Paulo, Brasil | 2-hydroxyethyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate | Methylene Blue | [adsorbate] = 50 mg/L, [adsorbent] = 1 g/L, 5 min | Q = 9 mg/g | Ferreira et al. (2017) |
| Commercial Montmorillonite | Sodium eicosenoate, cetyltrimethylammonium chloride and Fe3O4 | Methylene Blue | [adsorbate] = 50 mg/L, [adsorbent] = 0.4 g/L, pH = 7 | Q = 125 mg/g | Rahmani et al. (2019) |
| Commercial Montmorillonite | dodecyl sulfobetaine surfactant | Methylene Blue | [adsorbate] = 40 mg/L, [adsorbent] = 1 g/L, pH = 5 | Q = 250 mg/g | Fan et al. (2014) |
| Natural clay (kaolinite) from Shymkent deposit, KZ | Triethanolamine | Methylene Blue | [adsorbate] = 50 mg/L, pH 3.0, [adsorbent] = 0.25 g/L | 86% removal (equivalent to a Q = 159 mg/g\*) | Present study |

\*calculated according to [Saeed](https://doi.org/10.1016/j.micromeso.2019.109697%22%20%5Ct%20%22_blank%22%20%5Co%20%22Persistent%20link%20using%20digital%20object%20identifier) et. al. (2019)

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