Thermal Oxidation Synthesis of MoS_2/MoO_3 Composites for Cationic Dye Adsorption

Jéssica Cristina de Almeida [a,1], Thais Aparecida Rodrigues [a,1], Thais Mota de Souza [a], Douglas M.S.Del Duque [b], Tânia Regina Giraldi [c] and Vagner R. de Mendonça [a,b*]

[a] Federal University of São Carlos, Science, and Technology Center for Sustainability - UFSCar, 18052-780, Sorocaba, SP, Brazil.

[b] Federal Institute of Education, Science, and Technology of São Paulo – IFSP Campus Itapetininga,18202-000, Itapetininga, SP, Brazil.

[c] Federal University of Alfenas, Institute of Science and Technology 37715-400, Poços de Caldas - MG, Brazil.

[1] These authors contributed equally to this work.

[*]*Corresponding author e-mail*: vrm@ifsp.edu.br (Vagner R. de Mendonça)

Experimental section

Thermogravimetry TG and differential scanning calorimetry (DSC) analyses were performed at UNIFAL-MG with Jupiter® STA 449 F3 equipment in a temperature range of 20 to 800 °C under synthetic airflow 100 mL min^{-1}, applying a heating rate of 10 °C min^{-1}. The crystalline nature of the samples was analyzed at EMBRAPA Instrumentation by X-ray diffraction (XRD) using *Cu Kα* radiation (λ=1,5406Å) in the 2θ range from 10 to 70° employing a Rigaku Dmax 2500PC diffractometer. Raman spectra were obtained at EMBRAPA Instrumentation by an FT-Raman spectrometer (Bruker RAM II with a Ge detector) equipped with an Nd: YAG. It applied an excitation wavelength of 1064 nm, generating a power of 100 mW at a resolution of 2 cm^{-1}. Infrared (FTIR) spectra of the materials were obtained at EMBRAPA Instrumentation by a Spectrum 1000 spectrophotometer (Perkin Elmer) ranging from 400 to 4000 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}. The morphologies of the samples were verified by field emission scanning electron microscopy (FESEM) using a JSM 6701 F microscope (JEOL) operated at 5 kV with *Thermo Noran* for EDS. The specific surface area of the materials was obtained using nitrogen physisorption at 77 K (ASAP-2020, Micromeritics) and applying the data in the BET model. Before the analyses, the samples were degassed by heating at 70°C under a vacuum until reaching a pressure of less than 20 mmHg. The Zeta potential was measured at room temperature using a Zetasizer Nano-ZS analyzer (Malvern Instruments, UK).

Factorial Design

Factorial design is an analytical tool that allows rearranging the combinations of a given analytical event. It is intended to study the influence of more than one variable,

ensuring that most combinations will be investigated. The organizational basis for factorial design is represented by b^k, where k is the number of factors and b is the number of levels chosen. The simplest case of a factorial design is that the factor k is present at two levels, 2^k. In this case, the design can study k factors, each with two levels in a fully crossed manner, covering experimental points.

A commonly used technique in 2^k factorial design is to define a central point at which the average value of the levels of all variables is used. This is called Central Point Planning (CPP). This delimitation minimizes the risks of losing the non-linear relationship between the combinations of events and reducing the number of repetitions. For this work, the central point, 150 min at 300 ºC, was determined after observing the thermal events occurring in Thermogravimetry measurements. After that, other conditions were assigned by the geometric pattern in Figure S1, which shows the construction scheme of the predicted combinations for a factorial design with a central point. Additionally, Table S1 presents the applied levels for each variable studied.

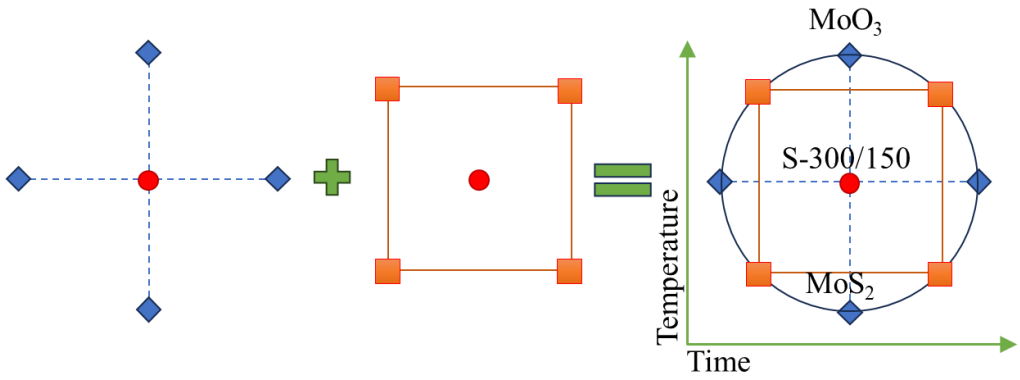

Figure S1. Illustration of the experimental runs of 2^k CPP design, including central points and combination runs.

Table S1: Applied levels for each variable studied in the 2^k factorial design with a central point.

Level	T (ºC)	t (min)
$-\sqrt{2}$	88	23
− 1	150	60
0	300	150
+1	450	240
$+\sqrt{2}$	512	277

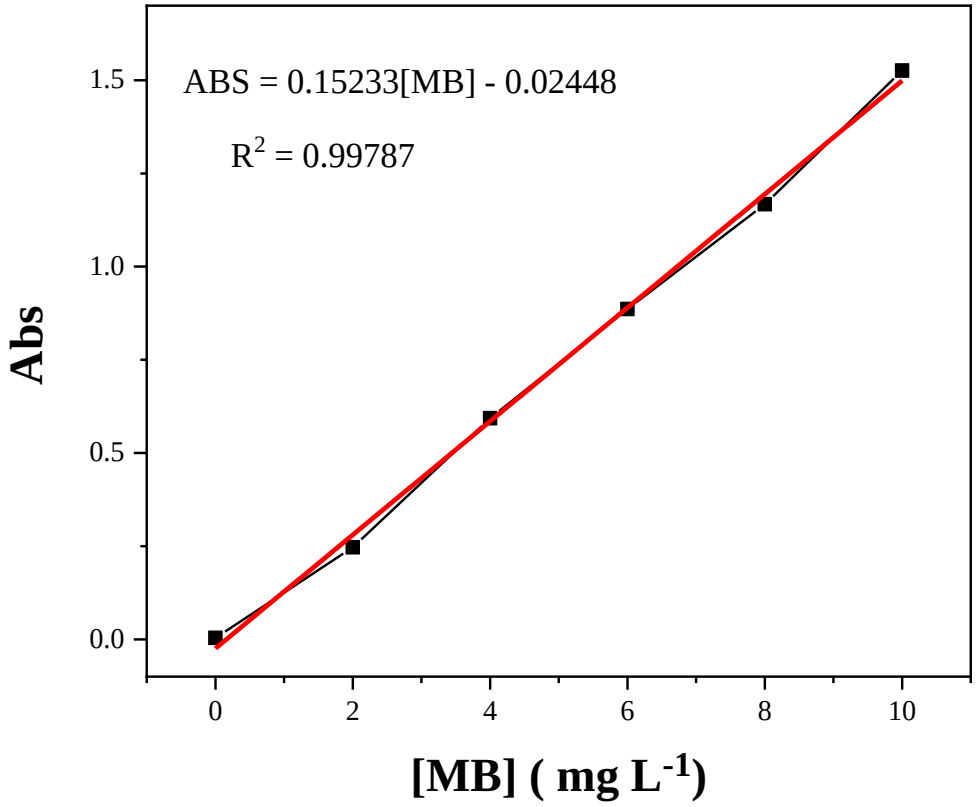

Figure S2. The analytical curve of methylene blue concentration.

Results and discussion

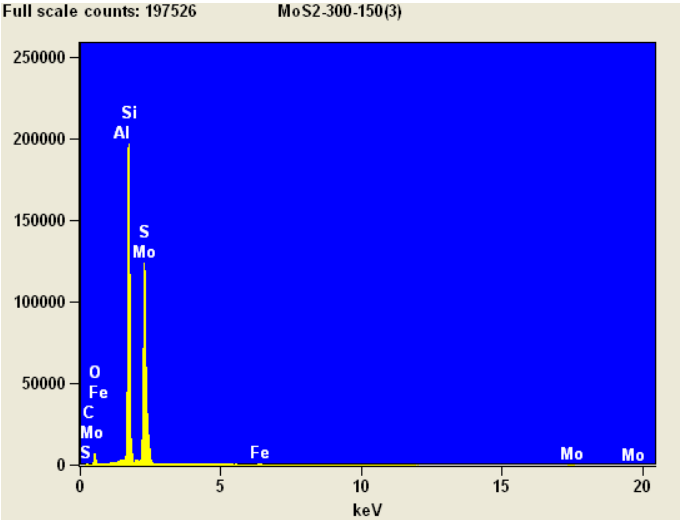

Figure S3. Elemental counts obtained by EDS technique.

Adsorption studies

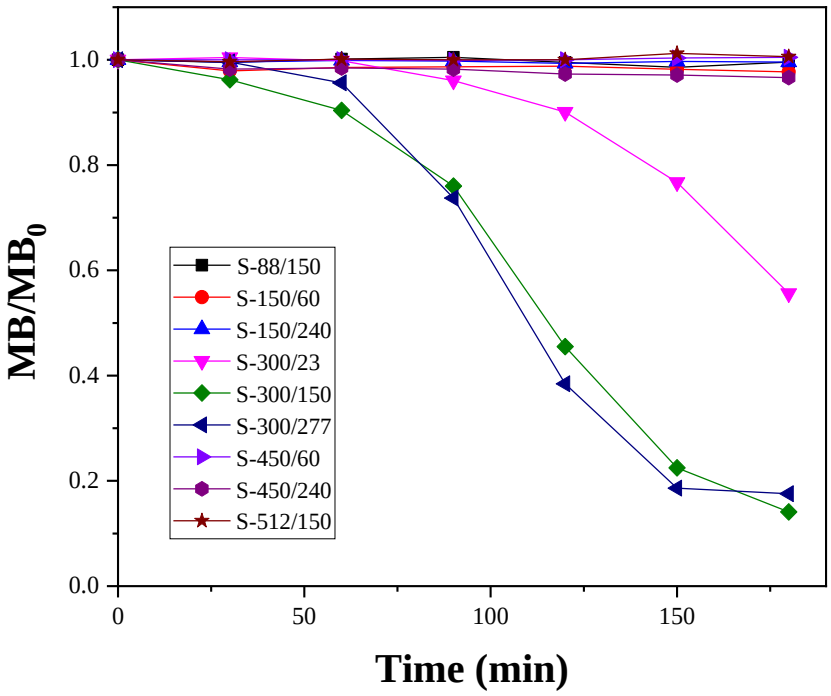

Figure S4. Adsorption kinetics of 6 mg of adsorbent in 40 mL of MB solution (10 mg L^{-1}) test without any equilibrium time in distilled water.

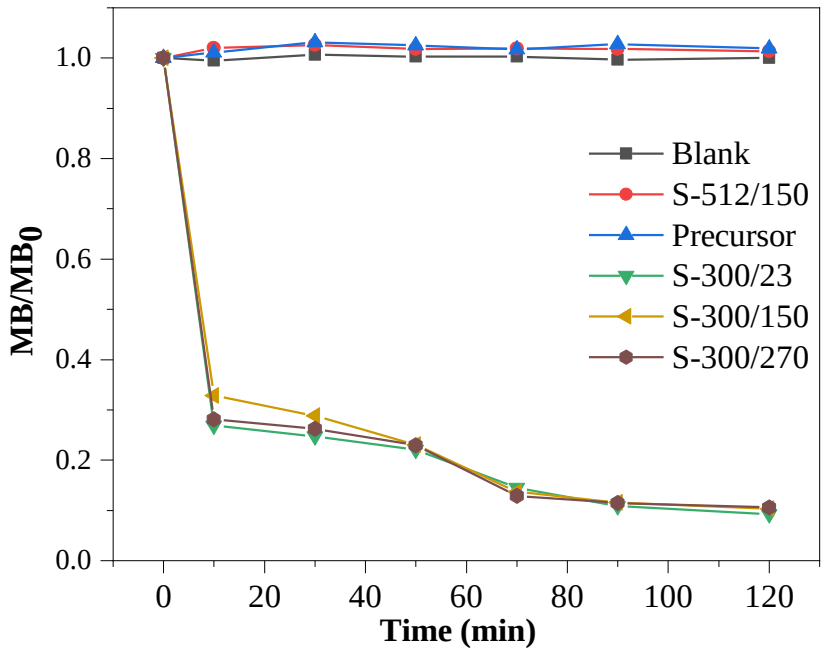

Figure S5. Adsorption kinetics of 6 mg of adsorbent in 40 mL of MB solution (10 mg L^{-1}) in distilled water after one hour of equilibrium.

The initial tests presented an inertia effect, as seen in Figure S4. This effect is overcome by the immersion of the adsorbent in distilled water for one hour before the beginning of the adsorption kinetic evaluation, as observed in Figure S5. This is because the equilibrium time in distilled water might assist in the diffusion of the dye molecules into the adsorbent particles.