**Bifunctional TiO2 – Cellulose Based Nanocomposites for Synergistic Adsorptive-Photocatalytic Removal of Methyl Orange: Response Modelling and Optimization**

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Table S1.Structure (chemical and 3D), general, optical, physicochemical features, and toxicity data of methyl orange (MO) [1-9].

|  |  |
| --- | --- |
| **Methyl Orange (MO) – Chemical and 3D Structures** | |
| undefinedA molecule model with blue and white balls  Description automatically generated | |
| **General Properties** | |
| Formula | C14H14N3NaO3S |
| Dye Category | Anionic, azo dye |
| Molar Mass | 327.33 g/mol |
| IUPAC Name | Sodium 4-[(4-(dimethylamino)phenyl]diazinyl]benzene-1-sulfonate |
| Other Names | Sodium 4-[(4-dimethylamino)phenylazo]benzenesulfonate; Orange III; C.I. Acid Orange 52; Gold Orange; Helianthin; Tropaeolin D |
| **Optical Properties** | |
| Color | Orange-yellow solid. Color in solution is pH – dependent (orange-red in acidic ‘pH ˂ 3.1’ and yellow in basic medium ‘pH > 4.4’) |
| Color Index (C.I.) | 13025 |
| λmax | 465 nm |
| **Physicochemical Features and Toxicity** | |
| Water Solubility | Soluble (˂ 1 mg/mL, at 64 °F) |
| pKa | 3.45 [5], 3.4 [7], 1.97 (pKa1) and 6.16 (pKa2) [8] |
| Melting Point | >300 °C |
| Density | 1.28 g/cm3 |
| Toxicity | Carcinogenic, mutagenic, causes GIT disorders, skin allergies |

**Table S2.** Setup of the BB design for MO removal using 3%TiO2@MP500

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Run Order** | **Block** | **Independent variables** | | | | | **Dependent variable** | |
| **pH** | **Dose** | **RT** | **%TiO2** | **[MO]** | **%RExp** | **%RPred** |
| 01 | 1 | 10 | 65 | 150 | 2 | 35 | 2.75 | 3.73 |
| 02 | 1 | 6 | 65 | 80 | 1 | 60 | 5.52 | 5.24 |
| 03 | 1 | 6 | 120 | 80 | 2 | 10 | 60.99 | 61.12 |
| 04 | 1 | 2 | 10 | 80 | 2 | 35 | 10.41 | 9.71 |
| 05 | 1 | 6 | 10 | 80 | 2 | 10 | 31.36 | 34.45 |
| 06 | 1 | 6 | 10 | 80 | 2 | 60 | 8.14 | 10.73 |
| 07 | 1 | 6 | 65 | 80 | 2 | 35 | 75.56 | 81.77 |
| 08 | 1 | 2 | 65 | 150 | 2 | 35 | 14.62 | 18.79 |
| 09 | 1 | 10 | 10 | 80 | 2 | 35 | 3.98 | 3.16 |
| 10 | 1 | 6 | 65 | 80 | 2 | 35 | 90.92 | 81.77 |
| 11 | 1 | 6 | 65 | 80 | 3 | 10 | 21.82 | 26.85 |
| 12 | 1 | 6 | 65 | 80 | 1 | 10 | 18.64 | 17.80 |
| 13 | 1 | 6 | 65 | 80 | 3 | 60 | 32.82 | 40.12 |
| 14 | 1 | 2 | 120 | 80 | 2 | 35 | 45.34 | 46.59 |
| 15 | 1 | 6 | 120 | 80 | 2 | 60 | 76.61 | 89.28 |
| 16 | 1 | 6 | 65 | 150 | 3 | 35 | 26.34 | 22.66 |
| 17 | 1 | 10 | 120 | 80 | 2 | 35 | 13.17 | 11.75 |
| 18 | 1 | 10 | 65 | 10 | 2 | 35 | 6.56 | 7.43 |
| 19 | 1 | 6 | 65 | 10 | 1 | 35 | 9.37 | 9.14 |
| 20 | 1 | 6 | 65 | 80 | 2 | 35 | 92.94 | 81.77 |
| 21 | 1 | 6 | 65 | 10 | 3 | 35 | 24.03 | 23.20 |
| 22 | 1 | 2 | 65 | 10 | 2 | 35 | 17.12 | 18.79 |
| 23 | 1 | 6 | 65 | 150 | 1 | 35 | 5.55 | 4.76 |
| 24 | 2 | 6 | 65 | 80 | 2 | 35 | 94.10 | 81.77 |
| 25 | 2 | 2 | 65 | 80 | 2 | 60 | 45.98 | 34.99 |
| 26 | 2 | 6 | 65 | 150 | 2 | 10 | 24.75 | 21.51 |
| 27 | 2 | 6 | 120 | 80 | 1 | 35 | 11.68 | 12.36 |
| 28 | 2 | 6 | 10 | 150 | 2 | 35 | 16.02 | 16.86 |
| 29 | 2 | 6 | 120 | 150 | 2 | 35 | 28.32 | 31.41 |
| 30 | 2 | 6 | 65 | 80 | 2 | 35 | 65.40 | 81.77 |
| 31 | 2 | 6 | 65 | 10 | 2 | 10 | 67.92 | 72.95 |
| 32 | 2 | 10 | 65 | 80 | 2 | 10 | 14.98 | 15.29 |
| 33 | 2 | 10 | 65 | 80 | 1 | 35 | 0.42 | 0.41 |
| 34 | 2 | 6 | 10 | 80 | 1 | 35 | 4.21 | 4.76 |
| 35 | 2 | 2 | 65 | 80 | 2 | 10 | 25.91 | 20.83 |
| 36 | 2 | 6 | 10 | 10 | 2 | 35 | 12.14 | 10.60 |
| 37 | 2 | 2 | 65 | 80 | 3 | 35 | 6.34 | 7.02 |
| 38 | 2 | 6 | 65 | 80 | 2 | 35 | 75.80 | 81.77 |
| 39 | 2 | 2 | 65 | 80 | 1 | 35 | 12.48 | 13.96 |
| 40 | 2 | 10 | 65 | 80 | 2 | 60 | 4.12 | 3.92 |
| 41 | 2 | 6 | 65 | 10 | 2 | 60 | 20.69 | 20.25 |
| 42 | 2 | 6 | 120 | 10 | 2 | 35 | 92.65 | 86.59 |
| 43 | 2 | 10 | 65 | 80 | 3 | 35 | 14.29 | 13.85 |
| 44 | 2 | 6 | 120 | 80 | 3 | 35 | 76.47 | 65.11 |
| 45 | 2 | 6 | 10 | 80 | 3 | 35 | 11.48 | 10.14 |
| 46 | 2 | 6 | 65 | 150 | 2 | 60 | 48.03 | 38.21 |

Table S3. Surface area analysis data.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameters** | **MP500** | **1%TiO2@MP500** | **2%TiO2@MP500** | **3%TiO2@MP500** |
| Multi-point BET SSA, (m2/g) | 2.19 | 54.69 | 111.87 | 184.61 |
| Total Pore Volume (cm3/g) | 0.0178 | 0.1004 | 0.1907 | 0.1881 |
| Average Pore Radius (Å) | 162.7 | 36.7 | 34.1 | 20.4 |

**TEXT S1:**

***Characterization and Measurements***

Morphologies and elemental composition were explored with the scanning electron microscope (SEM, Quanta 200, USA), and energy-dispersive X-ray spectrometric (EDS) analysis. Catalyst microstructure was investigated using transmission electron microscope (TEM, FEI Tecnai TF20, 200 kV, USA). Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, USA) and Raman spectroscopy (ThermoFisher Scientific, USA) were used for structure elucidation and doping with TiO2. Brunauer-Emmett-Teller, (BET, Micrometrics ASAP2020) was used to collect the relevant data on the adsorbent-photocatalyst surface attributes (surface area, pore volume, and radius). Thermal stability of the prepared samples up to 900 °C under a nitrogen atmosphere was evaluated using a thermogravimetric analyzer (TGA, PerkinElmer-TGA400, USA), using a heating rate of 10 °C/min. The crystallinity of the MP500 and TiO2@MP500 nanocomposites was examined using X-ray diffraction (XRD) analysis (PANalytical Co., the Netherlands).

For all pH measurements, a pH meter (Jenway 3305, UK) was used. Suspensions were filtered using a 0.45 µm nylon syringe filter. The concentration of MO dye before and after the adsorption was detected using a UV-Vis spectrophotometer (Agilent, USA). Photocatalysis experiments were conducted on a 4 W UV lamp operated using two wavelengths of 365 and 254 nm (Spectroline® CM UV, Sigma-Aldrich, USA).

**TEXT S2:**

***Comparison the Adsorption Efficiency of MP500 and* 3% TiO2@MP500**

Comparison of the adsorption efficiency towards MO using MP500 and 3% TiO2@MP500 was conducted under the following conditions: pH = 6, a dose of 120 mg, an [MO] of 35 ppm, and a reaction time of 80 min. The obtained solutions were filtered, and the absorbance was measured at a λmax of 462 nm. The %R for the two adsorbents was found to be 9.37% and 76.47% for MP500 and 3%TiO2@MP500, respectively. The obtained data confirm that loading TiO2 onto MP500 significantly increased the adsorption capability of the prepared nanosorbent.

Figure S1. **(a)** The obtained Raman spectra for the as-prepared samples, including MP500, 1%TiO2@MP500, 2%TiO2@MP500, and 3%TiO2@MP500, and **(b)** amplified spectrum of the same samples in the range between 100 and 1000 cm−1.

****Figure S2. FTIR spectra for MP500, 1% TiO2@MP500, 2% TiO2@MP500, and 3% TiO2@MP500 in the range from 3400 to 2500 cm−1.

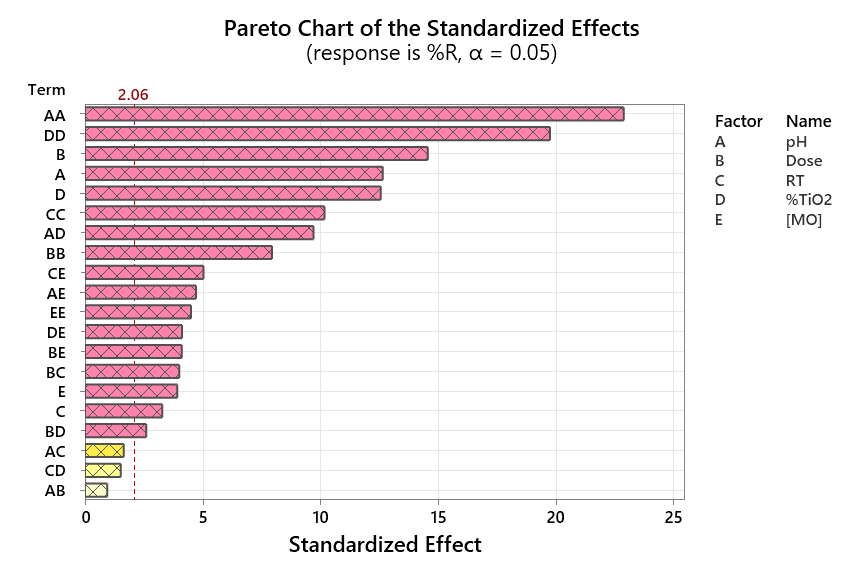


Figure S3.Quality tool - Pareto chart showing the cascade of variable significance.



Figure S4.Quality tool – Normal plot of effects.



Figure S5.Point of zero charge for the as-prepared samples.

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