**Terbium metal-organic frameworks for the efficient removal of tartrazine food dye from aquatic systems: Thermodynamics, kinetics, isotherm, and Box-Behnken Design optimization**

**1. Material and methods**

**1.1. Materials**

Table S1. Chemical name, formula, and company.

|  |  |
| --- | --- |
| **Chemical name** | **Company** |
| Terbium chloride hexahydrate | Sigma-Aldrich, Germany |
| 2-methyl imidazole | Sigma-Aldrich, Germany |
| Sodium hydroxide | LOBA CHEMIE PVT.LTD, India |
| Hydrochloric acid 37% | LOBA CHEMIE PVT.LTD, India |
| Ethanol | LOBA CHEMIE PVT.LTD, India |
| Methanol | LOBA CHEMIE PVT.LTD, India |
| Tartrazine | Sigma Aldrich (St. Louis, USA). |

**1.2. Instruments**

Table S2. Instruments and equipment's.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Test name** | **Abbrevation** | **Instrument name** | **Company** | **Illustration** |
| Fourier transformer infrared | FT-IR | A Nicolet IS10 Fourier transform infrared (FTIR) spectrometer | Thermo Fisher Scientific, Waltham, MA, USA | equipped with an attenuated total reflectance accessory and which ran in the 4000-400 cm–1 range was used to gather FTIR spectra |
| Powered X-ray diffraction | PXRD | Siemens diffractometer (model D500, Germany) | Germany | patterns were captured from powder samples through the use of a Siemens diffractometer (model D500, Germany) that was fitted with a Cu-K radiation source (wavelength 1.54 Angstroms (Å)) operating at 30 kV and 20 mA. |
| Scanning Electron Microscope | SEM | (JSM-6510LV, JEOL Ltd., Tokyo, Japan) | JEOL Ltd., Tokyo, Japan | The morphology of the investigated sorbents was analyzed with the use of a scanning electron microscope |
| X-ray photoelectron spectroscopy | XPS | K-ALPHA (Themo Fisher Scientific, USA) | Themo Fisher Scientific, USA | Used for determination the elemental analysis for the compound |
| Braunnar Emmet Teller | BET | Quantachrome Instruments, Anton Paar Quanta Tec, Inc., Boynton Beach, FL, USA | Quanta Tec, Inc., Boynton Beach, FL, USA | was utilised for surface and pore analysis (Brunauer Emmett-Teller (BET) surface area, porous volume, and pore size), and NovaWin Software (v11.0) was used for data interpretation.  The BET surface area of material adsorbents was obtained by the application of nitrogen adsorption-desorption isotherms at 77K through the use of a specific analyser (Quadrasorb–EVO, Quantachrome, USA). |
| UV-visible spectrophotometer | UV spectrophotometer | HACH LANGE DR5000 | HACH LANGE Germany | Measuring the concentration of the adsorbate soulution via using bear lambert law |
| Energy Dispersive X-ray | EDX | Leo1430VP microscope | Carl Zeiss AG, Jena, Germany | Elemntal analysis of the material |
| Transmission electron microscopy | TEM | TEM, FEI Teanci G2 F20, USA | FEI Teanci G2 F20, USA | Determination the morphology of the material and size |
| pH meter | pH | HANNA (model 211) | USA | Measuring the acidity or basicity of the solution |
| Sonication | Ultrasonic | Elmasonic P300H ultrasonic bath, continuous mode, power 380 W | Elma Schmidbauer GmbH, Singen, Germany | Sonication of the material as well as used ton disperse material on the solution as it decrease the particle size of the material |

Table S3. True variables, codes, and their BBD levels.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Code** | **Variables** | **-1** | **0** | **+1** |
| **A** | pH | 2 | 7 | 12 |
| **B** | Dose (g) | 0.02 | 0.135 | 0.25 |
| **C** | Time (min.) | 5 | 55.5 | 100 |

Table S4. Equations used in this work to fit the data of adsorption experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Serial** | **Equation** | **Namae** | **Description** | **Ref.** |
| 1 | qe **=** | Adsorption capacity | qe (mmol.g−1) Adsorption capacity, C0 initial concentration Ce equilibrium concentration | Eq. S1 |
| 2 | % R = | Removal efficiency | %R Removal efficiency, C0 initial concentration Ce equilibrium concentration | Eq. S2 |
| 1 |  | Langmuir | qe (mmol.g−1) Adsorption capacity, Ce equilibrium concentration, qm (mmol.g−1) is the monolayer saturation capacity constant and KL  (L.mmol−1) is the Langmuir constant associated with the free adsorption energy. | [1] |
| 2 |  | Freundlich | KF Freundlich isotherm constants (mmol.g−1), and 1/n are indicative of adsorption capacity and adsorption intensity, respectively. | [2] |
| 3 |  | Dubinin–Radushkevich | Where D-R constant β (mol2J−2) is associated with average adsorption energy per mole of the adsorbate, and ε denotes Polanyi sorption potential given by RT ln (1+1/Ce) | [3] |
| 4 | ln() | Temkin | Where bT (kJ.mol−1) is Temkin constant associated with sorption enthalpy, AT(L.g−1) is the Temkin equilibrium binding constant, R (kJ.mol−1K−1) is the gas constant and T is absolute temperature (K) | [4] |
| 5 |  | Pseudo-First-order kinetic | K1 is the rate constant for Pseudo second order constant for the adsorption processes (min−1) | [5] |
| 6 |  | Pseudo-Second-order kinetic | Rate constant for Pseudo first order constant for the adsorption processes (g.mg−1min−1) | [6] |
| 7 |  | Intraparticle diffusion | Ki were the rate constants for intraparticle diffusion (mg.g−1min1/2) | [7] |
| 8 |  | Elovich | The constants α chemical adsorption rate (mg.g−1min−1), and β Coefficient in relation with extension of covered surface | [8] |
| 9 | ∆Go = ∆Ho − T∆So | Gibbs free energy | ΔG°: Gibbs free energy change; Kd: equilibrium constant; R: gas constant; T: temperature. | [9] |
| 10 |  | Van’t Hoff | ΔS°: entropy change; ΔH°: enthalpy change. | [10] |

Table S5. List of abbreviation.

|  |  |
| --- | --- |
| Symbol | Definition |
| qe | the adsorbed amount of dye at equilibrium concentration (mmol.g−1) |
| qmL | the maximum sorption capacity (corresponding to the saturation of the monolayer, (mmol.g−1) |
| KL | Langmuir binding constant which is related to the energy of sorption (L.mmol−1) |
| Ce | is the equilibrium concentration of dyes in solution |
| KF | Freundlich constants related to the sorption capacity (mmol.g−1) (L.mmol−1)1/n |
| n | intensity |
| KDR | constant related to the sorption energy (J2mol−2) |
| qDR | theoretical saturation capacity (mmolg−1) |
| ε | Polanyi potential (J2mol−2) |
| R | Gas constant (8.314 J.mol−1K−1) |
| T | temperature where the adsorption occurs |
| AT | Temkin isotherm constant |
| bT | Temkin constant in relation to heat of adsorption (J.mol−1) |
| qt | is the amount of dye adsorbed (mmol.g−1) |
| K1 | Rate constant for Pseudo first order constant for the adsorption processes (min−1) |
| q2 | Maximum adsorption capacity for pseudo second order |
| K2 | Rate constant for Pseudo first order constant for the adsorption processes (g.mg−1min−1) |
| α | Chemical adsorption rate (mg.g−1min−1) |
| β | Coefficient in relation with extension of covered surface |
| ΔGo | Free Gibb’s energy |
| ΔHo | Enthalpy |
| ΔSo | Entropy |
| Kc | distribution coefficient |
| Ceq | Concentration at equilibrium (mg/L) |

Table S6. The parameter of the adsorption isotherm for TZ dye on Tb-MOF (Ci: 2.76x10-4 to 2.36x10−3 mmol, time: 100 min., dose: 0.02 to 0.25 g, volume: 25 mL, agitation speed 180 rpm, and temp.: 25 oC).

|  |  |  |
| --- | --- | --- |
| Isotherm | Parameters | Value |
| Langmuir | qm exp (mmol/g) | 1.53 |
| qm (mmol/g) | 1.55 |
| KL (L/mmol) | 119788.33 |
| RL | 0.04 |
| Reduced Chi-Sqr | 0.01763 |
| Residual Sum of Squares | 0.28212 |
| R-Square (COD) | 0.92982 |
| R2 | 0.92543 |
| Freundlich | 1/n | 0.0565 |
| KF (mmol/g)(L/mmol)1/n | 2.2 |
| Reduced Chi-Sqr | 0.00263 |
| Residual Sum of Squares | 2.62807 |
| R-Square (COD) | 0.73042 |
| R2 | 0.73015 |
| Dubinin–Radushkevich | QDR | 1.8 |
| KDR(J2/mol2) | 4.9E-10 |
| Ea (kJ/mol) | 23.78 |
| Reduced Chi-Sqr | 4.31996E-5 |
| Residual Sum of Squares | 0.04311 |
| R-Square (COD) | 0.99426 |
| R2 | 0.99426 |
| Temkin | bT (kJ/mol) | 1.49E-12 |
| AT (L/mg) | 33382.3 |
| Reduced Chi-Sqr | 997 |
| Residual Sum of Squares | 1.22783E-5 |
| R-Square (COD) | 0.01224 |
| R2 | 0.99766 |
| Khan | qm(mmol.g−1) | 1.23 |
| k | 0.813 |
| n | 319749.5 |
| Reduced Chi-Sqr | 0.00269 |
| Residual Sum of Squares | 2.68345 |
| R-Square (COD) | 0.48691 |
| R2 | 0.4864 |
| Sips | qm (mmol.g-1) | 1.53 |
| ks | 319749.51 |
| sp | 0.94 |
| Reduced Chi-Sqr | 3.88601E-32 |
| Residual Sum of Squares | 3.87435E-29 |
| R-Square (COD) | 0.992 |
| R2 | 0.995 |

Table S7. Models of TZ dye adsorption using kinetic parameters on Tb-MOF (Ci: 1.556x10−3 mmol, time: 5 to 100 min., dose: 0.02 g, volume: 25 mL, agitation speed 180 rpm, and temp.: 25 oC).

|  |  |  |
| --- | --- | --- |
| Model | Value of parameters | |
| Pseudo-First-order kinetic | *K1*(min−1) | 0.025 |
| qe (mmol/g) | 1.56 |
| Reduced Chi-Sqr | 1.92085E-4 |
| Residual Sum of Squares | 0.1917 |
| R-Square (COD) | 0.99874 |
| R2 | 0.99874 |
| Pseudo-second-order kinetic | *K2*(g.mg−1min−1) | 0.0094 |
| qe (mmol/g) | 1.57 |
| qe (exp) (mmol/g) | 1.53 |
| Reduced Chi-Sqr | 0.004 |
| Residual Sum of Squares | 0.07593 |
| R-Square (COD) | 0.97754 |
| R2 | 0.97636 |
| Intraparticle diffusion | Ki (mgg−1min1/2) | 0.15 |
| X (mg/g) | 0.98 |
| Reduced Chi-Sqr | 0.00262 |
| Residual Sum of Squares | 0.04979 |
| R-Square (COD) | 0.98721 |
| R2 | 0.98654 |
| Elovich | β (g/mg) | 0.47 |
| α (mgg−1.min−1) | 0.46 |
| Reduced Chi-Sqr | 0.00293 |
| Residual Sum of Squares | 0.05572 |
| R-Square (COD) | 0.98569 |
| R2 | 0.98494 |

Table S8. Thermodynamic parameters and their correlation coefficients for the adsorption.

|  |  |  |
| --- | --- | --- |
| Model | Equation | Illustration |
| Free Gibb’s energy (12) | ∆Go = ∆Ho − T∆So |  |
| Van't Hoff equation (13) |  | The values of ΔHO and ΔSO were calculated from the plots of ln Kc *vs.* 1/T |

**Table S9.** This is the thermodynamic parameter that controls TZ on Tb-MOF.

(Ci: 1.556x10−3 mmol, time: 5 to 100 min., dose: 0.02 g, volume: 25 mL, agitation speed 180 rpm, and temp.: 20 to 50 oC)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Adsorbate** | **T (K)** | **∆Ho**  **(kJ.mol−1)** | **∆So**  **(J.mol−1K−1)** | **-∆Go**  **(kJ.mol−1)** |
| **TZ** | 293 | 108.9 | 387.70 | 2.03 |
| 298 | 3.9 |
| 303 | 5.8 |
| 308 | 7.7 |
| 313 | 9.6 |
| 318 | 11.49 |

Table S10. Comparison of related adsorbents for absorption of TZ onto Tb-MOF [11].

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Adsorbent | pH | T | Q max | Reference |
| Bottom ash | 2 | 50 | 12.6 | [12] |
| Deoiled soya | 2 | 50 | 24.6 | [13] |
| Hean feather | 2 | 50 | 74.82 | [14] |
| Activated carbon | 2 | 50 | 90.9 | [15] |
| Polyaniline nanolayer composite | 2 | 25 | 2.74 | [16] |
| Cross-linked chitosan | 2.5 | 47 | 294.1 | [17] |
| Cht-PANI | 7.2 | 25 | 584 | [18] |
| La/Sn MOF | 4 | 25 | 694.72 | [19] |
| Tb-MOF | 4 | 25 | 817.63 | This search |

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