***Supplementary Information***

**Fabrication of carboxymethyl functionalized β-cyclodextrin-modified graphene oxide for efficient removal of methylene blue**

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## 2. Experimental section

**Characterization**

The X-ray photoelectron spectroscopy (XPS) were recorded on an XSAM800 (Kratos Company, UK). Prior to data analysis, charging effects were corrected on the basis of the binding energy of C 1s peak to 284.6 eV on each sample. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a Nicolet 6700 (Thermo Fisher Scientific, USA) FT-IR spectrometer (4000 cm-1 to 400 cm-1, 64 scans). Thermal gravimetric analysis (TGA) was performed on a TGA8000 analyzer (TG209F1 Iris; Netzsch, Selb, Germany) at a heating rate of 10 °C/min from 30 °C to 800 °C under nitrogen atmosphere. Raman spectroscopy was recorded from 4000cm-1 to 500 cm-1 on an inVia Raman microscope (Renishaw, UK) operated at a wavelength of 532 nm. An X’Pert PRO diffractometer (PANalytical, Holland) with Cu Kα1 radiation (λ=1.54056 Å, generator setting: 40 kV and 40 mA) was applied for the acquisition of powder X-ray diffraction (PXRD) patterns at 2θ between 5° and 50° (step size 0.01313°). Atomic force microscopy (AFM) data were collected by the Multi-Mode Nanoscope V controller (Bruker, USA) in tapping mode. The samples were dispersed in water and dropped onto the mica flakes, and dried at 40 ℃ for 12h. Morphology was observed using a scanning electron microscopy (SEM; JSM-7500F, JEOL, Japan).

## 3. Results and discussion

**Adsorption kinetics**

On the basis of solid capacity, the pseudo-first-order model describes the removal mechanism as adsorption through boundary diffusion. This model considers that adsorption is a first-order process partially related to the concentration of free sites, whereas the dye concentration varies proportionally with time. The pseudo-second-order model is built upon the assumption that adsorption follows a pseudo-second-order rate kinetic mechanism where the site occupation rate is proportional to the square of unoccupied site amounts. The expressions of pseudo-first-order (Eq. [3]) and pseudo-second-order (Eq. [4]) models in linear forms used in this study are as follows:

(1)

(2)

where *q*e and *q*t are the uptake capacity (mg g-1) at equilibrium and at time *t*, respectively; *k*1 (min-1) is the pseudo-first-order rate constant; *k*2 (g [mg·min]-1) is the pseudo-second-order rate constant.

**Adsorption isotherms**

For the Langmuir model, adsorption occurs at specific homogeneous binding sites with identical energy and affinity on the adsorbent surface, forming a monolayer adsorption. In the Freundlich model, the adsorbate is adsorbed into multilayer films on a non-uniform surface. The adsorption capacity increases infinitely with the increase in concentration. An important feature of Langmuir model is the separation factor (RL) (Eq. (3)), which is a dimensionless constant, proposed by Webbr and Chakkravorti. The adsorption process can be predicted by RL value: RL ＞ 1 (unfavorable), RL = 1 (linear), 0 ＜ RL ＜ 1 (favorable), and RL = 0 (irreversible).

(3)



**Fig. S1** Adsorption kinetics linear plots fitted with (a) pseudo-first-order and (b) pseudo second-order model for the adsorption of MB onto CM-β-CD-GO (100 mg L-1 MB, 0.5 mg mL-1 adsorbent dose, pH = 7.0).



**Fig. S2** Langmuir and Freundlich adsorption isotherm adsorption of MB onto CM-β-CD-GO (0.5 mg mL-1 adsorbent dose, pH = 7.0, t=3 h).



**Fig. S3** TGA and DTG curves of β-CD-GO (a) and CM-β-CD-GO (b).



**Fig. S4** SEM images of (a)GO 8000×, (b)CM-β-CD-GO 8000×, (c)GO 5000×, and (d)CM-β-CD-GO 3500×.

**Table S1** Comparative study of adsorption of dyes by several grapheme sorbents found in the literature.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Adsorbent | Adsorbate | Kinetic a | Isotherm | qm(mg g−1) | ΔH°(kJ mol−1) | pH | Reg. cycles | Reference |
| GO | Methylene Blue | PSO | Langmuir | 3373.59 | 0.28 | 11.5 | N/A | (Peng et al., 2016) |
| GO | Reactive Black5 | PSO | Langmuir-  Freundlich | 221.00 | 10.53 | 3.0 | N/A | (Travlou et al., 2013) |
| nGO-(NH)R | Reactive black 5 | PSO | Langmuir | 335.86 | 92.83 | 6.8 | 10 | (Fraga et al., 2020) |
| Fe3O4-GO | Methylene Blue | PSO | Langmuir | 131.10 | 38.66 | 9.0-10.0 | 8 | (Ganesan et al., 2018) |
| 3D reduced GO | Acid Red 1 | PSO | Langmuir | 277.01 | N/A | 7.0 | N/A | (Kim et al., 2015) |
| Agro-waste biomass GO | Crystal Violet | PSO | Langmuir | 24.93 | 494.13 | 8.1 | 8 | (Goswami et al., 2017) |
| Bi2O3-GO | Rhodamine B | IPD | Temkin | 387.44 | 62.94 | 4.0 | 7 | (Das et al., 2018) |
| β-cyclodextrin-Graphene | Methyl Orange | PSO | Langmuir | 328.20 | -22.14 | N/A | 6 | (Tan and Hu, 2017) |
| CM-β-CD-GO | Methylene Blue | PSO | Langmuir | 245.70 | 18.10 | 7 | 5 | This work |

a For kinetic models, PFO means pseudo-first-order; PSO, pseudo-second-order; and IPD, Intraparticle diffusion; N/A means “not available”.

**Table S2** The separation factor (RL) for Langmuir model of MB on CM-β-CD-GO.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *C*0 (mg/L) | 20 | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 180 | 200 |
| 25℃ | 0.0208 | 0.0105 | 0.0070 | 0.0053 | 0.0042 | 0.0035 | 0.0030 | 0.0027 | 0.0024 | 0.0021 |
| 35℃ | 0.0145 | 0.0073 | 0.0049 | 0.0037 | 0.0029 | 0.0024 | 0.0021 | 0.0018 | 0.0016 | 0.0015 |
| 45℃ | 0.0133 | 0.0067 | 0.0045 | 0.0034 | 0.0027 | 0.0022 | 0.0019 | 0.0017 | 0.0015 | 0.0013 |

**Table S3** Curve fitting results of XPS C1s, O1s and N1s.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Samples | Elements | Peaks | BE | Atom(%) |
| GO | C 1s | C-C/C=C | 284.60 | 39.72 |
|  |  | C-O | 286.56 | 48.65 |
|  |  | C=O | 287.13 | 2.12 |
|  |  | O-C=O | 288.16 | 9.54 |
| β-CD-GO | C 1s | C-C/C=C | 284.60 | 36.69 |
|  |  | C-O | 285.69 | 50.87 |
|  |  | O-C=O/N-C=O | 288.40 | 12.44 |
| CM-β-CD-GO | C 1s | C-C/C=C | 284.60 | 37.84 |
|  |  | C-O | 285.60 | 49.21 |
|  |  | O-C=O/N-C=O | 288.40 | 12.95 |
| CM-β-CD-GO-MB | C 1s | C-C/C=C | 284.60 | 32.49 |
|  |  | C-O | 285.67 | 55.87 |
|  |  | O-C=O/N-C=O | 288.46 | 11.65 |
| GO | O 1s | C=O/O-C=O | 531.01 | 9.44 |
|  |  | C-O/C-OH | 532.24 | 90.56 |
| β-CD-GO | O 1s | C=O/O-C=O | 530.66 | 39.56 |
|  |  | C-O/C-OH | 532.25 | 60.44 |
| CM-β-CD-GO | O 1s | C=O/O-C=O | 530.80 | 42.61 |
|  |  | C-O/C-OH | 532.34 | 57.39 |
| CM-β-CD-GO- MB | O 1s | C=O/O-C=O | 530.96 | 30.39 |
|  |  | C-O/C-OH | 532.42 | 69.61 |
| CM-β-CD-GO | N 1s | amide | 399.19 | 100.00 |
| CM-β-CD-GO- MB | N 1s | amide | 399.26 | 77.16 |
|  |  | amine | 399.90 | 20.29 |
|  |  | N+ | 401.64 | 2.55 |

**Table S4** Elemental composition and atomic ratios of GO, β-CD-GO and CM-β-CD-GO determined by XPS.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Elemental content | | | |
|  | C wt% | O wt% | N wt% | C/O |
| GO | 67.54 | 32.46 | - | 2.08 |
| β-CD-GO | 70.26 | 15.98 | 13.75 | 4.40 |
| CM-β-CD-GO | 72.98 | 15.15 | 11.87 | 4.82 |

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