Supporting Information Available:

Adsorption behavior and mechanism of sulfonamide antibiotics in aqueous solution on a novel MIL-101(Cr)@GO composite

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1. Synthesis of MIL-101(Cr)

The MIL-101(Cr) was synthesized by hydrothermal methods according to a literature procedure reported by Férey \(^1\) with a slight modification. To acquire larger output, the 10 times amount of each reaction reagent was selected in a Teflon-lined bomb, respectively (4 g \(\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\), 1.66 g terephthalic acid, 425 \(\mu\text{L}\) hydrofluoric acid and 48 mL ultrapure water), subsequently magnetic stirring for 15 min and ultrasonic dispersion for 15 min so as to these reagents can be mixed evenly and sufficiently. Then, the Teflon-lined bomb was sealed, placed in an oven, and kept at 210°C for 8 h. The resulting crystallized green powder was further purified by washing with DMF and hot ethanol, collected via centrifugation at 4000 rpm for 10 min after ultrasonic dispersion for 15 min. The procedure was repeated three times to remove the unreacted terephthalic acid from MIL-101(Cr). In the end, the MIL-101(Cr) was evacuated, activated under reduced pressure at 150°C for 12 h, and preserved under reduced pressure.
2. Synthesis of MIL-100(Fe)

The MIL-100(Fe) was synthesized with the same procedures referred by Yoon et al.\textsuperscript{2} Trimesic acid (687.5 mg), iron powder (299.5 mg), hydrofluoric acid (200 \( \mu \text{L} \)) and concentrated nitric acid (190 \( \mu \text{L} \)) were mixed with ultrapure water (20 mL) in a Teflon-lined bomb. The bomb was then sealed, placed in an oven and heated at 150°C for 12 h. The light orange crystallized powder was obtained by filtration and washing with ultrapure water and further purified by a two-step procedure using hot water and ethanol. To remove the residual unreacted substances, the powder was immersed into water at 80°C for 5 h and subsequently hot ethanol at 60°C for 3 h till no colored impurities in the mother liquor solution were detected. The highly purified MIL-100(Fe) was evacuated in vacuum at 150°C for 12 h to form activated MIL-100(Fe).
3. Characterization of MIL-101(Cr)

Figure S1. (A) Comparison of the XRD pattern of the prepared MIL-101 with the simulated one obtained by importing the crystal structure data from Ref. 3 into the software of Mercury 1.4; (B) TGA curve of the synthesized MIL-101(Cr); (C) SEM image of the synthesized MIL-101(Cr); (D) \( \text{N}_2 \) adsorption-desorption isotherms and the pore size distribution of MIL-101(Cr).

The experimental XRD pattern of the synthesized MIL-101(Cr) was in good agreement with the simulated one, confirming the accuracy of the prepared MIL-101(Cr). The TGA curve revealed that the MIL-101(Cr) was stable at temperatures below 390°C and showed a weight-loss step at 390°C due to collapse of the frameworks. The SEM images clearly showed that octahedral crystals were obtained. The nitrogen adsorption experiment demonstrated that the prepared MIL-101(Cr) gave a BET surface area of 3311.88 m\(^2\) g\(^{-1}\) with a pore volume of 1.5732 cm\(^3\) g\(^{-1}\).
4. Characterization of MIL-100(Fe)

Figure S2. (A) Comparison of the XRD pattern of the prepared MIL-100(Fe) with the simulated one obtained by importing the crystal structure data from Ref. 4 into the software of Mercury 1.4; (B) TGA curve of the synthesized MIL-100(Fe); (C) SEM image of the synthesized MIL-100(Fe); (D) N\textsubscript{2} adsorption–desorption isotherms and the pore size distribution of the synthesized MIL-100(Fe).

The experimental XRD pattern of the synthesized MIL-100(Fe) is in good agreement with the simulated one, showing the successful preparation of MIL-100(Fe). The TGA data reveal that the MIL-100(Fe) is stable up to 340°C. The prepared MIL-100(Fe) gave a BET surface area of 1225.53 m\textsuperscript{2} g\textsuperscript{-1} with a pore volume of 0.6224 cm\textsuperscript{3} g\textsuperscript{-1}. 
Graphite oxide (GO) was prepared from expandable graphite power according to the modified Hummers method.\textsuperscript{5} Firstly, 23 mL of concentrated sulfuric acid was added into a 250 mL flask and cooled by immersing it into an ice bath, and then 1.0 g of graphite powder and 1.0 g of NaNO\textsubscript{3} were gradually added into the flask and the electromagnetic stirring for 1 h was kept. Subsequently, 10 g of KMnO\textsubscript{4} was slowly added under stirring at temperature below 10°C, the stirring process maintained about 2 h. Next, the ice bath was removed out and the mixture was stirred at 35°C for 7 h. After that, the reaction mixture was cooled and kept at room temperature overnight. 40 mL cooled water was slowly added into the flask with continuous stirring and the temperature was maintained at 90°C in the water bath for 0.5 h. In the next step, 140 mL water and 10 mL of 30\% (\textit{v/v}) H\textsubscript{2}O\textsubscript{2} were added to terminate the reaction. Then, the centrifugation and the repeated rinsing with 10\% HCl were performed till the sulfate ion was thoroughly removed by adding BaCl\textsubscript{2} without the precipitation of BaSO\textsubscript{4} phenomenon. Finally, the generated brown powder of graphite oxide was dried at 80°C under vacuum for 12 h for further reaction.
6. Synthesis of MIL-101(Cr)@GO

The composite material MIL-101(Cr)@GO was prepared using hydrothermal method\(^6\): the obtained GO (0.566 g) was dispersed in 48 mL of deionized water and the mixture was ultrasonicated for 1 h to create a stable dispersion in the solution. After being added with Cr(NO\(_3\))\(3\)·9H\(_2\)O (4 g), H\(_2\)BDC (1.66 g), and HF (450 µL, 40%, w/w) in turn, the mixture was continuously sonicated for 1 h to acquire a homogeneously mixture. Subsequently, the mixture was transferred to a Teflon lined bomb. Then, the Teflon lined bomb was sealed and placed in an oven and kept at 210°C for 8 h. After the reaction, the bomb was naturally cooled down to room temperature. The raw material was purified by N, N-dimethylformamide and hot ethanol to remove the unreacted H\(_2\)BDC in the resulting crystalline solid for three times. Finally, MIL-101(Cr)@GO was isolated from the suspension by centrifuging and was dried at 80°C under vacuum for 12 h. MIL-101(Cr)@GO was directly ultrasonicated in methanol bath for 10 min and dried under air, then it was used for further characterization and mechanism study.
7. UV-vis spectrum of three sulfonamides.

SDZ \((c = 10 \text{ mg L}^{-1})\)  
SDX \((c = 10 \text{ mg L}^{-1})\)  
SMX \((c = 10 \text{ mg L}^{-1})\)

Figure S3. UV-vis spectrum of three sulfonamides at different pH.
8. Calibration curves of three sulfonamides.

The aqueous stock solution of SDZ, SDX, and SMX were diluted by deionized water to prepare seven standard solutions at concentration levels of 10, 20, 30, 40, 50 mg L\(^{-1}\). Then, 50 mL of a variety of concentrations of the sulfonamides solution was adjusted to pH value at 3, 4, 5, 6, 7, 8, 9 with 0.1 mol L\(^{-1}\) HCl or 0.1 mol L\(^{-1}\) NaOH. The absorbances of SDZ, SDX and SMX solutions were measured using UV-vis spectrophotometer at maximum absorption wavelength, respectively. Calibration curves were constructed by the least squares linear regression analysis of the absorbance \(y\) versus the concentration \(x\).

| Sulfonamide | pH | Calibration curve | \(R^2\) |
|-------------|----|-------------------|--------|
| SMX         | 3  | \(y=0.0831x+0.0098\) | 0.9991 |
|             | 4  | \(y=0.0837x+0.0098\) | 0.9995 |
|             | 5  | \(y=0.0825x+0.0024\) | 0.9997 |
|             | 6  | \(y=0.0849x+0.0145\) | 0.9990 |
|             | 7  | \(y=0.0902x+0.0248\) | 0.9984 |
|             | 8  | \(y=0.0857x-0.0085\) | 0.9989 |
|             | 9  | \(y=0.0856x+0.0061\) | 0.9985 |
| SDZ         | 3  | \(y=0.0837x-0.0107\) | 0.9978 |
|             | 4  | \(y=0.0874x-0.0136\) | 0.9997 |
|             | 5  | \(y=0.0862x+0.0096\) | 0.9991 |
|             | 6  | \(y=0.0864x-0.0213\) | 0.9994 |
|             | 7  | \(y=0.0922x-0.0014\) | 0.9999 |
|             | 8  | \(y=0.0089x-0.0017\) | 0.9986 |
|             | 9  | \(y=0.0956x-0.0094\) | 0.9996 |
| SDX         | 3  | \(y=0.0804x-0.0203\) | 0.9999 |
|             | 4  | \(y=0.0815x-0.0211\) | 0.9988 |
|             | 5  | \(y=0.0814x+0.0202\) | 0.9993 |
|   |   |   |   |
|---|---|---|---|
| 6 | $y=0.0816x-0.0085$ |     | 0.9999 |
| 7 | $y=0.0960x-0.0360$ |     | 0.9994 |
| 8 | $y=0.0888x-0.0084$ |     | 0.9990 |
| 9 | $y=0.0870x-0.0008$ |     | 0.9998 |
9. Characterization of GO

Figure S4. (A) N\textsubscript{2} adsorption-desorption isotherms and the pore size distribution of GO; (B) TGA curve of the synthesized GO.

As can be seen, the N\textsubscript{2} sorption–desorption isotherm and the pore size of GO distribution in Fig. S4 (A), the prepared GO was characterized by surface area and pore size analyzer. It can be seen that the BET surface area of GO is 98.382 m\textsuperscript{2} g\textsuperscript{-1} with total pore volume of 0.1044 cm\textsuperscript{3} g\textsuperscript{-1}. The TGA curve revealed that the GO was stable at temperatures below 200°C and showed a weight-loss step at 200°C due to the decomposition of surface groups.
10. Total pore volume of the synthesized MIL-101(Cr)@GO and MIL-101(Cr).

Figure S5. Total pore volume of the synthesized MIL-101(Cr)@GO and MIL-101(Cr).
11. Effect of solution pH on the Zeta potential of MIL-101(Cr)@GO composite.

Figure S6. Effect of solution pH on the Zeta potential of MIL-101(Cr)@GO composite.
12. Adsorption kinetics plots for adsorption of sulfonamides on MIL-101(Cr)@GO.

Figure S7. Pseudo-first-order kinetic (a), pseudo-second-order kinetic (b), and intra-particle diffusion (c) plots for adsorption of SDZ, SDX and SMX on MIL-101(Cr)@GO.
13. Effect of different initial concentration.

Figure S8. Effect of different initial concentration on the adsorption mass.
14. Value of separation factor $R_L$ of MIL-101(Cr)@GO towards three sulfonamides.

Figure S9. Value of separation factor $R_L$ of MIL-101(Cr)@GO towards three sulfonamides.
15. Van’ Hoff plots to get the $\Delta H$ and $\Delta S$ of MIL-101(Cr)@GO towards three sulfonamides.

Figure S10. Van’ Hoff plots to get the $\Delta H$ and $\Delta S$ of MIL-101(Cr)@GO towards three sulfonamides.
16. Comparison of the maximum adsorption capacities for SMX adsorption on MIL-101(Cr)@GO with other adsorbents.

Table S2 Comparison of the maximum adsorption capacities for SMX adsorption on MIL-101(Cr)@GO with other adsorbents.

| Target | Adsorbent                | Maximum adsorption capacity (mg g⁻¹) | Refs. |
|--------|--------------------------|--------------------------------------|-------|
| SMX    | Fe₃O₄@C                 | 92.7                                 | (7)   |
| SMX    | High silica zeolite      | 1.90×10⁻³                            | (8)   |
| SMX    | MWCNT-10                 | 71.8±3.4                             | (9)   |
| SMX    | Aligned-MWCNT           | 37.9±2.2                             | (9)   |
| SMX    | S-MWCNT-2040            | 8.2±0.5                              | (9)   |
| SMX    | L-MWCNT-2040            | 22.7±1.5                             | (9)   |
| SMX    | L-MWCNT-60100           | 16.3±1.5                             | (9)   |
17. References

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