

Supporting information

Sonochemical synthesis of cyclophosphazene bridged mesoporous organosilicas and their application in methyl orange, congo red and Cr(VI) removal

Pawan Rekha, Raesh Muhammad and Paritosh Mohanty*

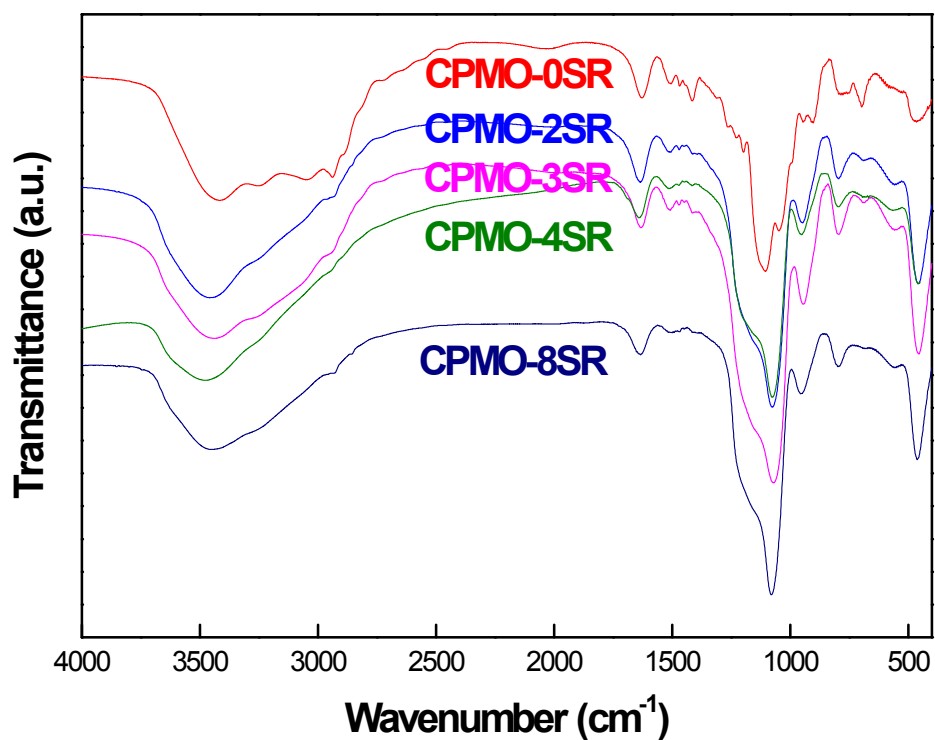


Figure S1. FT-IR of CPMOs

Table S1. Observed FT-IR band positions along with their assignments of CPMOs

| Band assignments | Wavenumber (cm ⁻¹) |
|--|--------------------------------|
| C-H stretching(APTES) | 2929-2856 |
| ν_{as} (P=N-P) | 1406-1418 |
| P=N | 1196-1209 |
| Si-O-Si and ν_{as} (P-NH-P) | 1237-1050 |
| ν_{as} (P-NH-P) and Si-OH | 950 |
| Si-O-Si | 800 |
| δ (P=N-P) | 544-555 |

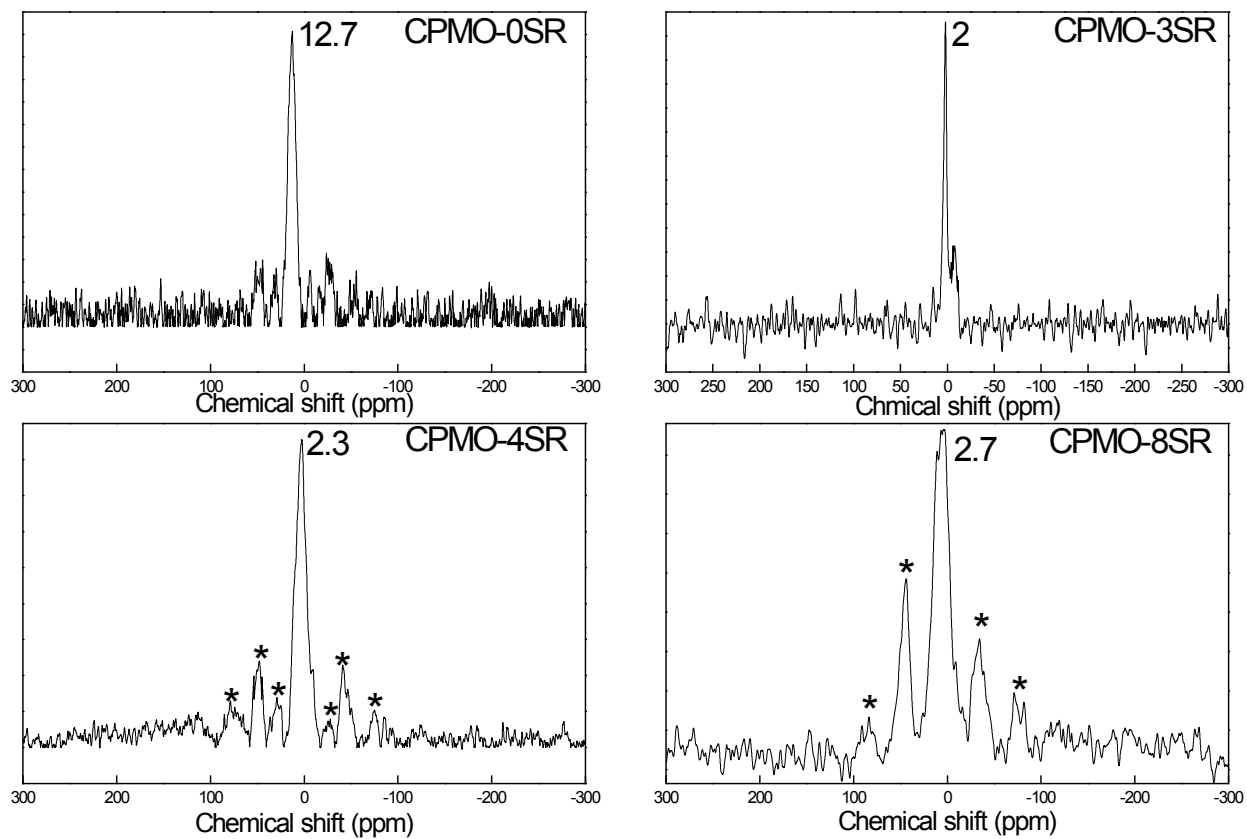


Figure S2. ^{31}P CPMAS NMR of CPMOs synthesized by sonication

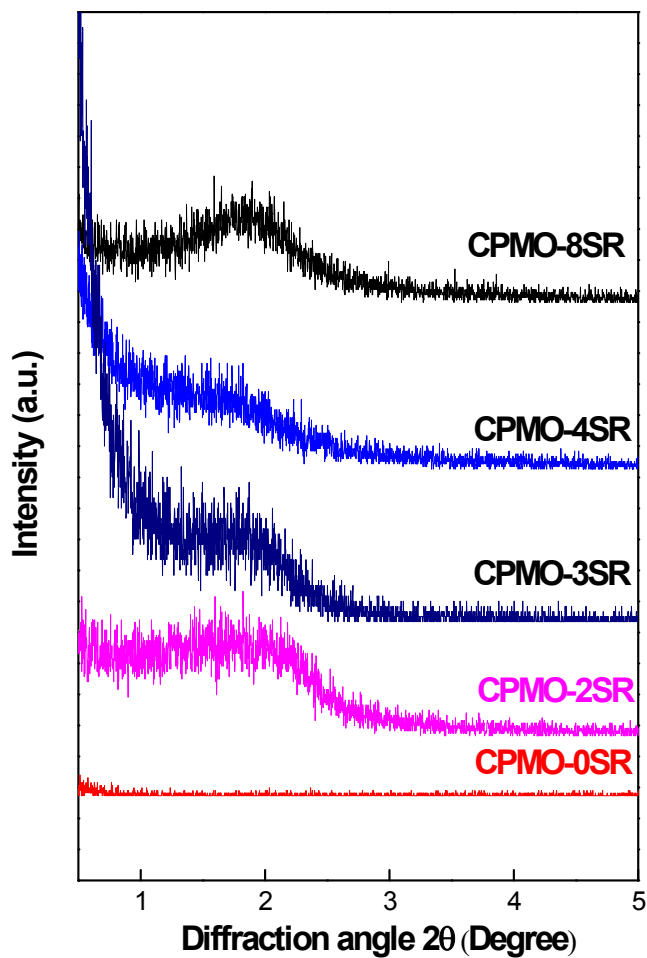


Figure S3. Small angle X-ray scattering pattern of CPMOs

Table S2. Position and % of the *T* and *Q* sites in different samples

| Sample ID | Position of <i>T</i> sites | | Position of <i>Q</i> sites | | |
|-----------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| | <i>T</i> ² (ppm), (%) | <i>T</i> ³ (ppm), (%) | <i>Q</i> ² (ppm), (%) | <i>Q</i> ³ (ppm), (%) | <i>Q</i> ⁴ (ppm), (%) |
| CPMO-0SR | -58, (27.6) | -66, (72.4) | -- | -- | -- |
| CPMO-4SR | -57, (20.1) | -66, (8.4) | -90, (8.1) | -100, (47.9) | -110, (15.5) |

Table S3. C, H and N elemental analysis of CPMOs

| Sample ID | N (wt%) | C (wt%) | H (wt%) | C/N ratio |
|-----------|---------|---------|---------|-----------|
| CPMO-0SR | 11.71 | 23.62 | 5.28 | 2.01 |
| CPMO-2SR | 6.19 | 11.85 | 3.17 | 1.91 |
| CPMO-3SR | 5.22 | 9.58 | 3.13 | 1.83 |
| CPMO-4SR | 5.14 | 8.93 | 2.85 | 1.73 |
| CPMO-8SR | 4.86 | 8.28 | 2.1 | 1.70 |

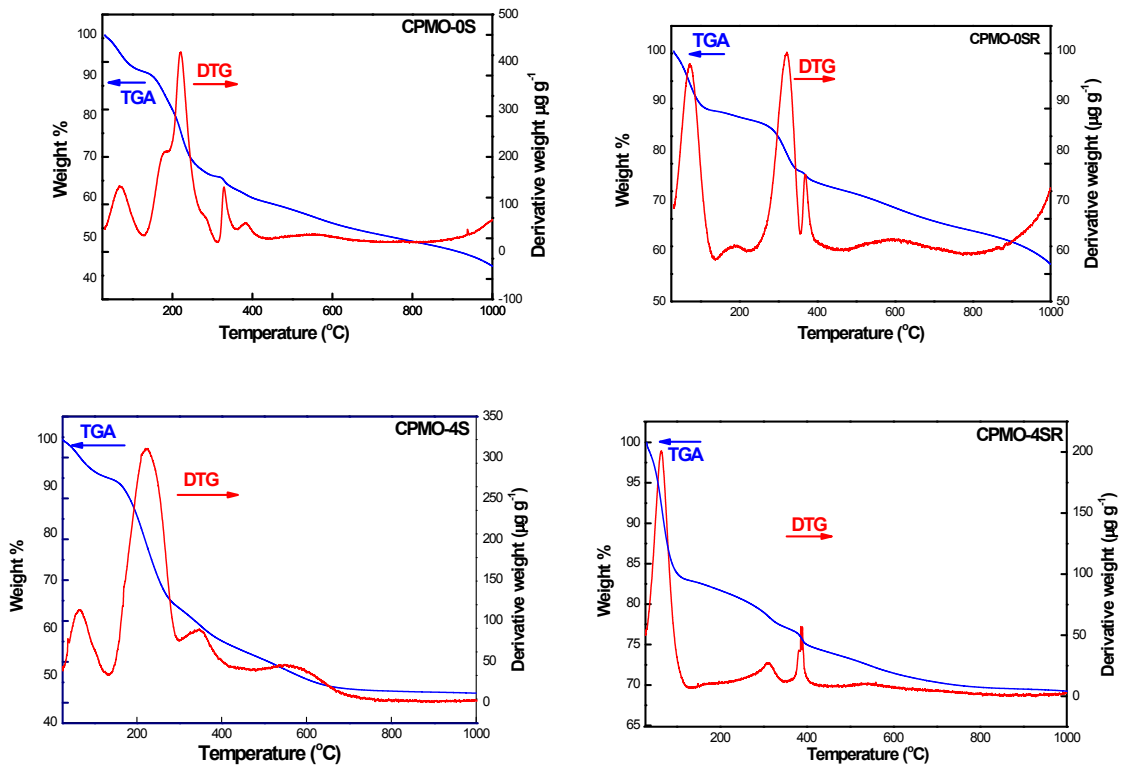


Figure S4. TGA and DTG thermograms of CPMOs measured in nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

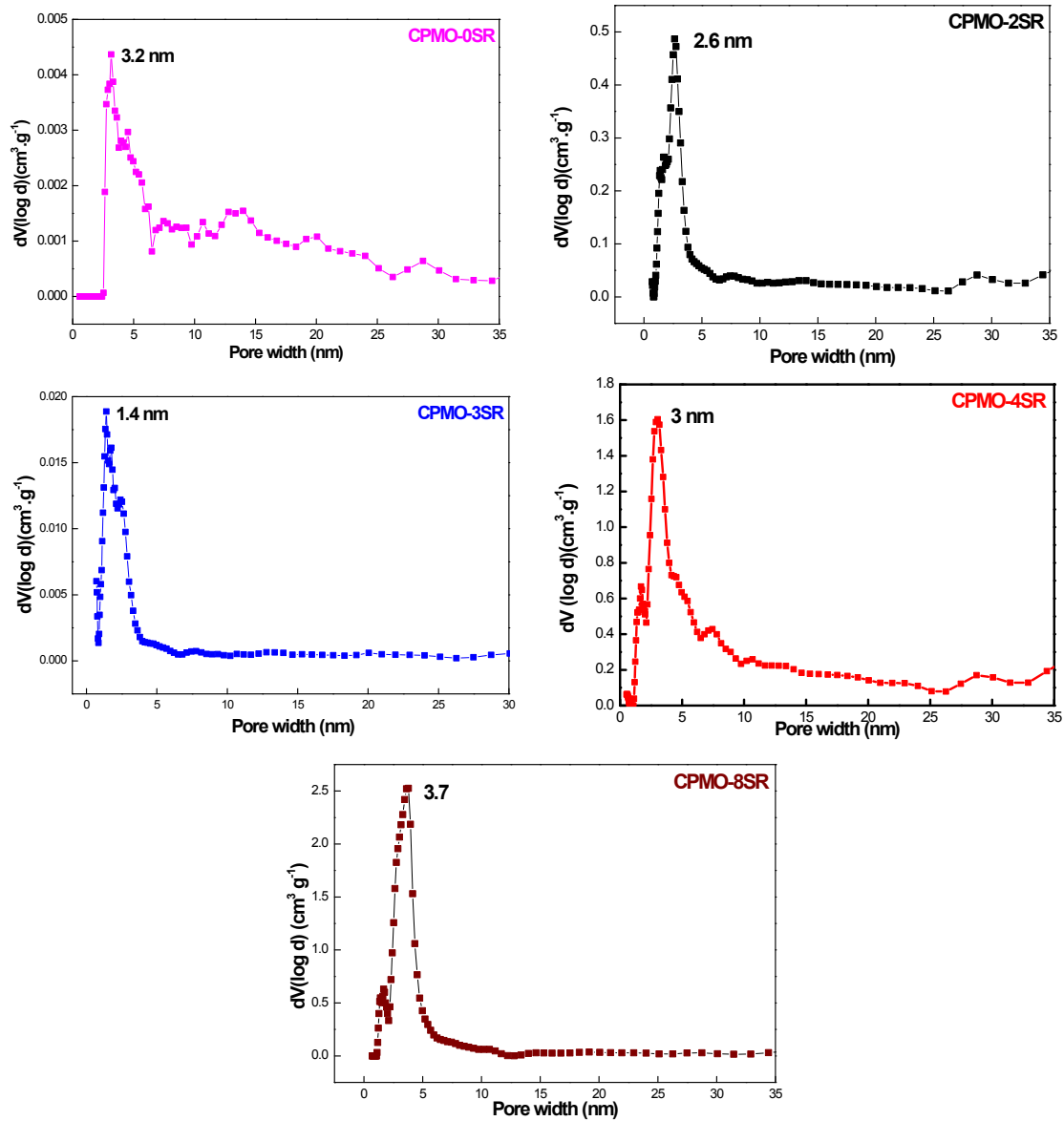


Figure S5. Pore size distribution of CPMOs

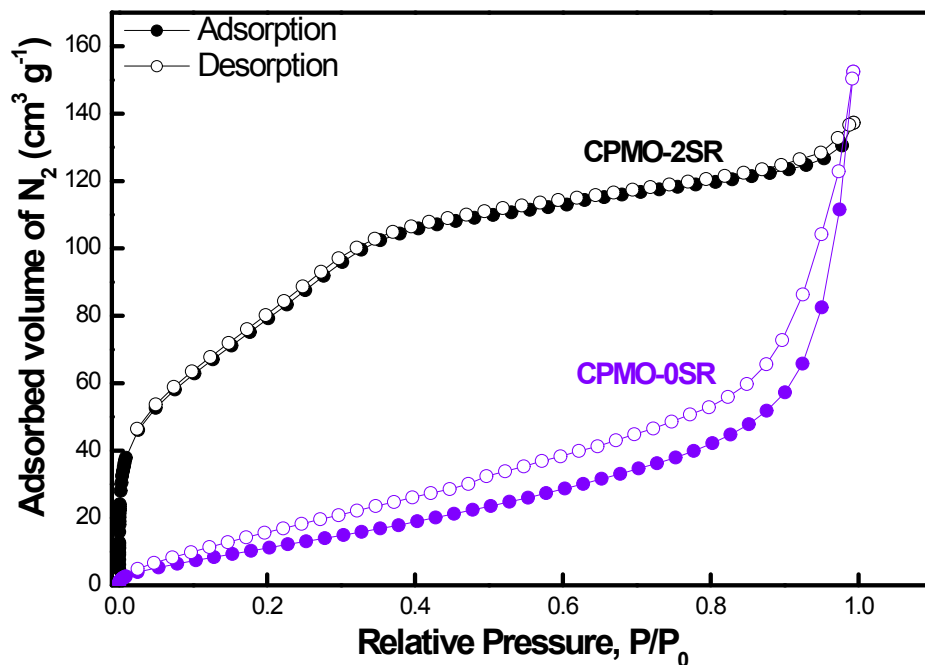


Figure S6. N_2 sorption isotherms of CPMO-0SR and CPMO-4SR measured at 77 K

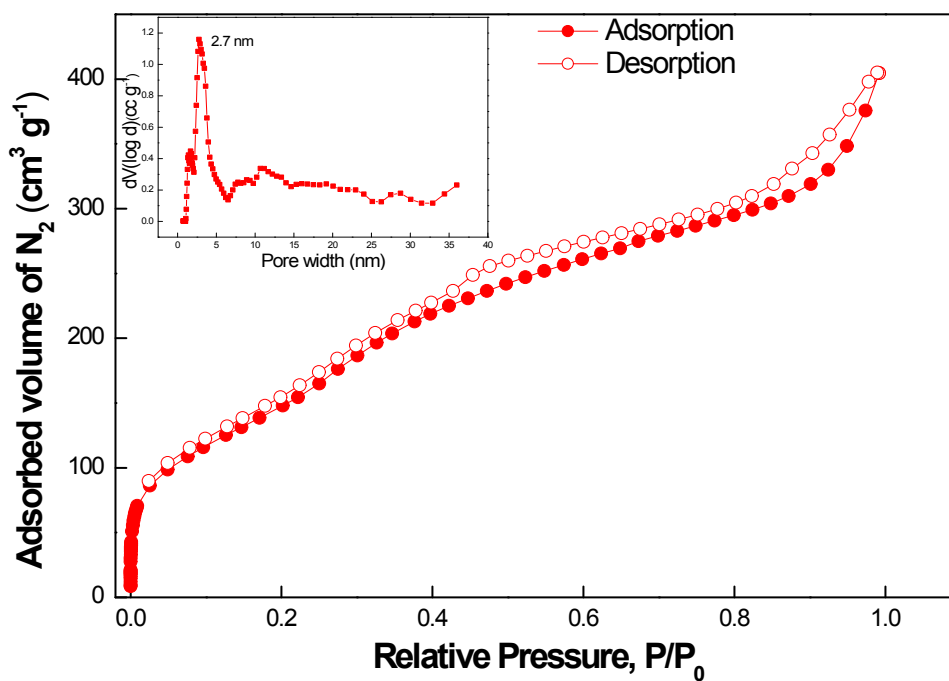


Figure S7. N_2 sorption isotherm of PMO-4S (without PNC) measured at 77 K

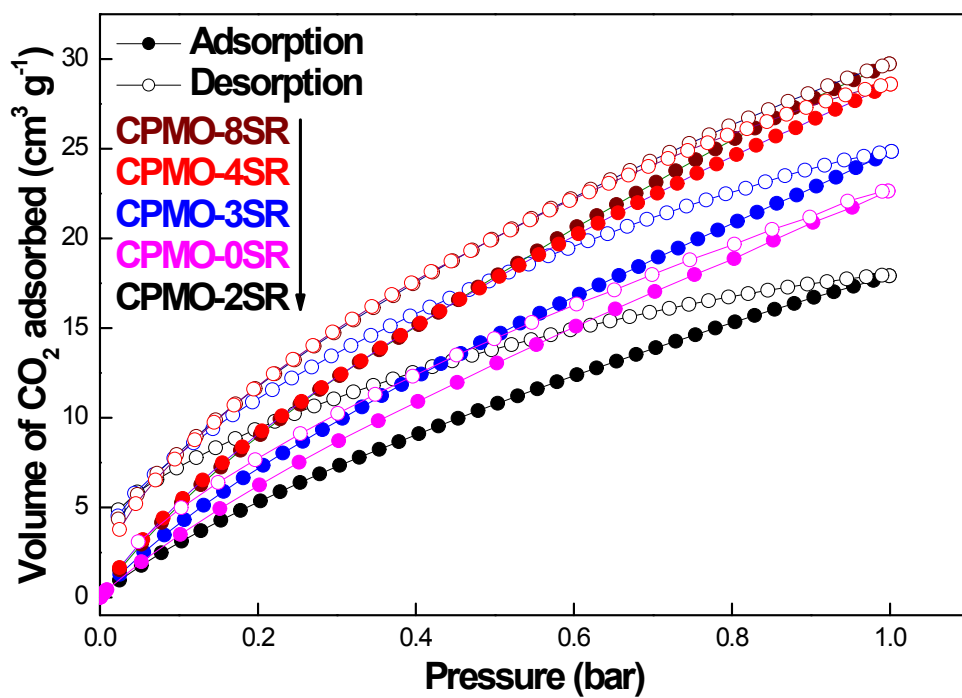


Figure S8. CO₂ sorption isotherms of CPMOs measured at 273K

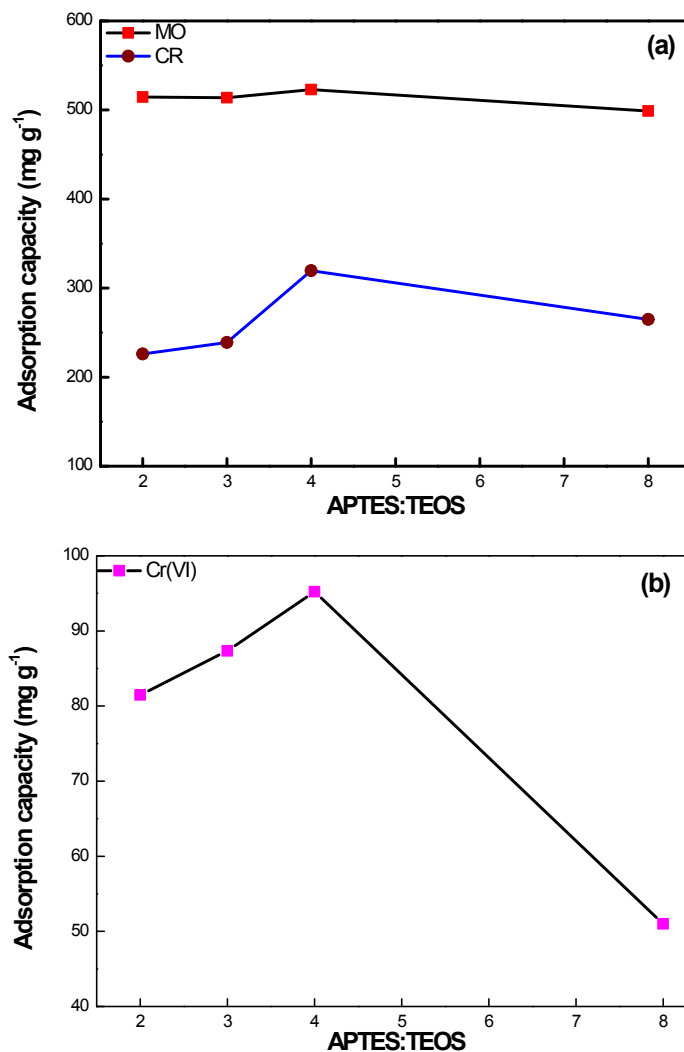


Figure S9. Comparison of adsorption capacity of CPMOs for (a) organic dyes and (b) Cr(VI) ions removal

Table S4. Comparison of adsorption capacities of CPMOs for (a) organic dyes and (b) Cr(VI) ions removal

| Sample ID | MO (q_{\max})(mg g ⁻¹) | CR (q_{\max})(mg g ⁻¹) | Cr(VI)(q_{\max})(mg g ⁻¹) |
|-----------|--|--|---|
| CPMO-2SR | 514.515 | 226 | 81.469 |
| CPMO-3SR | 513.857 | 239 | 87.338 |
| CPMO-4SR | 523 | 319.46 | 95.206 |
| CPMO-8SR | 498.817 | 264.79 | 51 |
| PMO-4S | 474.307 | 281.32 | 73.3 |

Table S5: Adsorption capacities q_{\max} for Cr (VI) removal of selected results from the literature

| Silica type | q_{\max} (mg g ⁻¹) | Ref. |
|--|----------------------------------|---------------------|
| 3 Aminopropyl functionalized MCM-48 | 65 | S1 |
| 6-amino-4-azahexyl functionalized MCM-48 | 119 | S1 |
| 9-amino-4,7-diazanonyl functionalized MCM-48 | 160 | S1 |
| AP-TMS modified MCM-45 | 40 | S2 |
| Amine-Functionalized Mesoporous Silica | 82 | S3 |
| Magnetic functionalized MCM-48 mesoporous silica with melamine | 115.6 | S4 |
| CPMO-4SR | 101 | Present work |

Table S6: Adsorption capacities q_{\max} for methyl orange removal of selected results from the literature

| Material type | q_{\max} (mg g ⁻¹) | Ref. |
|---|----------------------------------|---------------------|
| Ammonium-functionalized silica nanoparticle | 105.4 | S5 |
| Mesoporous carbon material | 294.1 | S6 |
| Alkali-activated multiwalled carbon nanotubes | 149 | S7 |
| Poly HEMA–chitosan-MWCNT nano-composite | 306 | S8 |
| CPMO-4SR | 523 | Present work |

Table S7: Adsorption capacities q_{\max} for congo red removal of selected results from the literature

| Silica type | q_{\max} (mg g ⁻¹) | Ref. |
|--|----------------------------------|---------------------|
| Modified xanthan gum/silica hybrid nanocomposite | 209.21 | S9 |
| Graphene oxide/chitosan fibers | 294.12 | S10 |
| Maghemite nanoparticles | 208.33 | S11 |
| Cu-BTC | 959.9 | S12 |
| Ni50/Cu-BTC | 1078 | S12 |
| CPMO-4 SR | 320 | Present work |

Table S8. Thermodynamic parameters for the adsorption of organic dyes and Cr(VI) ions by CPMO-4SR

| | MO | CR | Cr(VI) ion |
|-------|------------------------------------|------------------------------------|------------|
| T (K) | ΔG (kJ mol ⁻¹) | ΔG (kJ mol ⁻¹) | |
| 283 | -- | -0.292 | -- |
| 293 | -8.095 | -0.312 | -- |
| 298 | -8.254 | -0.324 | -7.4 |
| 303 | -8.384 | -0.321 | -- |
| 313 | -8.635 | -0.326 | -5.089 |
| 323 | -8.80 | -0.304 | -- |
| 333 | -9.04 | -0.301 | -1.58 |
| 343 | -- | -0.289 | -- |
| 353 | -- | -0.256 | -- |

Table S9. Thermodynamic parameters for the adsorption of organic dyes and Cr(VI) ions by CPMO-4SR

| Adsorbate | Thermodynamic parameters | |
|------------|------------------------------------|---------------------------------------|
| | ΔH (kJ mol ⁻¹) | ΔS [J (mol K) ⁻¹] |
| MO | -1.377 | 23 |
| CR | -0.461 | -0.498 |
| Cr(VI) ion | -7.096 | -172 |

References

- S1. T. Yokoi, Y. Kubota and T. Tatsumi, *Appl. Catal. A*, 2012, **421–422**, 14-37.
- S2. S. A. Idris, K. M. Alotaibi, T. A. Peshkur, P. Anderson and M. Morris, *Microporous Mesoporous Mater.*, 2013, **165**, 99-105.
- S3. X. Li, C. Han, W. Zhu, W. Ma, Y. Luo, Y. Zhou, J. Yu and K. Wei, *J. Chem.*, 2014, **2014**, 1-10.
- S4. M. Anbia, K. Kargosha and S. Khoshbooei, *Chem. Eng. Res. Des.*, 2015, **93**, 779-788.
- S5. J. Liu, S. Ma and L. Zang, *Appl. Surf. Sci.*, 2013, **265**, 393–398.
- S6. N. Mohammadi, H. Khani, V. K. Gupta, E. Amereh and S. Agarwal, *J. Colloid Interface Sci.*, 2011, **362**, 457–462.
- S7. J. Ma, F. Yu, L. Zhou, L. Jin, M. Yang, J. Luan, Y. Tang, H. Fan, Z. Yuan and J. Chen, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5749–5760.
- S8. H. Mahmoodian, O. Moradi, B. Shariatzadeha, T. A. Salehf, I. Tyagi, A. Maity, M. Asif, and V. K. Gupta, *J. Mol. Liq.*, 2015, **202**, 189–198.

- S9. S. Ghorai, A. K. Sarkar, A. B. Panda and S. Pal, *Bioresour. Technol.*, 2013, **144**, 485–491.
- S10. Q. Du, J. Sun, Y. Li, X. Yang, X. Wang, Z. Wang and L. Xia, *Chem. Eng. J.*, 2014, **245**, 99–106.
- S11. A. Afkhami and R. Moosavi, *J. Hazard. Mater.*, 2010, **174**, 398–403.
- S12. J. Hu, H. Yu, W. Dai, X. Yan, X. Hu and H. Huang, *RSC Adv.*, 2014, **4**, 35124–35130.