

Supplementary Information

Guanidinium based ionic porous organic polymer as a propitious material for inordinate uptake of permanganate ions from water

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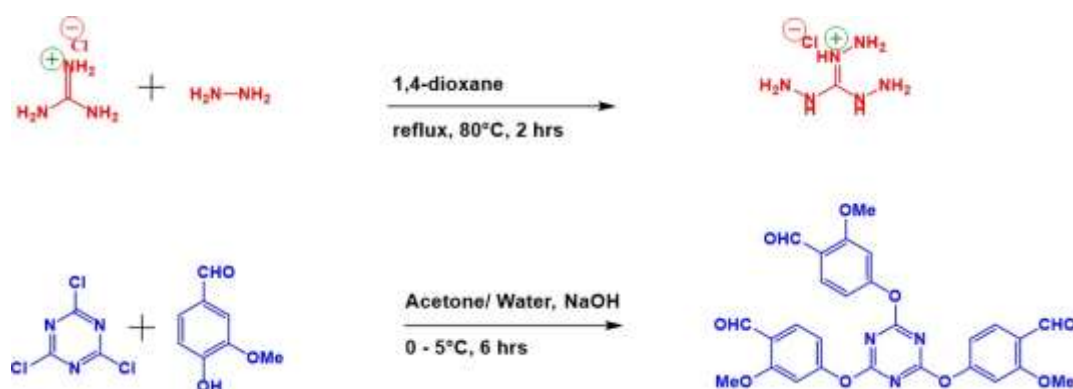
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1. Materials and methods

All the chemicals were purchased from Sigma Aldrich, Alfa Aeser, Spectrochem, Merck and TCI and used without further purification. FT-IR spectra were recorded using Shimadzu IR Tracer 100 with DLATGS and MCT detectors. CPMAS ^{13}C NMR was performed using 500 MHz JEOL model ECZ500R/S1. Thermogravimetric analysis were performed using Perkin Elmer Thermal Analyzer STA 8000. Powder X-ray diffraction were recorded using Rigaku XRD Smart Lab. Field Emission Scanning Electron Microscopy were obtained using Carl Zeiss model Gemini SEM 300. The absorption spectra of samples were captured using a BioTek EPOCH2 microplate reader.

2. Synthesis of monomers



Scheme S1. Synthesis of monomers **TGDM** (top), **TMB** (bottom)

2.1. Synthesis of triaminoguanidinium hydrochloride (TGDM)

TGDM was synthesized by reacting guanidinium hydrochloride and hydrazine hydrate using 1,4-dioxane as the solvent. 2 mmoles of guanidinium hydrochloride was dissolved in 10 mL of dioxane and transferred to a round bottom flask kept in an oil bath preheated to 100°C. 7 mmoles of hydrazine hydrate was then added dropwise. The reaction was continued for 2 hours.

The resulting solid product was filtered out and washed with 1,4-dioxane. The ^1H NMR spectra showed signals around $\delta = 2.32[2\text{H},\text{s}]$, $3.18[4\text{H},\text{s}]$, $4.32[2\text{H},\text{s}]$. The FT-IR spectra of **TGDM** shows characteristic vibrational bands around 3350 and 3180 cm^{-1} corresponding to NH_2 stretching and vibrational bands around 1690 cm^{-1} corresponding to imine stretching respectively.

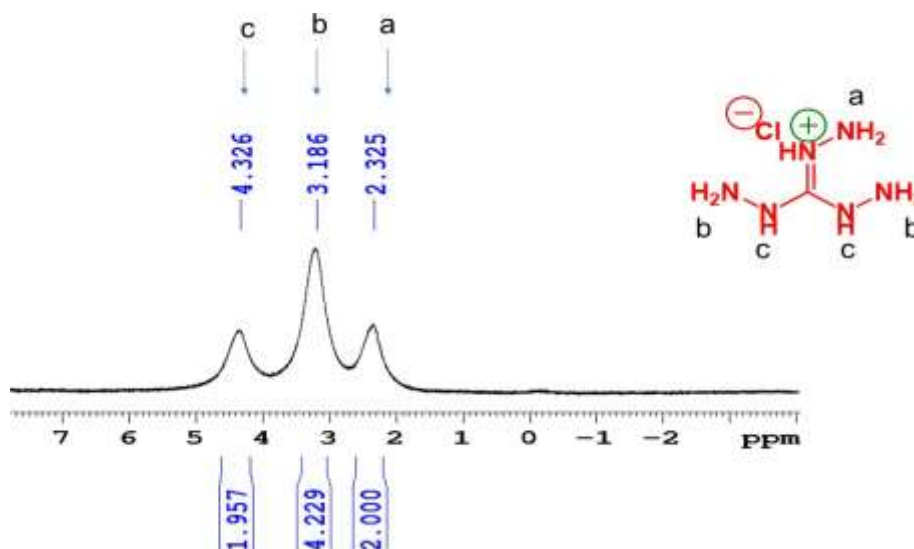


Figure S1. ^1H NMR spectra [400 MHz, DMSO-d_6] of **TGDM** monomer

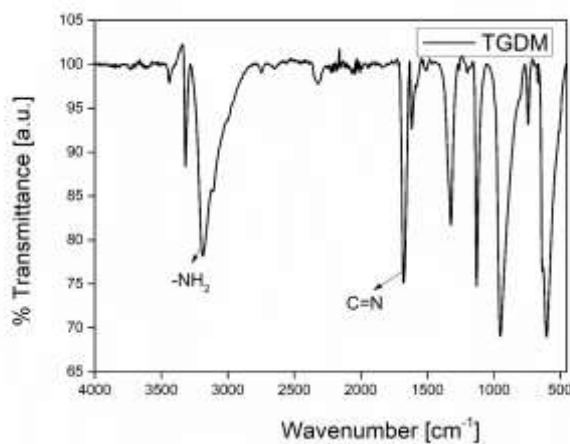


Figure S2. FT IR spectra of **TGDM** monomer

2.2. Synthesis of 4,4',4''-[1,3,5-triazine-2,4,6-triyltris(oxy)tris]3-methoxybenzaldehyde (TMB)

TMB was synthesized by reacting cyanuric chloride with vanillin using sodium hydroxide as base and acetone/water as solvent. 7.5 millimoles of vanillin was dissolved in 10 mL of acetone. 8.75 millimoles of sodium hydroxide was taken separately and dissolved in 10 mL of water. Sodium hydroxide solution was slowly added to vanillin dissolved in acetone, keeping in ice bath. 2.5 millimoles of cyanuric chloride was dissolved in acetone and added dropwise into the reaction flask kept in ice bath. Reaction was continued for 6 hours. The resultant white powder was filtered out using distilled water and characterized by NMR spectroscopy. ^1H NMR spectra showed signals at $\delta = 3.342[9\text{H},\text{s}]$, $7.47[3\text{H},\text{s}]$, $7.495[3\text{H},\text{d}]$, $7.971[3\text{H},\text{d}]$ and $9.989[3\text{H},\text{s}]$. The FT-IR spectra of the compound shows carbonyl stretching band at 1700 cm^{-1} . The vibrational band around 1570 cm^{-1} corresponds to triazine ring. The characteristic stretching vibration of C-O was observed around 1145 cm^{-1} . The absence of hydroxyl stretching and C-Cl stretching further confirms the complete conversion of the starting materials.

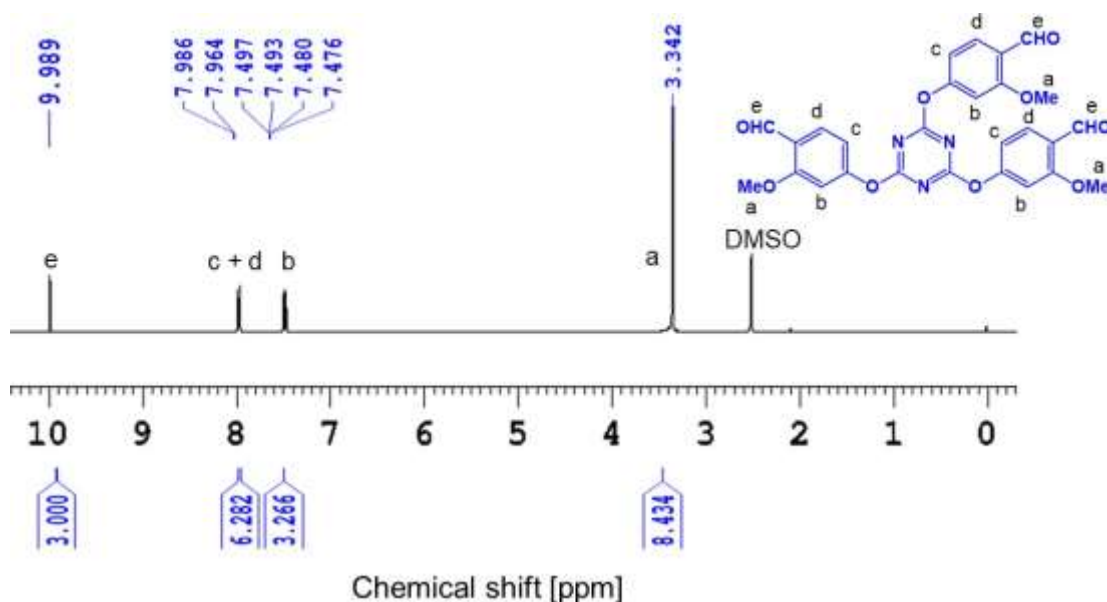


Figure S3. ^1H NMR spectra [400 MHz, DMSO-d_6] of **TMB** monomer

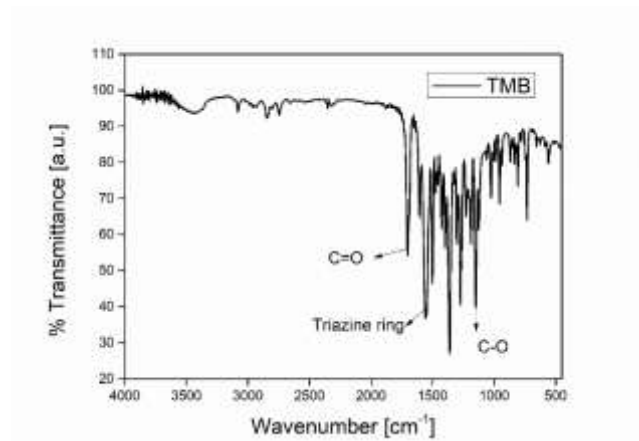


Figure S4. FT-IR spectra of **TMB** monomer

3. Solvothermal and mechanochemical synthesis of gn-ipop-cl

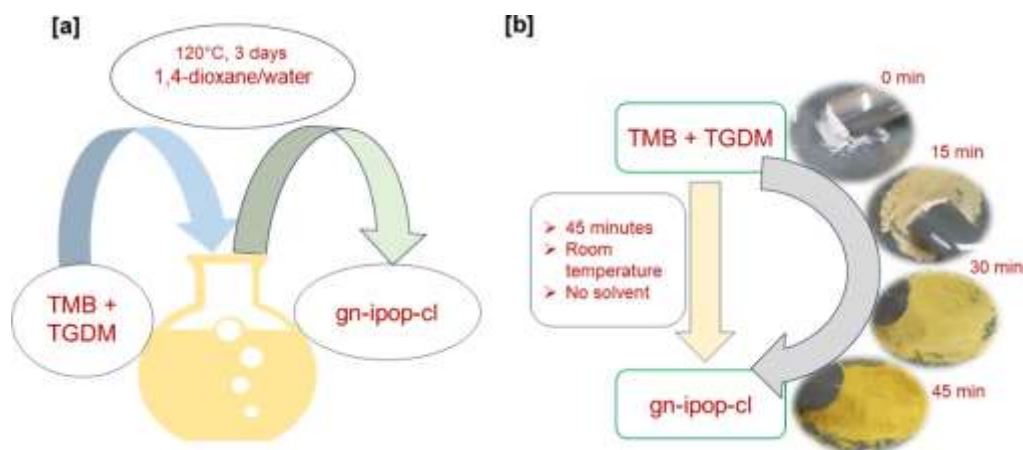


Figure S5. [a] Solvothermal and [b] mechanochemical methods of synthesis of **gn-ipop-cl**

The % yield of gn-ipop-cl was calculated with respect to monomer weight used.

$$\% \text{ yield} = [\text{Observed weight of polymer} / \text{Theoretical weight}] * 100$$

The polymerization gave 92 % yield.

4. Elemental analysis of gn-ipop-cl

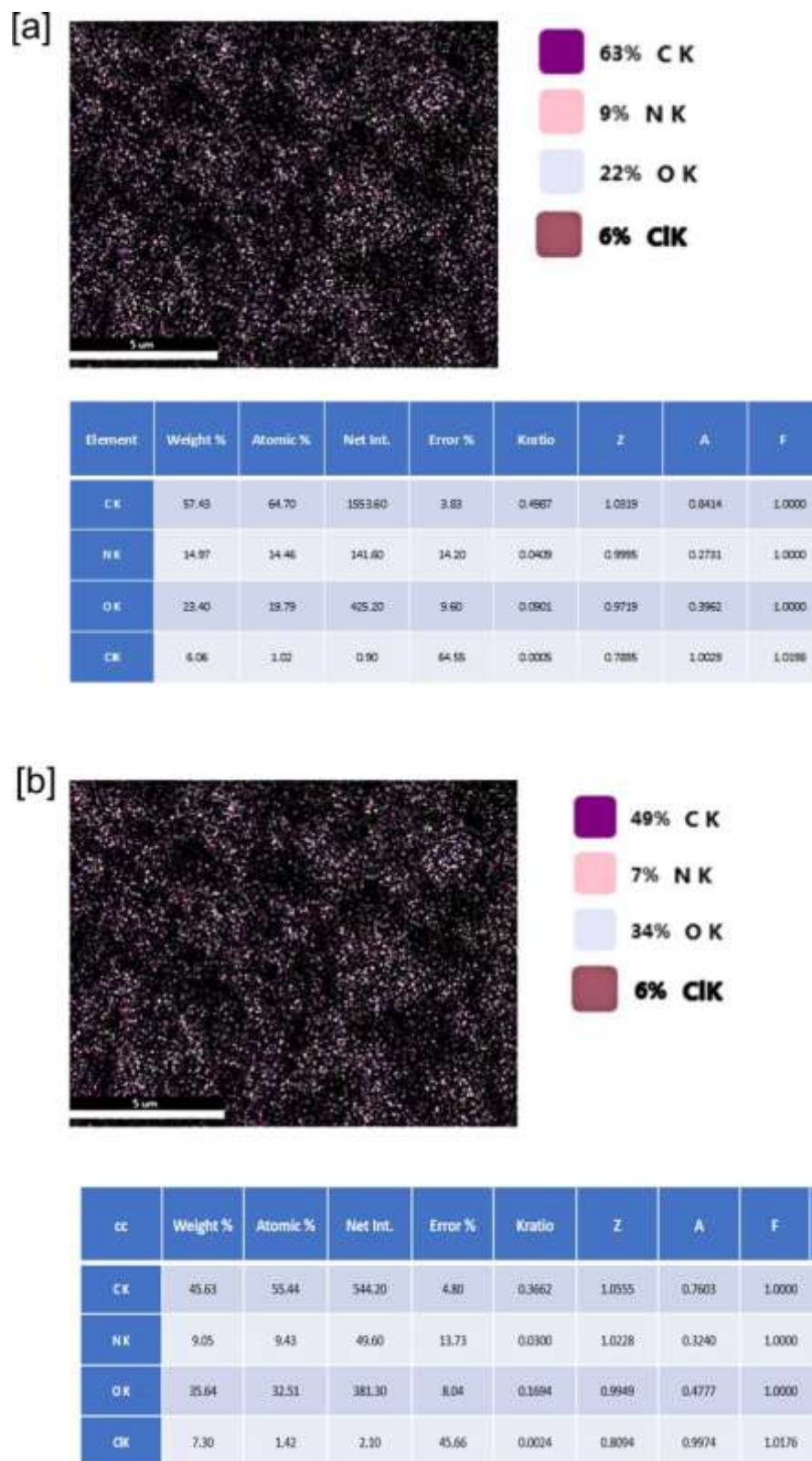


Figure S6. Elemental mapping of [a] gn-ipop-cl(MC) [b] gn-ipop-cl(ST)

5. Evaluation of chemical stability

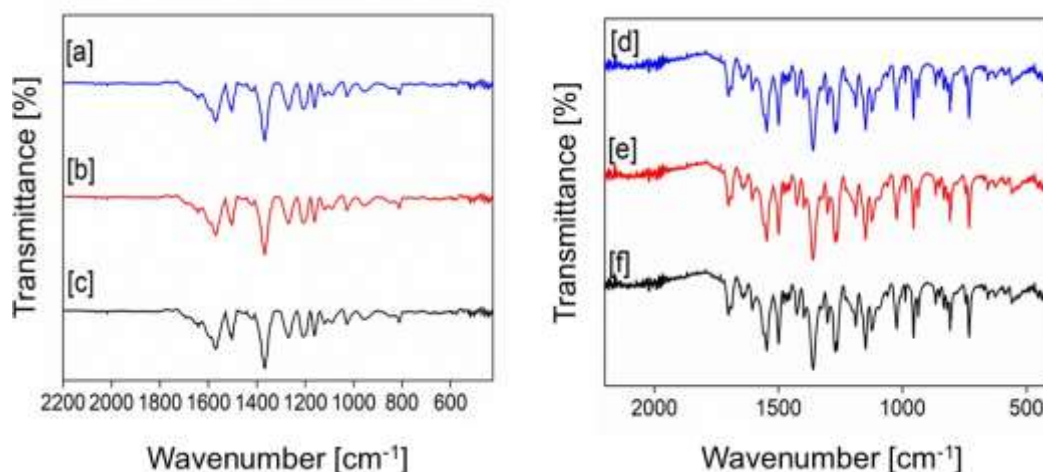


Figure S7. FT IR spectra of [a] **gn-ipop-cl(MC)**, [B] **gn-ipop-cl(MC)** treated with 2N HCl, [c] **gn-ipop-cl(MC)** treated with 2N NaOH, [d] **gn-ipop-cl(ST)**, [e] **gn-ipop-cl(ST)** treated with 2N HCl, [f] **gn-ipop-cl(ST)** treated with 2N NaOH

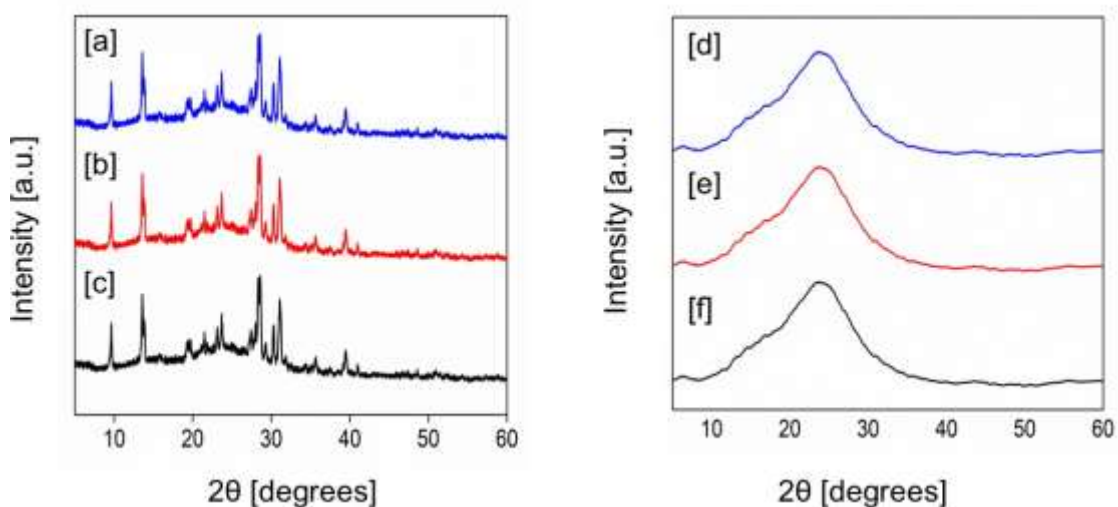


Figure S8. pXRD pattern of [a] **gn-ipop-cl(MC)**, [B] **gn-ipop-cl(MC)** treated with 2N HCl, [c] **gn-ipop-cl(MC)** treated with 2N NaOH, [d] **gn-ipop-cl(ST)**, [e] **gn-ipop-cl(ST)** treated with 2N HCl, [f] **gn-ipop-cl(ST)** treated with 2N NaOH

6. Permanganate adsorption studies

In a typical experiment, 5 mg of **gn-ipop-cl** was added into a 5 mL of permanganate solution prepared with specified concentration. The suspension was kept for stirring till maximum

adsorption monitored from UV-Vis spectra. The UV-Vis spectra of each sample was recorded after 10 times dilution of the original aliquots.

6.1. Kinetic studies

5 mg of polymer was mixed with 5 mL of 2.5 mM solution of potassium permanganate and kept for stirring. The adsorption was monitored at frequent time intervals. The obtained data was fitted with pseudo first order and second order kinetic equation.

6.2. Isotherm studies

5 mg of polymer was mixed with 5 mL of permanganate solution having different concentrations and kept for stirring until the adsorption equilibrates. The amount of permanganate adsorbed was calculated as

$$Q_e = [C_0 - C_e] * v / m$$

C_0 – initial concentration of permanganate in mg/L

C_e – equilibrium concentration of permanganate after adsorption in mg/L

v – volume of solution used in L

m – mass of adsorbent in g

7. Experimental results

7.1. KMnO_4 calibration curve

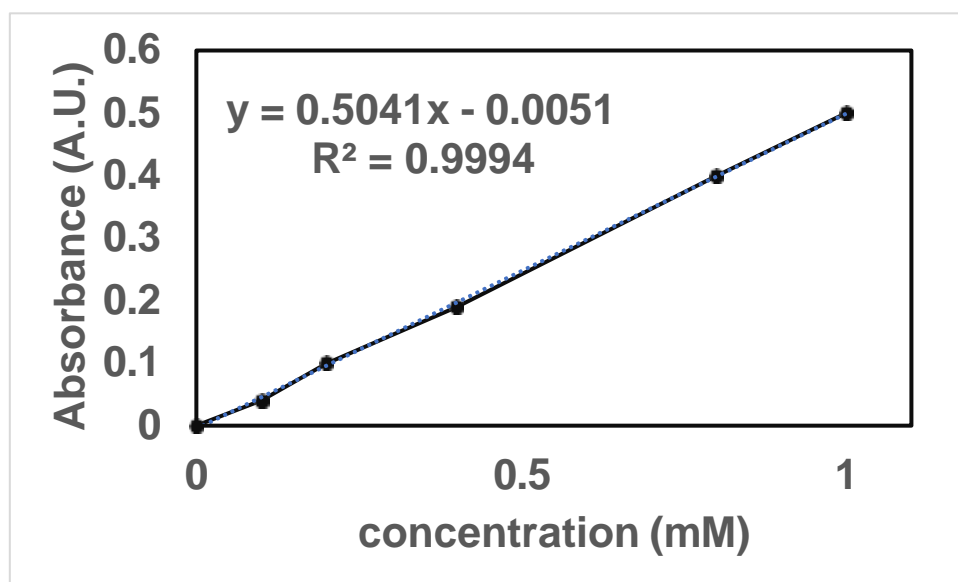


Figure S9. Calibration plot of potassium permanganate solution

7.2. Adsorption studies

The adsorption studies were performed using water as the solvent. The UV-Vis spectra indicates the decrease in absorbance of permanganate solution after adsorption. In each case black curve represents absorption spectrum before adsorption experiment and red curve represents absorption spectrum after adsorption.

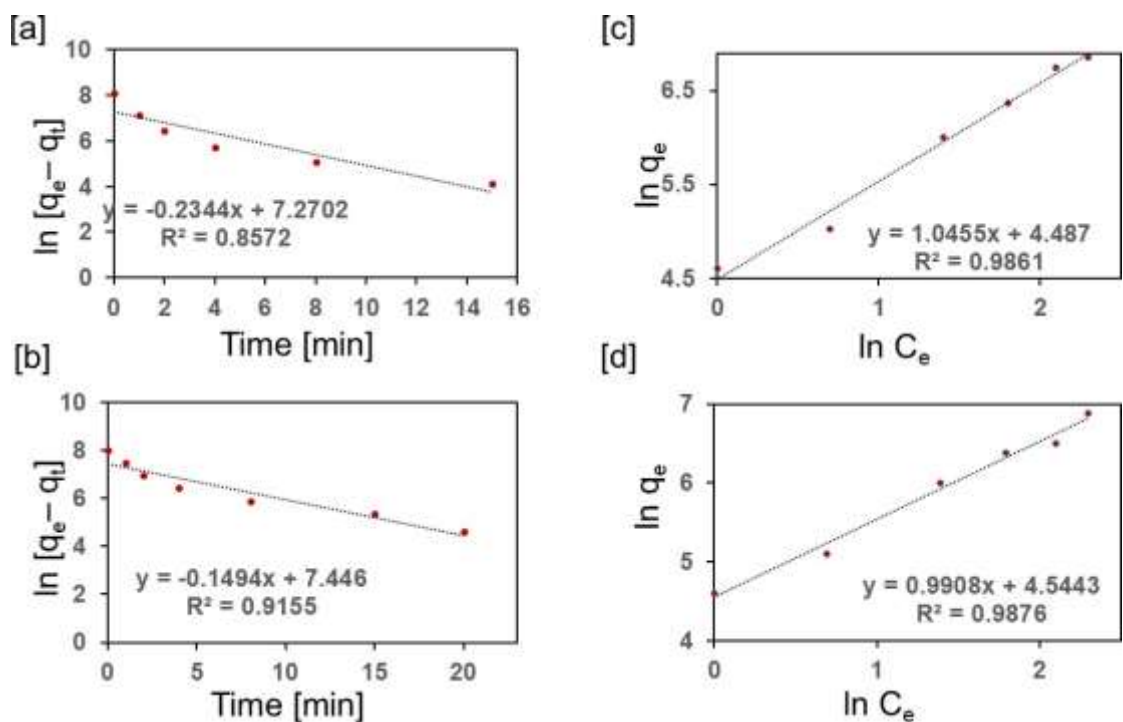


Figure S10. First order fitting for [a] **gn-ipop-cl(MC)**, [b] **gn-ipop-cl(ST)**, [c] Freundlich adsorption model evaluated for **gn-ipop-cl(MC)**, [d] Freundlich adsorption model evaluated for **gn-ipop-cl(ST)**

8. Study of effect of temperature on adsorption

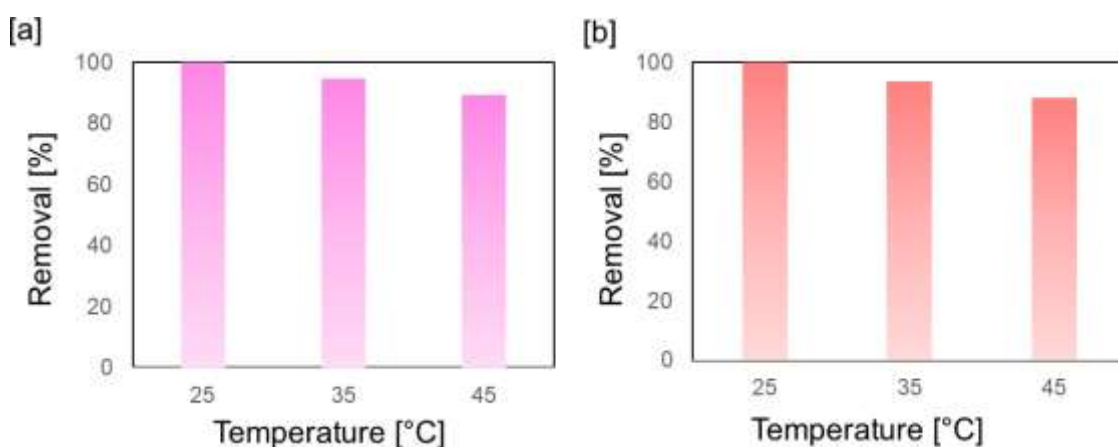


Figure S11. Temperature dependent removal of permanganate from water employing [a] **gn-ipop-cl(MC)**, [b] **gn-ipop-cl(ST)** (permanganate solution= 1 mM)

9. Characterization of KMnO₄ treated polymers

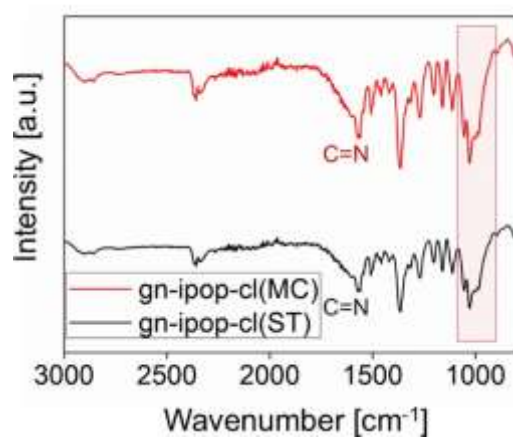


Figure S12. FT IR spectra of post treated polymer **gn-ipop-cl**

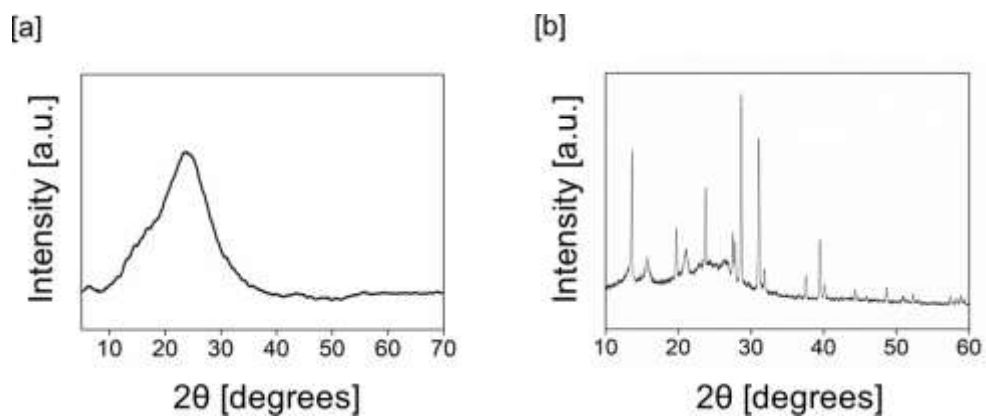


Figure S13. pXRD pattern for [a] post treated **gn-ipop-cl(ST)** [b] post treated **gn-ipop-cl(MC)**

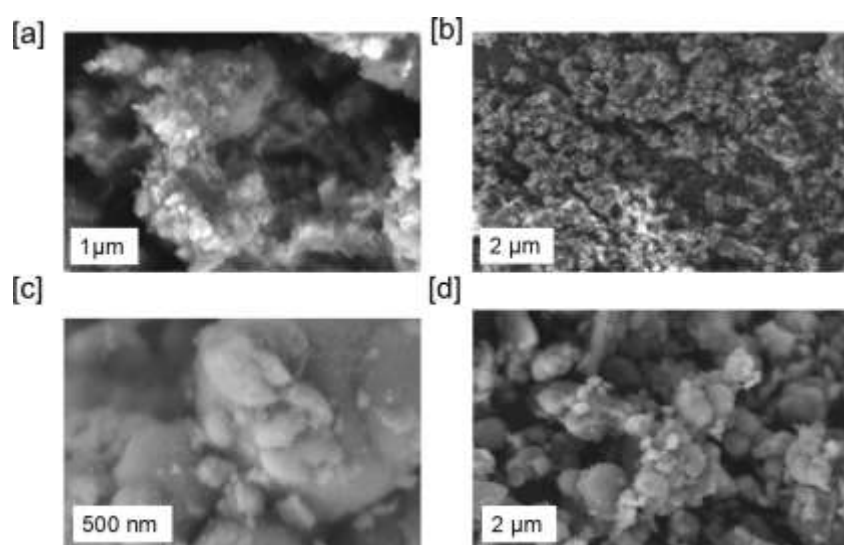


Figure S14. FE SEM analysis for [a,b] post treated **gn-ipop-cl(MC)**, [c,d] post treated **gn-ipop-cl(ST)**

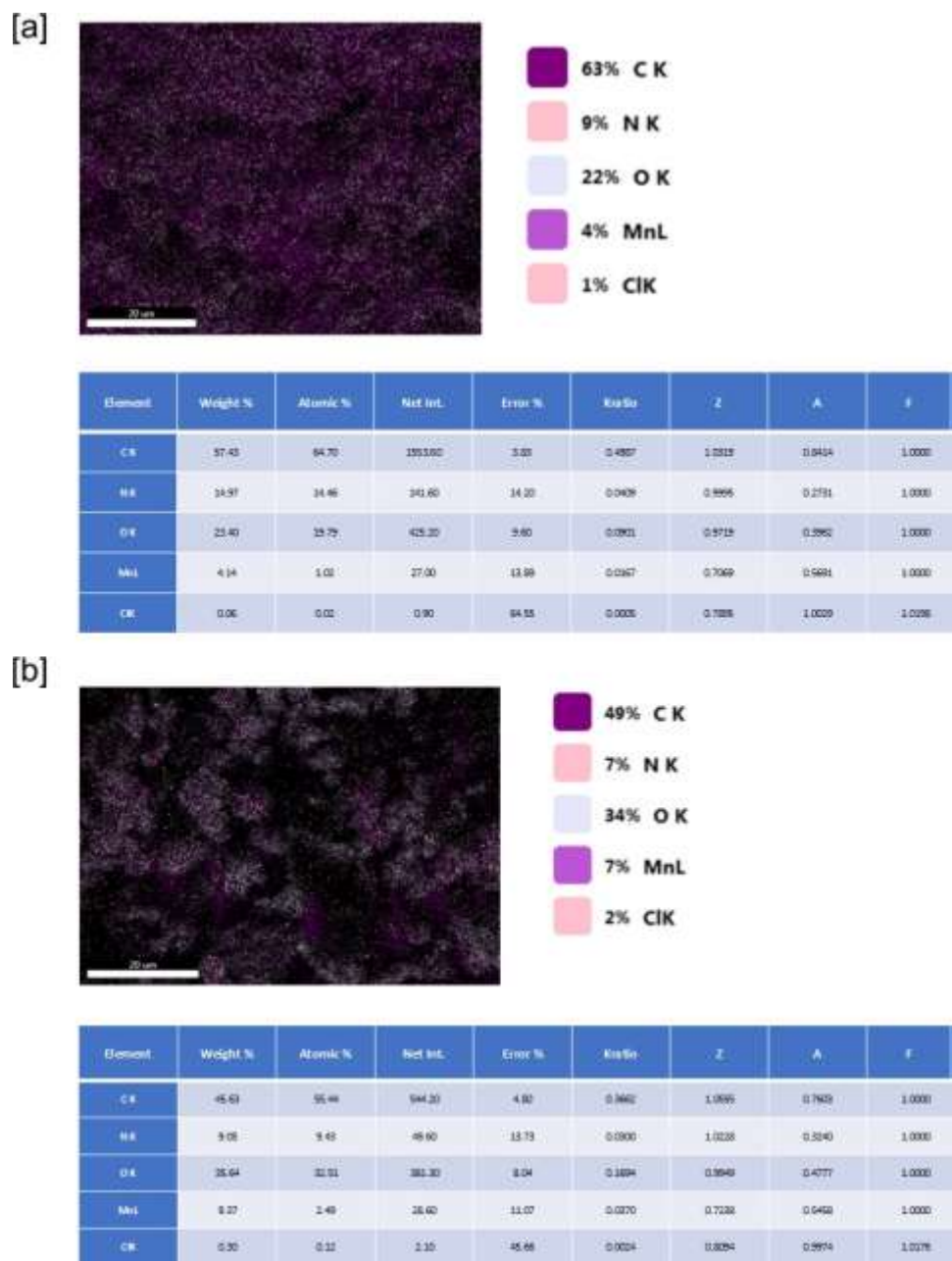


Figure S15. Elemental analysis for [a] post treated **gn-ipop-cl(MC)**, [b] post treated **gn-ipop-cl(ST)**

10. Literature reports on permanganate uptake

Table S1. Comparison of our polymer with the state-of-art materials with respect to the permanganate uptake capacity

Sl no.	Material	Uptake [g/g]	Reference
1	<i>Ocimum basilicum</i> Leaves Powder Modified by Zinc Chloride	0.7	[1]
2	powder of <i>Foeniculum vulgare</i> seeds	1.5	[2]
3	Zinc chloride modified sage leaves powder	0.9	[3]
4	Nitraria retusa leaves powder	0.3	[4]
5	Chemically modified Teucrium polium (Lamiaceae) plant	1	[5]
6	Neem leaves powder	1.06	[6]
7	Copper sulfide nanoparticles	1.25	[7]
8	Zinc oxide nanoparticles	0.05	[8]
9	EDTA-modified magnetic activated carbon nanocomposite	0.095	[9]
10	Ionic Viologen organic network	0.297	[10]
11	Pyridinium functionalized porous organic polymer	0.33	[11]
12	Ionic porous organic polymer	0.514	[12]
13	Bifunctional imidazolium functionalized ionic porous organic polymer	5.3	[13]
14	Guanidine based ionic porous organic polymer	9.4	This work

Reference:

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