Cellulose Acetate-nanoMOF Beads: A Safe, Sustainable and Scalable Solution for Lead Remediation in Complex Water Systems

Prathmesh Bhadane[ab], and Swaroop Chakraborty[a]*

[a]School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, B15 2TT, UK

[b]Materials Engineering, Indian Institute of Technology, Gandhinagar, India, 382355

*Corresponding author- s.chakraborty@bham.ac.uk

S1: Synthesis of BNMG-1 MOF

Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) [Sigma Aldrich] 1.619g in 12mL and 2-methylimidazole (2-MeIM) [Sigma Aldrich] 3.319g in 48mL were dissolved separately in ultrapure water, followed by mixing under vigorous stirring for 30 minutes. The resulting precipitate was washed with ultrapure water to remove unreacted residues, vacuum-dried at 60°C, and further activated at 110°C to remove residual solvents. The structural and compositional properties of the BNMG-1 MOF were confirmed via physicochemical characterization techniques.

S2: Equations:

- $$Adsorption\ Efficiency\ (RE)(\%) = \frac{C_0 - C_e}{C_0} \times 100$$ Eq. S1
- $$Adsorption\ capacity\ (q_e) = \frac{C_0 - C_e}{m} V$$ Eq. S2
- $$Distribution\ Coefficient\ (K_d) = \frac{C_0 - C_e}{C_e} \times \frac{V}{m}$$ Eq. S3
- Separation factor (SF)= $\frac{K_d(metal-1)}{K_d(metal-2)}$ Eq. S4

Where, C_0 and C_e (mg/L) represents initial and equilibrium concentration of the REE ion in supernatant respectively. m (g) is adsorbent mass, V (mL) is solution volume, K_d (mL/g).

Kinetics studies

Pseudo first-order kinetics:

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \qquad \text{Eq. S5}$$

Pseudo second-order kinetics:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad \text{Eq. S6}$$

Where, q_e and q_t represents the adsorption capacity at equilibrium and time t (mg/g), respectively. k_1 (min^{-1}) and k_2 (g $mmol^{-1}$ min^{-1}) represents parameters for kinetic rate constants for pseudo-first order and pseudo-second-order model, respectively.

Adsorption isotherm studies

Langmuir adsorption isotherm:

$$\frac{C_e}{Q} = \frac{C_e}{Q_{max}} + \frac{1}{k_L Q_{max}} \qquad \text{Eq. S7}$$

Freundlich adsorption isotherm:

$$log\ Q_e = log\ K_f + \frac{1}{n} log\ C_e \qquad \text{Eq. S8}$$

Where, Qmax and Qe represents the maximum (theoretical) and equilibrium adsorption capacity (mg/g) respectively, Ce is adsorbate concentration at equilibrium (mg/L), K_L (L/mg) and K_F (L/mg).

S3: Complex aqueous system

- Composition of Artificial Sea Water (ASW)

  NaCl (24.60 g); $NaHCO_3$ (0.180 g); KCl (0.670 g); $CaCl_2$(1.360 g); $MgSO_4.7H_2O$ (6.290 g), (pH- 7.5) (1L)

- Canal Water Sampling Location: The water samples were collected from the Selly Oak Railway Bridge, Birmingham, United Kingdom (B15 2TT). A recent dissertation by Wai-Chun Leung et al., titled "Environmental Inequality and Heavy Metal in Birmingham Canals: A Quantitative Analysis," provides comprehensive quantitative measurements of heavy metal ions in both the water and sediments of Birmingham Canals. A detailed report on the constituent elements of the canal water is included in the attached document, which was submitted on August 27, 2024. [https://www.cieh.org/media/mpjgbzni/birmingham-wai-leung.pdf]

  Some of the physicochemical parameters measured are as follows-

  pH- 7.8

  Conductivity- 600 μS/cm

Microbial load- was not measured.

Experimental Conditions: In an experiment where canal water was spiked with 10 ppm Pb(II), the measured concentration of lead was found to be 13.5 mg/L. The water also contained other coexisting ions, including sodium (Na(I)) at 48.9 mg/L, calcium (Ca(II)) at 148.6 mg/L, and magnesium (Mg(II)) at 32.9 mg/L.

Figures and Tables

Table S1: *EDS analysis of CA-BNMG-1 composite beads*

Element	Atomic %	Atomic % Error	Weight %	Weight % Error	Net Counts
C	50.7	0.6	18.6	0.2	12 168
N	9.5	0.8	4.1	0.3	1 269
O	0.0	---	0.0	---	0
Cu	39.0	0.3	75.8	0.6	65 052

Figure S1: *SEM-EDS analysis of CA-BNMG-1 composite beads with composition mentioned in Table S1.*

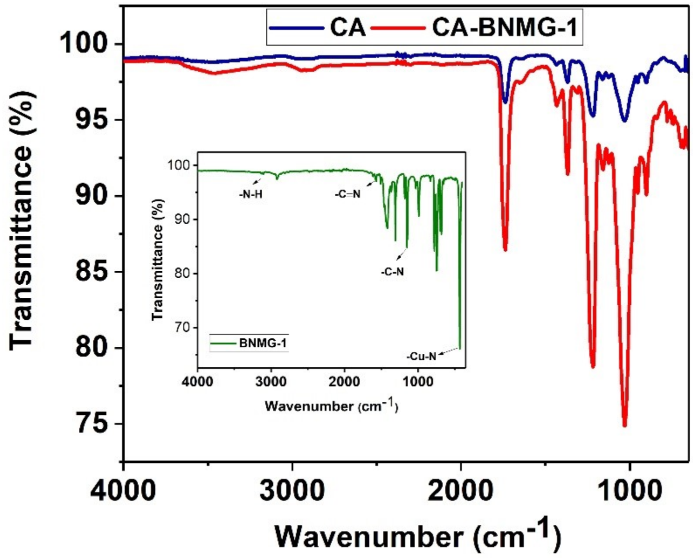


Figure S2: *FTIR analysis of BNMG-1, CA and CA-BNMG-1 composite beads*

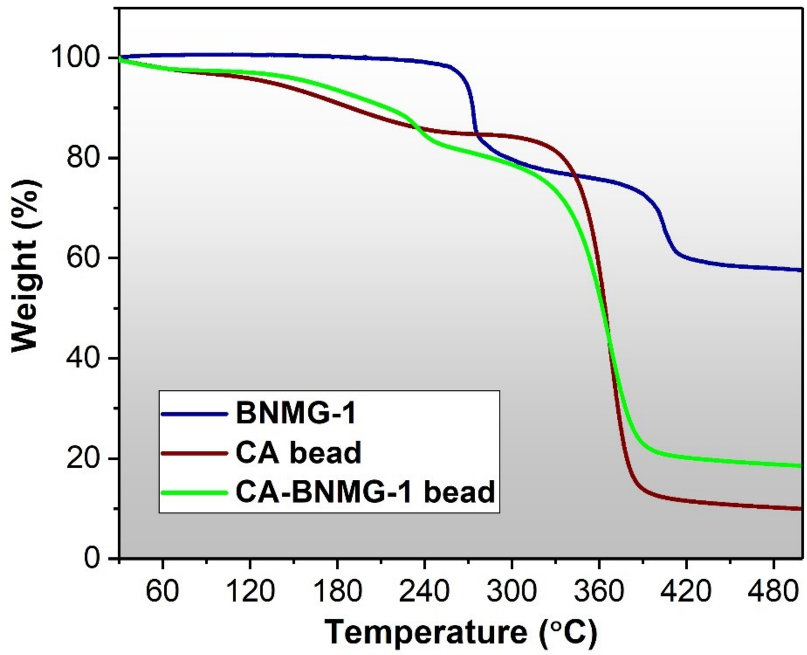


Figure S3*: TGA analysis of BNMG-1, CA and CA-BNMG-1 composite bead*

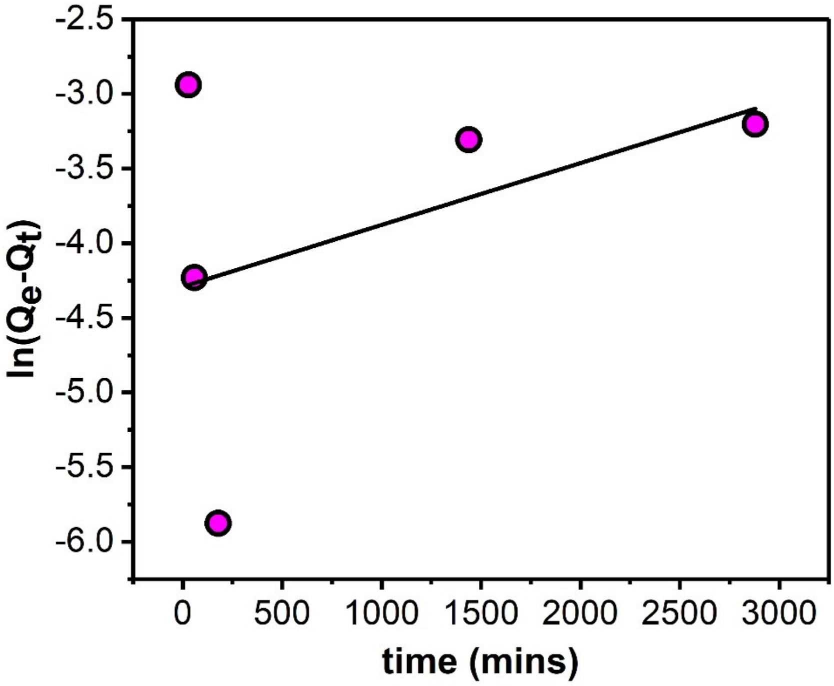


Figure S4: *Pseudo first order kinetics model fitting using adsorption kinetics data for composite bead using 10 mg/L Pb(II) aqueous solution with 5 beads/mL*

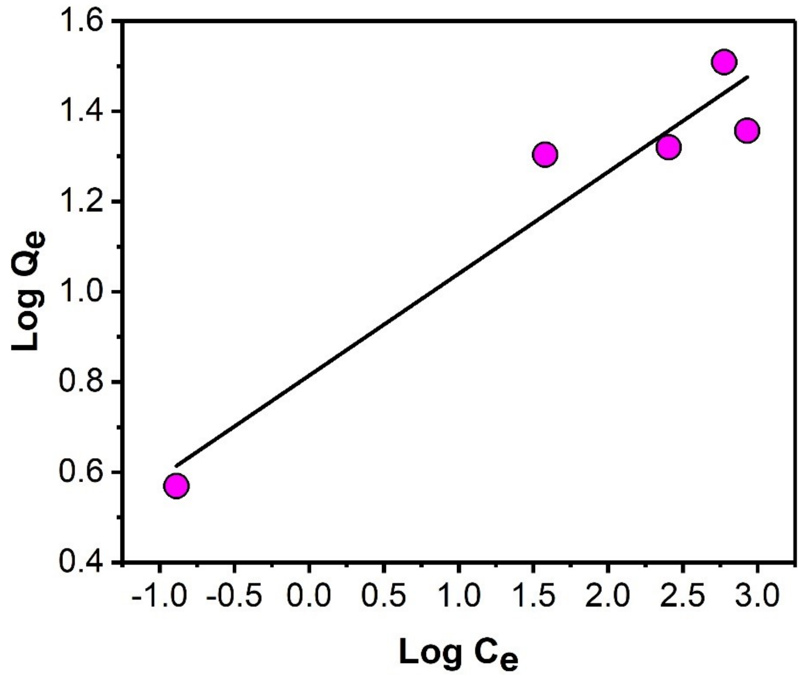


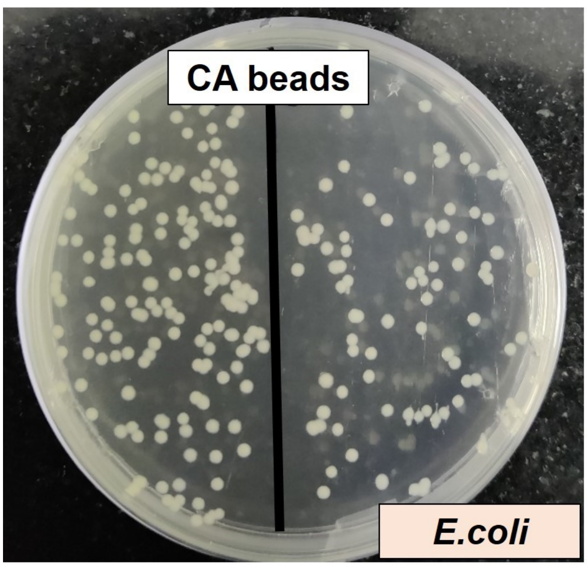
Figure S5: *Freundlich adsorption isotherm fitting using adsorption isotherm data obtained by varying Pb(II) concentration for constant adsorbent dosage*

Table S2: *Adsorption Kinetics and adsorption isotherm parameters for Pb(II) removal using CA-BNMG-1 beads.*

	Pseudo-first order			Pseudo-second order		
	K1 (min)	Qe (mg/g)	R^2	K2 {g/ (mg* min)}	Qe (mg/g)	R^2
Pb(II)	-4.14E(-4)	0.01368	0.18388	0.04579	0.807	0.99929
	Langmuir Model			Freundlich Model		
	Qmax (mg/g)	K_L (L/mg)	R^2	K_f (L/mg)	n	R^2
Pb(II)	24.9	0.87419	0.95101	6.5218	4.433	0.92638

S4: Antibacterial activity of CA-BNMG-1 composite beads:

The CA-BNMG-1 beads were immersed in 2 mL of mid-log phase E. coli (ATCC 25922), culture and incubated at 100 rpm for 6 hours. Pure cellulose acetate (CA) beads were used as a control. Following incubation, the culture medium was collected, serially diluted, and 20 µL of the diluted solution was spread onto Mueller-Hinton agar (MHA) plates. Each petri dish was divided into two sections, representing two replicates of the experiment. The plates were then incubated at 37°C for 16 hours, after which visible bacterial colonies were counted to assess bacterial viability. The results demonstrated >99% bacterial reduction, confirming the strong antibacterial activity of the CA-BNMG-1 beads. The antibacterial effect is attributed to Cu leaching, a well-established mechanism where Cu^{2+} ions disrupt bacterial membranes, induce oxidative stress via reactive oxygen species (ROS) generation, and inactivate intracellular enzymes, ultimately leading to cell death.



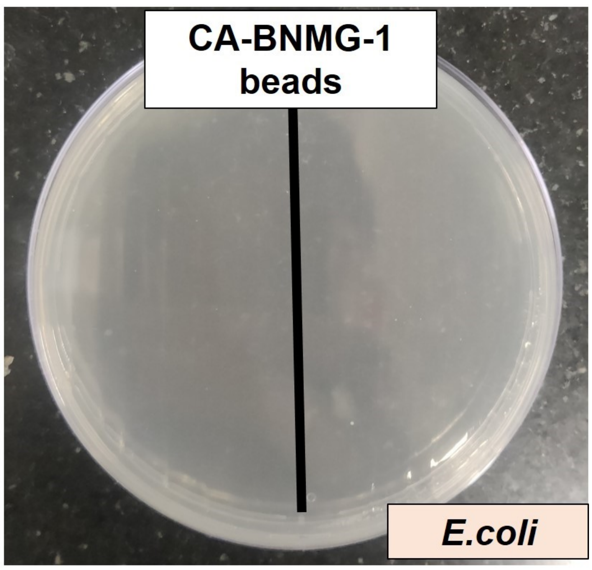


Figure S6. *Antibacterial activity of (a) CA beads and (b) CA-BNMG-1 beads against E. coli, showing >99% reduction in (b).*