

Supporting Information

Porous, pH Responsive, and Reusable Hydrogel Beads of Bovine Serum Albumin_Au Hybrid as Smart Nanofactories for the Removal of Organic and Inorganic Pollutants from Water: A Detailed Demonstration by Spectroscopy and Microscopy

Aekta Upadhyay and Chebrolu Pulla Rao*

Bioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai – 400 076, India, E-mail: cp Rao@iitb.ac.in

Contents

SI 01: Synthesis of BSA_Au NCs	S2
SI 02: Adsorption kinetics	S2
SI 03: Photograph of BSA, BSA_Au NCs and BSA_Au beads	S2
SI 04: TGA of <i>Bead_a</i> and <i>Bead_b</i>	S3
SI 05: Pore size distribution plot of <i>Bead_a</i> and <i>Bead_b</i>	S3
SI 06: Mapping of different elements of lyophilised <i>Bead_a</i> by SEM	S3
SI 07: Mapping of different elements of <i>Bead_a</i> dispersed in water by STEM	S4
SI 08: Time dependent UV-Visible spectra of supernatant solution of dyes upon incubation with <i>Bead_a</i>	S4
SI 09: Table showing the adsorption kinetic parameters	S4
SI 10: Kinetics and isotherm fitting for <i>Bead_a</i> @ EY.	S5
SI 11: Time dependent adsorption spectra of R6G and MB by <i>Bead_b</i>	S5
SI 12: Adsorption kinetics parameters for <i>Bead_b</i> @ MB and <i>Bead_b</i> @R6G	S5
SI 13: Langmuir and Freundlich isotherm fitting for <i>Bead_b</i> @ MB	S6
SI 14: Desorption of EY and MB from <i>Bead_a</i> and <i>Bead_b</i> at different temperatures	S6
SI 14: UV-Vis spectra of EY and MB before and after passing through column set-up	S6
SI 15: Maximum adsorption capacity of Pb ²⁺ , Cd ²⁺ and Hg ²⁺ by <i>Bead_b</i>	S7
SI 16: Maximum adsorption capacity of KMnO ₄ , K ₂ PdCl ₄ and HAuCl ₄ by <i>Bead_a</i>	S7

SI 01: Synthesis of BSA_Au NCs: In 20 ml vial, 100 mg/ml BSA was dissolved in 5 ml water. To this solution, five ml of (50 mM) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was dropwise added under stirring at 450 rpm. The solution was kept under stirring at room temperature for 10 minutes and thereafter dropwise addition of 1 M NaOH was done to make the pH of the solution 12. The solution was stirred for another 48 hours at RT to form a dark red colour solution. The solution was stored at 4°C and characterised.

SI 02: Adsorption kinetics: Different terms used

$$q = \frac{C_0 - C_t}{M} \times V \left(\frac{\text{mg}}{\text{g}} \right)$$

Adsorption capacity (q)

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$

Pseudo first order rate kinetics

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Pseudo second order rate kinetics

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

Langmuir isotherm

$$\ln q_e = \ln k_f + \ln \frac{C_e}{n}$$

Freundlich isotherm

SI 03: Photograph of BSA, BSA_Au NCs and BSA_Au beads under visible and UV light

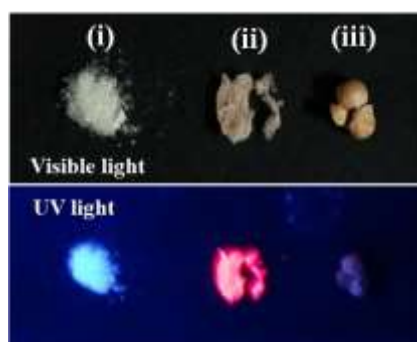


Figure S1: Photograph of (i) only BSA, (ii) lyophilised BSA_Au NC and (iii) lyophilised Bead_a under visible and UV light.

SI 04: TGA of *Bead_a* and *Bead_b*

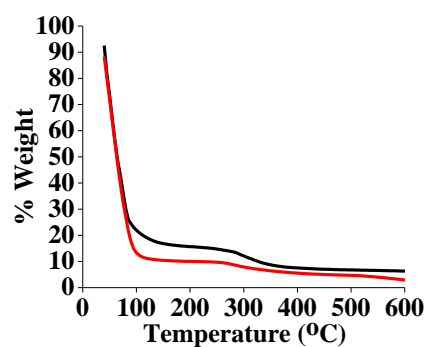


Figure S2: TGA of *Bead_a* (Black) and *Bead_b* (Red).

SI 05: Pore size distribution plot of *Bead_a* and *Bead_b*

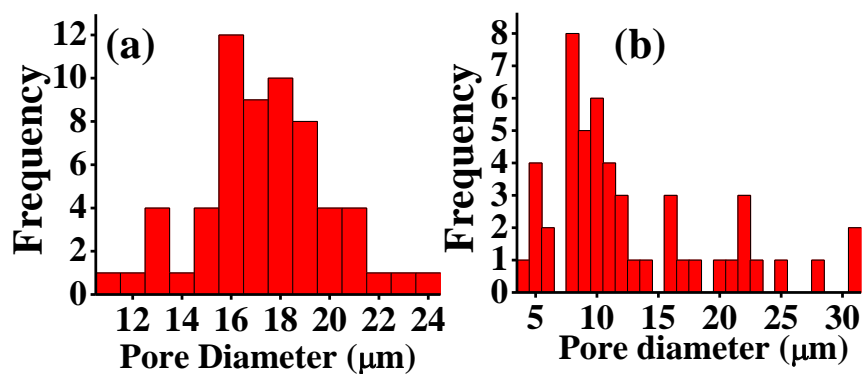


Figure S3: Pore size distribution plot of (a) *Bead_a* and (b) *Bead_b* calculated by imageJ software from SEM micrograph.

SI 06: Mapping of different elements present in lyophilised *Bead_a* by SEM



Figure S4: Mapping of different elements present in lyophilised *Bead_a* by SEM

SI 07: Mapping of elements present in *Bead_a* by STEM

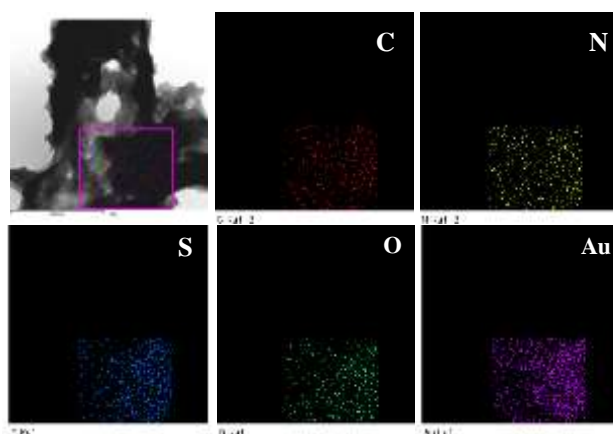


Figure S5: Mapping of elements present in *Bead_a* by STEM.

SI 08: Time dependent UV-Visible spectra of supernatant solution of dyes upon incubation with *Bead_a*.

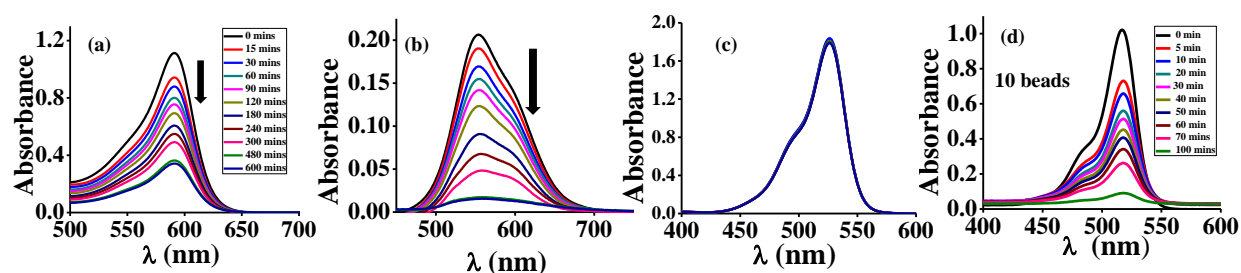


Figure S6: UV Visible spectrum of (a) BB, (b) CBB and (c) R6G when 1 bead is used and (d) EY when 10 beads are used as adsorbent.

SI 09: Table showing the adsorption kinetic parameters by *Bead_a*.

Dyes	First order			Second order		
	R ²	K ₁	q _{cal} (mg/g)	R ²	K ₂	q _{cal} (mg/g)
EY	0.96	4.6 x 10 ⁻³	127.46	0.97	8.6 x 10 ⁻⁵	175.43
BB	0.938	6.9 x 10 ⁻³	168.15	0.978	5 x 10 ⁻⁵	194.93
CBB	0.876	9.6 x 10 ⁻³	328.1	0.95	1.4 x 10 ⁻⁵	313.47

Table S1: R², K₁, K₂ and q_{cal} for *Bead_a* adsorbed dyes (EY, BB and CBB).

SI 10: Kinetics and isotherm fitting for *Bead_a*@EY.

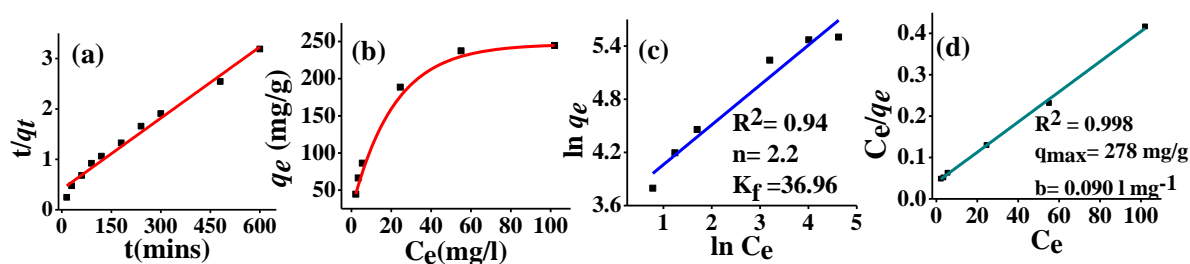


Figure S7: (a) Pseudo second order fit for *Bead_a*@EY. (b) Plot of q_e versus C_e for adsorption of EY by *Bead_a*. (c) Freundlich and (d) Langmuir isotherms fit for adsorption of EY by *Bead_a*.

SI 11: Time dependent adsorption spectra of R6G and MB upon incubation by *Bead_b*

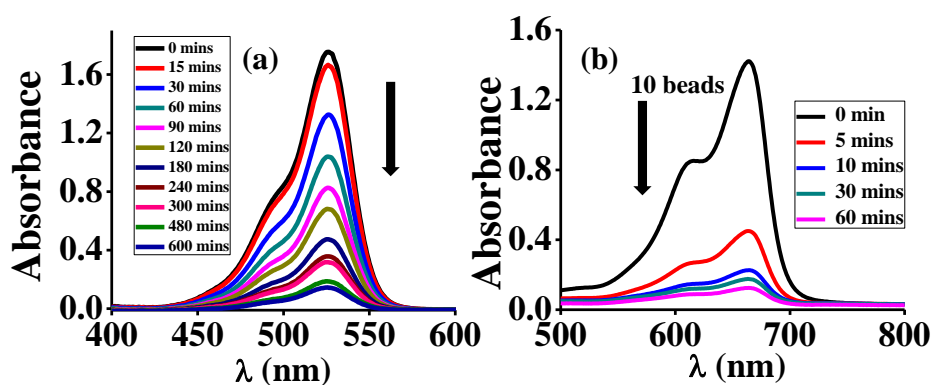


Figure S8: UV-Visible spectrum of supernatant of (a) R6G with respect to time when incubated with one *Bead_b* and (b) MB when incubated with 10 beads.

SI 12: Adsorption kinetics parameters for *Bead_b*@ MB and *Bead_b*@R6G.

Dyes	First order			Second order		
	R^2	K_1	q_{cal} (mg/g)	R^2	K_2	q_{cal} (mg/g)
MB	0.98	6.6×10^{-3}	184.92	0.998	3.6×10^{-5}	333
R6G	0.987	7.6×10^{-3}	171.85	0.988	3.6×10^{-5}	227

Table S2: R^2 , K_1 , K_2 and q_{cal} for *Bead_b* @ MB and *Bead_b* @ R6G

SI 13: Langmuir and Freundlich isotherm fitting for *Bead_b* @ MB.

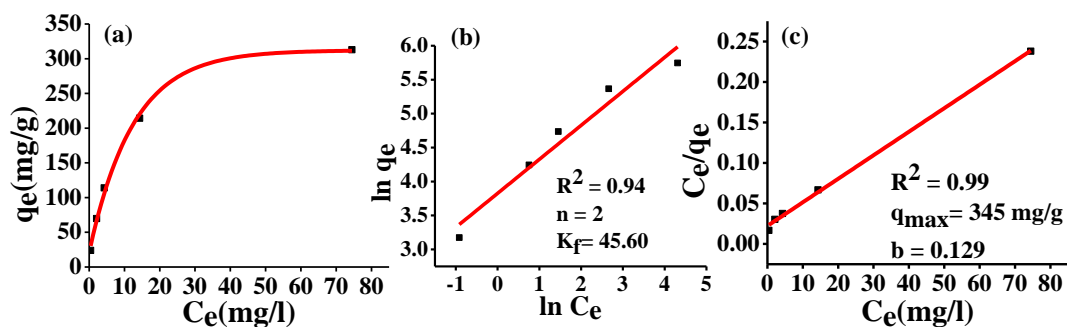


Figure S9: (a) Plot of q_e versus C_e for adsorption of MB by *Bead_b*. (b) Freundlich and (c) Langmuir isotherms for adsorption of MB by *Bead_b*.

SI 14: Desorption of EY and MB from *Bead_a* and *Bead_b* at different temperatures

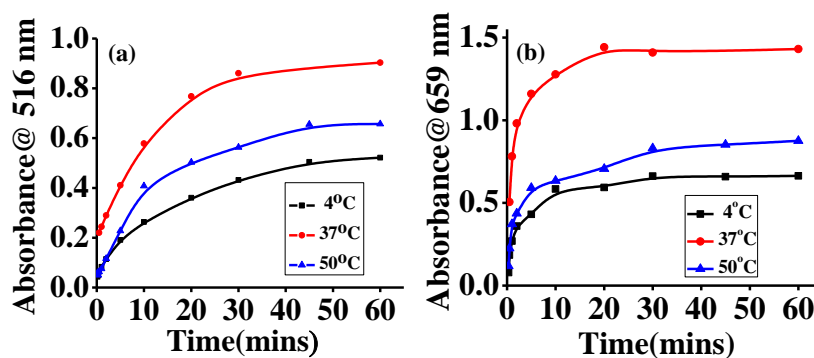


Figure S10: Plot of λ_{\max} of corresponding dye versus time taken for desorption at different temperature in case of (a) EY (from *Bead_a*) and (b) MB (from *Bead_b*).

SI 15: UV-Vis spectra of EY and MB before and after passing through column set-up.

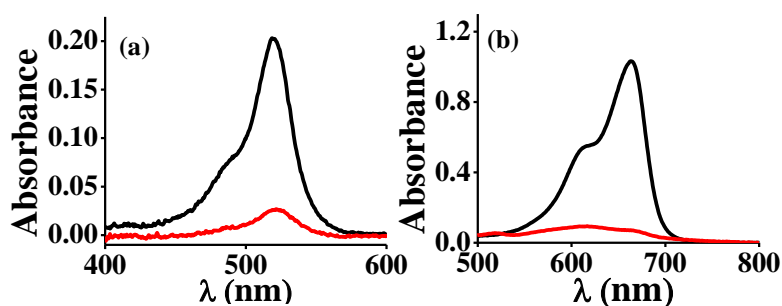


Figure S11: UV-Vis spectra of (a) EY and (b) MB before (Black line) and after (Red line) being adsorbed by beads.

SI 16: Maximum adsorption capacity of Pb^{2+} , Cd^{2+} and Hg^{2+} by *Bead_b*

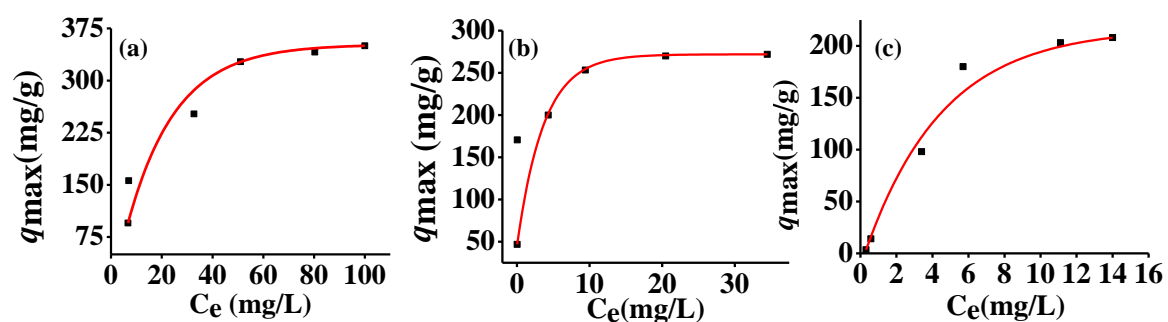


Figure S12: Plot of q_{max} versus C_e for (a) Cd^{2+} , (b) Pb^{2+} and (c) Hg^{2+}

SI 17: Maximum adsorption capacity of KMnO_4 , K_2PdCl_4 and HAuCl_4 by *Bead_a*

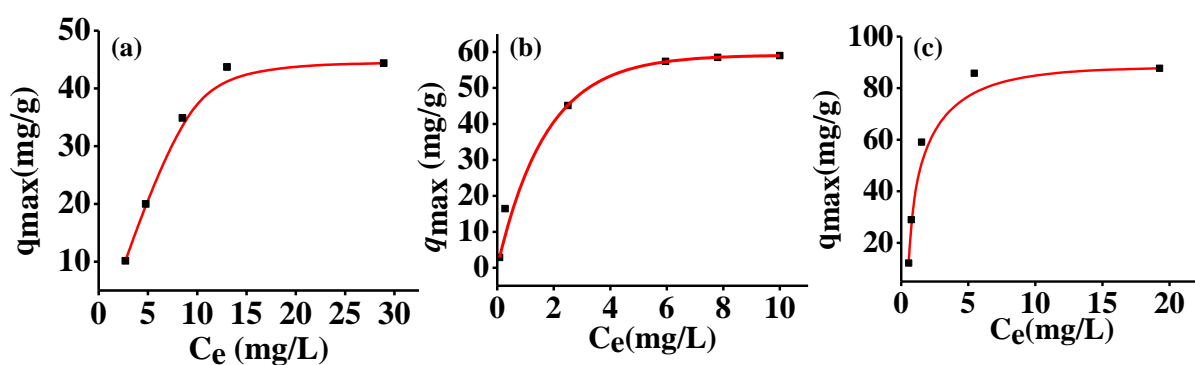


Figure S13: Plot of q_{max} versus C_e for (a) KMnO_4 , (b) K_2PdCl_4 and (c) HAuCl_4