Facile design of dextran derived polyurethane hydrogel & metallopolymer: sustainable approach for elimination of organic dyes and reduction of nitrophenols

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1.1 Protocol for assessment of adsorption

Briefly, known amount of dried hydrogel were immersed in distilled water to attain equilibrium swelling state. The swollen hydrogel was then added into 50 mL of aqueous dye solutions of predetermined concentrations (50, 100, 150, 200 and 250 mg L^{-1}) under stirring at room temperature for 24 hours. To determine the optimum amount of hydrogel to be used for further experiments different quantities of hydrogel (25, 50, 100, 150, 200mg) were added to 100mg L^{-1} of MB and MO solution respectively. For pH variation study 100 mg L^{-1} of dye solutions with different pH values were prepared and 100 mg of hydrogel was added to determine the fate of adsorption. The pH adjustments were done using NaOH and HCl solutions.

Using the optimized conditions kinetics experiments were performed at different time intervals. The effect of temperature on adsorption was also determined by performing the experiments at 35 °C and 45°C. For quantification of adsorption, supernatants were collected by

filtration after each set of adsorption experiment and measured using UV-Vis spectrophotometer (wavelength scan range: 200-800 nm) at λ_{max} = 664 for MB and λ_{max} = 460 for MO. The volume of supernatant removed is replenished by same volume of fresh dye solution to maintain uniform concentration of dye throughout the experiments. All the experiments were conducted in triplicate and mean values have been reported. The adsorption capacity, removal percentage and adsorption at particular time‘t’ were calculated using the formula:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad \text{--------- (3)}$$

$$\%R_e = \frac{C_0 - C_e}{C_e} \times 100 \quad \text{--------- (4)}$$

$$q_t = \frac{C_t - C_e}{m} \times V \quad \text{--------- (5)}$$

where q_e is the adsorption capacity (mg/g), %Re denote removal efficiency and q_t represents the adsorption capacity at particular time ‘t’ (mg/g); $C_0$is the initial concentration(mg L^{-1}), C_e is equilibrium concentrations (mgL^{-1}) and C_t denotes concentration at time ‘t’(mg L^{-1}) of dyes in aqueous solution; ‘V’ represent the volume of dyes solution (L); and ‘m’ denotes the weight of the hydrogel (g).

1.2 Protocol for determining the swelling characteristics

1.2.1 Swelling Kinetics

100 mg air dried uniformed sized hydrogel was weighed and immersed in distilled water. Swollen gels were withdrawn from water and excess of solvent on surface was wiped off using tissue paper and weighed at predetermined time intervals. Weight determination was carried out upto the attainment of constant weight. Equilibrium Water Absorbency (EWA) was calculated using the formula:

$$WA = \frac{W_t - W_0}{W_0} \quad \text{-------- (1)}$$

Where, W_0 (mg) and W_t (mg) are the weight of dry and swollen hydrogel samples.

1.2.2 pH and salt sensitivity

100 mg of dried hydrogel sample was immersed in buffer solution of different pH (2-12) at room temperature for assessment of pH dependent EWA. The pH values of buffer solutions were adjusted using 1 mol L^{-1} NaOH and 1 mol L^{-1} HCl. The equilibrium water absorbency was calculated using equation (1) at each pH value. Different concentration of KCl solution (0.2, 0.6, 1.0 wt %) was used to determine water uptake ability of hydrogel in salt solution using the same method.

1.2.3 Water Retention Capacity

To study the water retention capacity of the hydrogel at equilibrium known amount of air dried hydrogel sample was kept in distilled water for one day. Swollen hydrogel was removed and weighed at regular time interval to investigate water retention capacity. Water retention ratio was calculated using the formula:

$$WR(\%) = \frac{(W_t - W_0)}{(W_e - W_0)} \times 100 \quad \text{---------- (2)}$$

Where, $\mathbf{W_0}$ is the weight of initial dried hydrogel, $\mathbf{W_e}$ is the weight of swollen hydrogel at equilibrium and $\mathbf{W_t}$ is the weight of swollen hydrogel at time‘t’.

FIGURES

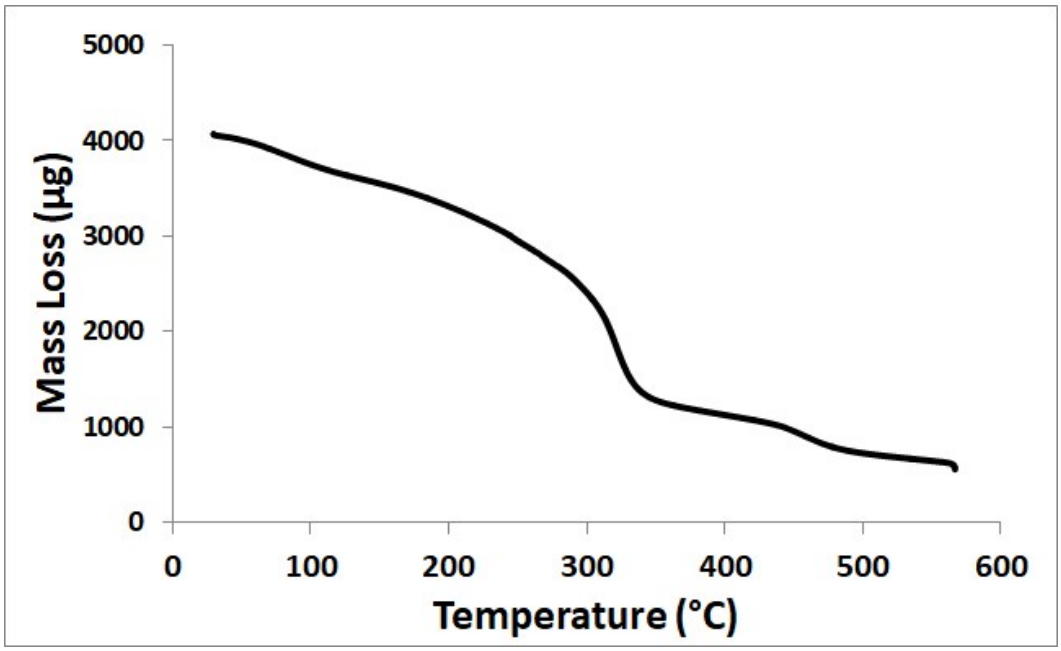

Figure S1: Thermogravimetric Curves for Hydrogel

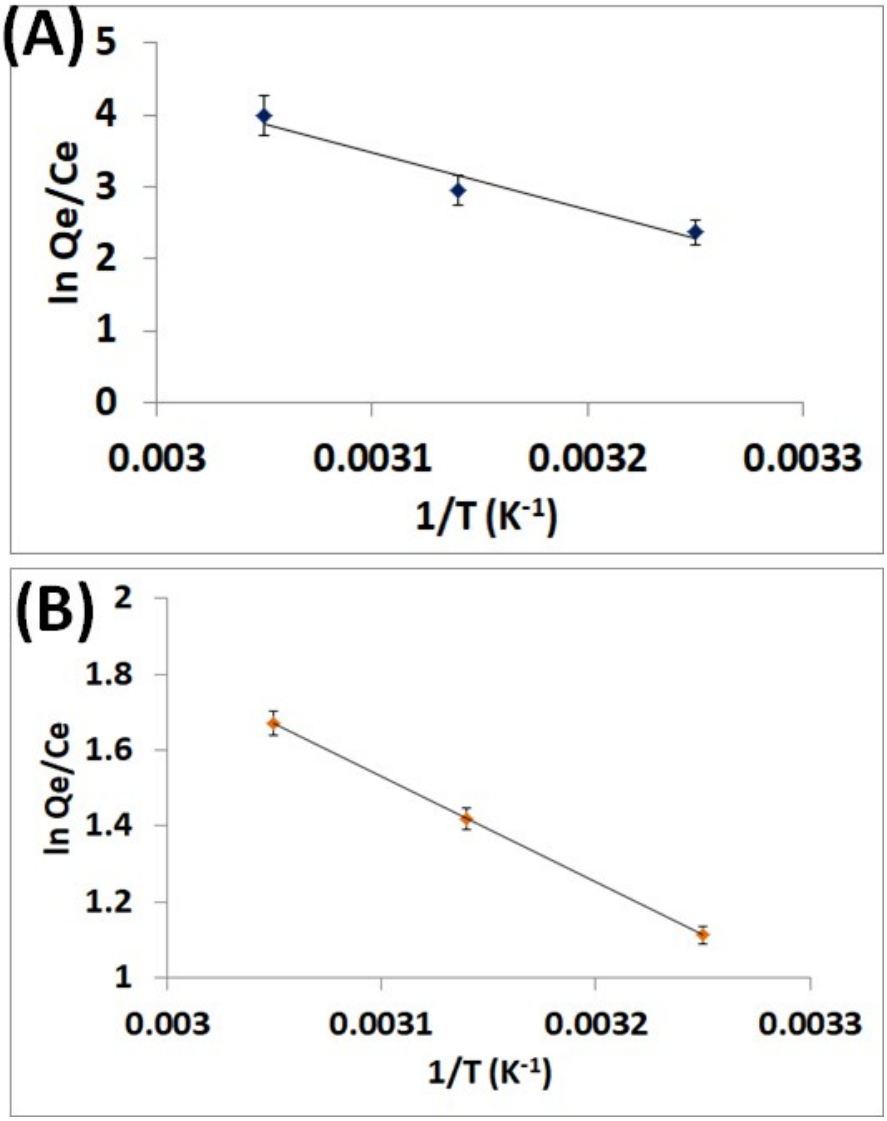

Figure S2: Thermodynamic plot for removal of (A) MB and (B) MO using hydrogel

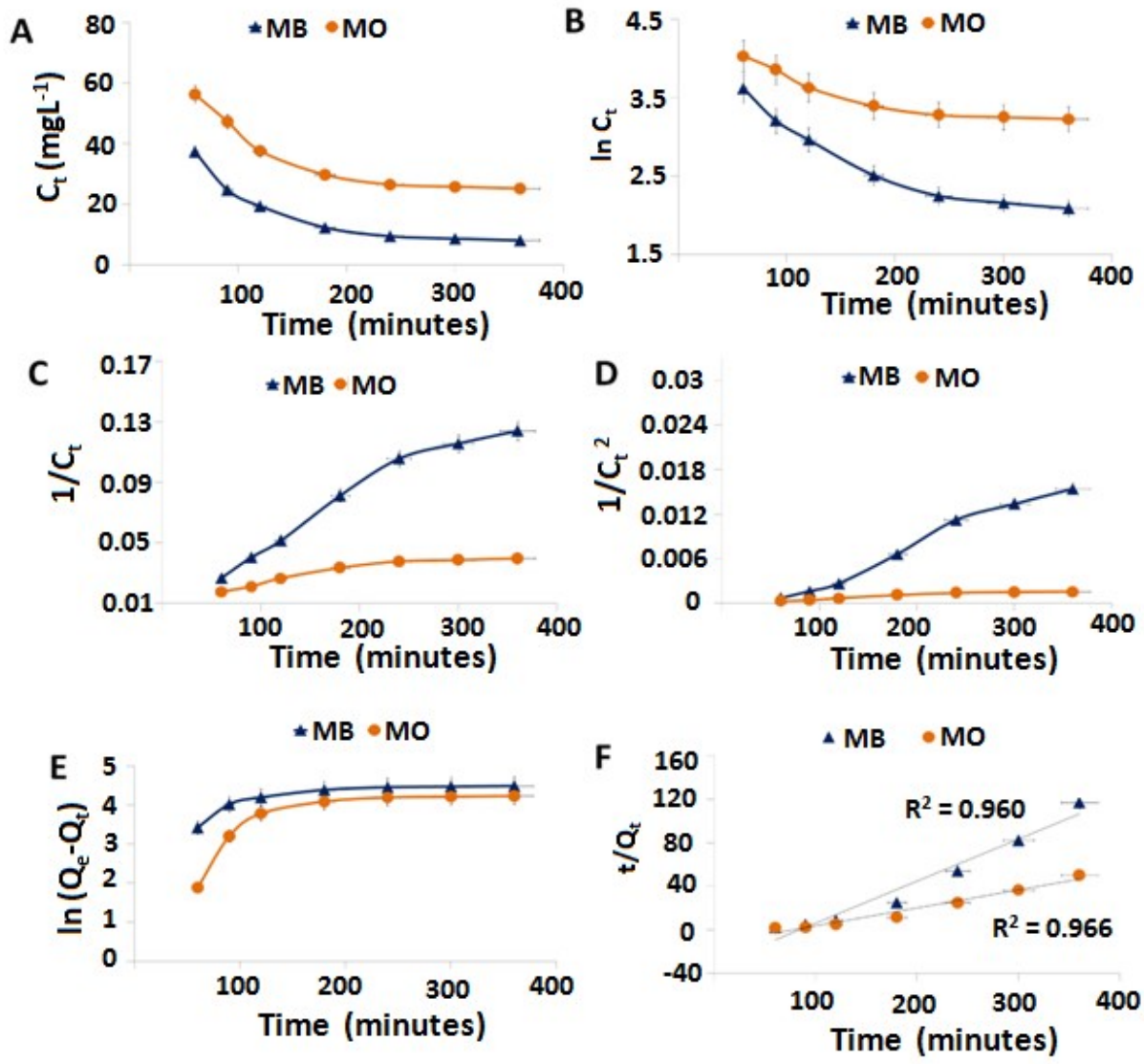

Figure S3:Graphs of (A)zero (B)first (C) second (D) third (E) pseudo first (F) pseudo second order kinetic models for adsorption of MB and MO on hydrogel (conditions: initial concentration 100 mgL^{-1}, adsorbent dosage 0.1g at room temperature)

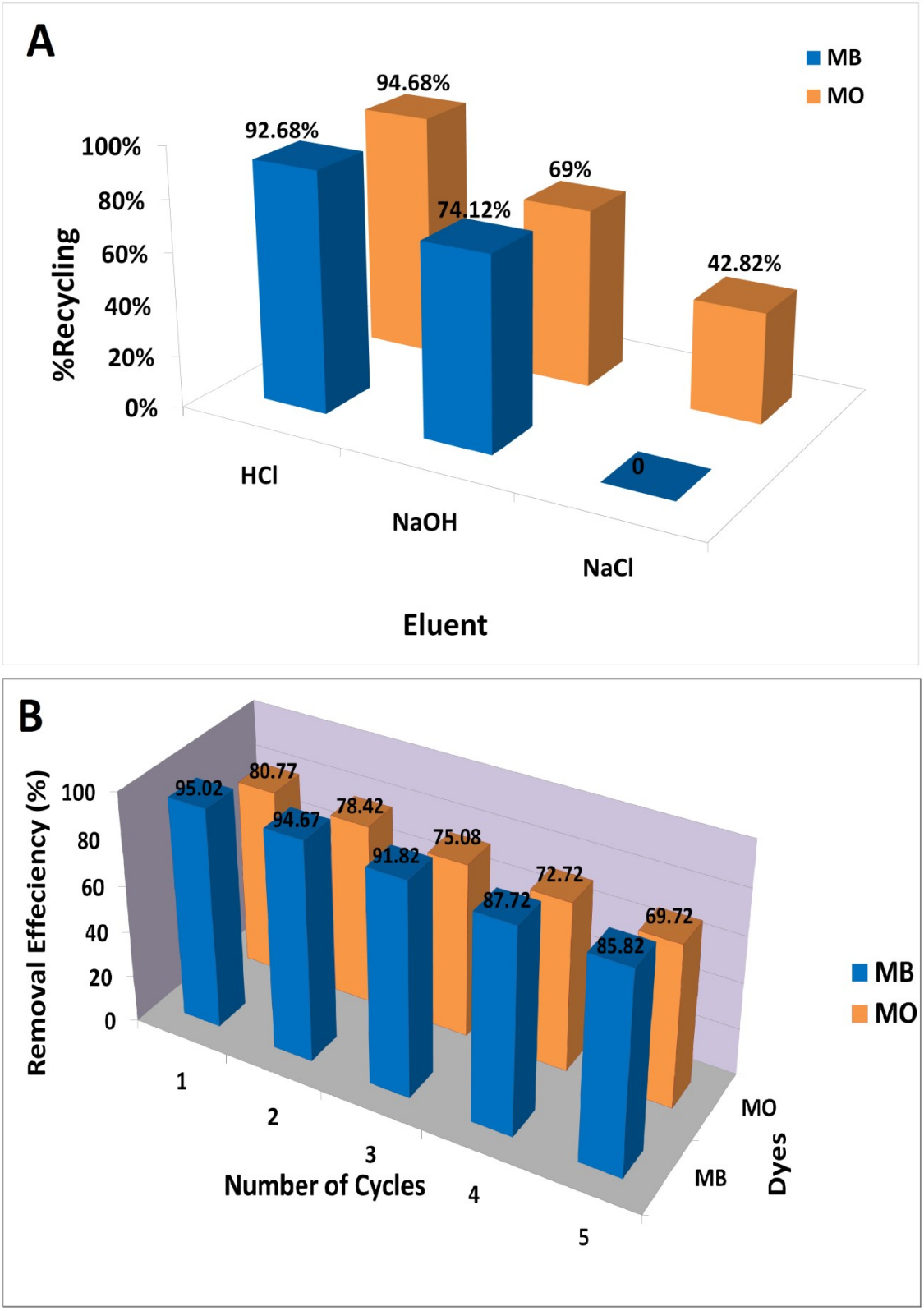

Figure S4: (A) Studies for desorption of dyes in different eluents (B) assessment of recyclability of the hydrogel

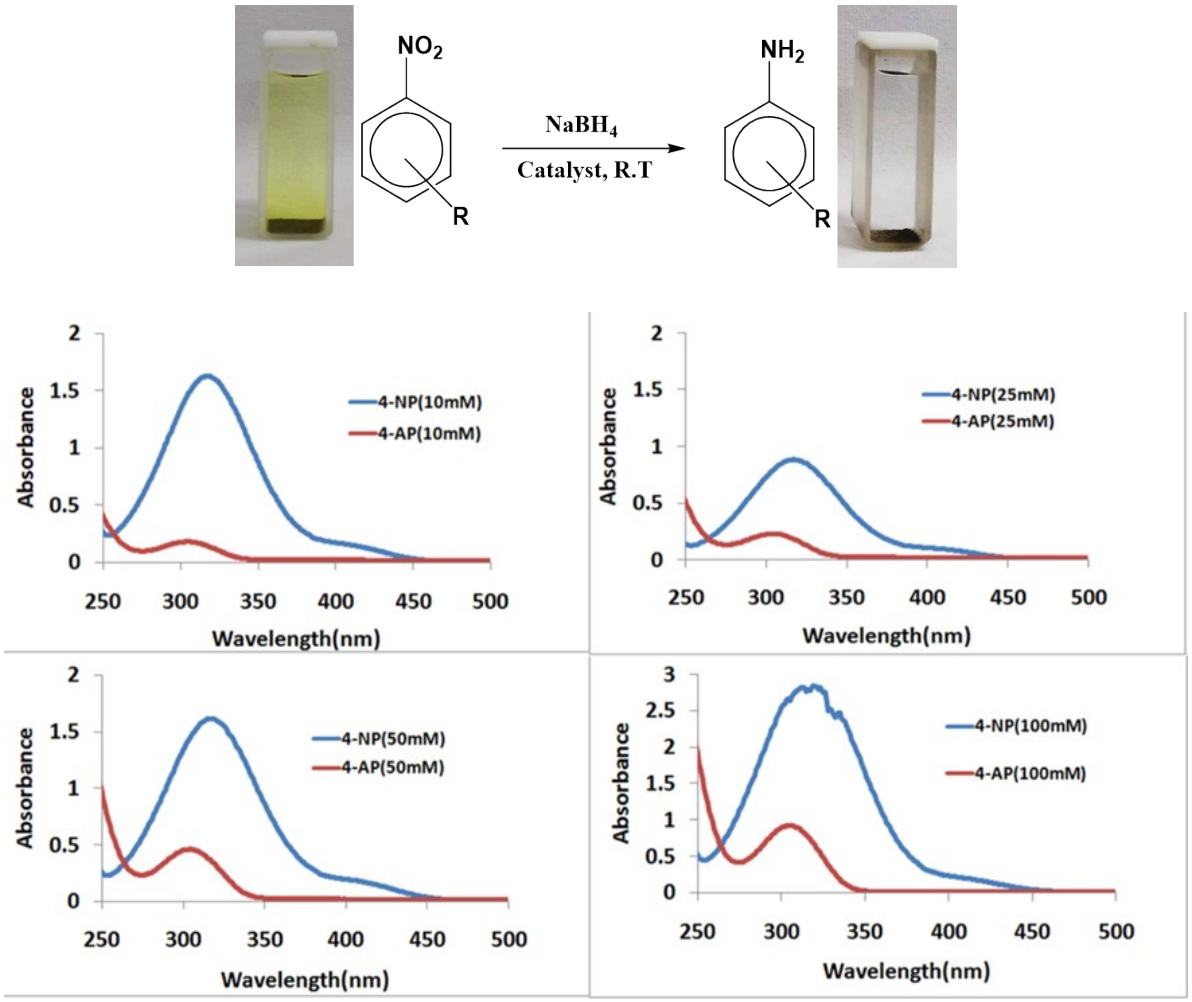

Figure S5: General scheme for the reduction of nitroaromatics and UV-vis spectrophotometric determinations for reduction of varying concentrations of 4-NP using Ag@Hydrogel

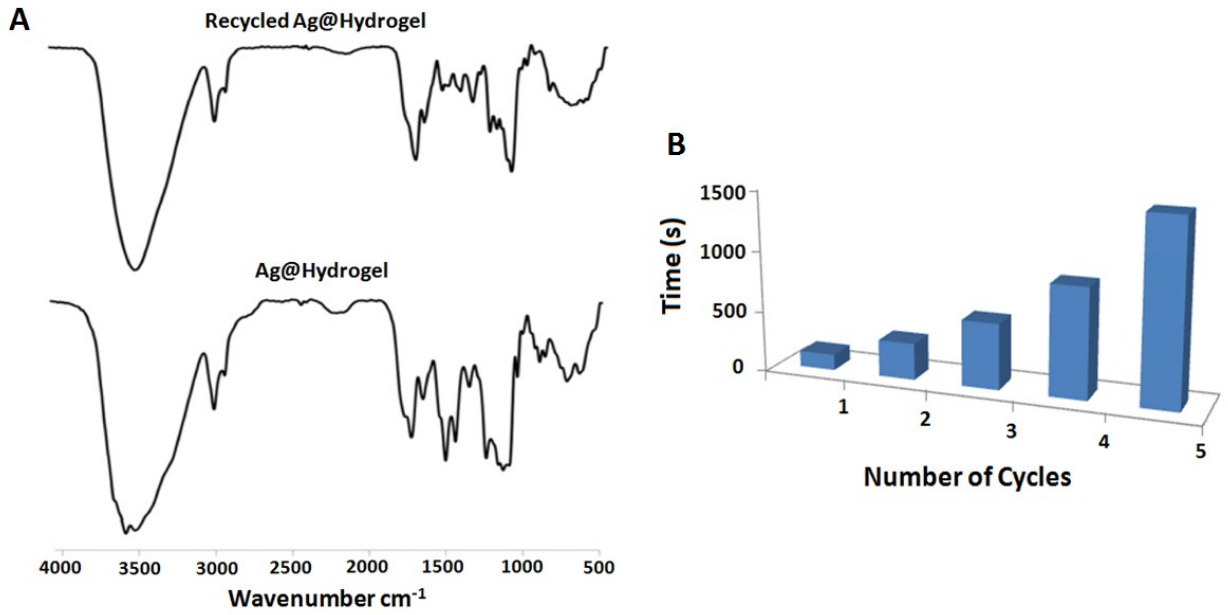

Figure S6: (A) FT-IR overlay of fresh and recycled metallopolymer (B) Recycling studies

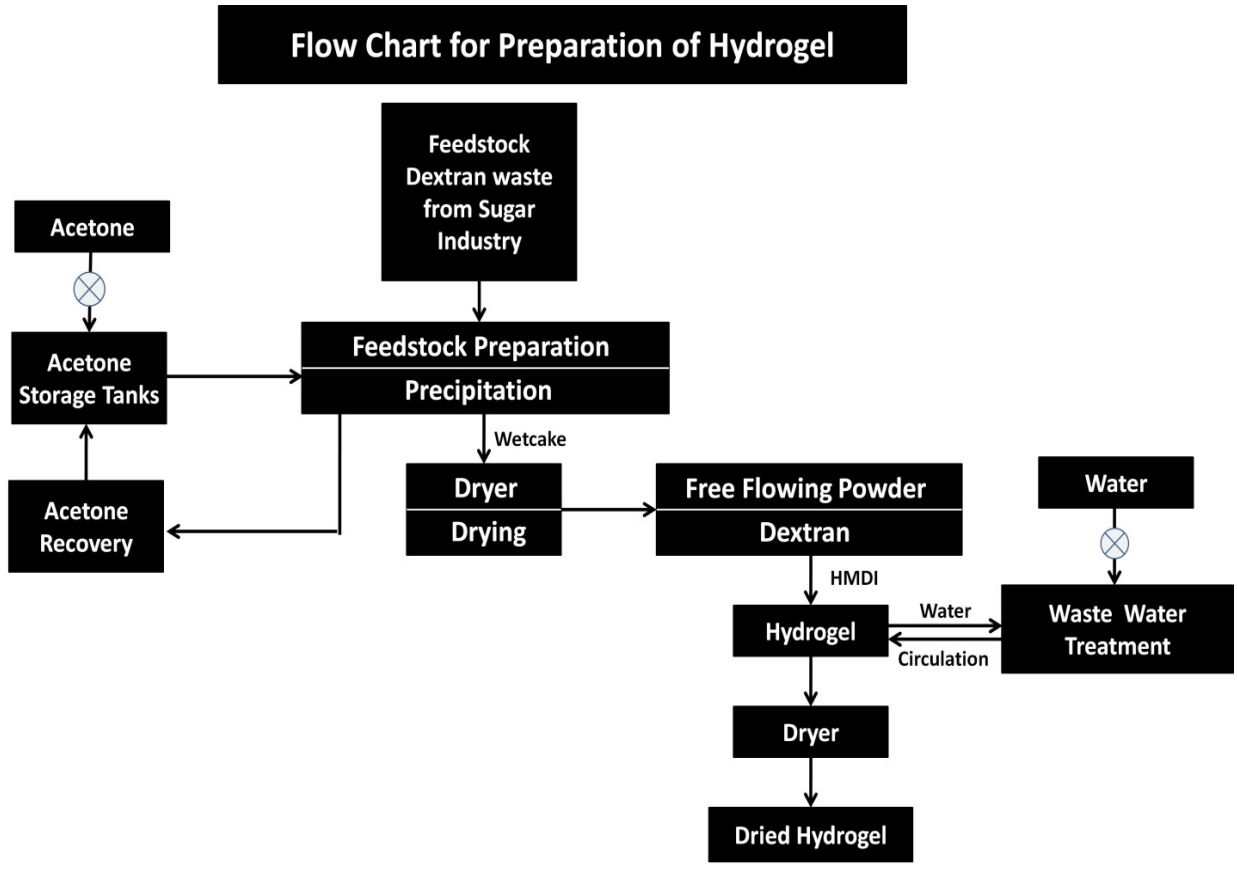

Figure S7: Process flow diagram for commercial production of dextran derived Hydrogels

TABLES

Table S1: Elemental Composition of Recycled Hydrogel following Adsorption/Desorption Cycle

Material	C (wt-%)	N (wt-%)	O (wt-%)	Na (wt-%)	S (wt-%)	Cl (wt-%)
Hydrogel +MB	*51.90*	*2.74*	*45.23*	*0*	*0.11*	*0.02*
Hydrogel +MO	*54.83*	*0.67*	*44.26*	*0.10*	*0.14*	*0*

Table S2: Comparison of Removal Efficiencies of Hydrogel with Literature Reports:

Sr. No	Adsorbent	Dye	Concentration	Q_e	Reference
1	DexG (Amphiphilic Cationic Dextran hydrogel)	Methyl Orange	*1.5* mM	*650-730* mg/g	[49]
2	Alg/PASAP (alginate/polyapartate hydrogel beads)	Malachite Green,Methylene Blue,MethylOrange	*10* mg/L	*600-700* mg/g MB, *300-350* mg/g MG	[47]
3	Poly (N-isopropylacrylamide/ Acrylic Acid/N-allylisatin) hydrogel nanoparticles	Methylene Blue (300mg L-1), AuramineO(200 mg L-1), Chrysoidine G (150mg L-1)	*250* mg/L	*584* mg/g	[50]
4	poly(acrylic acid) (PAA)-based super-adsorbent nanocomposite Hydrogel	Methylene Blue	*100* mg/L	*2000* mg/g	[28]
5	Salecan/PAD hydrogels	Methyl Orange	*10* mg/L	*56.2* mg/g	[17]
6	Supramolecular Complex of Graphene Oxide and Sulfonatocalix[4]areneHydrogel	Methyl Orange	*20*mg/L		[2]
7	Graphene/Chitosan based Hydrogel	Congo Red (CR)	*100* mg/L	*356* mg/g	[51]
8	GO-hydrogel porous nanocomposites	Methylene Blue	*100* mg/L	*714.29* mg/g	[52]
9	graphene oxide/sodium alginate/ polyacrylamide nanocomposite hydrogel	Methylene Blue Methyl Orange		*2.62* mg/g, *1.24* mg/g	[53]
10	Sodium alginate poly itaconic acid (NaAlg/IA) hydrogel	Methylene Blue	*80* mg/L	*12.77* mg/g	[54]
11	β – Cyclodextrin-	Nickel,	*100* mg/L	*18.6* mg/g	[55]

	Cellulose / Hemicellulose-Based Hydrogels	Cadmium		*42* mg/g	
12	Magnetic bentonite/ carboxymethyl chitosan/sodium alginate hydrogel beads	Copper	*50* mg/L	*56* mg/g	[56]
13	Dextran Hydrogel	Methylene Blue, Methyl Orange	*100*mg/L	*98* mg/g *84* mg/g	This Work

Table S3: Elemental Composition of Ag@Hydrogel

Material	C (wt %)	N (wt %)	O (wt %)	Ag (wt %)
Hydrogel	*50.67*	*0*	*49.33*	*0*
Ag@Hydrogel	*43.55*	*2.99*	*42.93*	*10.93*

Table S4: Reduction of 4-NP at Different Concentrations using Ag@Hydrogel as Catalyst

Sr.no	Quantity of Ag@hydrogel (mg)	Concentration of 4-Nitrophenol (mM)	Time (s) At room temperature	Time (s) In presence of sunlight
1	*10*	*10*	*21*	*10*
2		*25*	*55*	*40*
3		*50*	*85*	*48*
4		*100*	*130*	*52*

Reaction conditions: All the reactions were carried using 50 µL of 0.1 M 4-NP, $5x10^{-3}$M $NaBH_4$.