

Underwater superoleophobic and magnetic hydrogel for cascade chemical reactions

Experimental Section

Materials:

The following chemicals were purchased from Sigma Aldrich (Bangalore, India): branched polyethylenimine (BPEI, M_n : 25,000 Da), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, molecular weight: 207.25 g/mol), poly(ethylene glycol) diacrylate (PEGDA, average M_n 575), α -Ketoglutaric acid (molecular weight: 146.10 g/mol), acrylamide (AAm, molecular weight: 71.08 g/mol), vanillin (molecular weight: 152.15 g/mol), and propylamine (molecular weight: 59.11 g/mol). Ferric chloride anhydrous ($FeCl_3$) was obtained from Research Lab Fine Chem Industries, and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) from Merck Specialties Private Limited. Alfa Aesar, India provided methanol, acetone, and dichloroethane. Sodium hydroxide, sodium chloride, sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB) were supplied by Emparta (Merck Specialties Pvt. Ltd.). $NaBH_4$ was purchased from Spectrochem Pvt. Ltd. Milli Q purified water was used for all syntheses. Neodymium alloy magnet (100 mT) was purchased from Amazon India Pvt. Ltd.

Characterization:

The FTIR-ATR (Fourier transform infrared attenuated total reflectance) spectra were recorded in Perkin Elmer spectrometer equipped with ZnSe ATR accessory. Scanning electron microscopic images of hydrogel samples were taken using a field emission scanning electron microscope (FESEM, Sigma Carl Zeiss). Freeze dried samples were coated with a thin layer of gold prior to FESEM imaging. LABCONCO 4.5 lyophilizer was used to freeze dry the hydrogel samples. The high-resolution transmission electron microscopic (HRTEM) images, corresponding selected area diffraction (SAED) and inverse fast Fourier transition (IFFT) micrograph were recorded using FETEM (JEOL, Model :2100F). Very thin slice of swelled hydrogel was casted on the TEM copper grid and then dried prior to image acquisition. The X-ray diffraction studies (XRD) of the as-prepared magnetic hydrogels were performed using Philips-PW1800 X-ray diffractometer, utilizing $Cu K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) in thin film mode. The KRUSS Drop Shape Analyzer-DSA25 equipment with an automatic liquid dispenser was used to measure the contact angle under ambient lighting conditions using sessile drop method. ZwickRoell (model: Z005TN) was used to record tensile stress-strain relation of prepared hydrogels. Vibrating Sample Magnetometer (VSM, Lakeshore, Model:7400 series) was used for magnetic characterization of the prepared hydrogel samples. The digital images and videos were captured by a Canon Powershot SX420 IS digital camera. Image J software was used for image processing.

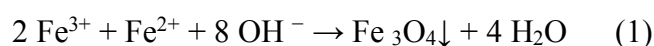
Synthesis of hydrogel:

To synthesize hydrogel with interpenetrated network, the following two-step procedure was followed. For a typical composition, 1.5 mL of BPEI solution was prepared by dissolving 0.05 g (2.18 μmol) BPEI into 1.5 mL D.I. water. Then 0.45 g (2.16 mmol) of AMPS was added to the above aqueous BPEI solution followed by addition of 5 mol% (with respect to the AMPS monomer) PEGDA crosslinker and 1 mol% (with respect to the AMPS monomer) of α -ketoglutaric acid initiator and vortexed for 5 min. The pre-gel solution was then transferred into glass moulds and kept under UV light (365 nm, 30 W) for 4 h to form the hydrogel.

The above as-synthesized hydrogel was taken out of the mould, immersed in 10 mL aqueous solution of acrylamide (2M) having 1 mol% PEGDA crosslinker and 1mol% of α -ketoglutaric acid. After swelling for 3 h in a dark condition, the hydrogel was kept under UV light for 4h to obtain hydrogel with interpenetrated network. Then the hydrogel samples were dipped into distilled water for 24 h. Water was changed 2 to 3 times over 24 h duration after regular intervals to washout the unreacted monomers.

Synthesis of Magnetic Hydrogel (MH):

The as-synthesized above hydrogel was first deswelled by air drying. Then it was immersed in an aqueous solution of selected iron salt varying the molar ratios of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ferric chloride anhydrous (FeCl_3) specifically in ratios of 1:2, 1:3, and 1:6 for 12 hours to promote soaking of iron salts in the prepared hydrogels. Once swollen, the hydrogel was exposed to an alkaline solution (0.5 M sodium hydroxide) for 15 min, which triggers the *in-situ* formation of iron oxide nanoparticles within the hydrogel matrix. The hydrogel with the embedded nanoparticles is then washed with water to remove any unreacted chemicals and by-products. The plausible chemical reaction for iron oxide MNPs formation may be written as equation 1;



Measurement of water content of the magnetic hydrogel:

The water content of a hydrogel was determined by gravimetric method using the following equation-

$$\text{Water content} = \frac{W_s - W_d}{W_s} \times 100\%$$

Where, W_s is the weight of as-synthesised magnetic hydrogel fully equilibrated with water and W_d is the weight of the same hydrogel after lyophilization.

Magnetic characterization of MH:

Magnetic hysteresis measurements were conducted at room temperature (300 K) using a Lakeshore 7410 series VSM magnetometer. Magnetic hydrogel samples initially were wiped with blotting paper and inserted into the probe for measurements which undergo magnetized

by being exposed to a cycle of magnetic fields ranging from -15 kOe to + 15 kOe at an average sweep rate of 10 Oe/s. The raw data collected from these measurements were then converted into magnetic moment per gram (emu g^{-1}) of the used samples.

Measurement of angle of deflection of MH:

A cantilever bending beam actuator model was used to demonstrate actuation behaviour of magnetic hydrogel to an external magnetic field. A magnetic hydrogel beam (dimension: L= 30 mm, W= 4 mm and T= 4 mm) was suspended by attaching its one end to a support kept underwater. A permanent (Neodymium alloy) magnet (100 mT) was brought close (2 cm) to the actuator and the deflection angle of the actuator-tip was measured from subsequent image analysis using Image J software.

Chemical durability test of MH:

The chemical durability of the MH was evaluated by swelling measurements after immersing it in various complex aqueous environments- including acidic (pH 1), alkaline (pH 12), surfactants (SDS and DTAB) solution (1 mM). After prolonged exposure for 7 days, the swelling ratio was measured following equation-

$$\text{Swelling ratio (\%)} = \frac{W_2 - W_1}{W_1} \times 100\%$$

Where, W_2 denotes the weight of the swollen hydrogel, and W_1 represents the weight of the dry hydrogel.

Mechanical property:

Hydrogel samples with rectangular shapes (L= 7 cm, W= 5 mm) and ~95wt% water content was utilized for tensile measurement. The samples were mounted using a pincer grip and stretched uniaxially at a machine speed of 5 mm min^{-1} in electromechanical universal testing machine ZwickRoell (model: Z005TN) equipped with 5 kN load cell. The tensile stress was calculated by dividing the measured force with the cross-sectional area of the sample. Young's modulus was calculated from the slope of stress versus strain curve. The toughness value was calculated from the area under a tensile stress versus strain curve using Origin Pro.

Underwater droplet manipulation by MH actuator:

A lab-made prototype was developed using a MH actuator having a tail and an arch-shaped head. The MH was attached to an oil-repellent hydrogel bed that allows oil droplets to move freely without sticking when the whole setup kept under water. By applying an external magnetic field by a permanent Neodymium magnet (100 mT), the MH can precisely manipulate

an oil droplet movement by pushing it in an angular direction. This same setup was utilized for manipulation and mixing multiple oil droplets with different droplet volumes (5- 20 μL).

Cascade chemical reaction using MH actuator:

Using the above-mentioned setup, droplets of propylamine, vanillin, and a reducing agent (NaBH_4) in dichloromethane were beaded on the hydrogel bed under water. The MH actuator was then guided by an external neodymium magnet (100 mT) to merge these droplets step-by-step. The mixing of droplets having vanillin and propylamine yielded a Schiff base. Thereafter, its coalescence with NaBH_4 by MH actuator, reduced the imine bond present in the schiff base.

Table S1: Comparing the performance of prepared MH with recent relevant literatures on magnetic hydrogels.

Composition	Wettability Contact angle ($^\circ$)	Alkaline and acidic stability	Mechanical strength (MPa)	Saturation Magnetization (emu g^{-1})	References
Fe_3O_4 - NH_2 /gelatin/PVA hydrogel	$\theta_{\text{water}} = 83^\circ$	-	0.61	75	Ref. 1
SEBS/ COCe/ PMMA Polymer	-	-	30	13.7	Ref. 2
Fe_3O_4 /GelMA hydrogels	-	pH 10	0.23	-	Ref. 3
γ - Fe_2O_3 /PNIPAm matrix	-	-	3.7	72	Ref. 4
Silk fibroin (RSF)/TA/ Fe_3O_4 hydrogel	-	-	-	6.5	Ref. 5
Fe_3O_4 /Nanofibre/PVA hydrogel	-	-	2.4	30	Ref. 6
DMAPS/ MAA CNC nanoparticles	-	-	1.25	0.05	Ref. 7
Ferrofluid Gelatinmethacryloyl hydrogel	-	-	-	8	Ref. 8
Fe_3O_4 /PAAm-silane	$\theta_{\text{oil}} = 155^\circ$	-	0.025	42	Ref. 9
Fe_3O_4 /PNIPAm hydrogel	-	-	0.001	5	Ref. 10
MH	$\theta_{\text{oil}} = 160^\circ$	pH 1 to 12	0.55	85	This work

Reference:

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Supporting Figures:

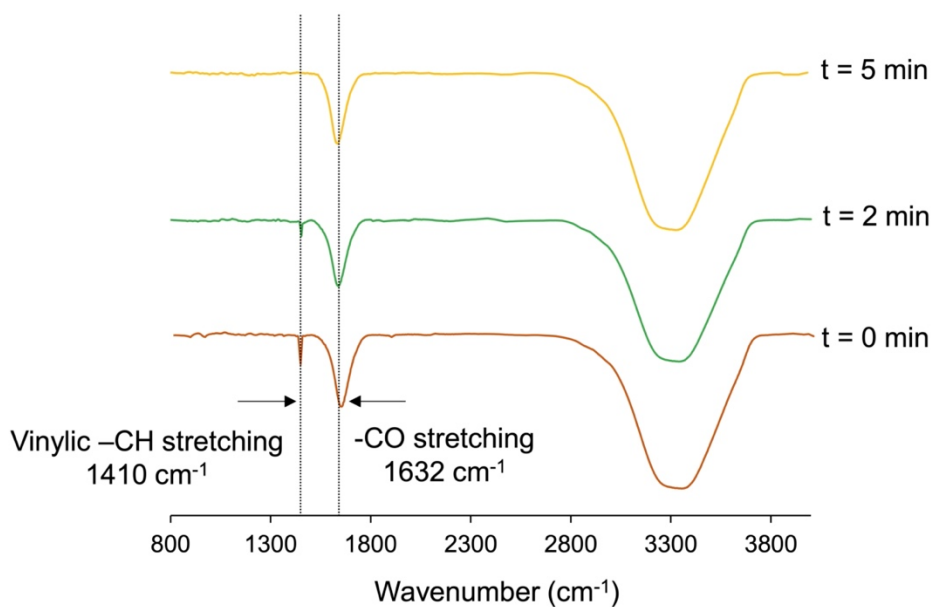


Figure S1: FTIR spectra of the reaction mixture of BPEI and PEGDA is recorded at different time. The broad absorption around 3400 cm⁻¹ appeared due to the O-H stretching vibration of the water present in the aqueous reaction mixture of BPEI and PEGDA.

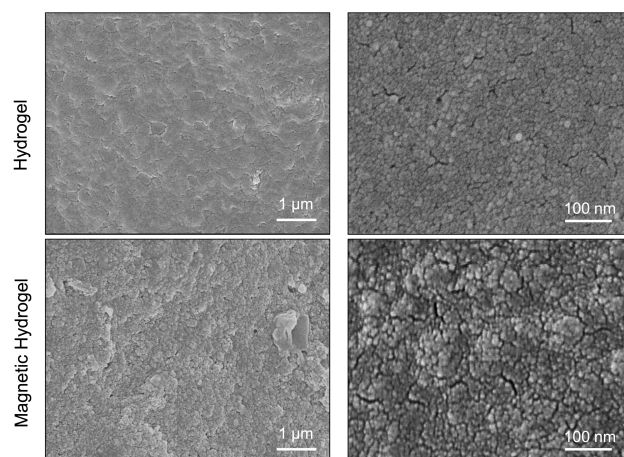


Figure S2: FESEM images of hydrogel and magnetic hydrogel (MH) in low and high magnifications.

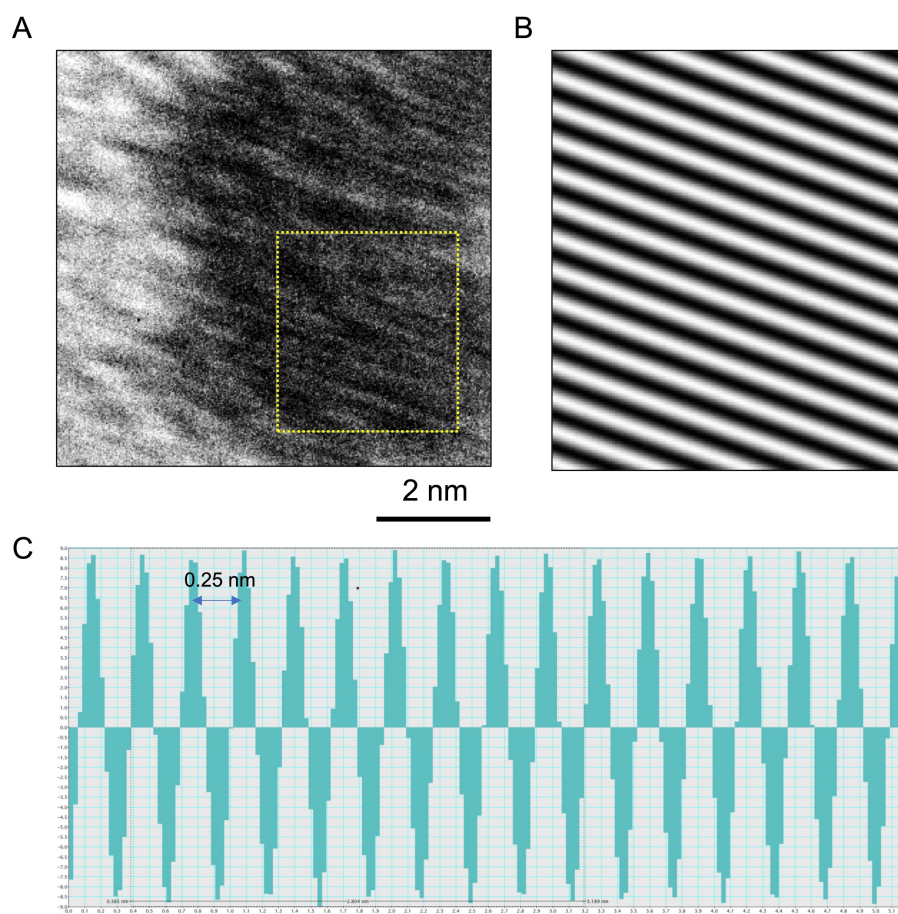


Figure S3: A) HRTEM image of magnetic hydrogel. B) Inverse Fast Fourier Transition (IFFT) micrograph of MH derived from the selected area (indicated by dotted box in Figure S3A) of the corresponding HRTEM image. C) IFFT profile plot indicating d-spacing as 0.25 nm.

Table S2: Indexing the lattice interplanar distance (d) of diffraction planes in the SAED micrograph of magnetic nanoparticle embedded hydrogel in reference to the JCPDS: 190629

Calculated value from SAED of MH				Standard value	
1/D [#] (1/nm)	1/r [§] (1/nm)	d [†] (nm)	d (Å)	d (Å) JCPDS: 190629	Crystal plane hkl
13.511	6.755	0.1480	1.480	1.484	440
12.491	6.245	0.1601	1.601	1.615	511
9.524	4.762	0.2099	2.099	2.099	400
7.933	3.966	0.2521	2.521	2.532	311
6.731	3.365	0.2971	2.971	2.967	220

[#]Reciprocal of diameter of the diffraction rings calculated from SAED micrograph analysis using ImageJ software. [§] Reciprocal of radius of the diffraction rings. [†]Radius of the diffraction rings or lattice interplanar distance (d).

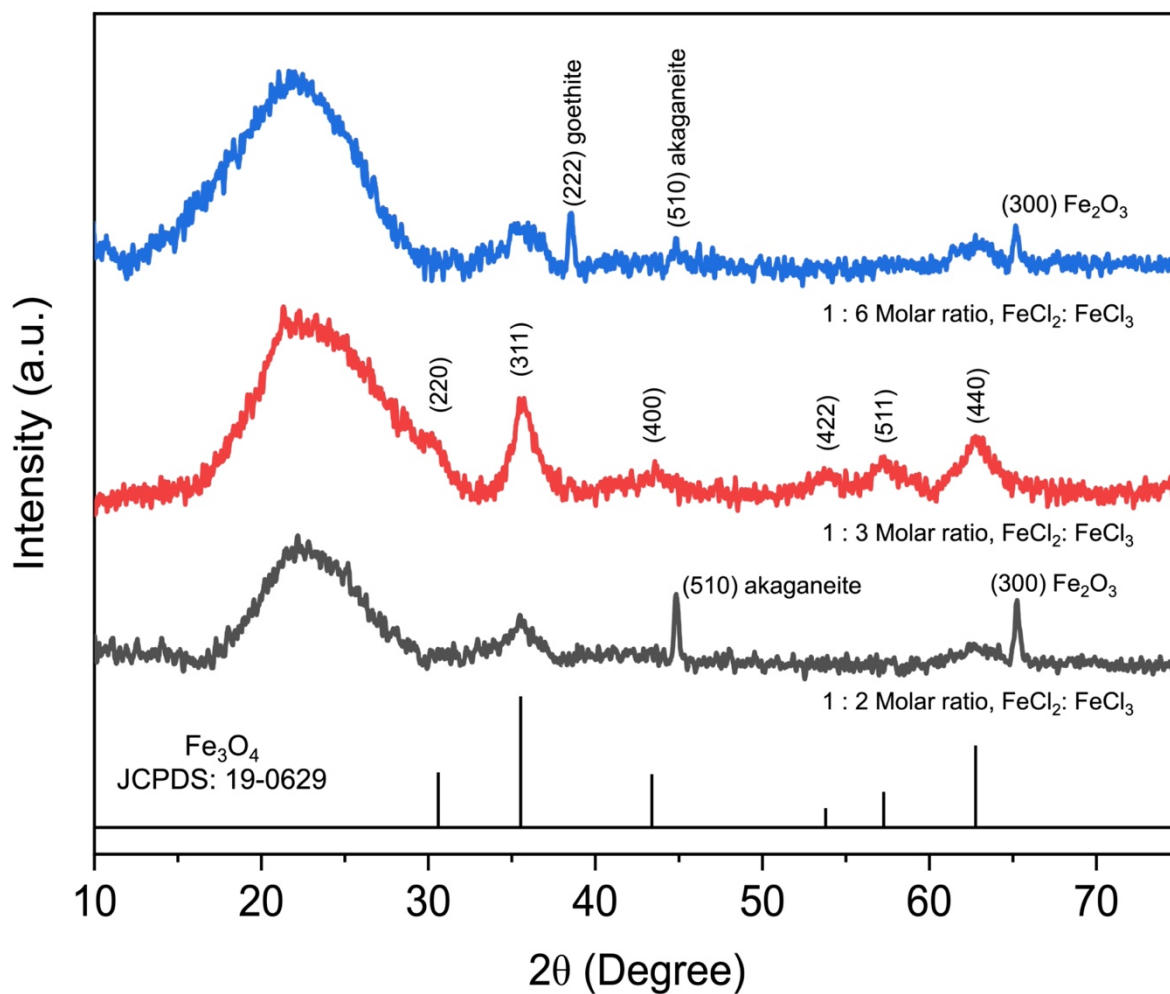


Figure S4: X-ray diffraction patterns (XRD) of different MHs that were prepared by varying the molar ratio of selected iron salts.

Table S3: Accounting the crystallite size of MNPs and magnetic properties of different MHs that were prepared by varying the molar ratio of selected iron salts.

FeCl ₂ : FeCl ₃ salt composition	Mol ratio	Total Fe content solution	M _S (emu/g)	Avg. crystallite size (d nm)
0.1 M : 0.2 M	1:2	0.3 M	50	4.1
0.1 M : 0.6 M	1:6	0.7 M	63	5.2
0.2 M : 0.6 M	1:3	0.8 M	85	5.8

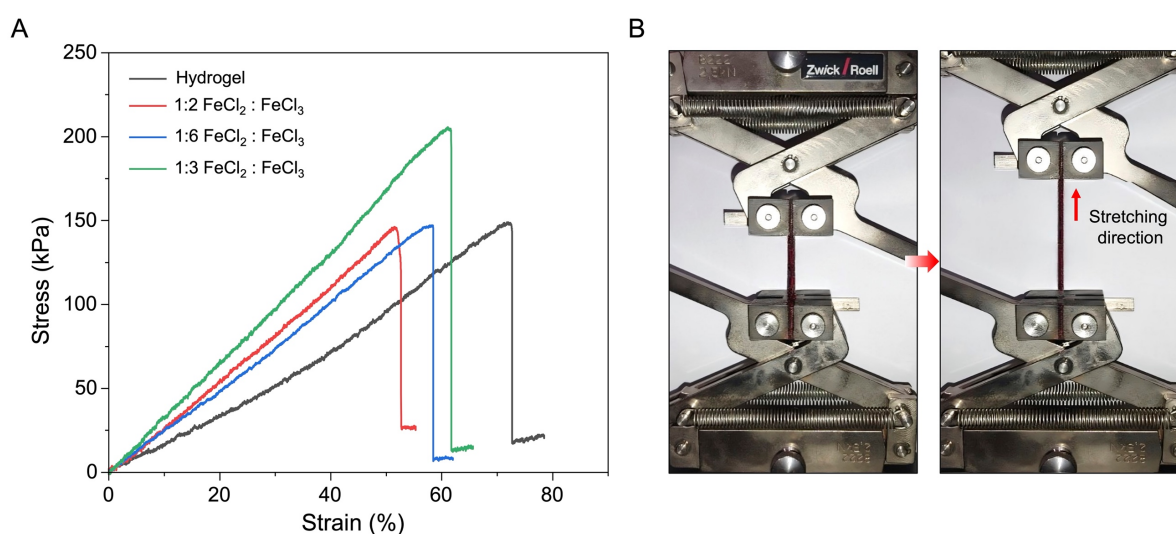


Figure S5: A) Stress-strain curve of hydrogel (without MNPs) and different MHs that were prepared by varying the molar ratio of selected iron salts. B) Digital image showing the tensile test of a MH sample in universal tensile machine, where sample is being stretched until failure to get tensile stress versus strain data.

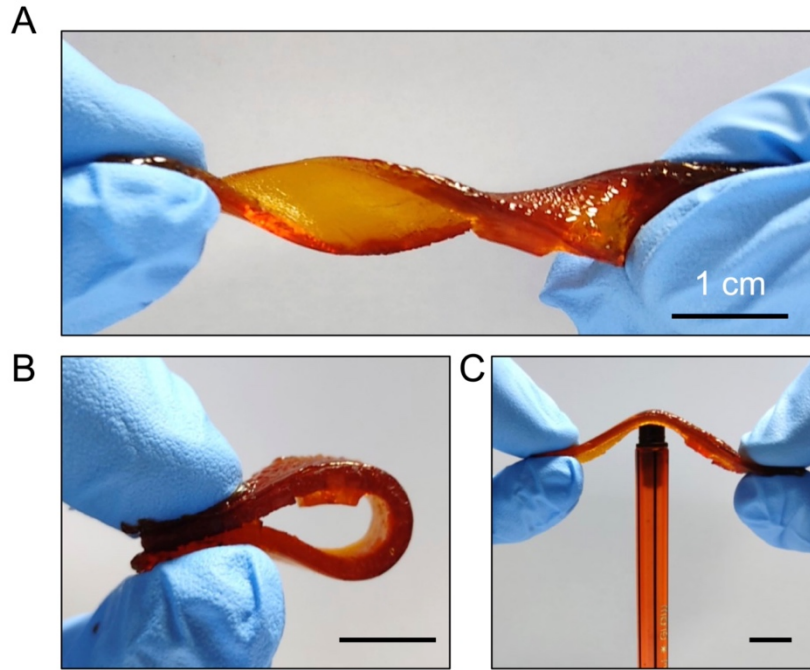


Figure S6: Digital images of magnetic hydrogel (MH) during different mechanical deformations: A) multiple twisting, B) folding, C) puncture test by a cylindrical object (i.e. pen) with diameter of 8 mm, (scale bar: 1 cm)

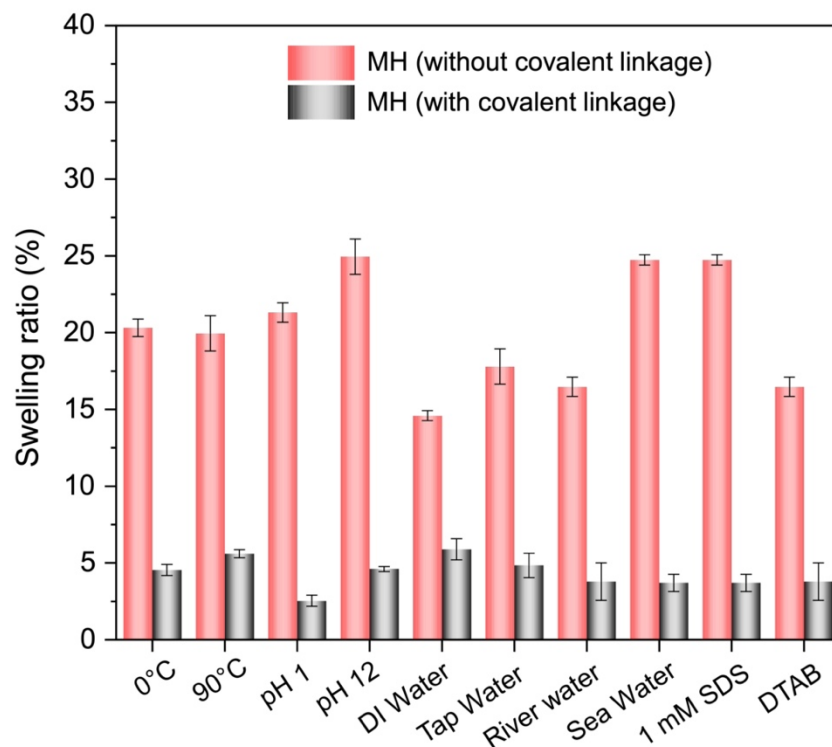


Figure S7: Accounting swelling of MH with and without covalent linkages in different and complex aquatic conditions.

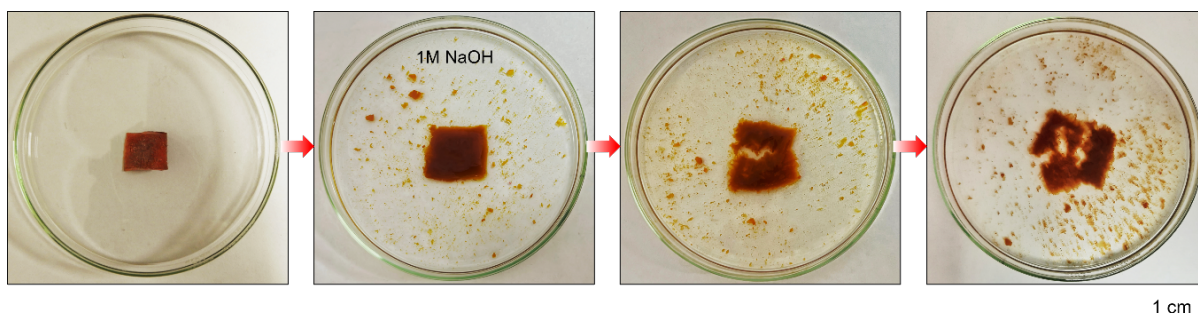


Figure S8: Digital images of the hydrogel prepared by directly mixing an aqueous solution containing iron salts with BPEI, AMPS, PEGDA, a photoinitiator, and AAm, depicting its response to alkaline (1M NaOH) exposure for the in-situ growth of MNPs. The images revealed high swelling and disintegration of the hydrogel.

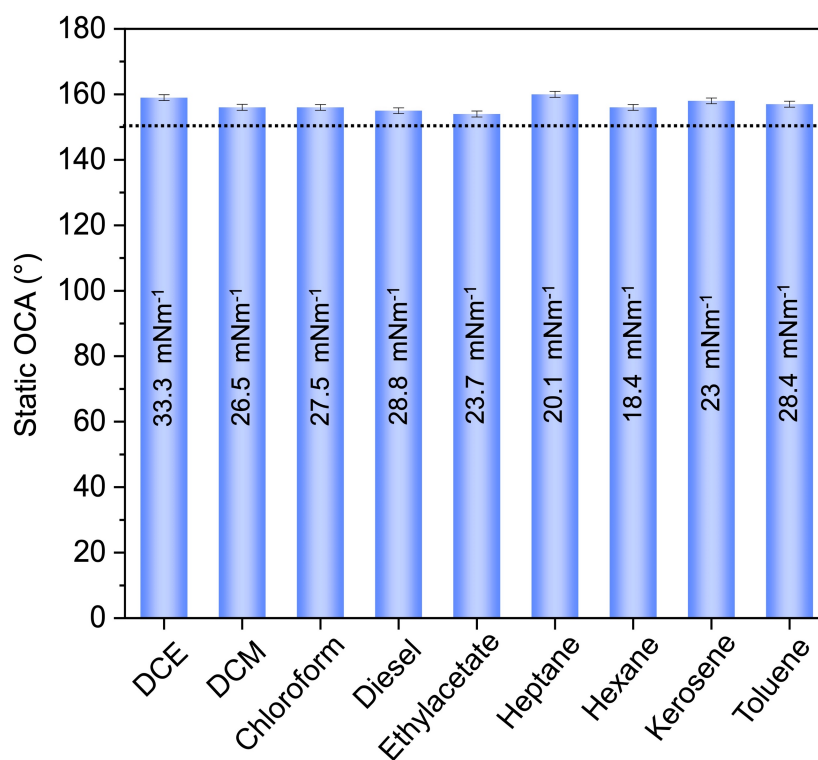


Figure S9: Static oil contact angle of beaded droplets of different oils and organic solvents on MH.

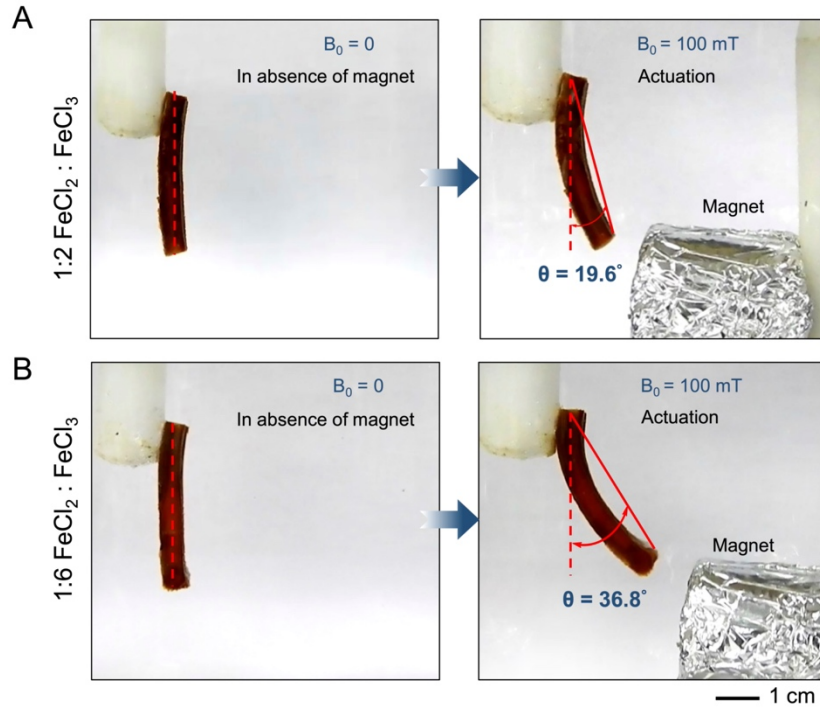


Figure S10: Digital images of different MH beam actuator prepared the varying iron salt composition-A) 1:2 and B) 1:6 of FeCl_2 and FeCl_3 , showing difference in the tip deflection by a permanent neodymium alloy magnet of 100 mT placed of a distance of $\sim 2\text{cm}$.

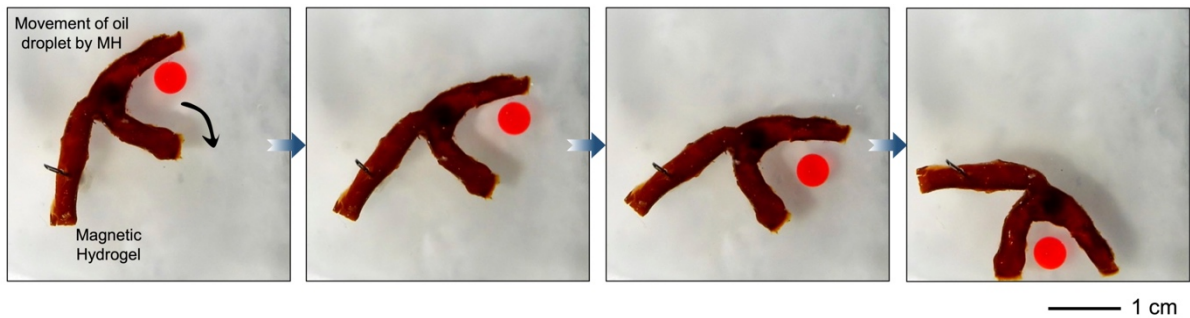


Figure S11: Digital images accounting no loss transfer of oil droplet in an angular direction using a MH in presence of external magnet.

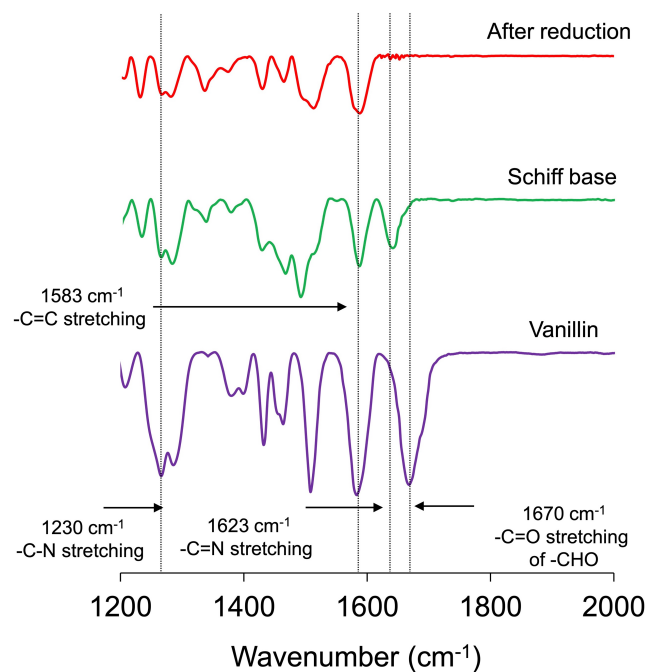


Figure S12: FTIR spectra of Schiff base formed by mutual reaction between amine (from propylamine) and aldehyde (from Vanillin), and its reduction by NaBH₄ via sequential coalescence of droplet having appropriate reactants and reagent.