Single step fabrication of a dual-sensitive chitosan hydrogel by C-Mannich reaction: Synthesis, physicochemical properties, and screening of its Cu^{2+} uptake

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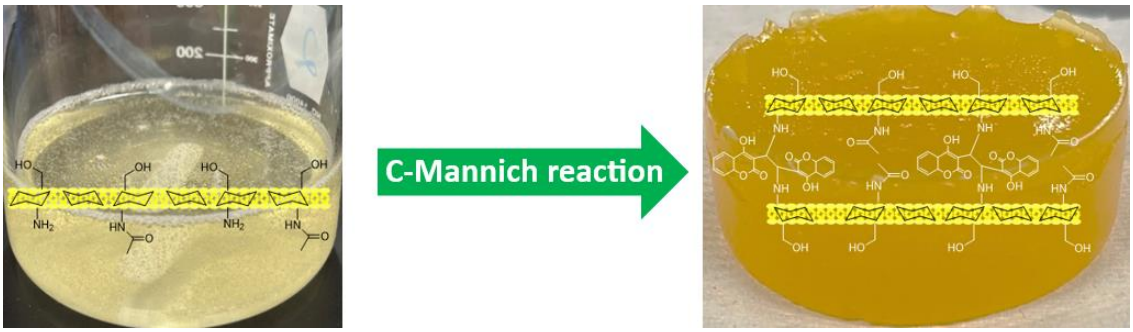

Abstract: Uncovering the value of waste materials is one of the keys to sustainability. In this current work, valorization of chitosan was pursued to fabricate a novel modified chitosan functional hydrogel using a process efficient protocol. The fabrication proceeds by a one-pot and single step C-Mannich condensation of chitosan (3% w/v), glutaraldehyde (20 eq.), and 4-hydroxycoumarin (40 eq.) at 22^0C in 3% v/v acetic acid medium. The Mannich base modified chitosan hydrogel (CS-MB) exhibits a dual-responsive swelling behavior in response to pH and temperature that has not been observed in any other hydrogel systems. Combining the pre-defined optimal swelling pH (pH=4) and temperature (T=22^0C), the CS-MB was screened for its Cu^{2+} adsorption capacity at this condition. The CS-MB achieved an optimal adsorption capacity of 12.0 mg/g with 1.2 g/L ad-sorbent dosage after 36 hours with agitation. The adsorption of Cu^{2+} in the surface of CS-MB was verified by EDS and an overview of the adsorption sites was exhibited by FT-IR. The simply fabricated novel CS-MB hydrogel under investigation presents a unique response to external stimuli that exhibits a promise in heavy metal removal from aqueous media.

Keywords: chitosan; hydrogel; dual responsive; Mannich reaction; water treatment; environmental engineering; heavy metal removal

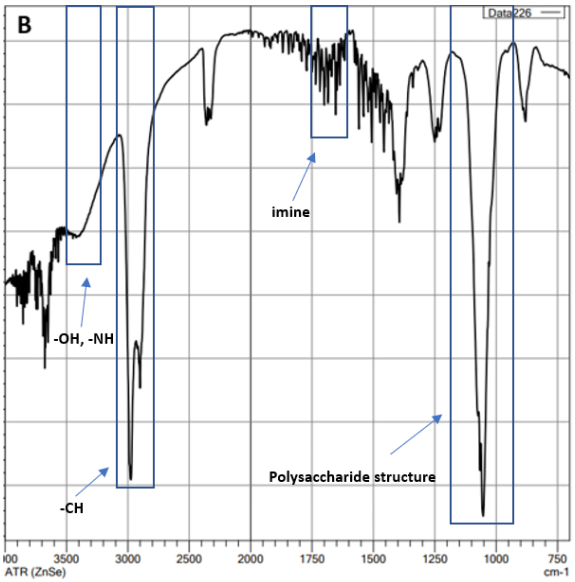

Figure S1. FT-IR of CS-MB (1 eq. CS, 20 eq. Glu, 20 eq. 4-HC)

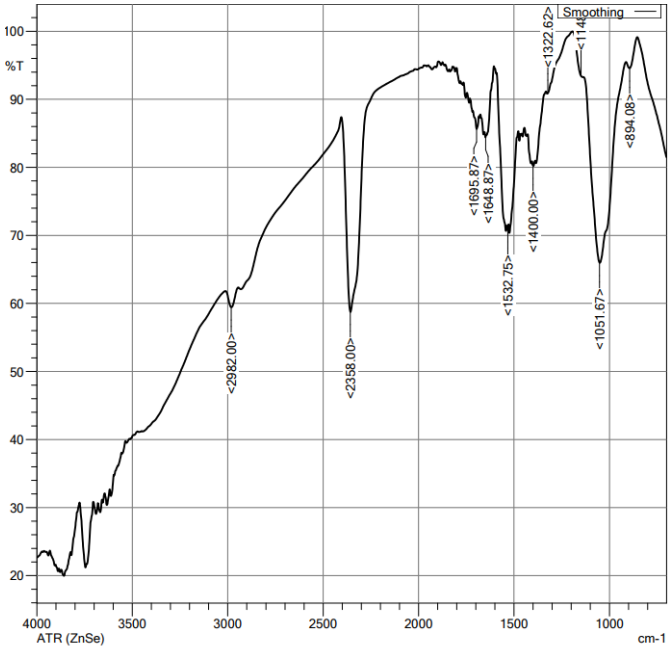

Figure S2. FT-IR of CS hydrogel film

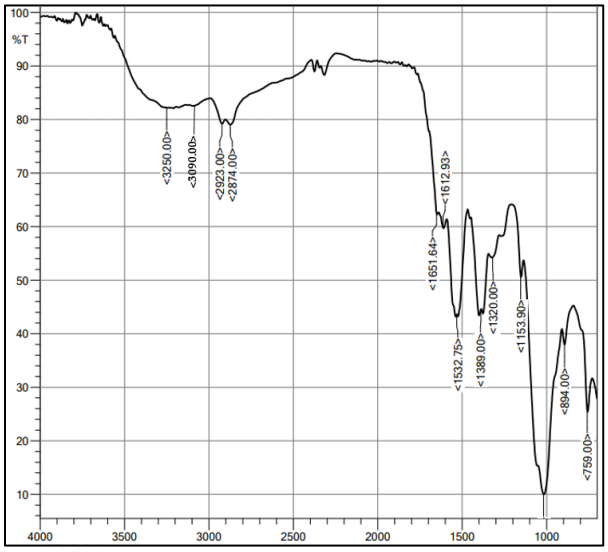

Figure S3. FT-IR of fresh CS-MB (1 eq. CS, 20 eq. Glu, 40 eq. 4-HC)

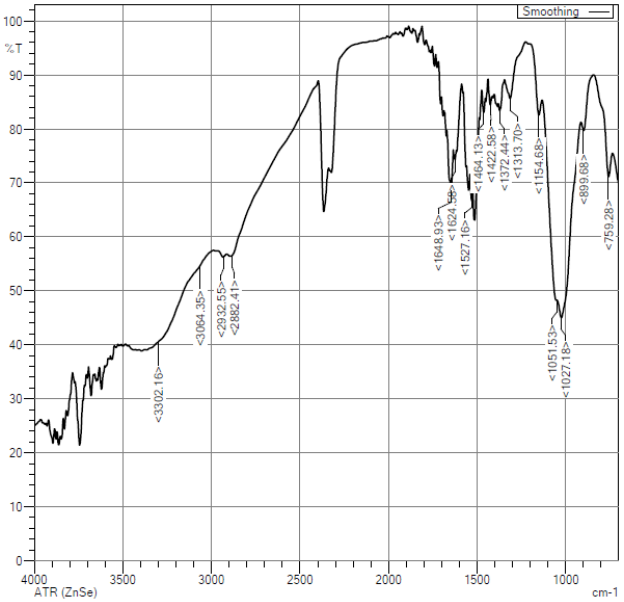

Figure S4. FT-IR of exhausted CS-MB swelled at pH 2.4

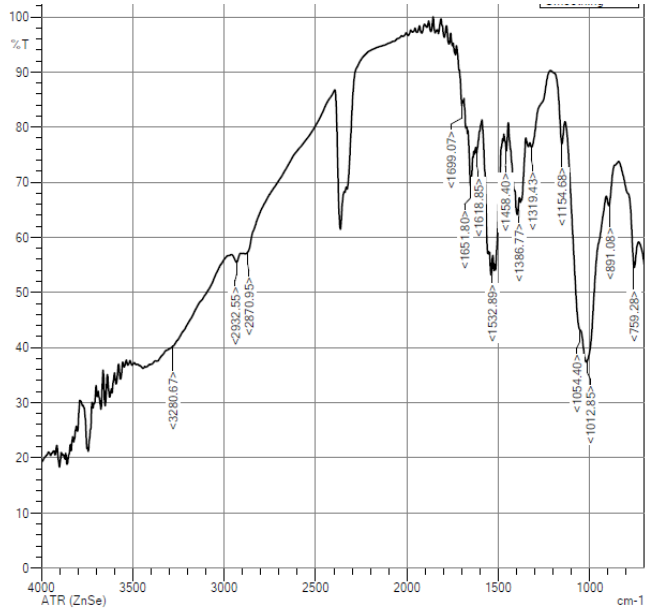

Figure S5. FT-IR of exhausted CS-MB swelled at pH 4.0

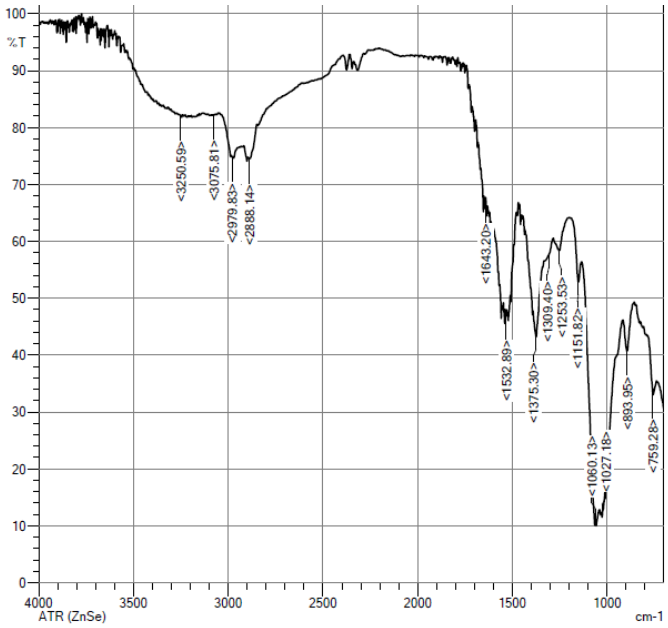

Figure S6. FT-IR of exhausted CS-MB swelled at pH 7.4

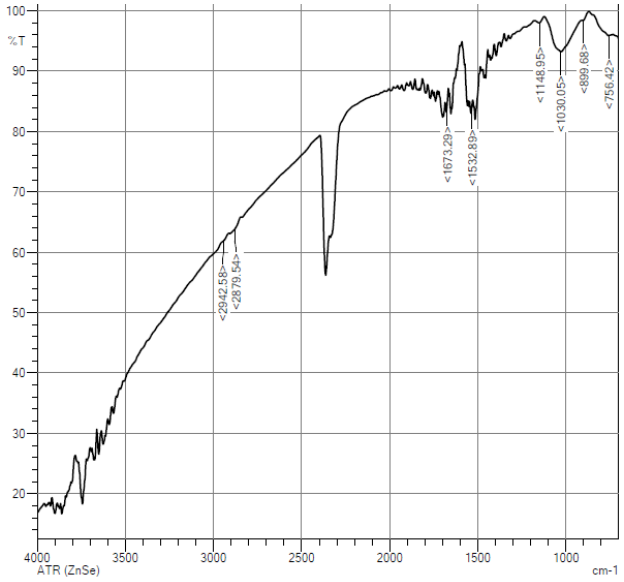

Figure S7. FT-IR of exhausted CS-MB swelled at pH 8.1

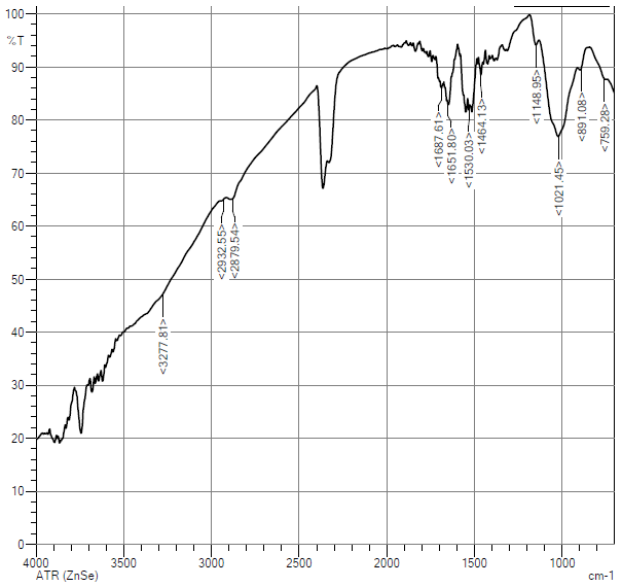

Figure S8. FT-IR of exhausted CS-MB swelled at pH 10.0

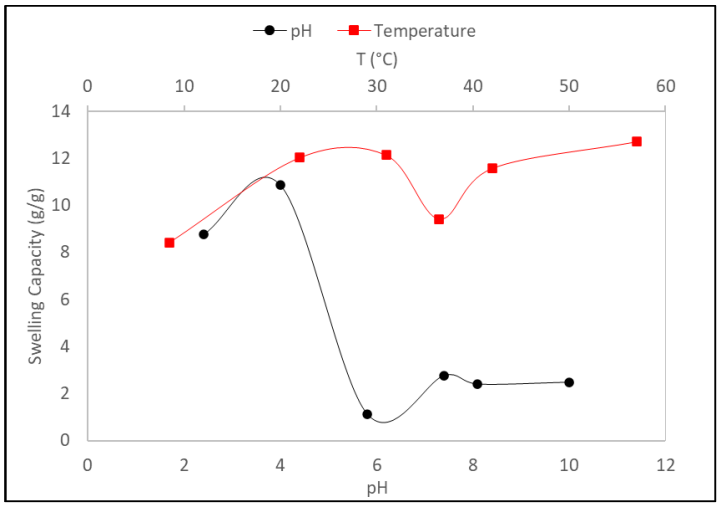

Figure S9: Influence of pH and temperature of water on the equilibrium swelling capacity of CS-MB.

Table S1: Copper speciation in AcOH/NaOAC buffered system (pH =4.0, 0.1 M) simulated from Visual MINTEQ ver. 3.1 (released 2014) J. P. Gustafsson.

Cu- species	Total Concentration (%)
Cu^{2+}	99.30
$CuOH^{+}$	0.025
$CuCl^{+}$	0.487
Cu-Acetate^{+}	0.184

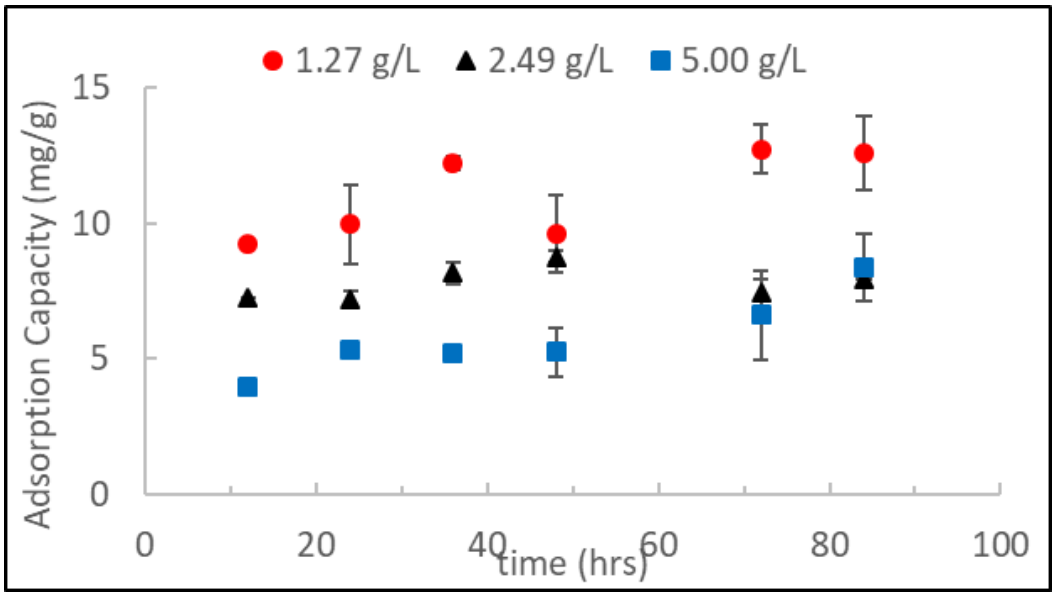

Figure S10: Adsorption equilibrium studies in batch mode with different CS-MB dosage. Conditions: [Cu^{2+}] = 120 mg/L adjusted to pH 4 with AcOH/NaOAc, 20 mL working volume, 22^{0}C, 140 rpm shaker speed.

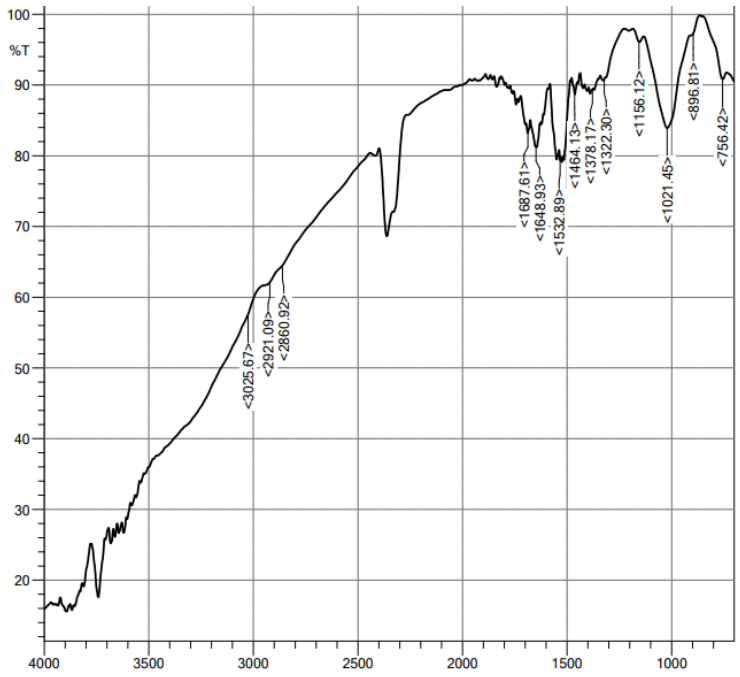

Figure S11: FT-IR of spent CS-MB

Table S2: EDC elemental analysis (Wt %) of fresh and spent CS-MB.

Samples	C	N	O	Cl	Cu	Total
CS-MB area #1	55.49	4.80	39.63	0.08	0.00	100.00
CS-MB area #2	53.24	5.86	40.88	0.02	0.00	100.00
CS-MB area #3	55.91	5.76	38.25	0.07	0.00	100.00
CS-MB-spent area #1	51.50	4.50	35.88	0.20	7.93	100.00
CS-MB- spent area #2	53.91	5.18	31.14	0.29	9.48	100.00
CS-MB- spent area #3	53.28	5.23	32.32	0.16	9.01	100.00