

Single-step fabrication of a dual-sensitive chitosan hydrogel by C-Mannich reaction: Synthesis, physicochemical properties, and screening of its Cu²⁺ uptake

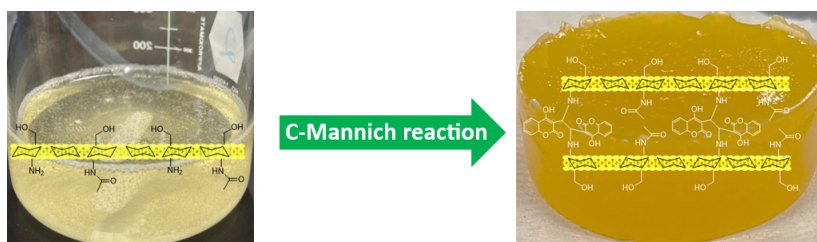
John Rey Apostol Romal ^{1,2,*} and Say Kee Ong ²

¹Department of Chemistry, Grand View University, Des Moines, IA 50316, USA

²Department of Civil, Construction, and Environmental Engineering, Iowa State University, Ames, IA 50011, USA

*Correspondence: jromal11@iastate.edu; jromal@iastate.edu

Field Code Changed



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°C in 3% v/v acetic acid. 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°C), the CS-MB was screened for its Cu²⁺ adsorption capacity at this condition. The CS-MB achieved an optimal adsorption capacity of 12.0 mg/g with 1.2 g/L adsorbent dosage after 36 hours with agitation. The adsorption of Cu²⁺ 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

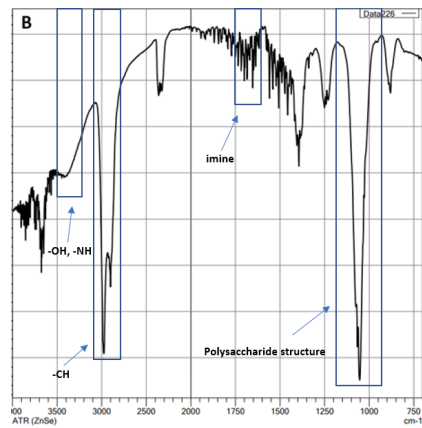


Figure S1. FT-IR of CS-MB (1 eq. CS, 20 eq. Glu, 20 eq. 4-HC)

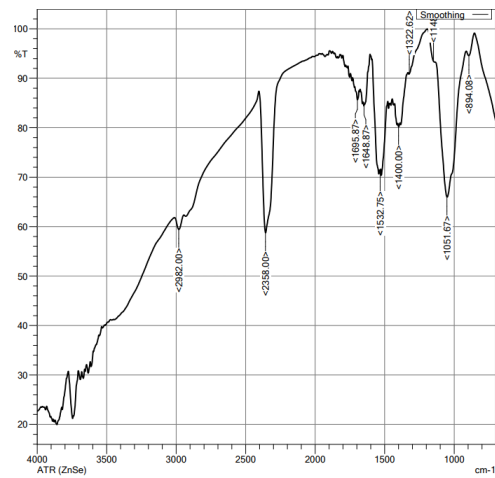


Figure S2. FT-IR of CS hydrogel film

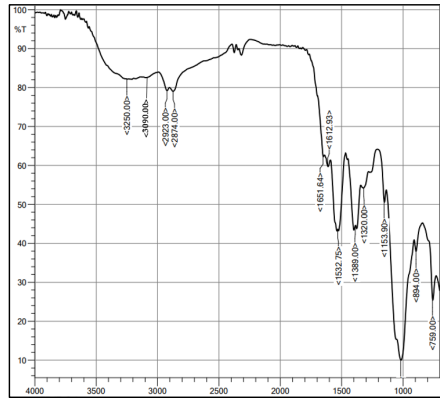


Figure S3. FT-IR of fresh CS-MB (1 eq. CS, 20 eq. Glu, 40 eq. 4-HC)

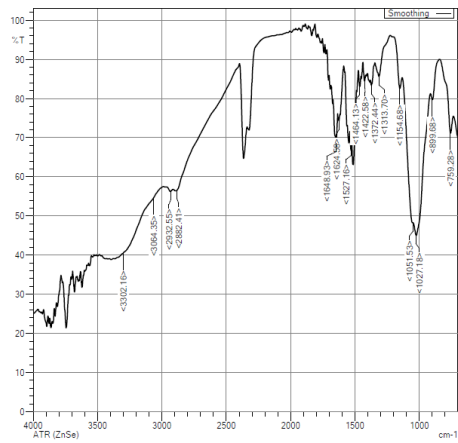


Figure S4. FT-IR of exhausted CS-MB swelled at pH 2.4

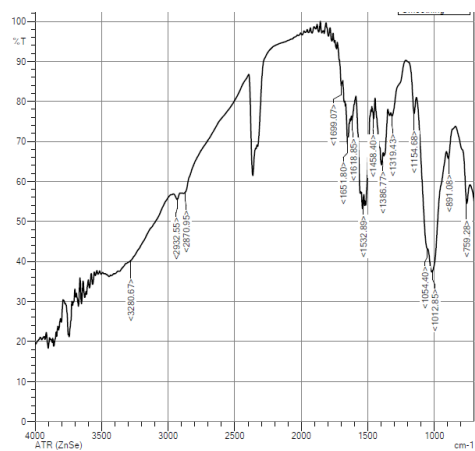


Figure S5. FT-IR of exhausted CS-MB swelled at pH 4.0

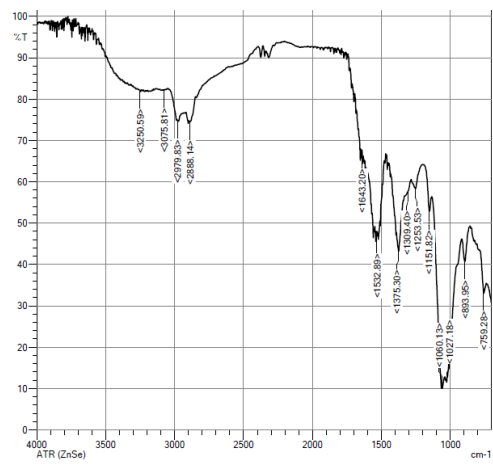


Figure S6. FT-IR of exhausted CS-MB swelled at pH 7.4

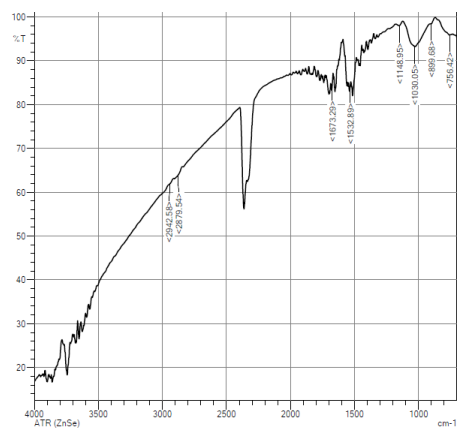


Figure S7. FT-IR of exhausted CS-MB swelled at pH 8.1

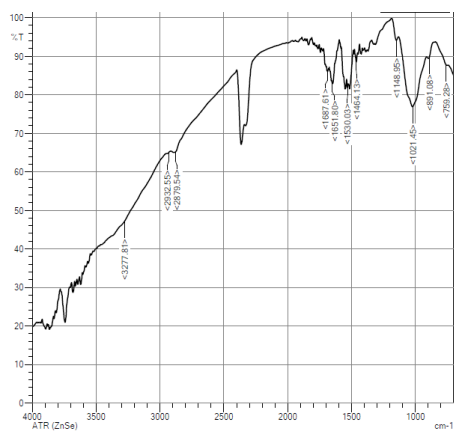


Figure S8. FT-IR of exhausted CS-MB swelled at pH 10.0

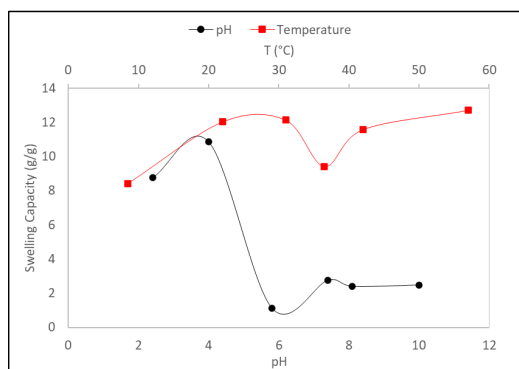


Figure S9: Influence of pH and temperature of water on the equilibrium swelling capacity of CS-MB.

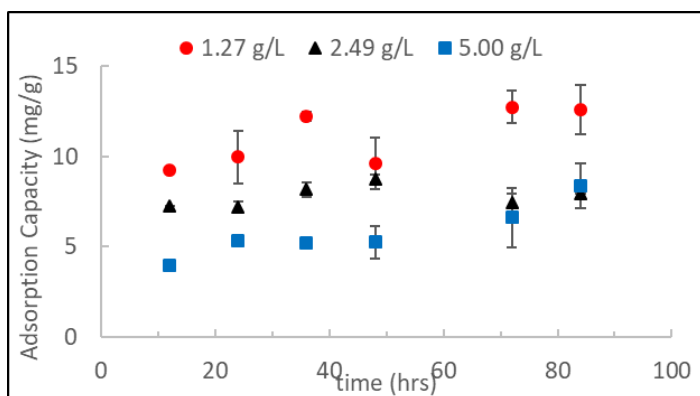


Figure S10: Adsorption equilibrium studies in batch mode with different CS-MB dosage. Conditions: $[Cu^{2+}] = 120$ mg/L adjusted to pH 4 with AcOH/NaOAc, 20 mL working volume, 22°C, 140 rpm shaker speed.

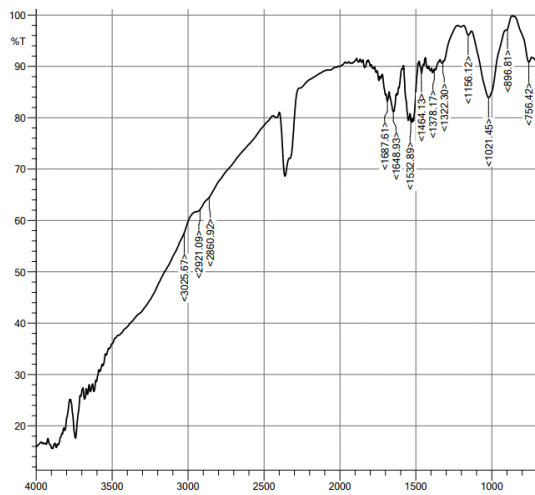


Figure S11: FT-IR of spent CS-MB

Table S1 : pH-sensitivity of CS-MB at 22°C at normal atmospheric pressure

pH	Observations/Explanations
2.4 > pH < 3.8	<ul style="list-style-type: none"> At pH =2.4, the amine groups in the CS-MB have a high degree of deprotonation. The lower swelling capacity of the CS-MB at this pH than at pH 3.8 is due to the excessive electrostatic repulsion caused by the fully-charged amine group (NH₃⁺). The excessive NH₃⁺ repulsion hinders the attractive interaction between the oxygen atom in the water molecule and the nitrogen atom in NH₃⁺. The gradual increase in pH decreases the degree of amine protonation and electrostatic repulsion allowing ion-dipole interaction between water and NH₃⁺ resulting in the improved swelling capacity.
3.8	<ul style="list-style-type: none"> Optimal pH for the swelling capacity of CS-MB hydrogel at 22°C and is time dependent until swelling equilibrium is established.
5.5	<ul style="list-style-type: none"> An inflection point is observed and the swelling capacity converges to a single quantity independent of the swelling time, which is identified as the pK_a of the amine group in the CS-MB.
5.5 < pH < 6.9	<ul style="list-style-type: none"> In this range, it is expected that the CS-MB is uncharged in this range causing a very minimal electrostatic interaction between water molecules and the polar groups of the hydrogel resulting in low water retention. It is observed that the swelling capacity decreases slightly with time. With the absence of electrostatic interactions at this condition, this trend may be speculated to be caused by a constant efflux of water out of the hydrogel overtime.
7.5	<ul style="list-style-type: none"> A second inflection point is observed and the swelling capacity converges to approximately the same value independent of the swelling time, which is identified as the pK_a of the hydroxyl group of the 4-HC in the CS-MB. Nowak et al. [1] reported that the pK_a of the non-substituted 4-HC was reported to be 4.06, whereas enhancing the stabilizing interaction between the hydroxyl of the 4-HC and proton-stabilizing substituent in the C-3 substituted 4-HC increases the pK_a. Possible proton-stabilizing interaction for CS-MB system can include OH...π interaction, OH...OH hydrogen bonding, OH...NH hydrogen bonding, and CH...O (crosslinking carbon).
7.5 < pH < 8.1	<ul style="list-style-type: none"> In this range, it is expected that there is a partial deprotonation of the hydroxyl groups from the 4-HC allowing the ion-dipole interaction between deprotonated hydroxyl group and the hydrogen atom of the water molecule, allowing water retention. Swelling capacity also improves with time, but not as much as when the system is at pH 3.8 that could be due to the stronger anion repulsion (relative to NH₃⁺ repulsion) between the partially deprotonated hydroxyl that influence the accessibility of water molecules for ion-dipole interaction.
>8.1	<ul style="list-style-type: none"> This pH range is the least operational condition for hydrogel in terms of swelling capacity. As the hydroxyl approaches a high degree of deprotonation, the oxyanion-oxyanion repulsion also becomes dominant overtime that may lead to complete inaccessibility of oxyanion for ion-dipole interaction with water.

Table S2: 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

Table S3: 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

References

[1] Nowak, P.M.; Sagan, F.; Mitoraj, M.P. Origin of Remarkably Different Acidity of Hydroxycoumarins—Joint Experimental and Theoretical Studies. *J Phys Chem B* 2017, *121*, 4554–4561, doi:10.1021/acs.jpcc.7b01849.