Sustainable Approach to Synthesis Phosphonated Chitosan Using Ball Milling and Its Application for Oilfield Scale Management

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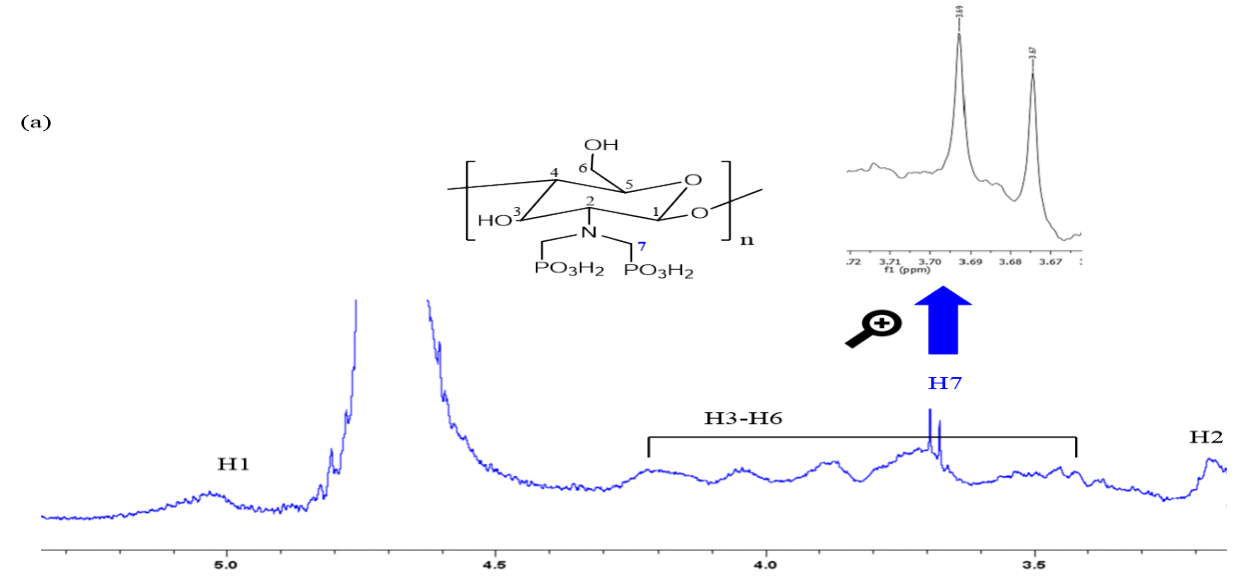
Figure S1. Schematic diagram of NMR spectra of the **PCH** under ball-milling conditions**:** (a) ^{1}H NMR spectrum of **PCH** and zoom in on a spectral region corresponded to -C**H**$_2$-PO_3H_2 and (b) ^{31}P NMR spectrum of **PCH**.



(b)

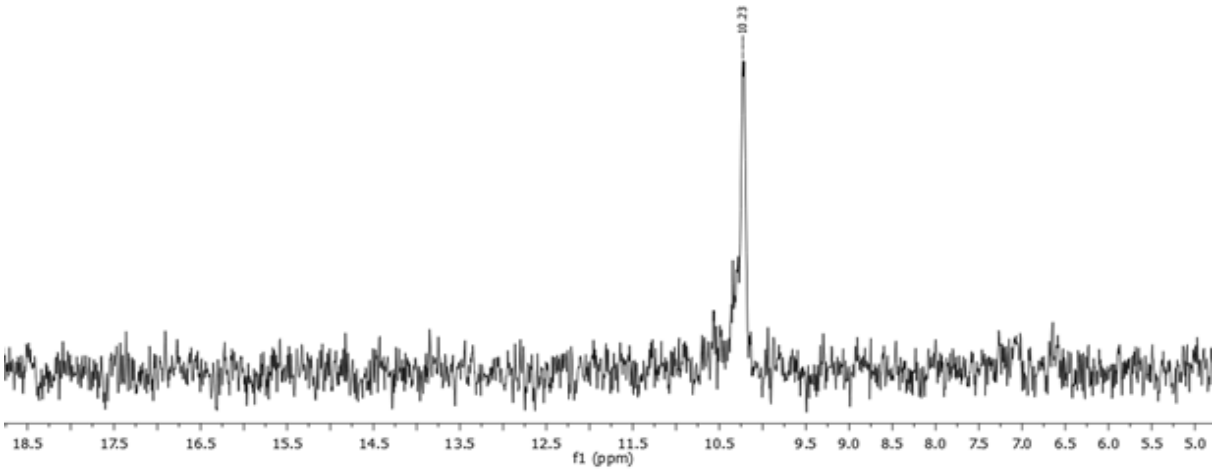


Figure S2. Schematic diagram of FTIR spectra of the **PCH**.

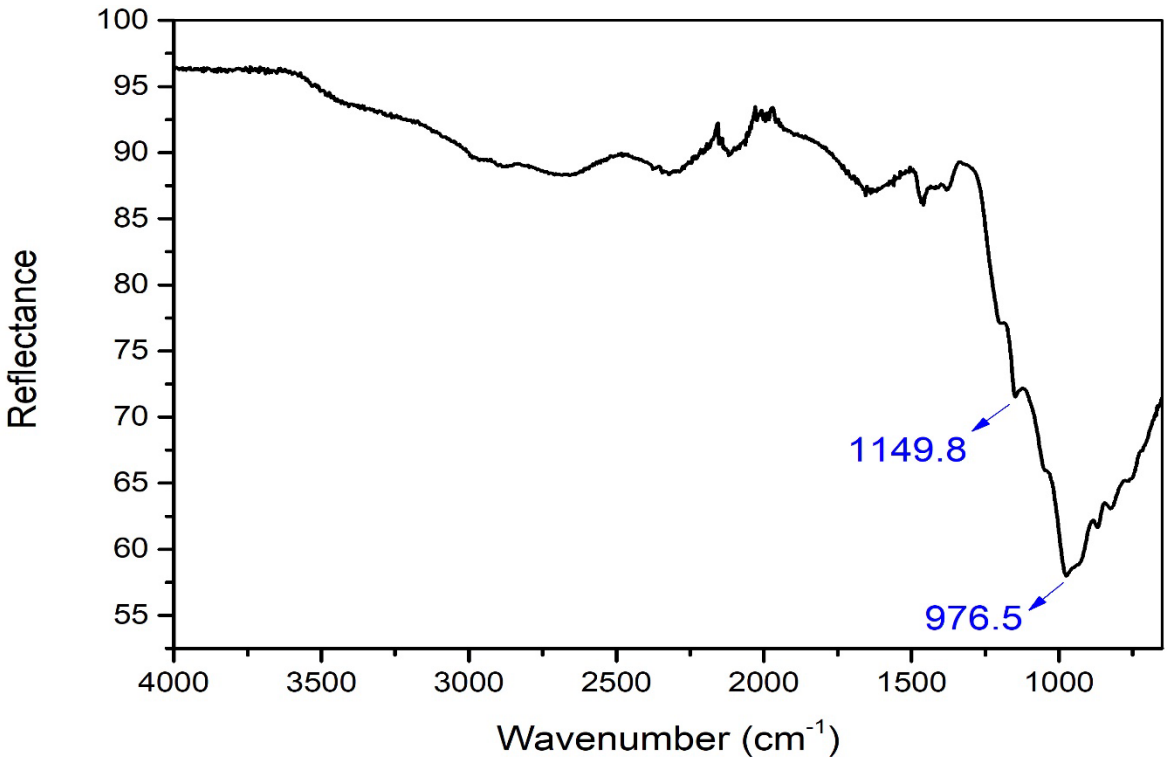


Figure S3. The optimized structures of **ATMP** in conformation I, in which the two phosphonates are bi-chelating Ca^{2+}. Key bond lengths are shown in Å, and the atomic color code is presented.

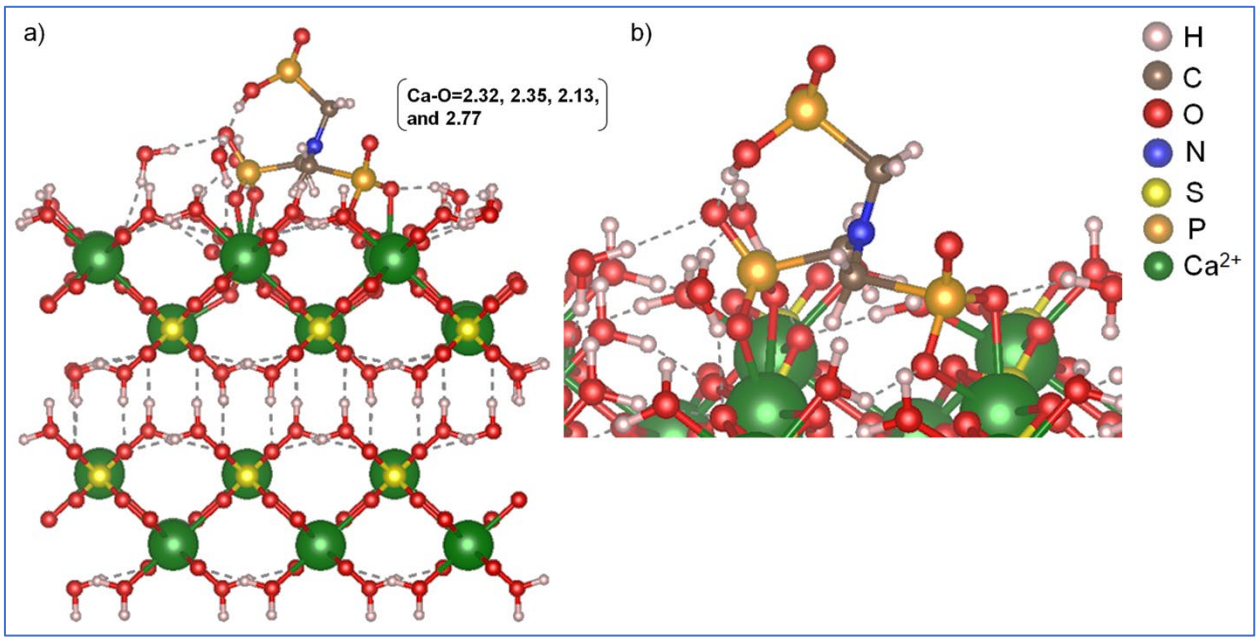


Table S1. Elemental analysis and substitution degree of **CH** and **PCH**.

	C	N	H	C/N	DS
CH	40.46	7.28	7.4	6.48	
PCH	23.16	3.63	4.96	7.438	0.956

Table S2. Calcium tolerance tests at 30000 ppm (3 wt%) NaCl for **PCH**.

SI	Ca^{2+} dose (ppm)	SI dose (ppm)	Appearance				
			after mixing	30 minutes	1 hour	4 hours	24 hours
PCH	100	100	clear	clear	clear	clear	clear
		1000	clear	clear	clear	clear	clear
		10000	clear	clear	clear	clear	clear
		50000	clear	clear	clear	clear	clear
	1000	100	clear	clear	clear	clear	clear
		1000	clear	clear	clear	clear	clear
		10000	clear	clear	clear	clear	clear
		50000	clear	clear	clear	clear	clear
	10000	100	clear	clear	clear	clear	clear
		1000	clear	clear	clear	clear	clear
		10000	clear	clear	clear	clear	clear
		50000	clear	clear	clear	clear	clear

The ratio of the molecular weight of the PCH to CH:

The molecular weight of the chitosan and phosphonated chitosan was determined using the Mark–Houwink–Sakurada equation.[1,2]

$$[\eta] = kMv^{a} \quad (1)$$

Where

$[\eta]$ = intrinsic viscosity, cm^3/g

M_v = the viscosity-average molecular weight, g/mol

k and a = The Mark-Houwink* constants for a given solute-solvent system

the values of the constants a (0.74) and k (0.00181 cm^3/g) and were found in the literature for 0.1 m acetic acid /0.2 m nacl 0.2 mol/l (medium 2) at 25 °c [3].

Intrinsic viscosity is defined as:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \quad (2)$$

η_{sp} = the specific viscosity

c = the concentration

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \eta_r - 1 \quad (3)$$

$$\eta_r = \frac{\eta}{\eta_o} \quad (4)$$

where

η_{sp} = the specific viscosity

η_r= the relative viscosity

η = the solution viscosity

η_o = the viscosity of the pure solvent

The ratio of the intrinsic viscosity of the phosphonated chitosan to the intrinsic viscosity of the chitosan is found to be 0.74. Moreover, the ratio of the molecular weight of the phosphonated chitosan to the chitosan is 0.67.

Refernces

1 H. Mark, *Hirzel, Leipzig*, 1938, **103**, 391–456.
2 R. Houwink, *Journal für praktische Chemie*, 1940, **157**, 15–18.
3 C. N. Costa, V. G. Teixeira, M. C. Delpech, J. V. S. Souza and M. A. S. Costa, *Carbohydrate Polymers*, 2015, **133**, 245–250.