Supplementary Materials: Anti-scale Performance and Mechanism of Valonia Tannin Extract for Calcium Carbonate in Circulating Cooling Water System

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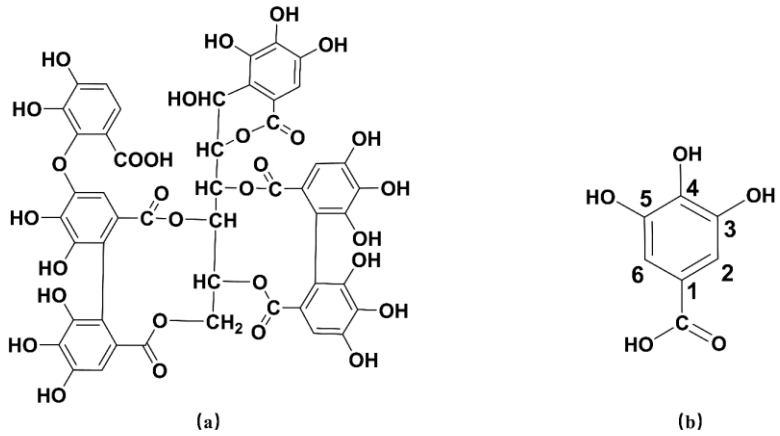

Figure S1. The typical structures of valonia tannin extract (a) along with its representative unit structural (b).

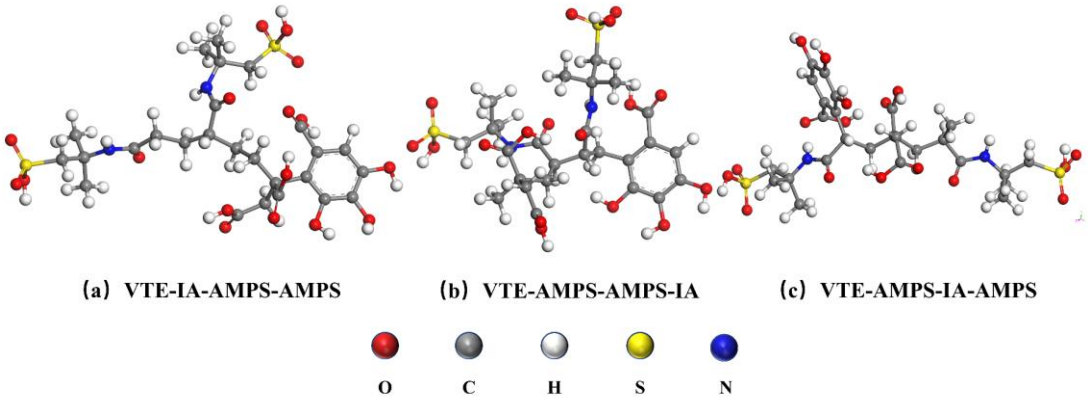

Figure S2. Three random molecular structures of MVTE. (a) VTE-IA-AMPS-IA; (b) VTE-AMPS-AMPS-IA; (c) VTE-IA-AMPS-AMPS.

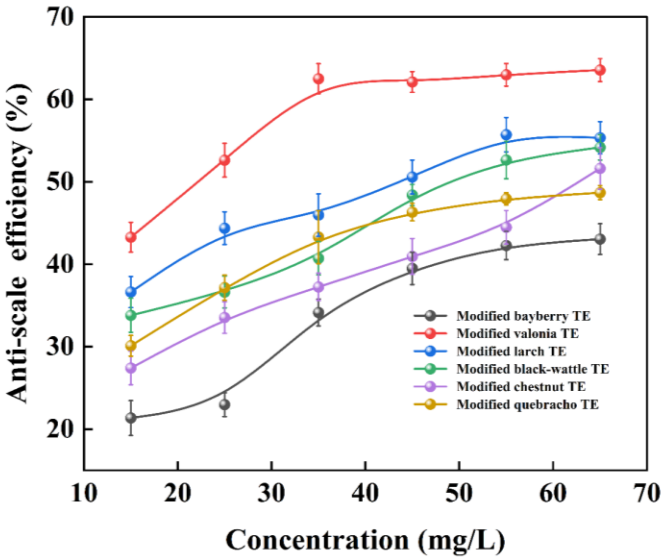

Figure S3. The anti-scale performance of six different modified tannin extracts for $CaCO_3$ scales at pH = 8.

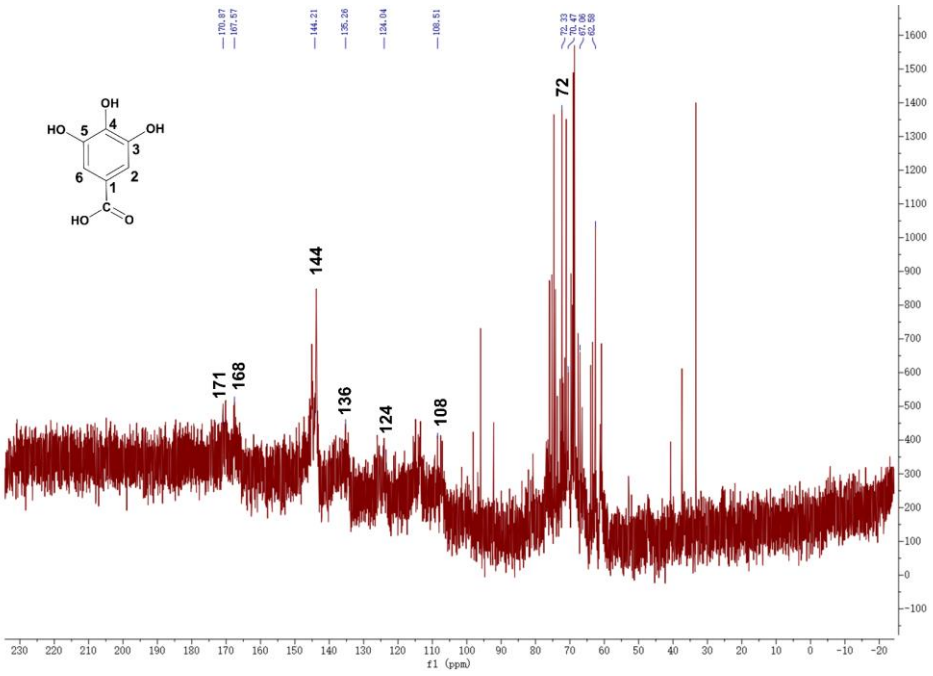

Figure S4. ^{13}C-NMR spectra of valonia tannin extract (VTE).

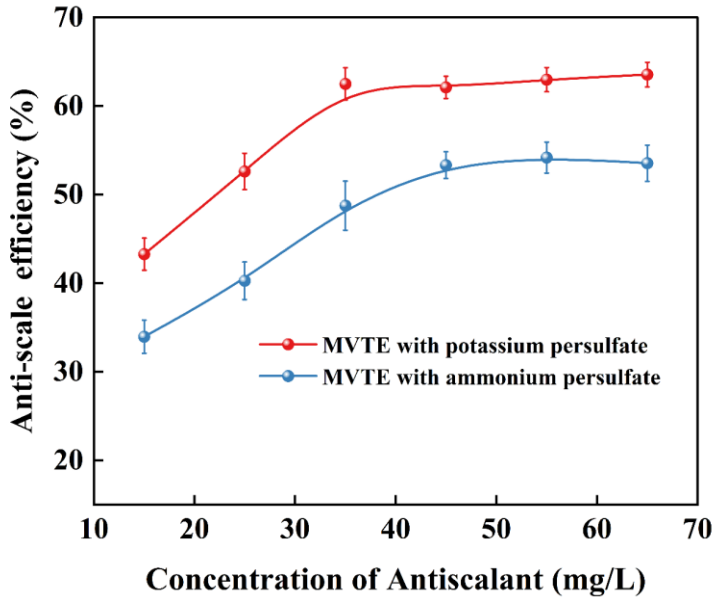

Figure S5. The anti-scale performance of modified valonia tannin extract (MVTE) with either ammonium persulfate or potassium persulfate against $CaCO_3$ scales.

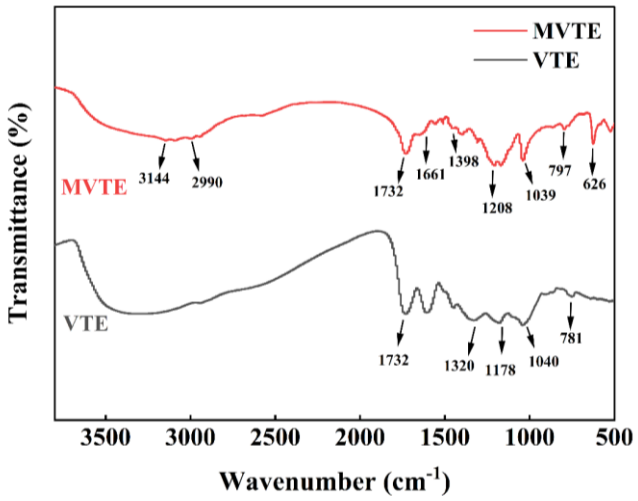

Figure S6. The FT-IR characterizations of MVTE and VTE.

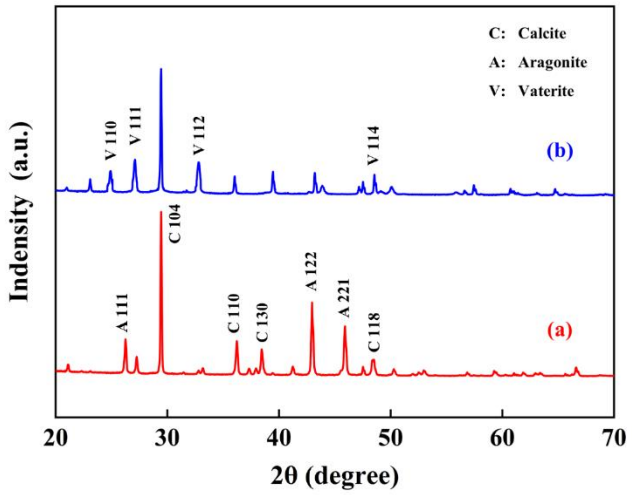

Figure S7. XRD patterns of $CaCO_3$: (a) without and (b) with MVTE.

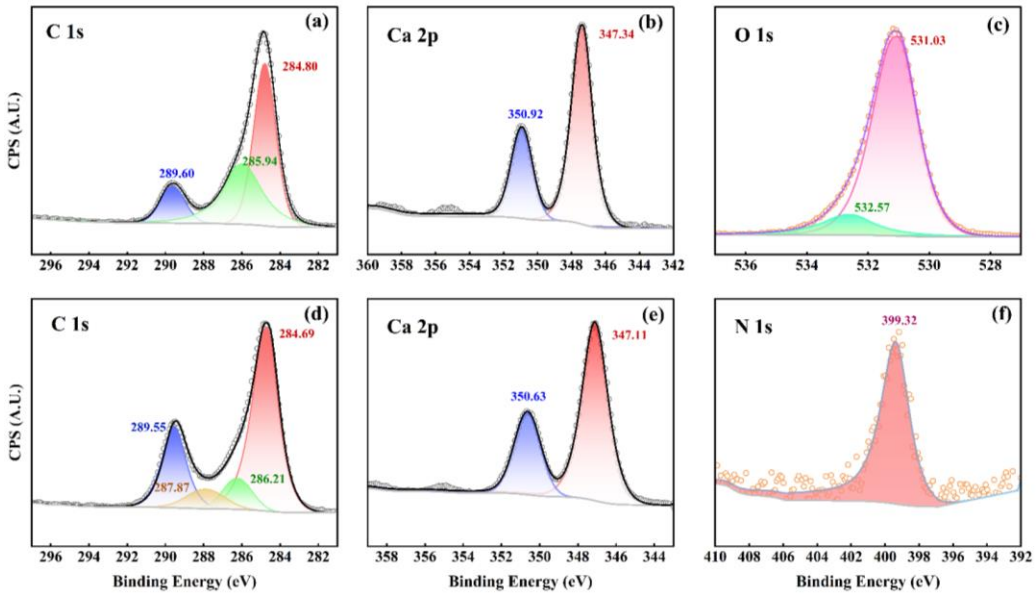

Figure S8. XPS spectra of $CaCO_3$ in the blank: C 1s (a) and Ca 2p (b) as well as in the presence of 35 mg/L MVTE: C 1s (c), Ca 2p (d), O 1s (e), and N 1s (f).

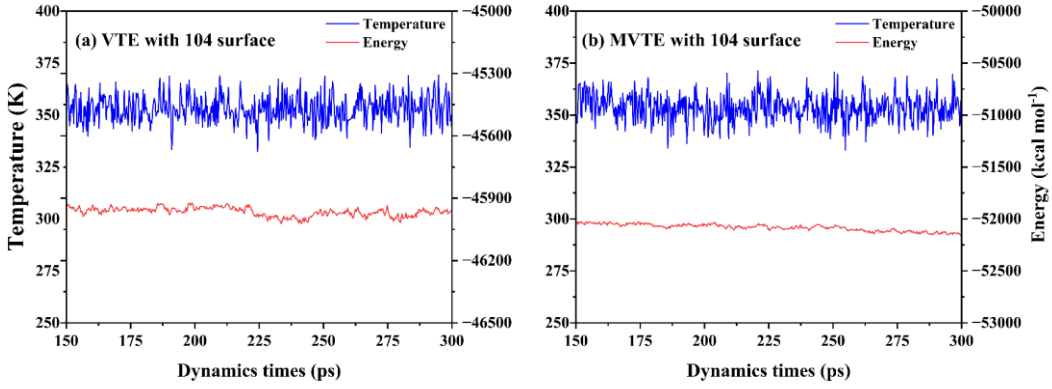

Figure S9. Energy fluctuation and temperature fluctuation of binding process of VTE (a), MVTE (b) onto

the (110) surface of calcite.

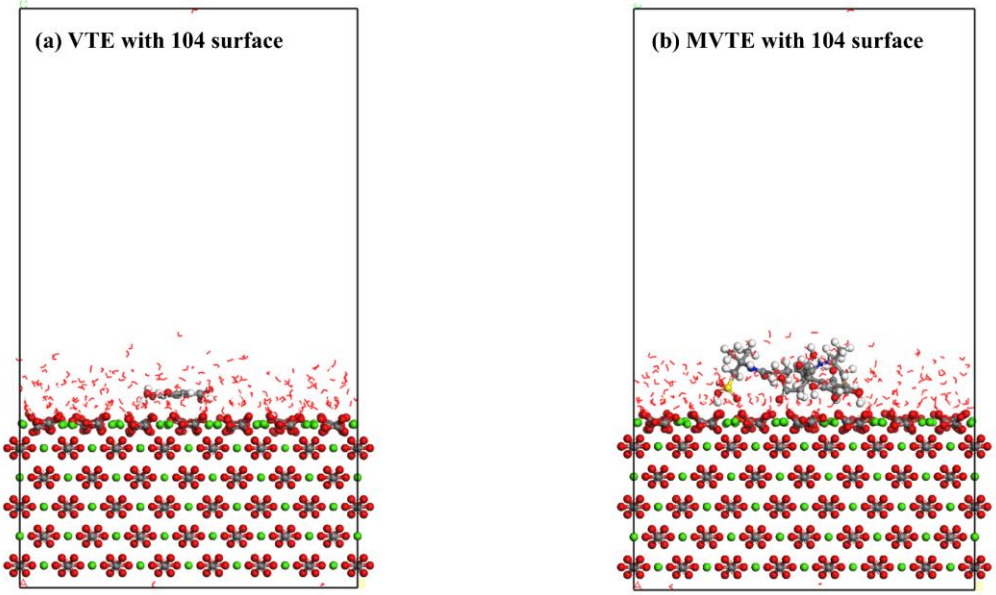

Figure S10. Equilibrium models of the VTE (a), MVTE (b) with (104) surface of calcite.

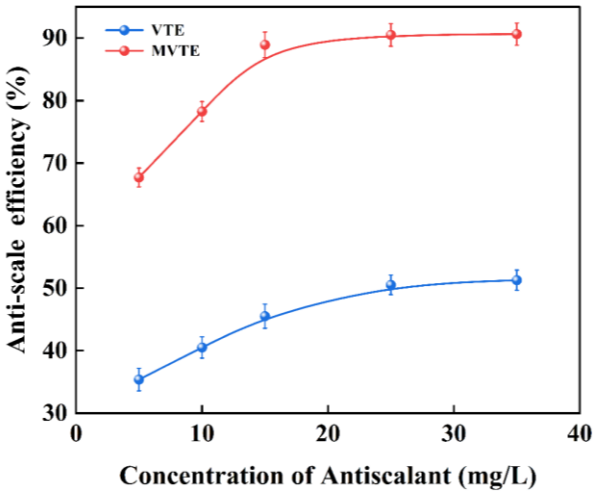

Figure S11 The anti-scale efficiency of VTE on $Ca_3(PO_4)_2$.

Table S1. The components of six common tannin extract.

Category	Tannin extracts	Content of tannin (%)	Content of non-tannin substance (%)
Condensed tannin	Bayberry	70～72	26～28
	Larch	55～57	37～41
	Black-wattle	72～74	18～22
	Quebracho	70～74	8～12
Hydrolyzed tannin	Chestnut	68～72	18～21
	Valonia	70～73	17～23

Table S2. The contents (%) of C, N and S of MVTE.

Element	C	N	S
Theoretical value	40.86	4.56	10.24
Estimate value	37.26	4.20	10.23

Table S3. Molecular weight of MVTE.

Sample	Mw	Mn	PDI
MVTE	4776	3995	1.22

Text S1. Details of the 13C-NMR spectra of VTE.

For the ^{13}C-NMR spectra of VTE(Figure S4), the peak at 171 ppm was relevant to the bands of C=O in gallic acid, the 144 ppm was assign to C_3 and C_5[1]. The peak at 168 ppm belonged to the carboxyl group of gallic acid, and the 136 ppm belonged to C_4[2]. Moreover, the peak at 124 ppm was responsible for C_1 of gallic acid[1]. Additionally, C_2 and C_6 of gallic acid were observed at 108 ppm, and the peak at 72 ppm was attributed to the C-O-C bridges of VTE[3].

References

[1] Resins T formaldehyde, Li J, Li C, et al. Reactivity of Larch and Valonia Tannins in Synthesis of Tannin-Formaldehyde Resins[J]. bioresources, 2016, 11(1): 2256-2268.

[2] Abdalla S, Pizzi A, Bahabri F, et al. Analysis of valonia oak (Quercus aegylops) acorn tannin and wood adhesives application[J/OL]. BioResources, 2015, 10(4): 7165-7177.

[3] Kang SW, Kang K, Kim MA, et al. Phytoestrogenic activity of Aceriphyllum rossii and rapid identification of phytoestrogens by LC-NMR/MS and bioassay-guided isolation[J/OL]. European Food Research and Technology, 2014, 239(2): 237-246.