Electronic Supplementary Material (ESI) for RSC Advances.

Immobilization of heavy metals in tannery sludge by the formation of tobermorite in subcritical water treatment with rice husk silica

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Supplementary Tables

Table S1 Experimental conditions for analyzing the efficacy of SCW treatment.

Experiment runs (code)	Amount of tannery sludge (g)	Amount of silica (g) 95% purity	Amount of $Ca(OH)_2$ (g)
SRC (control)	10	-	-
SR200/30	10	10.5	8
SR240/30	10	10.5	8
SR280/30	10	10.5	8

Table S2: Experimental setup for the formation of tobermorite

Experiment runs (code)	Amount of tannery sludge (g)	Amount of silica (g) 95% purity	Amount of $Ca(OH)_2$ (g)
SR200/60/S	10	10.5	8
SR200/180/S	10	10.5	8
SR200/360/S	10	10.5	8
SR200/360/D	10	21.0	16
SR200/540/S	10	10.5	8
SR240/180/S	10	10.5	8
SR240/180/D	10	21.0	16
SR240/360/S	10	10.5	8
SR240/360/D	10	21.0	16
SR280/60/S	10	10.5	8
SR280/90/S	10	10.5	8

Table S3 Risk assessment code (RAC) for heavy metals in tannery sludge.

Category	RI=(Fl+F2)/total × 100	Risk level
1	< 1	No risk
2	1-10	Low risk
3	11-30	Medium risk
4	31-50	High risk
5	> 50	Very high risk

Table S4 Chemical compositions of rice husk and metal oxides in rice husk ash.

Rice husk		Rice husk ash	
Composition	Contents (%)	Oxides	Contents (%)
Cellulose	31.12	SiO_2	93.19
Hemicellulose	22.48	K_2O	3.84
Lignin	22.34	MgO	0.87
Mineral ash	13.87	Al_2O_3	0.78
Water	7.86	CaO	0.74
Extractives	2.33	Fe_2O_3	0.58

Table S5 Relationship among fractions, eco-toxicity, and bioavailability of HMs [1].

Fractions	Binding strength	Eco-toxicity	Bioavailability
F1+F2	Weakly bound	Direct toxicity	Bio-available
F3+F4	Relatively stable	Potential toxicity	Potential bio-available

F5	Stable	No toxicity	Non-bio-available

Supplementary Figures

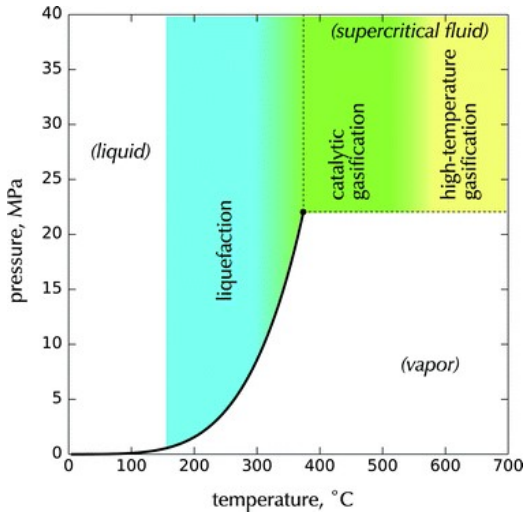


Fig. S1 Pressure-temperature phase diagram of water [2].

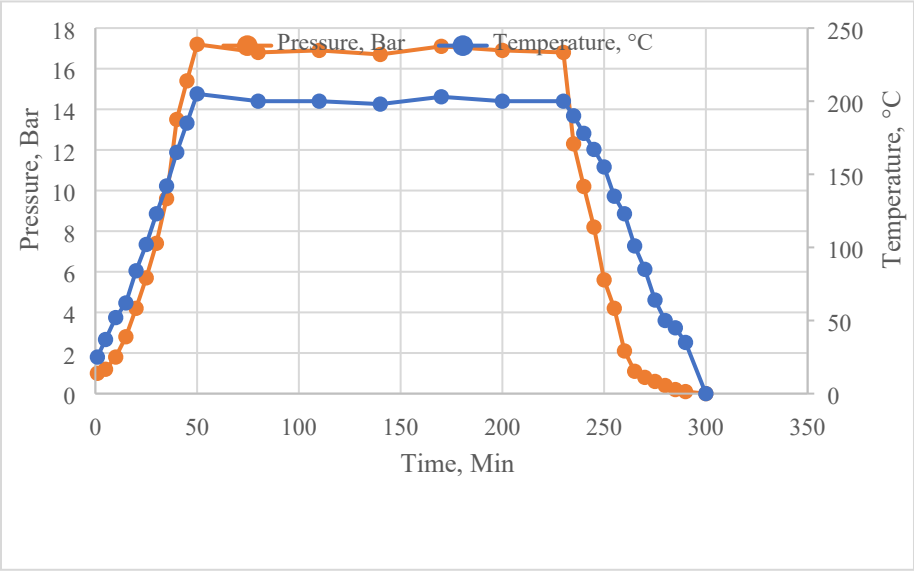
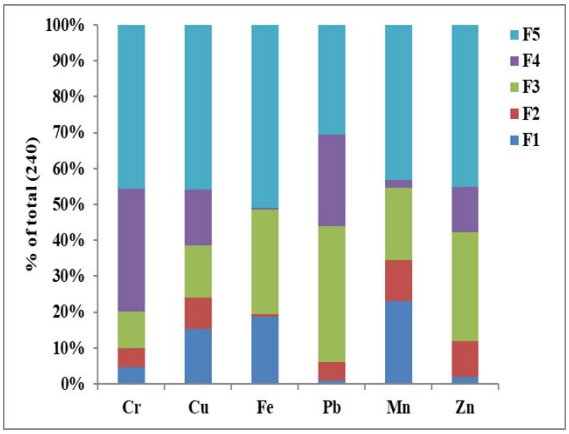
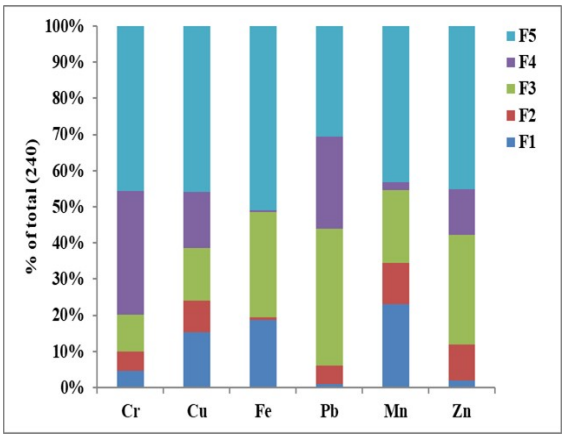


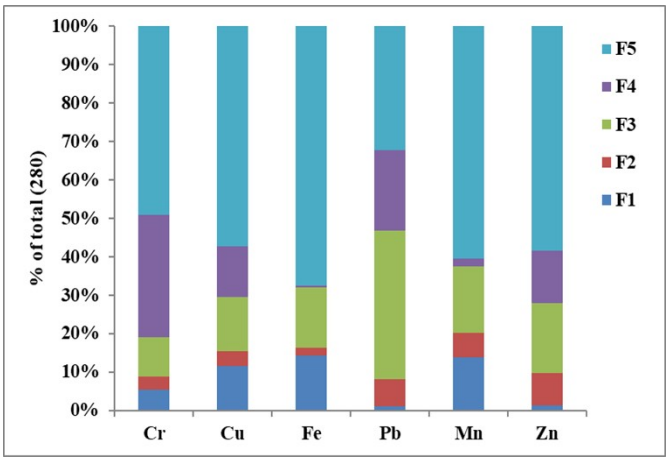
Fig. S2. SCW treatments pressure and temperature profile with time.



(a) 200℃ for 30 min

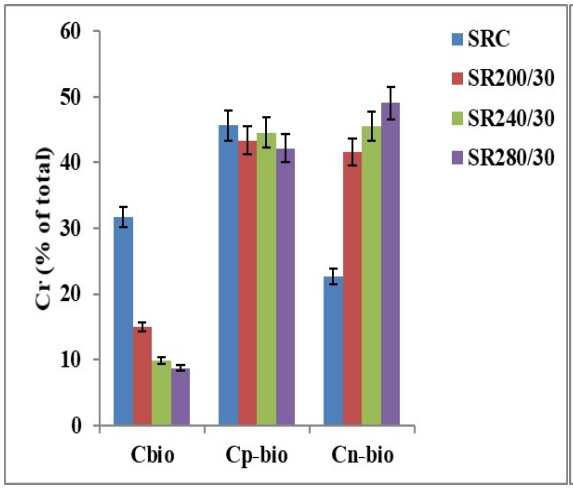


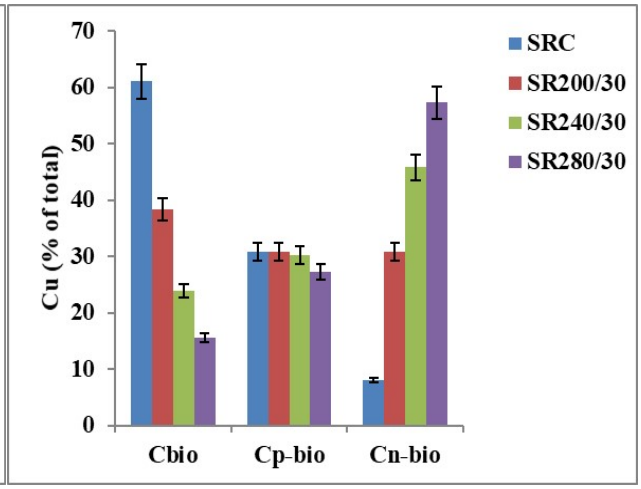
(b) 240℃ for 30 min

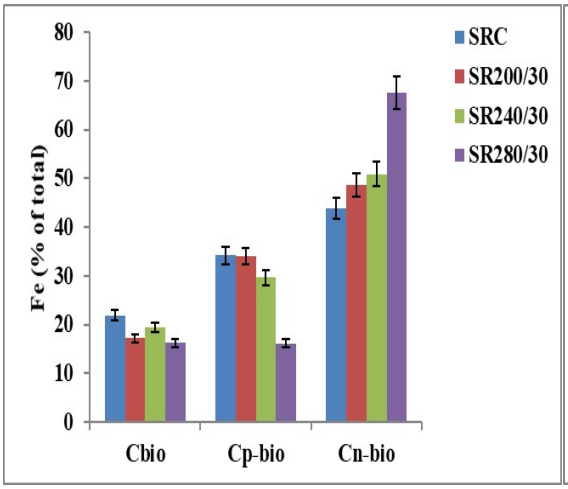


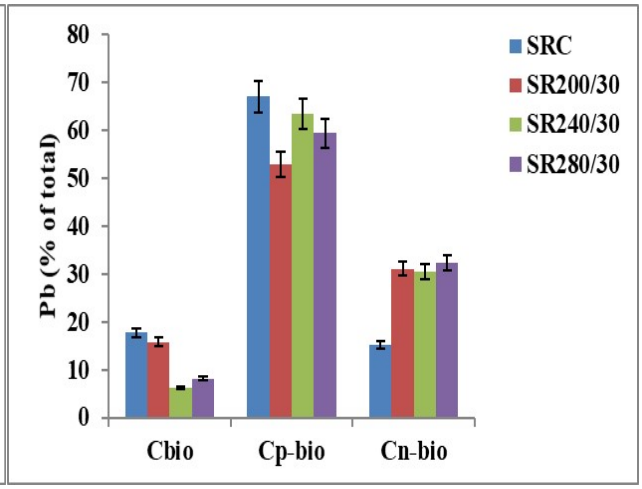
(c) 280℃ for 30 min

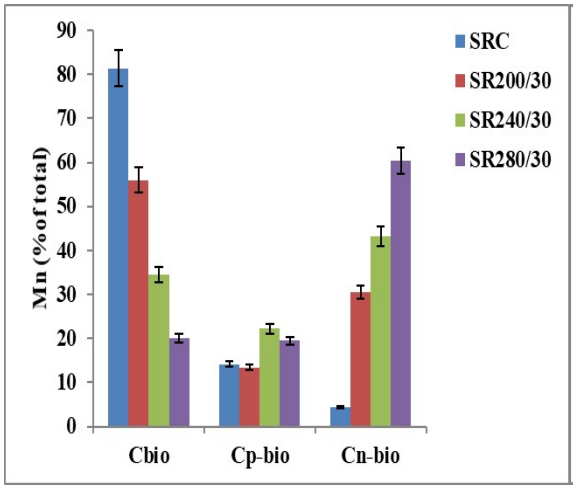
Fig. S3. Fractional distribution of heavy metals in the tannery sludge SCW at 200℃, 240℃, and 280℃, for 30 min.


Cr (% of total)
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30


Cu (% of total)
70
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30


Fe (% of total)
80
70
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30


Pb (% of total)
80
70
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30


Mn (%of total)
90
80
70
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30

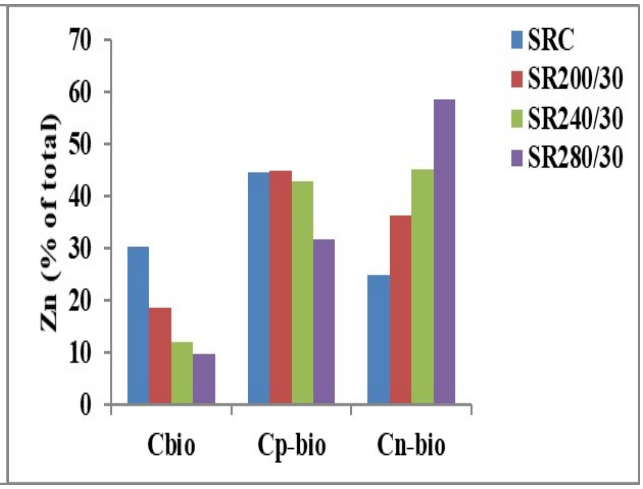

Zn (% of total)
70
60
50
40
30
20
10
0
Cbio
Cp-bio
Cn-bio
SRC
SR200/30
SR240/30
SR280/30

Fig. S4. Distribution of heavy metals, Cr, Cu, Fe, Pb, Mn, and Zn in bio-available (C_{bio}), potential bio-available ($C_{P\text{-}bio}$), and non-bio-available ($C_{N\text{-}bio}$) fractions before and after SCW treatment.

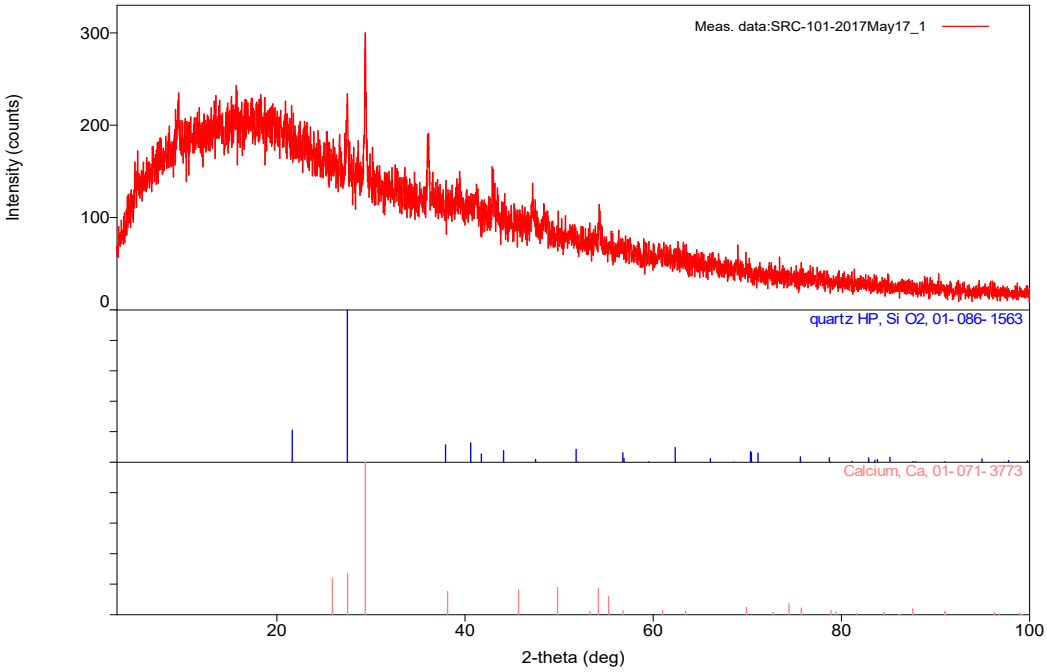
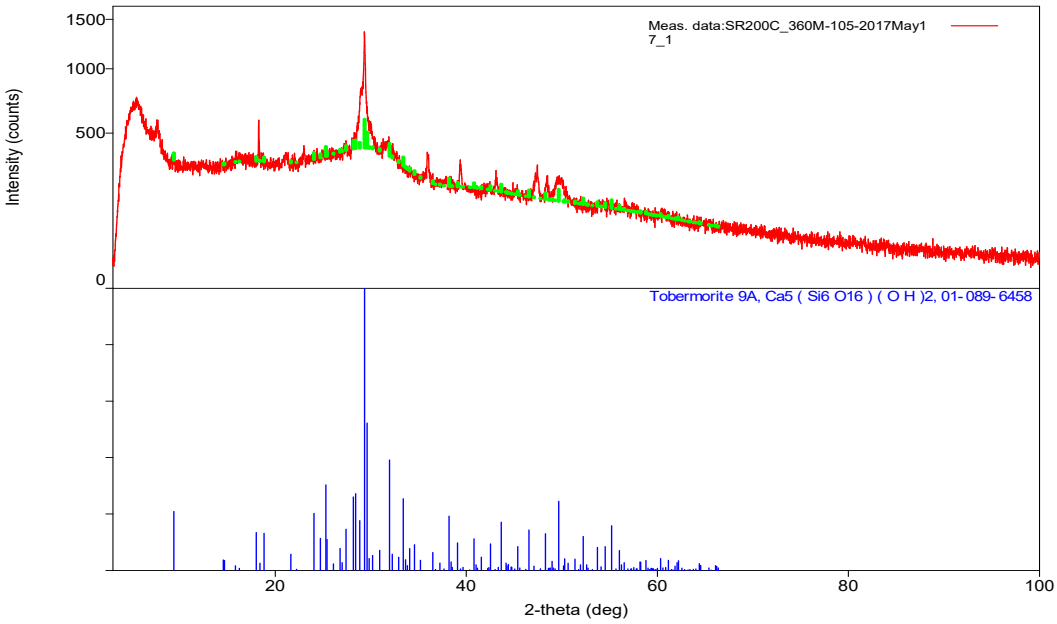
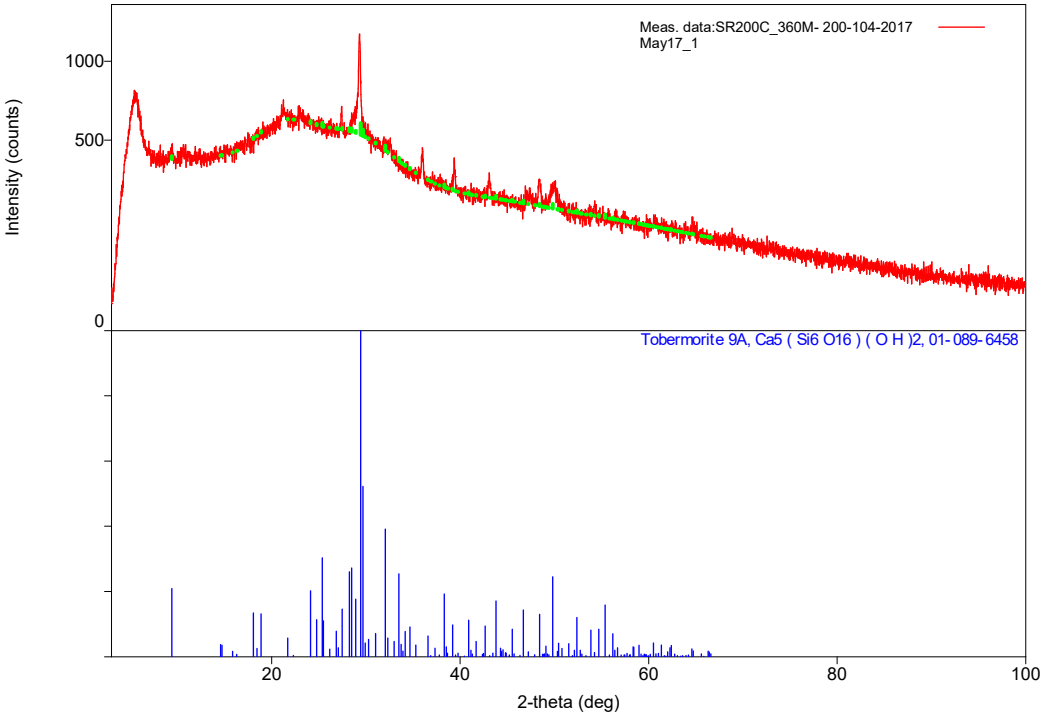


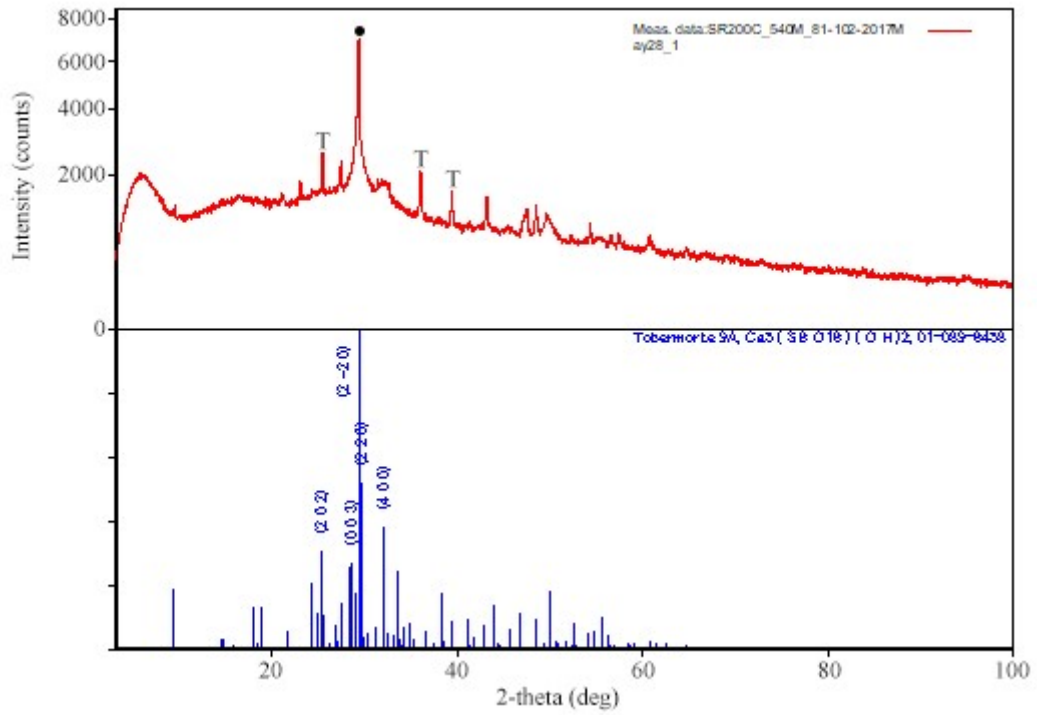
Fig. S5. XRD pattern of raw tannery sludge without SCW treatment (SRC).


Meas. data:SR200C_360M-105-2017May17_1
Tobermorite 9A, Ca5 (Si6 O16) (O H)2, 01-089-6458
Intensity (counts)
2-theta (deg)
1500
1000
500
0
20
40
60
80
100

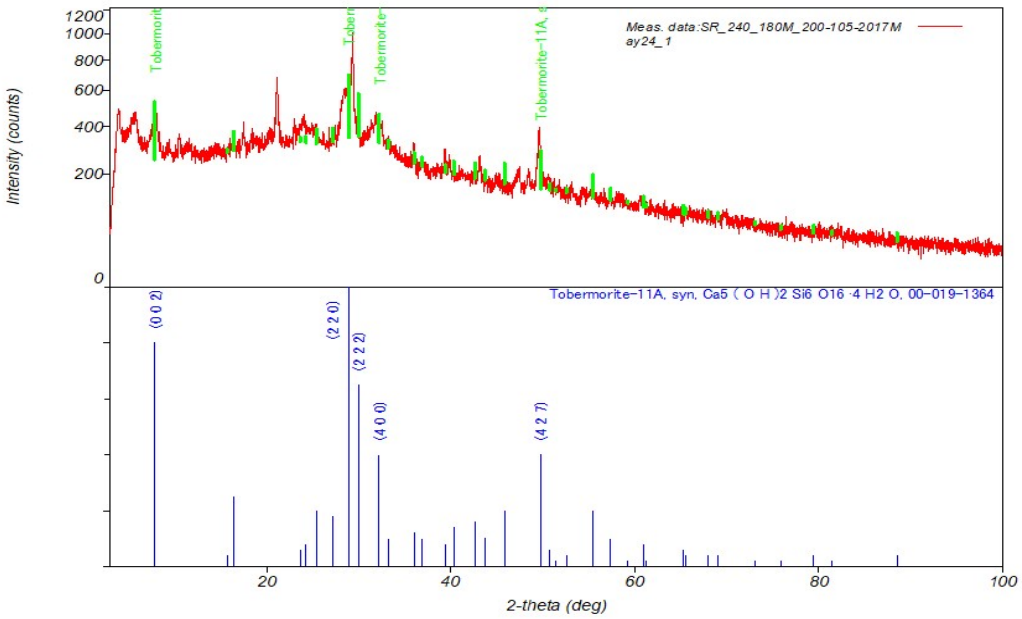
(a)


Meas. data:SR200C_360M- 200-104-2017 May17_1
Tobermorite 9A, Ca5 (Si6 O16) (O H)2, 01-089-6458
Intensity (counts)
2-theta (deg)
1000
500
0
20
40
60
80
100

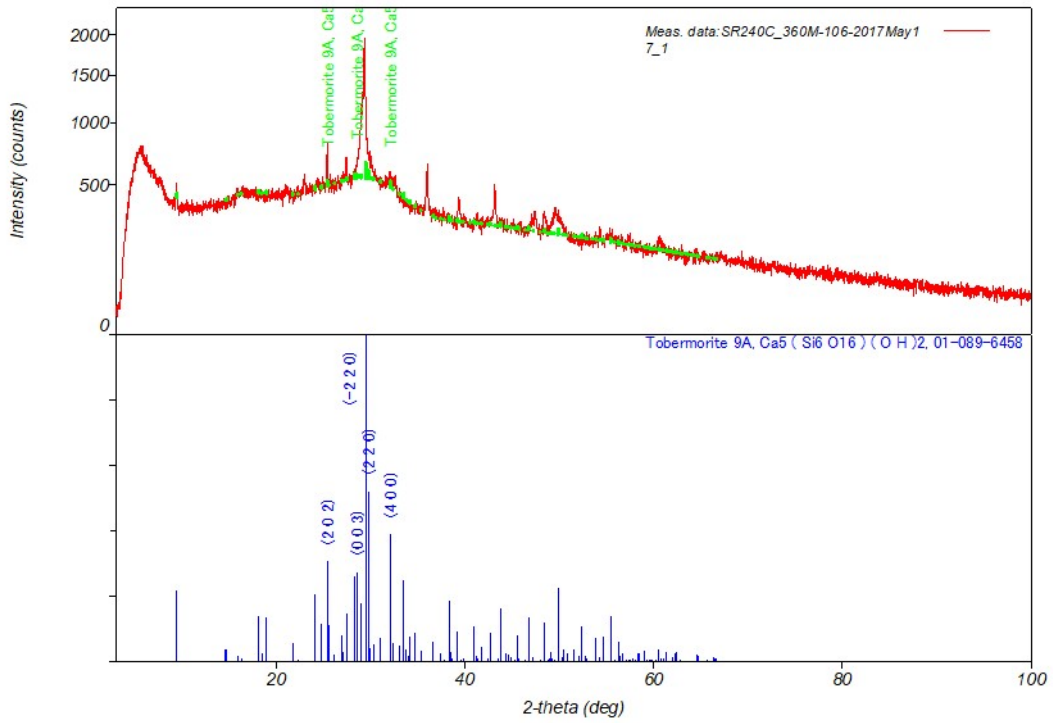
(b)


Meas. data:SR200C_540M_81-102-2017M
ay28_1
Intensity (counts)
8000
6000
4000
2000
0
T
T
T
Tobermorite 9A, Ca5 (Si6 O16) (O H)2, 01-089-8458
(2 -2 0)
(2 2 0)
(0 0 3)
(4 0 0)
20
40
60
80
100
2-theta (deg)

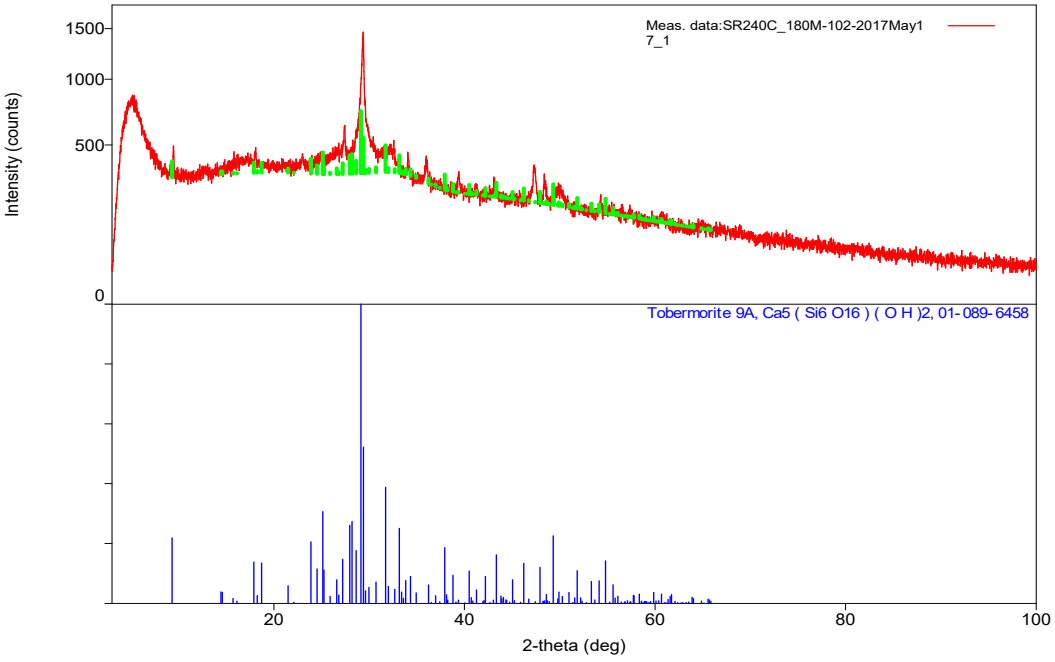
(c)


Meas. data:SR_240_180M_200-105-2017M
ay24_1
Intensity (counts)
1200
1000
800
600
400
200
0
Tobermorite
Tobermorite
Tobermorite-11A,
Tobermorite-11A, syn, Ca5 (O H)2 Si6 O16 ·4 H2 O, 00-019-1364
(0 0 2)
(2 2 0)
(2 2 2)
(4 0 0)
(4 2 7)
20
40
60
80
100
2-theta (deg)

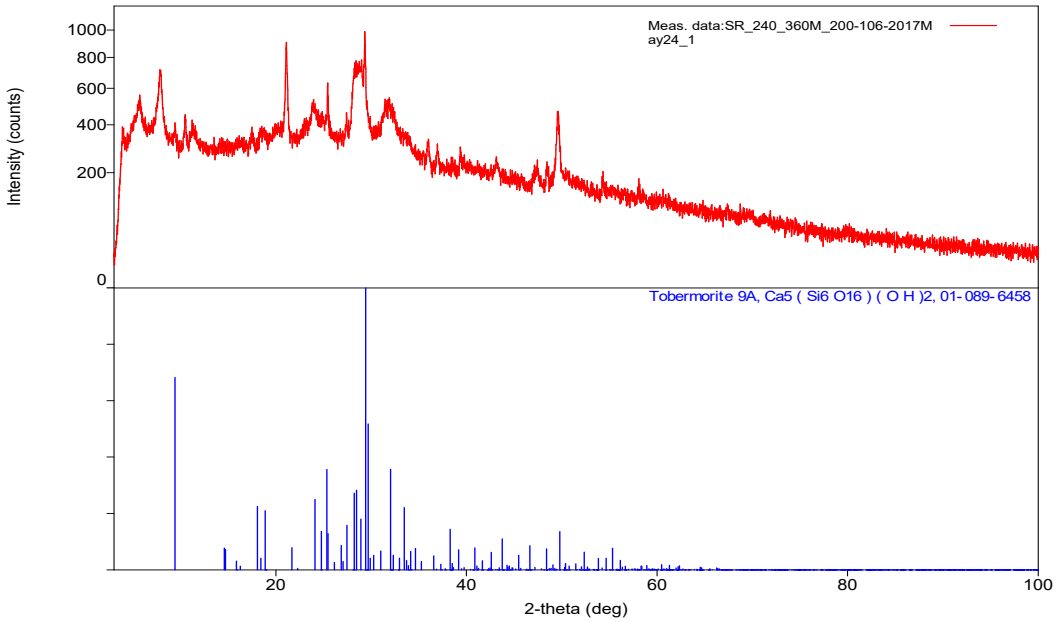
(d)


Meas. data:SR240C_360M-106-2017May17_1
Tobermorite 9A, Ca5 (Si6 O16) (O H)2, 01-089-6458
(-2 2 0)
(2 2 0)
(4 0 0)
(2 0 2)
(0 0 3)
Intensity (counts)
2-theta (deg)

(e)


Meas. data:SR240C_180M-102-2017May17_1
Tobermorite 9A, Ca5 (Si6 O16) (O H)2, 01-089-6458
Intensity (counts)
2-theta (deg)

(f)



(g)

Fig. S6. XRD pattern of SCW-treated tannery sludge. A: SR200/360/S, B: SR200/360/D. XRD pattern of SCW treated solid portion. C: SR200/540/S, D: SR240/180/D, E: SR240/360/D, F: SR240/180/S, G: SR240/360/D.

References

[1] L. Li, Z.R. Xu, C. Zhang, J. Bao and X. Dai, Bioresour. Technol. **121**, 169-175 (2012). https://doi.org/10.1016/j.biortech.2012.06.084

[2] A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, M.J. Antal and J.W. Tester, Energ. Environ. Sci. **1(1)**, 32-65 (2008).