

Supporting material for

Sustainable Fertiliser Mesh, '4D'-Precision Engineered by Flow Chemistry: Minimising Agrochemical Pollution

Tu Nguyen Quang Le^{a,b}, Chang Nong Lim^c, Ian Fisk^{b,e}, Nam Nghiep Tran^{a,e}, Volker Hessel^{*a,f}, Karen Robertson^{*c,g}

^a School of Chemical Engineering, Faculty of Sciences, Engineering and Technology, The University of Adelaide, Adelaide SA 5005, Australia.

^b International Flavour Research Centre, Division of Food, Nutrition and Dietetics, University of Nottingham, Sutton Bonington Campus, Loughborough LE12 5RD, United Kingdom.

^c Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park Campus, Nottingham NG7 2RD, United Kingdom.

^d International Flavour Research Centre (Adelaide), School of Agriculture, Food and Wine and Waite Research Institute, The University of Adelaide, PMB 1, Glen Osmond, South Australia 5064, Australia.

^e School of Chemical Engineering, Can Tho University, Vietnam.

^f School of Engineering, University of Warwick, Library Rd, Coventry, United Kingdom.

^g Advanced Material Research Group, Faculty of Engineering, University of Nottingham, University Park Campus, Nottingham NG7 2RD, United Kingdom.

*Corresponding authors: karen.robertson@nottingham.ac.uk; volker.hessel@adelaide.edu.au

Pages: 7; Tables: 3, Figures: 6

Table S1. Summary of soil properties

Table S2. Kinetic of cross-linking of chitosan and citrate ion

Table S3. Value of r_0 , D_r and $t_{0.8}$ of different samples obtained from the logistic growth model with a damping coefficient for the releasing behaviour of both composites in aqueous media

Figure S1. Schematic illustration of chitosan cross-linked citrate ion

Figure S2. SEM images of apatite nanoparticles

Figure S3. Optical microscopy image of passive merging channel

Figure S4. Viscosity titration of citrate ion 0.15 M in 15 mL of Chitosan 1% (w/v). Measurement performed at 24.1°C at 1000 s⁻¹.

Figure S5. Elemental mapping images of section (inside) of the capsule on the necklace of S7_5.25_0.5_1.25_CS sample

Figure S6. SEM-EDS results for fertiliser with different initial conditions

Table S1. Summary of soil properties

Analysis	Result	Guideline	Interpretation	Comments
pH	8.1	6.0	High	High. An alkaline environment will reduce the availability of certain nutrients - particularly P, K, B, Co, Cu, Fe, Mn and Zn. An elevated pH will also impact on beneficial soil fungal populations and activity.
Phosphorus (ppm)	21	16	Normal	(Index 2.5) 20 kg/ha P ₂ O ₅ (16 units/acre).
Potassium (ppm)	131	121	Normal	(Index 2.1) Adequate level for grazing system.
Magnesium (ppm)	89	51	Normal	(Index 2.8) PRIORITY FOR LIVESTOCK HEALTH. Apply 25 kg/ha MgO (20 units/acre) every three to four years. Further applications may be required if there is a history of hypomagnesaemia.
Calcium (ppm)	2244	2000	Normal	Adequate level.
Sulphur (ppm)	18	10	Normal	Adequate level.
Manganese (ppm)	46	110	Very Low	Consider treatment for optimum grass growth.
Copper (ppm)	4.5	8.0	Low	PRIORITY FOR LIVESTOCK HEALTH.
Boron (ppm)	1.25	0.50	Normal	Adequate level.
Zinc (ppm)	5.3	7.0	Slightly Low	PRIORITY FOR LIVESTOCK HEALTH.
Molybdenum (ppm)	0.05	<0.5	Normal	No problems anticipated.
Iron (ppm)	614	50	Normal	Adequate level.
Sodium (ppm)	19	90	Very Low	PRIORITY FOR LIVESTOCK HEALTH.
C.E.C. (meq/100g)	12.3	15.0	Slightly Low	Cation Exchange Capacity indicates a slightly low nutrient holding ability - soil applied nutrients could be readily leached. Where possible foliar applied nutrients should be recommended.

Table S2. Kinetic of cross-linking of chitosan and citrate ion

$$-r = k [\text{Chitosan}]^x [\text{Citrate}]^y [\text{Acetic}]^z \Rightarrow \begin{cases} k = 9.92 \times 10^{-4} \\ x = -2.1 \\ y = 2.35 \\ z = 0 \end{cases}$$

$$k = A \times e^{\frac{-E_a}{RT}} \Rightarrow \begin{cases} A = 5.43 \times 10^7 \\ E_a = 61.08 \text{ KJ.mol}^{-1} \end{cases}$$

Temp. Concentrations					Equilibrium time
°C	Citrate M	Chitosan (w/v)	% Acetic acid M	Fitting	s
24.1	0.15	1	0.1	$y = 9.36681 + 50.50092.e^{-x/28.15465}$	255
24.1	0.075	1	0.1	$y = 14.08345 + 33.18494.e^{-x/96.30774}$	781.5
24.1	0.075	0.5	0.05	$y = 5.61841 + 18.3832.e^{-x/17.05091}$	132
24.1	0.075	0.5	0.1	$y = 9.31094 + 12.36181.e^{-x/16.96054}$	127.5
18.1	0.15	1	0.1	$y = 9.36778 + 54.06066.e^{-x/46.29918}$	424.5

The modified equation for the releasing behaviour model has been adapted for this study and is as follows:

$$H = 1 - e^{-\frac{r_0}{C_{inf}} \times t^{1-D_r}}$$

Where, H : releasing efficiency
 r_0 : initial releasing rate (mg mL⁻¹ min⁻¹)
 C_{inf} : equilibrium concentration (mg mL⁻¹)
 D_r : damping coefficient

Table S3. Value of r_0 , D_r and $t_{0.8}$ of different samples obtained from the logistic growth model with a damping coefficient for the releasing behaviour of both composites in aqueous media.

Sample	Aqueous media	r_0 (mg L ⁻¹ min ⁻¹)	D_r	R^2	$t_{0.8}$
CFI-made-CAC	Deionised water	0.0048	0.85325	0.9403	69 days
	Acetate buffer	84.4152	0.81139	0.9541	9.4 mins
sheath-made-CAC	Deionised water	0.0012	0.74135	0.9669	2422 days
	Acetate buffer	20.1872	0.83865	0.9779	62 days

Figure S1. Schematic illustration of chitosan cross-linked citrate ion

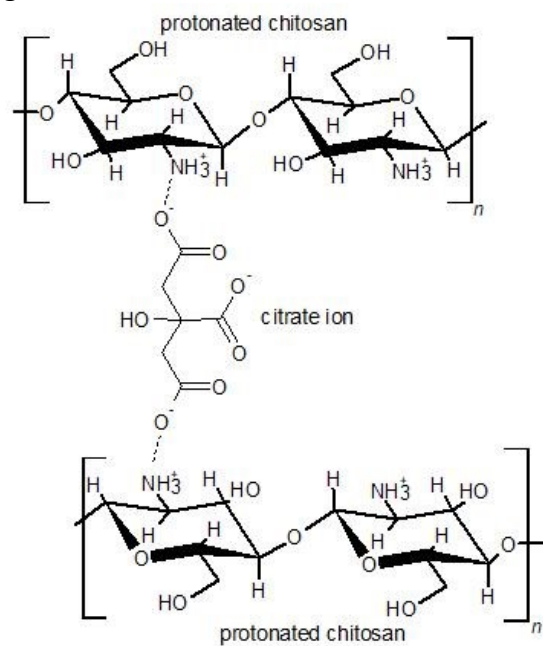


Figure S2. SEM images of apatite nanoparticles

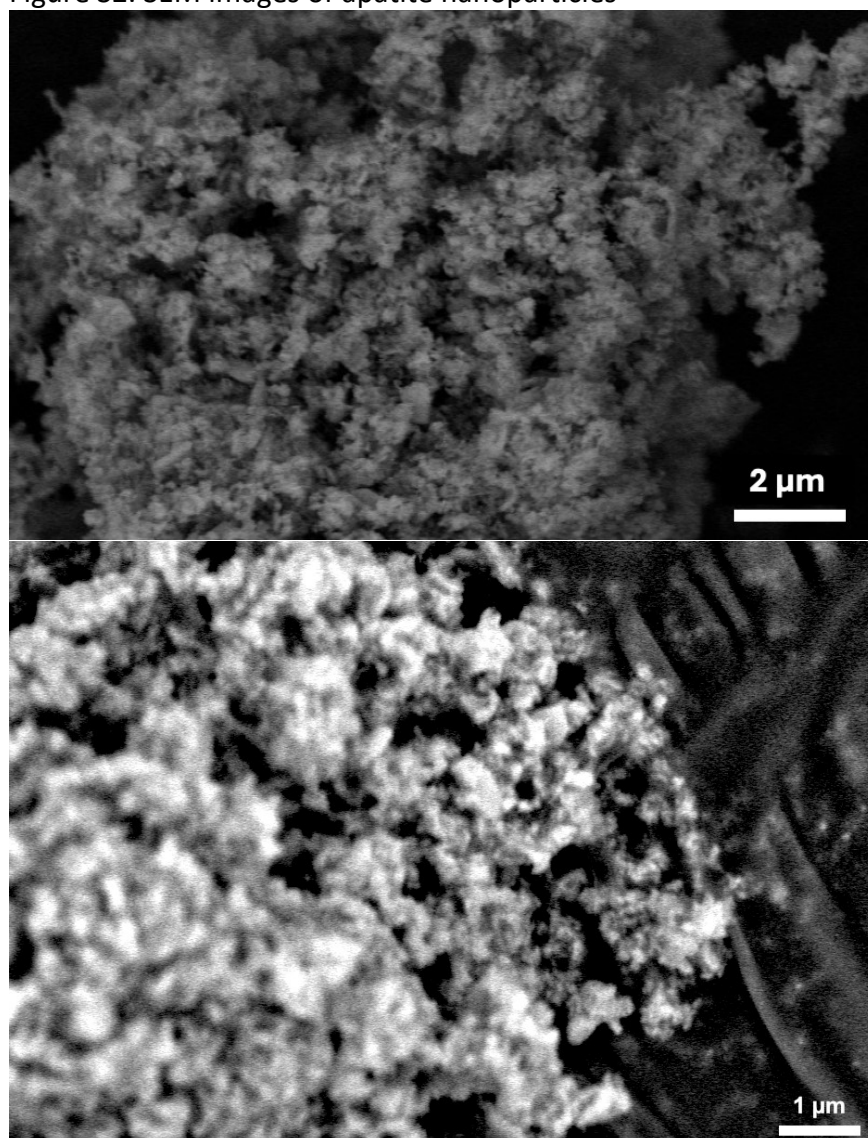


Figure S3. Optical microscopy image of passive merging channel

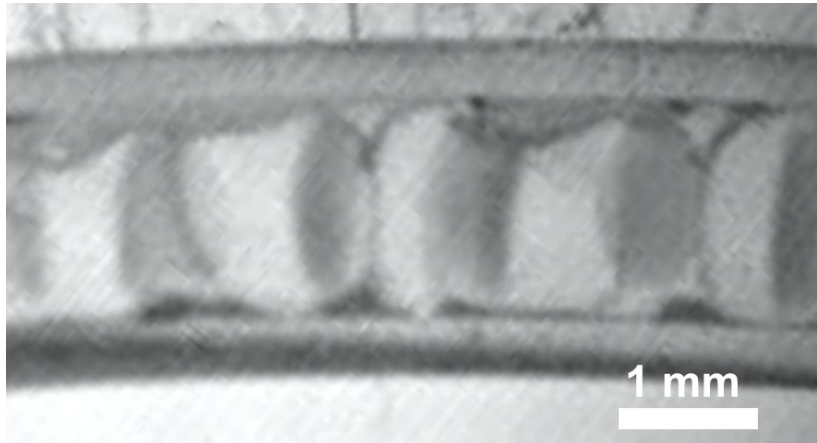


Figure S4. Viscosity titration of citrate ion 0.15 M in 15 mL of Chitosan 1% (w/v). Measurement performed at 24.1°C at 1000 s⁻¹.

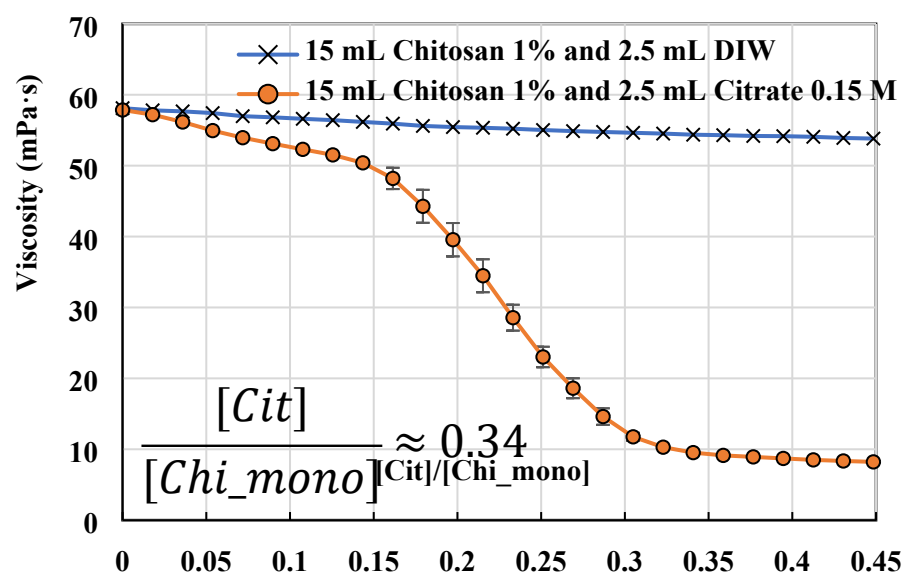


Figure S5. SEM-EDS results for fertiliser with different initial conditions

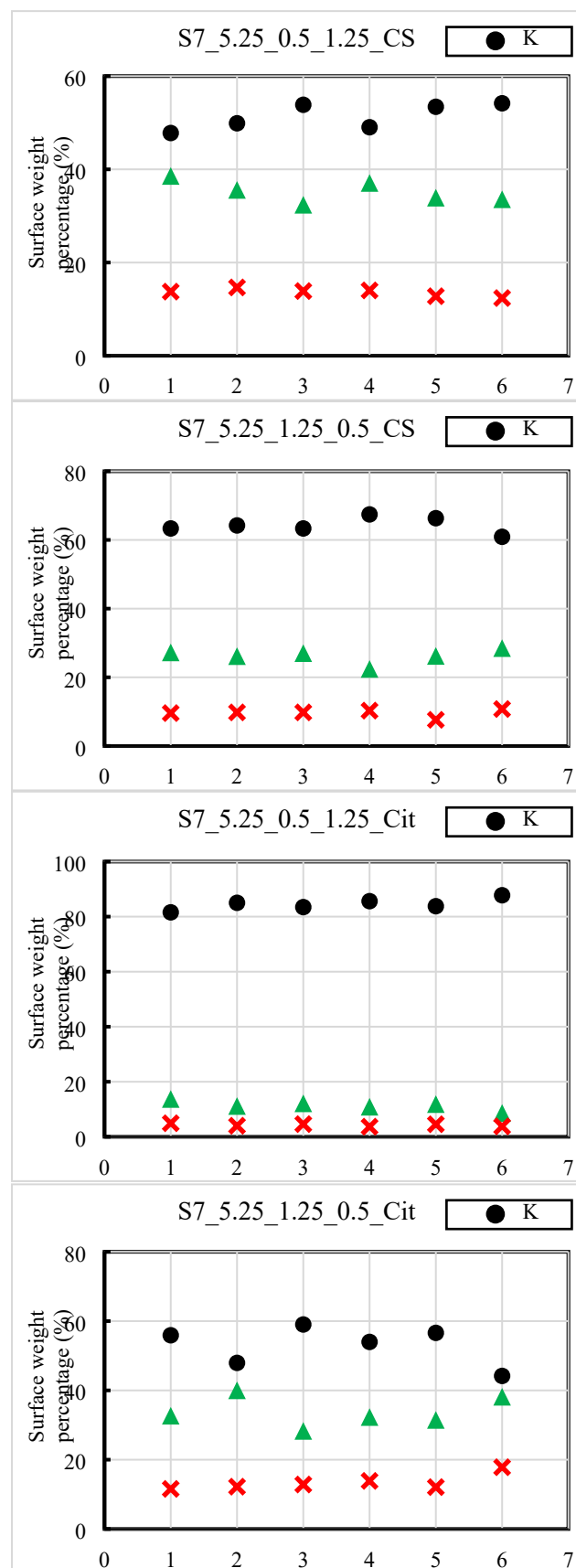


Figure S6. Elemental mapping images of section (inside) of the capsule on the necklace of S7_5.25_0.5_1.25_CS sample

