Copper-binding of alginate beads effects on oxidative stability of vegetable oil

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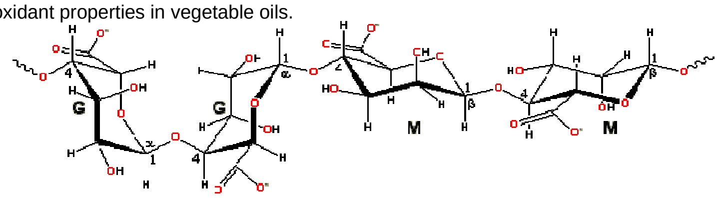
Introduction

Alginate is a polysaccharide produced from brown algae and is composed of β-D-mannuronic acid and α-D-guluronic acid, the residues being grouped in long mono-polymeric or hetero-polymeric sequences. Alginate has the capacity to form gels/beads in the presence of divalent cations such as **copper (Cu)**(Rui Rodrigues, et al. (2006).

The gelation process is highly dependent on the type of alginates used and the cross-links are grouped into egg-box structures in which each metallic ion binds to two carboxyl groups on adjacent alginate molecule Morris (1990), leading to a viscoelastic solid behaviour.

Micronutrient fortification has been challenging and strongly dependent on the chemical interactions between the food components and the bioavailable cation sources, causing undesirable flavours by promoting **oxidation of fats/oils**, as well as metallic taste, unappealing colour, degradation of vitamins and minerals.

The present study examined the copper binding of alginate beads and their anti-oxidant properties in vegetable oils.



Alginate structure: β-(1→ 4)-linked D-mannuronic acid (M) and α-(1→ 4)-linked L-guluronic acid (G) residues

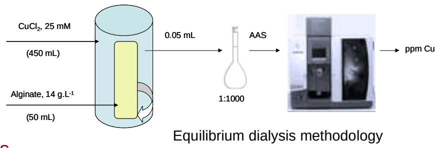
OBJECTIVE

Assess the effect of the water soluble micronutrients, copper, on the oxidative stability of model oil systems containing alginate beads.

Materials and Methods

Alginate (90 g sodium alginate kg^{-1} powder) was obtained from Inotech (Basel, Switzerland). Alginate solution (14 $g.L^{-1}$) was prepared in Milli® Q water at room temperature, followed by filtration through a 0.20 µm Sartolab-P20 plus filter (Sartorius, Germany).

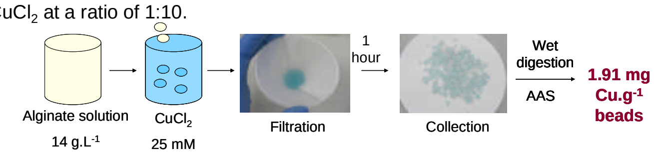
Equilibrium dialysis of the Alginate solution (14 $g.L^{-1}$) was conducted against $CuCl_2$ solution (25 mM). The amount of copper bound was detected using an Atomic Absorption Spectrophotometer (Varian SpectrAA-240, Australia) at times 0-72 hours, following the method derived from Alexa *et al.* (2010).



Equilibrium dialysis methodology

Preparation of alginate beads

Alginate beads were formed by pipetting drops of the above solution into 25 mM $CuCl_2$ at a ratio of 1:10.



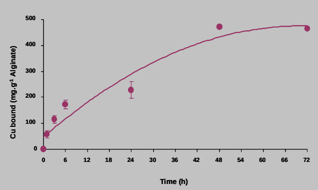
Crude water-in-oil emulsions were prepared by partially replacing the aqueous phase with equivalent levels of Cu-Alginate beads in order to give a final Cu concentration of 0, 0.1, 0.3, 1, 3, 10 mM reported to the total quantity (0.1 kg). The oil phase (600 $g.kg^{-1}$) contained commercial corn or sunflower oil. Control samples were prepared in the same way, the aqueous phase containing free Cu from 200 mM $CuCl_2$ solution.

Peroxide value of the emulsions – PV (mEq $O_2.kg^{-1}$ oil) – oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) ion by hydroperoxides in the presence of ammonium thiocyanate to produce ferric thiocyanate – quantified spectrophotometrically (Cary 100 Bio instrument) at 505 nm.

Results & Discussion

1. Binding capacity of Alginate

Equilibrium dialysis



✓High electrostatic binding capacity of divalent cations (Cu^{2+}) with 56.98 mg Cu bound by 1 g Alginate after 1 hour

✓Equilibrium reached after 72 hours, with approximately 420 mg Cu bound by 1 g Alginate

2. Characterisation of Cu-Alginate beads

✓The beads used for the present study were prepared at macro scale (~ 2 mm in diameter)

✓Developing micro-beads (~250 µm) to entrap micronutrients, such as Cu, can be successfully done using an Inotech encapsulator (Basel, Switzerland), with possible functionality application in food systems (Fig. 1)

Fig 1. Alginate beads formed in 200 mM $CuCl_2$, using a 200 µm nozzle

3. Oxidation assay

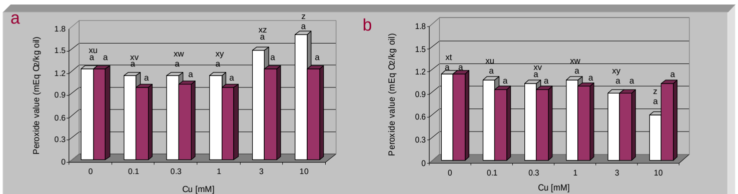


Fig 2. Effect of Copper on the oxidation of an unbound Cu/corn oil system ( ) and Cu-Alginate beads/corn oil system ( ) after a) 3 hours and b) 7 days. Letters a, b, c represent significant differences within treatment means between 3 hours and 7 days days. Letters u, v, w, x, y, z represent significant differences between treatment means after 3 hours and 7 days. Means with the same letter do not differ significantly at *P < 0.05.

✓Corn oil systems were relatively stable against oxidation

✓Cu-Alginate beads did not have a significant effect on the reduction of peroxide values

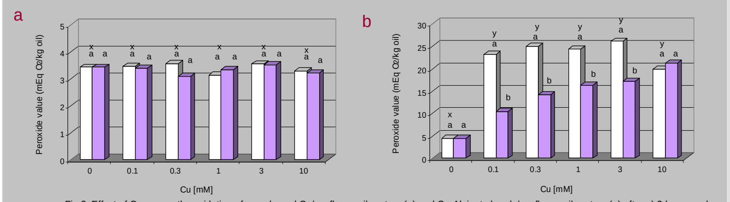


Fig 3. Effect of Copper on the oxidation of an unbound Cu/sunflower oil system ( ) and Cu-Alginate beads/sunflower oil system ( ) after a) 3 hours and b) 7 days. Letters a, b, c represent significant differences within treatment means between 3 hours and 7 days. Letters u, v, w, x, y, z represent significant differences between treatment means after 3 hours and 7 days. Means with the same letter do not differ significantly at *P < 0.05.

✓The more unsaturated Sunflower oil system was less stable than corn oil system

✓Samples containing Cu-Alginate beads showed a significant reduction (***P<0.001) in the peroxide values after 7 days as compared to the controls (unbound Cu).

Conclusions

✓Alginate-mineral delivery systems can be developed following the microencapsulation techniques
✓Copper is an important micronutrient but can promote lipid oxidation of the fat component of oil systems
✓The binding of Copper to alginate beads can be used to reduce the lipid oxidation of highly unsaturated oils such as Sunflower oil.

References

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