

Copper(II)–mediated thermolysis of alginates: A model kinetic study on the influence of metal ions in the thermochemical processing of macroalgae

J. S. Rowbotham^a, P. W. Dyer^{a*}, H. C. Greenwell^b, D. Selby^b, M. K. Theodorou^{c,d}

^a Centre for Sustainable Process Chemistry, Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom

^b Department of Earth Sciences, Durham University, South Road, Durham, DH1 3LE, United Kingdom

^c Centre for Process Innovation, Wilton Centre, Wilton, Redcar, TS10 4RF, United Kingdom

^d School of Biological and Biomedical Sciences, Durham University, South Road, Durham, DH1 3LE, United Kingdom

Summary

Thermochemical processing methods such as pyrolysis are of growing interest as a means of converting biomass into fuels and commodity chemicals in a sustainable manner. Macroalgae, or seaweed, represent a novel class of feedstock for pyrolysis that, but due to the nature of the environments in which they grow coupled with their biochemistry, they naturally possess high metal contents. Although the impact of the presence of metals upon the pyrolysis of terrestrial biomass is well documented, their influence upon the thermochemical conversion of marine-derived feeds is largely unknown. Furthermore, these effects are inherently difficult to study owing to the heterogeneous character of natural seaweed samples. The work described in this paper utilises copper(II) alginate, together with alginic acid and sodium alginate as model compounds with which to explore for exploring the effects of metals upon macroalgae thermolysis. A TGA-FTIR study revealed that, unusually, Cu²⁺ ions promote the onset of pyrolysis in the alginate polymer, with copper(II) alginate initiating rapid devolatilisation at 143 °C, 14 °C lower than alginic acid and 61 °C below the equivalent point for sodium alginate. Moreover, this effect was mirrored in a sample of wild *L. digitata* that had been doped with Cu²⁺ ions prior to pyrolysis, thus validating the use of alginates as model compounds with which to study the thermolysis of macroalgae. These observations indicate the varying impact of different metal species on thermochemical behaviour of seaweeds and offer insight into the pyrolysis of brown macroalgae used in phytoremediation of metal containing waste streams.

Keywords: alginate, biofuel, copper, pyrolysis, thermochemistry, seaweed

1. Introduction

The search for sources of fuels and chemicals that are sustainable, in both an environmental and economic sense, is rapidly intensifying as demands on fossil fuel-based resources increase. Here, biofuels represent one of a number of renewable technologies that aim to alleviate an over dependence on fossil-fuel-derived hydrocarbons. However, in recent years, the social, financial,

climatological, ecological and political impacts of certain biofuels, such as corn-derived ethanol and palm oil-based biodiesel, have been highly contested [1].

With this in mind, so-called “advanced” biofuels, derived primarily from feedstocks such as waste and non-edible plant matter, have awoken been met interest from the scientific community and beyond [2].

Though advanced biofuels are naturally more sustainable than their earlier counterparts, there are inevitable technological difficulties associated with the requirement to treat Advanced biofuels are derived primarily from feedstocks such as waste and non-edible plant matter, and aim to be readily integrated into existing infrastructures within society in a significantly more sustainable fashion than earlier biofuel counterparts. Options for the production of advanced biofuels do, however, present significant technological challenges, demanding the treatment of complex, heterogeneous, multi-component feedstocks, which may be difficult to upgrade using conventional biomass processing techniques such as fermentation and anaerobic digestion [3]. Consequently, thermochemical processing methods such as pyrolysis, hydrothermal liquefaction and gasification (all of which utilise heat to convert the feed) have come to the fore as versatile treatment options owing to their versatility and ability to tolerate virtually any feedstock with an appreciable organic content [4]. Consequently In this context, a diverse range of raw materials have now been considered for thermochemical processing for the production of fuels and chemicals; from including woods [5], bagasse [6] and, rice husks [7], to tyres [8], duck weed [9], and sewage sludge [10].

One type of feedstock that has demonstrated considerable potential in thermochemical processing, are macroalgae [11–14]. Macroalgae, often referred to as *seaweed*, are a group of fast growing aquatic organisms that include some 9000 species world-wide [15]. Owing to the need for structural flexibility in turbulent coastal environments, macroalgae consist predominantly of elastic polysaccharides such as laminarin, carrageenan, agarose and alginic acid [16,17]; a stark contrast to the rigid lignocellulosic support required by terrestrial flora. This constitution is in stark contrast to terrestrial flora, which have evolved in an environment where a rigid lignocellulosic structural support is essential. Clearly, tThese differences in biochemical composition mean that macroalgae offer unique opportunities both in terms of thermochemical processing and in the resulting products compared to their land-based counterparts. ManyMoreover, seaweeds also have the added advantages of being morevery high photosynthetically efficienciest (up to four times greater than terrestrial plants) and not competing with forestry and agriculture for land and fresh water [18,19].

Pheophyceae (brown macroalgae, of which the Orders Laminariales and Fucales are colloquially known as *kelp*) are common around the coasts of Britain, Ireland, Iceland, Greenland, and much of Northern Europe and grow well at temperate latitudes [16]. Consequently, there has been with considerable interest in their utilisation as a feedstock for manufacturing commodity chemicals, something that dates back to the early 17th Century when seaweeds were harvested in order to provide potassium (potash) and sodium carbonates (soda ash) [20]. More recently, work has demonstrated that kelps (including such as *Laminaria digitata*) show promise in thermochemical processes such as pyrolysis because of their abundance, their diverse range of products they can afford and their relatively low thermal decomposition temperatures [11,12]. However, comparative investigations of macroalgae in thermochemical applications are hampered by the inherent heterogeneous nature of the samples collected for study [11]. This is particularly problematic since both the carbohydrate and metal contents vary considerably as a function of season, geographic location, local environment, induced stress conditions and by species [21–23]. Consequently, meaning studies that examine only a single sample of seaweed can be severely restricted in the generality and applicability of their conclusions. As a result, investigations that employ appropriate model compounds rather than whole biomass are of interest. Such an approach as they circumvents the problems associated with natural variance in biochemical composition and reveal fundamental trends, such as including the origins of various products and the key decomposition temperatures of certain constituents, thereby allowing pyrolysis processes to be better understood and, ultimately, optimised [24].

One particular area where model compounds may be able to assist is in the prediction of the thermochemical behaviour of a biomass feedstock as a function of metal content. This parameter is particularly important since the presence of naturally occurring metals has been found to greatly influence greatly the pyrolysis behaviour of various biomass types [25,26]. For example, metal ions such as potassium, that are inherently present in some biomass feedstocks have been found to alter the potassium ions have been demonstrated to alter the kinetics of thermolysis (lowering both the first order activation energy and on-set temperature of the onset of rapid pyrolysis) in the case of short rotation willow coppice, as well as promoting the conversion of complex molecules such as levoglucosan, to more simple compounds, including acetic and formic acid [26,27].{Merging Citations}[27][26]..

Despite the significant established impact of metal ions in biomass thermochemical processing, their role is generally not well understood and has only been investigated for a very few types of feedstock. However, developing such insight for macroalgae feedstocks where the metal concentrations can be remarkably high (in the order of 10 – 20 % of the dry weight [12]), it is imperative that a greater knowledge of the influence of metal ions on the thermochemistry is acquired [12]. Indeed, the impetus to develop a better understanding in this area is increasing as the number of studies on the pyrolysis

behaviour of seaweed biomass continues to grow, especially as very Indeed, Ssignificantly, few of these investigations to-date feature a full analysis of the metal profile in the feedstock [28–30]. However, it should be noted that these types of studies are complicated since samples of metal-free macroalgae are not readily accessible as metal ion extraction (by acid washing for example) typically results in significant alteration of the biomolecular matrix that is under investigation [31,32]. Furthermore, a number of recent studies have started to probe the effects of directly incorporating metal-based catalysts into various biomass pyrolysis processes (including macroalgal studies [33]) with a view to influencing the resulting product distributions and selectivity [34,35]. Again, hHowever, in order to optimise catalyst integration in an effective manner a clear understanding of the nature and impact of naturally occurring metals is of great importance.

Undertaking this type of fundamental study into the role of metals in seaweed thermochemistry is particularly complex due to the inherent problems of sample heterogeneity, as mentioned previously. Such studies are further complicated by the fact that the metals cannot easily be removed (through processes like acid washing) without significantly altering the biopolymer matrix in the macroalgae that is under investigation [34,35]. Consequently, iIn order to circumvent the issues associated with macroalgal sample heterogeneity and metal ion removal for thermolysis studies, alginic acid (consisting of alternating blocks of unbranched binary copolymers of 1,4-linked α -D-mannuronic (M) and β -L-guluronic (G) acid residues) and the corresponding metal alginate salts, constitute a promising set of compounds with which to model the effects of metals on seaweed thermolysis. This is not only because aAlginate materials constitute typically not only constitute between 10-40 wt.% of the dry weight of many common kelps [22], but they are also largely responsible for the metal sequestering properties of brown macroalgae (Fig.1) [36]. Thus, studies of discrete metal alginate salts can be used to offer potential as substrates for modelling macroalgae macroalgal thermal degradation, as they can demonstrateexemplifying the effects of a particular metal ion on pyrolysis, without the results being convoluted by processes related to the decomposition of other compounds in the rest of the biomass.

With this in mind, aA number of studies have explored the effects of a various metals on alginate thermal stability using thermogravimetric analysis (TGA), a technique that effectively measures the volatilisation of a sample by recording the decrease in its mass loss as it is heated to the point of decompositionas a function of temperature [37–44]. However, many of these TGA-based investigations have been carried out under oxidative conditions, where combustion is the predominant reaction, usually to examine the flame retardant properties of alginates. Consequently, these studies are not goodpoor models for understanding pyrolysis behaviour, which requires an inert environment.

Of the few literature examples where an inert atmosphere has been used to study the thermolysis behaviour of alginates, one of the most comprehensive was However, Oone study carried out by Ross and co-workers , who examined both the pyrolysis (in inert nitrogen atmosphere) and oxidation (in air) of alginic acid alongside that of the corresponding sodium and calcium alginate salts [44]. They concluded that the metal ions had a dramatic effect on both the rate of pyrolysis and the resulting products. This study showed that calcium alginate was found to degrade at a higher temperature compared to the sodium alginate counterpart, which decomposes at a temperature closer to that of the parent acid. Both salts. While pyrolysis of the calcium salt though generated similar pyrolysis products to those obtained from alginic acid., the sodium salt, however, decomposes at a temperature closer to that of the parent acid, but equivalent gives, although the sodium salt equivalent gives rise to a significantly higher proportion of cyclopentenone derivatives. These observations raise the question of indicate the influence that other metal ions may also have on pyrolysis kinetics (*i.e.* key temperatures, rate of pyrolysis, Arrhenius parameters) and resultant products from alginates and, crucially, raise the question of the degree to which these effects are mirrored during the pyrolysis of whole macroalgal biomass.

The work presented in this paper here, aims to build on further the understanding gained by earlier investigations into the impact of alkali and alkali earth metals on alginate thermolysis to include d-block elements, which are found in some seaweed samples at concentrations many thousands of times higher than the surrounding seawater [45]. Studies to probe such effects are complex since, despite the passive nature of the biosorption process, macroalgae show preferences for certain metals above others, with the relative affinities (shown in Figure 2) having been calculated for divalent metal species. The observed This trend is not easily explained, but it is thought that this to originate from lie in the so-called “egg box” model of divalent cation binding to alginates [46], in which some M^{2+} ions are thought to fit the anionic cavities provided by two parallel strands of β -L-guluronic acid better than others (Fig. 3) [47]. Indeed, brown macroalgae harvested from copper-polluted water exhibit particularly high concentrations of Cu^{2+} ions, which is a direct consequence of the high affinity of alginates for copper [48][49].

Accordingly, studies on the thermochemical behaviour of copper(II) alginate provide a unique model system with which to probe the effects of this d-block metal on the thermolysis of macroalgae. To this end, the following study will examine the effects of Cu^{2+} ions on the slow pyrolysis (*i.e.* pyrolysis with a heating rate less than around $50\text{ }^{\circ}\text{C min}^{-1}$ [50]) of alginates *via* TGA. However, in addition to this, it is also desirable to analyse the degree to which these findings are applicable to the outcomes of the thermal treatment of samples of real seaweed biomass. In order to facilitate such a comparison, the metals inherently present in a sample of macroalgae can be almost completely ion-exchanged with Cu^{2+} ions by soaking the seaweed in a copper-containing solution and, subsequently, the resulting copper(II)-doped macroalgae can be subjected to the same TGA treatment as the model copper(II)

alginate compound. This approach will allow for a wider discussion on the methodological validity of using model compounds for studying biomass pyrolysis and, also, the importance of characterising the full metal content of a feedstock prior to its thermal analysis, a practice that is not currently commonplace.

2. Materials & Methods

Alginic acid (H-Alg) and sodium alginate (Na-Alg) were obtained in powdered form from Sigma Aldrich and used as received.

2.1 Preparation of copper(II) alginate (Cu-Alg)

Copper(II) alginate (Cu-Alg) was prepared *via* an ion exchange protocol by suspending sodium alginate (2.0 g) in a solution of $\text{Cu}(\text{NO}_3)_2$ (100 mL, 1.0 M) and stirring vigorously for 6 hours at room temperature (Eqn. 1). The resulting light blue gelatinous precipitate was subsequently isolated by filtration, washed thoroughly with deionised water and dried to a constant weight at 80 °C, which led to the isolation of a dark green solid.

2.2 Thermal Analysis of H-Alg, Na-Alg and Cu-Alg

The alginic acid and two metal alginate powders were ground and sieved to 250 μm . The three samples were then subsequently dried at 105 °C overnight, immediately prior to the TGA analyses, in order to attain similar moisture contents since both the alginate materials and alginic acid are hygroscopic. TGA analyses were carried out on the dried, ground samples of the H-, Na-, and Cu-Alg using a Perkin Elmer Pyris 1 analyser by loading 20.0 ± 0.5 mg of the sample evenly into a platinum pan and subsequently heating from 25 °C to 900 °C at 5, 10, 20, 30 and 40 °C min^{-1} under a flow of dry N_2 at 25 mL min^{-1} . The first derivative of the TGA data yielded the differential thermogravimetric profile (DTG). Coupled TGA-FTIR analyses of the three alginate samples was also carried out by heating the powders to 1000 °C at 10 °C min^{-1} on a TA Q500 V6.7 Build 203 coupled to a Nicolet IS 10 Infra Red Spectrometer.

Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments DSC analyser (Q1000, V9.9, build 303) by placing around 5.0 ± 0.5 mg of sample into an aluminium sample pan, crimping it shut and then heating from 30 to 500 °C at 10 °C min^{-1} under a flow of dry N_2 at 50 mL min^{-1} .

For comparison, TGA analyses of powdered samples of Na₂CO₃, CaCO₃ and CuCO₃ (each obtained from Sigma Aldrich and used as received) were also undertaken.

2.3 Kinetic Analysis

TGA analyses of H-, Na-, and Cu-Alg were carried out at five different heating rates (β), in order to determine values for the energy of activation (E_a) and pre-exponential factor (A) for the thermal degradation of the samples at certain points in the pyrolysis process. This was achieved by adopting a simple, previously used method, based on the approach described below [51]:

During thermolysis a sample will lose mass through volatilisation. Hence, a degree of conversion α_n of the sample at a temperature T_n can be defined:

$$\alpha_n = \frac{m_0 - m_n}{m_0 - m_\infty} \quad [(\text{Eqn. 2})]$$

where m_0 is the initial mass of the sample, m_n is the mass at temperature T_n and m_∞ is the final mass. Thus, the rate of thermolysis, or the rate of change of α with time, t , can be described by a temperature-dependant Arrhenius expression, $k(T)$, scaled by a function $f(\alpha)$, the *conversion function*:

$$\frac{d\alpha}{dt} = f(\alpha) k(T) \quad [(\text{Eqn. 3})]$$

The conversion function reflects the mechanistic nature of the thermolysis process that is taking place. Assuming, crudely, that there is a single first order reaction taking place at any particular temperature during the pyrolysis being studied, and which occurs uniformly throughout the biomass sample, this may be defined as:

$$f(\alpha) = (1 - \alpha) \quad [(\text{Eqn. 4})]$$

The constant rate at which the sample is heated, β , can simply be defined as the change of temperature, T , with time, t :

$$\beta = \frac{dT}{dt} \quad [(\text{Eqn. 5})]$$

Combining equations [2] and [4] gives:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} (1 - \alpha) k(T) \quad [(\text{Eqn. 6})]$$

Since the Arrhenius function $k(T)$ has the form:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad [(\text{Eqn. 7})]$$

it is possible to define:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} (1 - \alpha) A \exp\left(\frac{-E_a}{RT}\right) \quad [(\text{Eqn. 8})]$$

and thus the experimentally-determined turning points of the DTG profile represent the maximum volatilisation rates:

$$i.e. T = T_{\max} \text{ when } \frac{d^2\alpha}{dT^2} = 0 \quad [(\text{Eqn. 9})]$$

Hence, by rearrangement the following expression is obtained:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{RA}{E_a}\right) - \frac{E_a}{RT_{\max}} \quad [(\text{Eqn. 10})]$$

And so, from a graph of $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ versus $\frac{1}{T_{\max}}$, the values of E_a and A can be calculated [51].

2.4 Preparation of macroalgae (*laminaria digitata*)

Samples of *L. digitata* were harvested from Marsden Bay, South Shields, UK (54° 58' 42.58" N, 1° 23' 0.97" W) on 28th October 2011 (Fig. 4). The samples were washed in distilled water to remove the majority of the sand and grit, and frozen at −18 °C within 4 hours of harvest. After being allowed to thaw naturally at room temperature for 8 hours, the macroalgae were shredded, dried to a constant weight at 80 °C, and ground and sieved to 250 µm. The dry, powdered macroalgae samples were either used immediately or returned to storage at −18 °C.

2.5 Cu²⁺ Ion exchange in *L. digitata*

The alkali and alkali earth metals inherently present in a sample of wild *L. digitata* were replaced with Cu²⁺ ions via an ion-exchange process: the *L. digitata* (as prepared in section 2.4) were suspended in a solution of Cu(NO₃)₂ (100 mL, 1.0 M) and stirred vigorously for 6 hours at room temperature. The ion-exchanged macroalgae were subsequently isolated by filtration, washed thoroughly with deionised water (100 mL), and dried to a constant weight at 80 °C.

2.6 Thermal analysis of *L.digitata*

Both the untreated *L.digitata*, and the Cu²⁺ ion-exchanged *L.digitata* were dried overnight at 105 °C immediately prior to analysis. TGA analyses were carried out on the dried, ground seaweed samples using a Perkin Elmer Pyris 1 analyser. Around 20.0 ± 0.5 mg of sample was loaded into a platinum pan and spread evenly. The sample was subsequently heated from 25 °C to 900 °C at a heating rate (β) of 10 °C min⁻¹ under a flow of dry N₂ at 25 mL min⁻¹. The first derivative of the TGA plot yielded the DTG profile.

Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments DSC analyser (Q1000, V9.9, build 303) by placing around 5.0 ± 0.5 mg of samples into an aluminium sample pan, crimping it shut and then heating from 30 to 500 °C at 10 °C min⁻¹ under a flow of dry N₂ at 50 mL min⁻¹.

2.7 Elemental Analyses

C, H and N compositions of all samples were determined by combustion on an Exeter Analytical CE440 Elemental analyser by the Analytical Department of the Chemistry Department, Durham University.

The concentrations of 26 common metals in the *L.digitata* (known to be present in significant concentrations from previous investigations [22,23]) were determined *via* ICP-MS analysis using a Thermo Fisher X-Series II analyser; the analysed samples were prepared by Carius tube digestion in a concentrated, ultrapure HNO₃:HCl mix (3:1 by volume). The Cu and Na concentrations in H-, Na- and Cu-Alg were also determined using this method. Fluka analytical TraceSELECT[®] ultra-pure acids and standards were employed in the analyses and high purity deionised water was used throughout.

3. Results and Discussion

3.1 Pyrolysis of alginic acid and alginates

Samples of alginic acid (H-Alg), sodium alginate (Na-Alg) and copper(II) alginate (Cu-Alg) were prepared as in Section 2.1. An examination of their elemental analysis profile (Table 1) reveals that the exchange of sodium for copper ions occurred almost completely, with the equilibrium depicted in

Equation 1, lying predominantly to the right hand side, an effect predicted in earlier studies on the affinity of alginates for Cu^{2+} ions (see Section 1) [47,48].

A comparison was made of the pyrolysis behaviour of Cu-Alg against that of H-Alg and Na-Alg in order to probe the effect of the Cu^{2+} ions in the alginate structure [36]. Broadly, it was found that for all three compounds thermal degradation occurred in three discrete temperature windows (phases 1-3) defined by T_i (the onset of rapid pyrolysis) and T_f (the end of rapid pyrolysis). However, despite this apparent similarity, it was also found that the behaviour of the different materials within these three temperature regimes varied dramatically, as demonstrated by the DTG (Fig. 5a) and TGA (Fig. 5b) curves. In particular, a detailed analysis of the three distinct pyrolysis regions highlights the dramatic influence exerted by the presence of the metal ions on the pyrolysis of the alginic acid polymer.

i) Phase 1: $25\text{ }^{\circ}\text{C} \leq T < T_i$

The small mass loss (around 5 wt.%) observed in this region for H-, Na-, and Cu-Alg is attributed to simple dehydration loss of moisture, which was had re-absorbed following drying to a constant weight at $105\text{ }^{\circ}\text{C}$ prior to the TGA analysis, as a result consistent with of the hygroscopic nature of these materials [24,28,52–54]. This is further confirmed by the in agreement with the large endothermic peak during this temperature region on the DSC curve featured in Figure 6, which is induced as water results from molecules water evaporate evaporating from the sample.

ii) Phase 2: $T_i < T < T_f$

The region of the TGA profile that lies between T_i and T_f is arguably the most important when considering biomass pyrolysis in general (and that of related model materials) since it is within this window that the maximum degree of volatilisation takes place, with between 40 – 50 wt.% of the initial mass of the sample being lost. T_i corresponds to the temperature where rapid pyrolysis begins to take effect. With a heating rate, β , of $10\text{ }^{\circ}\text{C min}^{-1}$ the value of T_i varies with Cu-Alg ($150\text{ }^{\circ}\text{C}$) < H-Alg ($161\text{ }^{\circ}\text{C}$) < Na-Alg ($207\text{ }^{\circ}\text{C}$). During this period of rapid pyrolysis, several notable features appear at T_{max} (the temperature at which the maximum mass loss rate occurs) signified by an intense peak in the DTG curve. A summary of the values of T_i , T_f and T_{max} for H-Alg, Na-Alg and Cu-Alg recorded at five different heating rates (β) is given in Table 2. It can be seen that the H-Alg and Cu-Alg samples show two peaks ($T_{\text{max}1}$ and $T_{\text{max}2}$), whereas the Na-Alg only shows one (simply T_{max}), which represents a much greater rate of mass loss and occurs at a similar temperature to H-Alg $T_{\text{max}2}$. This indicates that the first step in the pyrolysis pathway is somehow inhibited (relative to H-Alg) by the Na^+ ions until some critical temperature ($207\text{ }^{\circ}\text{C}$), after which the subsequent reactions occur very rapidly. Many of the reactions that cause the rapid volatilisation of the solid feedstock are not well understood

and there is still much work to be done to gain a better understanding of this pyrolysis phase, both in the case of alginates and for biomass in general [55]. Interestingly, however, the DSC profiles for H-Alg, Na-Alg and Cu-Alg during this phase of pyrolysis (Fig. 6) all show sharp exothermic peaks, revealing that the net effect of the reactions that lead to the rapid volatilisation stage is to release heat, presumably as more thermodynamically stable compounds are formed from the decomposition.

T_f marks the end of the period of rapid volatilisation and varies as with Cu-Alg ($270\text{ }^{\circ}\text{C}$) < H-Alg ($275\text{ }^{\circ}\text{C}$) < Na-Alg ($283\text{ }^{\circ}\text{C}$); this is a much smaller temperature range of temperatures than that for T_i , where $\sim 60\text{ }^{\circ}\text{C}$ separates Cu-Alg from Na-Alg. This appears to be because the Na-Alg demonstrates a much higher mass loss rate during the period T_i to T_f . Consequently, although the onset of rapid pyrolysis for Na-Alg begins at a higher temperature than for both Cu-Alg and H-Alg, volatilisation of the sodium salt proceeds very quickly with mass loss ending at a temperature only slightly higher than those of copper(II) alginate and alginic acid.

iii) Phase 3: $T_f < T \leq 1000\text{ }^{\circ}\text{C}$

The region from T_f onwards is generally regarded as being a period of slower, sustained degradation in biomass pyrolysis. Reaction processes occurring within this region are thought to consist mainly of secondary pyrolysis reactions, tar cracking, char formation and the degradation of thermally robust inorganic constituents [24,28,52–54]. Consequently, the rate of mass loss is considerably lower than that in Phase 2, with the final mass achieved corresponding to the amount of char produced.

For biomass such as macroalgae, the residual char is primarily comprised of carbon and inorganic materials, such as metal oxides and metal carbonates, which form as the metal ions bound to the alginates react with the organic matrix upon degradation [44]. Some of the inorganic salts may be products of secondary reactions, such as the formation of metal carbonates from the reaction between CO_2 (released throughout the pyrolysis process) and other metal oxides. To survive to the char stage, however, the inorganic constituents need to be thermally robust, and some may degrade prior to $1000\text{ }^{\circ}\text{C}$. Figure 7 shows the TGA/DTG profiles of some of the inorganic constituents (namely copper, sodium and calcium carbonate) that may be expected to form during the pyrolysis of the Na-Alg and Cu-Alg. CuCO_3 degrades to CuO and CO_2 at around $300\text{ }^{\circ}\text{C}$ (with a later, much smaller mass loss at around $900\text{ }^{\circ}\text{C}$, as the CuO begins to form Cu_2O [56]) (Fig. 7). Consequently, no peak is seen that corresponds to the degradation of CuCO_3 in the pyrolysis of Cu-Alg between T_f and $1000\text{ }^{\circ}\text{C}$. Conversely, pure Na_2CO_3 , which melts at around $850\text{ }^{\circ}\text{C}$, does not start to significantly volatilise until temperatures above $1000\text{ }^{\circ}\text{C}$ [57] and hence no features arising from this material were observed.

However, a high temperature thermal decomposition feature is apparent during the pyrolysis of Na-Alg, something that has been attributed to small quantities of calcium ion impurities present in the alginate that initially react to form CaCO_3 [44], and which subsequently decomposes at temperatures around 700 °C (Fig 7) [58]. The H-Alg material contains only trace inorganic content and is virtually completely degraded by 650 °C. Thus, in the higher temperature regions (> 650 °C), there are no regions of significant mass loss in the TGA profile that correspond to the degradation of inorganic salts.

As expected, the inorganic materials present in the Cu-Alg and Na-Alg materials are not fully volatilised by 1000 °C. Metal oxides that form during pyrolysis such as Cu_2O , CuO , and Na_2O remain un-degraded intact, something that results in higher char yield for the Cu-Alg and Na-Alg samples (14.6 and 17.0 wt.%, respectively) compared to that from H-Alg (1.1 wt.%) [12]. Consequently, by using TGA data directly it is difficult to compare the effects of metals in the thermal degradation of metal-rich biomass samples, as the relative mass loss is smaller as a result of the significant amounts of inorganic char formed. Thus, to gain a deeper insight into the rate of volatilisation of the important organic constituents of the biomass occurring during pyrolysis a plot of the degree of conversion α (defined in Eqn. 3) against temperature, as depicted in Figure 5c, can be informative. This degree of conversion (α) does not include the amount of residual char and only considers matter that is volatilisable below the maximum temperature used in the experiment, 1000 °C. Consequently, samples such as Cu-Alg and Na-Alg, which have comparably high inorganic content (with 10-15 wt.% consisting of metal ions), can be compared directly with H-Alg, which is almost entirely organic. Thus, whereas the TGA profiles suggest that the extent of mass loss of Na-Alg with temperature is consistently lower than for H-Alg, when the mass lost is considered as a fraction of the total amount volatilised (*i.e.* the degree of conversion), it can be seen that there is a period between 240 – 330 °C where the Na-Alg has lost a greater proportion of its volatilisable mass than has H-Alg, indicating that the Na^+ ions promote pyrolysis between these temperatures.

Furthermore, the TGA data suggest that the H-Alg and Cu-Alg materials are comparable in terms of the extent of mass lost upon pyrolysis to 285 °C. However, if the degree of conversion data α are examined it becomes apparent that the samples of H-Alg and Cu-Alg do not achieve the same value until a pyrolysis temperature of 480 °C. This latter observation indicates that the Cu^{2+} ions promote pyrolysis of the organic matter over a much wider temperature range than would be apparent from the TGA profile alone. Indeed, the data presented in Figure 5c also clearly demonstrate that the presence of Cu^{2+} ions inhibits the later stages (Phase 3) of alginic acid pyrolysis quite considerably (*cf.* H-Alg and Na-Alg) and severely slows down the rate of volatilisation above ~500 °C.

This observation contradicts previous studies, where the presence of mono- (Na^+) and di- (Ca^{2+} , Co^{2+}) valent metal ions have all been shown to inhibit the onset of pyrolysis of alginates relative to that of the parent acid [43,44]. In contrast, the results presented here indicate that Cu^{2+} ions clearly shift the onset of pyrolysis to a lower temperature with respect to the (practically) metal-free alginic acid. To explain this phenomenon, however, requires a better understanding of the interaction of the metal ions with both the mannuronic and guluronic acid residues that comprise the alginates as it appears that, though the alginic acid shows a high affinity for Cu^{2+} ions, the presence of such ions also serve to destabilise the polymer at higher temperatures. In order to better quantify the observed trend in thermal stability (*i.e.* $\text{Cu-Alg} < \text{H-Alg} < \text{Ca-Alg}$), a kinetic study was carried out for the second stage of pyrolysis for all three compounds. The mathematical details of the model used are elaborated in section 2.3, but the principle behind the analysis was to plot $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ versus $\frac{1}{T_{\max}}$ where $T_{\max}$ represents a point of maximum mass loss rate (identified as a turning point of the DTG profile) for five different heating rates ($\beta = 5, 10, 20, 30$ and $40\text{ }^\circ\text{C min}^{-1}$).

From this plot (Fig. 8), the gradient can be used to extract the energy of activation, E_a , for the reaction(s) occurring at that point in the pyrolysis, with the intercept giving the pre-exponential factor, A . The plots in Figure 9 show the DTG profiles at the five different heating rates (β). As β increases, the DTG curve maintains a similar shape, but is shifted to a higher temperature; this is a well-documented effect that arises due to the delay in heat transfer to the samples being analysed [59]. The results of the kinetic analyses are summarised in Table 2. The energy of activation, E_a , was calculated for two points in the pyrolysis ($T_{\max1}$ and $T_{\max2}$) for H-Alg and Cu-Alg, and at one point ($T_{\max}$) for Na-Alg obtained from the peaks in the DTG profiles (Fig. 5a). The values of E_a give an indication of the energy required to initiate the reaction(s) occurring at that temperature in the pyrolysis, and so, they provide a useful comparison of the ease of volatilisation of the compounds relative to each other. It is unsurprising then that the trends in the values of E_a reflect the trends in the values of T_i ($T_{i(\text{Cu-Alg})} < T_{i(\text{H-Alg})}$), thus $E_a(T_{\max1})_{\text{Cu-Alg}} < E_a(T_{\max1})_{\text{H-Alg}}$ and $E_a(T_{\max2})_{\text{Cu-Alg}} < E_a(T_{\max2})_{\text{H-Alg}}$ and thus the kinetic data further corroborates the observation that Cu^{2+} ions promote volatilisation in the rapid pyrolysis phase with respect to H-Alg. Further comparison with Na-Alg is not straightforward however, as the DTG profiles (Fig. 9c) are not well resolved. Consequently, only one value of $T_{\max}$ (and thus E_a) can be determined for Na-Alg (Table 2) from the single, broad peak, which is clearly associated with a larger number of reactions than the separate, narrower peaks in the Cu-Alg and H-Alg spectra. This gives rise to the correspondingly large value of E_a for sodium alginate, which cannot meaningfully be correlated with the values of E_a determined for the other compounds.

Finally, coupled TGA-Fourier transform infrared spectroscopic (TGA-FTIR) analysis gives insight into aspects of the thermal degradation pathways of H-Alg, Na-Alg and Cu-Alg, and the differences between them. Figure 10 shows that the primary volatile component product for this “slow” pyrolysis,

in all three cases, is CO₂, as evidenced by the intense absorbance at 2360 cm⁻¹; this observation has been reported previously from studies using coupled TGA-gas-chromatography/mass spectrometer (Py-GC-MS) [42,44]. Interestingly, if the intensity of the IR absorbance at 2360 cm⁻¹ is plotted against temperature during the pyrolysis of H-Alg, Na-Alg and Cu-Alg over the temperature range 150-300 °C (Fig. 11a), the trace can be seen to completely replicate the trend in mass loss shown in the equivalent section of the TGA curve (Fig. 11b). Thus, it is possible that the rapid period of pyrolysis that begins at T_i (discussed above) is most likely attributable to decarboxylation of the carboxylate group of the alginates, which explains the rapid release of CO₂.

Beyond this temperature region 150 – 300 °C, the CO₂ evolved is seen to increase to a maximum in the case of Cu-Alg and H-Alg, but decrease in the case of Na-Alg. This decrease is a consequence of the reaction between CO₂ and sodium salts like Na₂O, from which Na₂CO₃ can form, thus retaining the CO₂ until decomposition at much higher temperatures (Fig. 11c) [44]. Of course, the formation of carbonates is not possible in the case of the Cu-Alg since CuCO₃ is not stable at these temperatures (Fig. 7), and for H-Alg, which does not contain significant metallic species for carbonates to form. The amount of CO₂ released is highest in H-Alg (as evidenced by the larger area under the curve in Figure 11c), which is expected due to the higher carbon content of the starting material compared to the metal salts.

Other minor peaks in the TGA-FTIR profile indicate that a number of other compounds may be evolved in the pyrolysis processes. Earlier studies have suggested that the minor peaks observed between 1500-1800 cm⁻¹ in the FTIR spectrum that begin to appear after around 300 °C (absorbance around 0.02) could be due to a mixture of small, volatile, organic molecules bearing carbonyl groups such as formaldehyde, acetone and furfural, amongst others [42,44].

3.2 Influence of Metals on the Pyrolysis of Macroalgae

In order to test the applicability of the results from the study of model biomass compounds (H-Alg, Na-Alg, Cu-Alg) described in section 3.1, whereby Cu²⁺ ions were shown to promote the onset of pyrolysis of alginic acid, an actual sample of macroalgal biomass should be subject to thermal degradation to test for similar effects. Indeed, previous studies have examined the role of metals in macroalgae pyrolysis by removing them completely and analysing the metal-stripped materials. However, this approach requires the macroalgae to be treated *via* washing with acid, something that has the additional detrimental effect of removing a significant fraction of the soluble organic constituents such as mannitol and fucose and potentially hydrolysing some of the carbohydrates [31,32]. Consequently, it is very difficult to determine which effects upon the pyrolysis are due to the presence or absence of the metals, and which result from the removal of the soluble biomolecules.

Here, we present a different and novel approach whereby instead of removing the metals, samples of seaweed are saturated with one particular metal species (in this case copper) to determine the effects on pyrolysis with minimal alteration to the volatilisable organic matter. This methodology is especially suited to the study of brown macroalgae, which have an extremely high affinity of for Cu^{2+} ions, making it possible to achieve very high levels of ion-exchange with relative ease [48].

To this end, a sample of wild *L. digitata* was subject to a metal ion exchange process, which resulted in replacement of around 93% of the alkali, alkali earth and other trace metals by Cu^{2+} ions. Table 3 depicts the elemental compositions of the *L. digitata* samples pre- and post-impregnation *via* ion exchange. It was found that the original seaweed, as collected, contained around 122000677 (± 106300) $\text{mg}_{\text{metal}}/\text{kg}_{\text{dry-seaweed}}$, which was increased to 161000112 (± 100045) $\text{mg}_{\text{metal}}/\text{kg}_{\text{dry-seaweed}}$ after copper-ion-exchange, accompanied by a slight decrease in carbon content (2.0 wt.%). The data reported in Table 3 also suggest that, within experimental uncertainty, electroneutrality of the seaweed was maintained according to Equation 1. Furthermore, the low nitrate content of the ion-exchanged material indicates that the copper detected was bound to the biomass and not residual $\text{Cu}(\text{NO}_3)_2$ used for impregnation, which was removed during the washing stages.

The two samples of *L. digitata* (the unadulterated sample and its Cu-exchanged counterpart) were pyrolysed under the same experimental conditions as described above for H-, Na- and Cu-Alg described above; the results are shown in the TGA/DTG plots in Figure 12. Broadly, these analyses reveal that the Cu-doped macroalgae sample shows the same mass loss regions as the H-, Na-, and Cu-Alg samples; dehydration, rapid pyrolysis and slow degradation phases are readily identifiable. Notably, although the onset of rapid pyrolysis occurs at a higher temperature for the real macroalgae biomass samples relative to those of the model compounds, the Cu^{2+} ions are seen to exert a similar influence and Cu-doped macroalgae ($T_i = 164^\circ\text{C}$) is observed to begin rapid pyrolysis at a lower temperature compared with the unadulterated macroalgae ($T_i = 180^\circ\text{C}$). The same trend is also true for the values of T_{max} $\{(T_{\text{max}}(\text{Cu(II)- L.dig}) = 236^\circ\text{C}$ compared to $T_{\text{max}}(\text{L.dig}) = 254^\circ\text{C})\}$. However, at T_j , the two seaweed samples begin to show remarkably similar mass loss profiles, which something that continues until around 650°C , where the unadulterated macroalgae shows a very slight additional mass loss relative to the Cu-exchanged. This latter mass loss is most likely to be a result of thermolysis of CaCO_3 (as shown by the data presented in Fig. 7), which forms due to the sizeable concentration of Ca^{2+} present in the biomass (2.5 wt.%). Thus, the conclusions drawn from the kinetic studies on the model alginate compounds are also true in the case of actual macroalgal biomass: the presence of Cu^{2+} ions promotes pyrolysis at lower temperatures, but does not assist in the later stages of high temperature volatilisation.

The similarities between the thermal behaviour of the model compound, copper(II) alginate, and the real biomass, copper(II)-doped *L. digitata*, can be further demonstrated by reference to the DSC

profiles (Fig. 13a). These analyses show that, broadly, the major exotherms for the Cu-Alg overlap with those of the copper(II)-doped *L.digitata* with the peaks in the heat flow to the latter material being less pronounced due to the presence of other (thermally stable) compounds in the rest of the biomass. The main difference between the two thermograms is a small endothermic event beginning at around 170 °C in the DSC of Cu-Alg, which, when compared with the TGA data for Cu-Alg (Fig. 6c), is apparently associated with the onset of rapid devolatilisation. The event is not, however, a feature of the DSC curve of the copper(II)-doped seaweed due to the smaller proportion of alginate in the sample coupled with potential insulating effects and, conceivably, exothermic events originating from other components present in the biomass. Thus, when these complicating factors are accounted for, it can be seen that the Cu-Alg effectively mimics the thermal behaviour of the copper(II)-doped *L.digitata*, and the sharp exothermic event at around 235 °C in the pyrolysis of the real biomass can easily be assigned to the degradation of the alginate. An interesting comparison can then be made between the results of the DSC analysis of the copper-doped seaweed sample with those of the unadulterated *L.digitata* (Fig. 13b), for which the latter material displays a much less well defined profile. It can be seen that the peaks in the thermogram of the unadulterated *L.digitata* are generally broader in places and more numerous, reflecting the varying influences of the many different metal ions on the thermolysis of the biomass, with some inhibiting that stage of decomposition (such as Ca^{2+}) and some promoting it (such as Cu^{2+}).

These results therefore demonstrate the validity of using alginates as model compounds with which to predict the thermochemical behaviour of brown seaweed biomass. Thus, the kinetic parameters established in Section 3.1 could potentially have utility can be used in the development of larger scaled-up macroalgae processing operations, particularly in the modelling of low temperature slow pyrolysis or torrefaction as a pre-treatment in biomass gasification [60]. Clearly, however, much more work is required, predominantly in determination of the product stream and the effects of reaction conditions, before a more complete model can be employed to analyse large scale thermochemical processes and the economic and energetic implications.

When all of the results in this report are taken into account, they suggest Together, the data presented here show that macroalgae that have been exposed to copper-enriched aqueous environments (such as some industrial waste water streams [61,62]) should be easier to pyrolyse than samples rich in alkali and alkali earth metals. Indeed, it is conceivable that macroalgae could be utilised in the remediation of waste water streams contaminated with other metals (such as cadmium) and then ion-exchanged in a copper solution prior to pyrolysis . Of course, the exception to this proposition would be for macroalgae enriched in Pb^{2+} ions (for which alginates show an even higher affinity than for Cu^{2+} ions, Fig. 2) [63]. The effects of Pb^{2+} ions on macroalgae thermolysis will, consequently make for an

interesting comparison with Cu^{2+} , but there is an inherent difficulty in such experiments owing to the toxicity of lead. Such studies, if achievable, may even help to shed light on the interactions between alginates and divalent cations.

Conclusions and Outlook

The complex nature of the thermal behaviour of seaweeds demonstrated throughout this study, indicate that their thermolysis pathways are not straightforward and that the TGA and DSC profiles encompass a myriad of diverse reactions. Thus the requirement to make comparative studies with model compounds is very relevant, as they can reduce and isolate help to pinpoint the important factors necessary for the study of biomass pyrolysis without the complication of sample heterogeneity. In this respect, copper(II) alginate was found to be a convincing compound with which to model the effects of Cu^{2+} ions on a sample of brown macroalgae. Consequently, though only samples of *L. digitata* were examined, the agreement between the model study and the study utilising whole biomass suggest that the findings in this paper should be applicable to most brown (alginate-containing) macroalgae.

In this respect Here, Cu^{2+} ions have been found to have a dramatic impact on the thermal stability of polymeric alginic acid; promoting the onset of pyrolysis where other mono- and di- valent cations have been found to inhibit it. This effect is evidenced by a reduction in temperature of the onset of rapid pyrolysis of copper(II) alginate compared to the parent alginic acid, which that, as might be expected, is also accompanied by a lowering of the activation energies of activation at various points in the conversion. It is not accurate, however, to describe the copper as acting catalytically towards the pyrolysis of the alginic acid as, at elevated temperatures ($> 500\text{ }^{\circ}\text{C}$), the Cu^{2+} ions clearly begin to inhibit conversion of the solid into volatile compounds. Indeed, with such a multitude of reactions taking place over the course of the pyrolysis process, the exact role of the copper is almost impossible to discern, but it clearly appears to destabilise the alginate polymer and, consequently, is beneficial during the early stages of pyrolysis, which are the region that is of most importance for the production of biofuels and chemicals.

Given the high affinity of alginates and, consequently, macroalgae for Cu^{2+} ions, it is anticipated that other samples of brown seaweed grown in or around copper- contaminated waste water streams will demonstrate similar effects to those described above. This highlights the importance of establishing the metal profile of a sample of macroalgae prior to analysis, especially in the case of comparative studies, such as those that compare different species or the effects of different catalysts. It is likely that a greater understanding of the destabilising effects of Cu^{2+} ions reported in this paper will be

accompanied by a better understanding of the interaction of seaweed biomass with metal ions as a whole, which in turn may lead opens the way to better utilisation of macroalgae as a resource.

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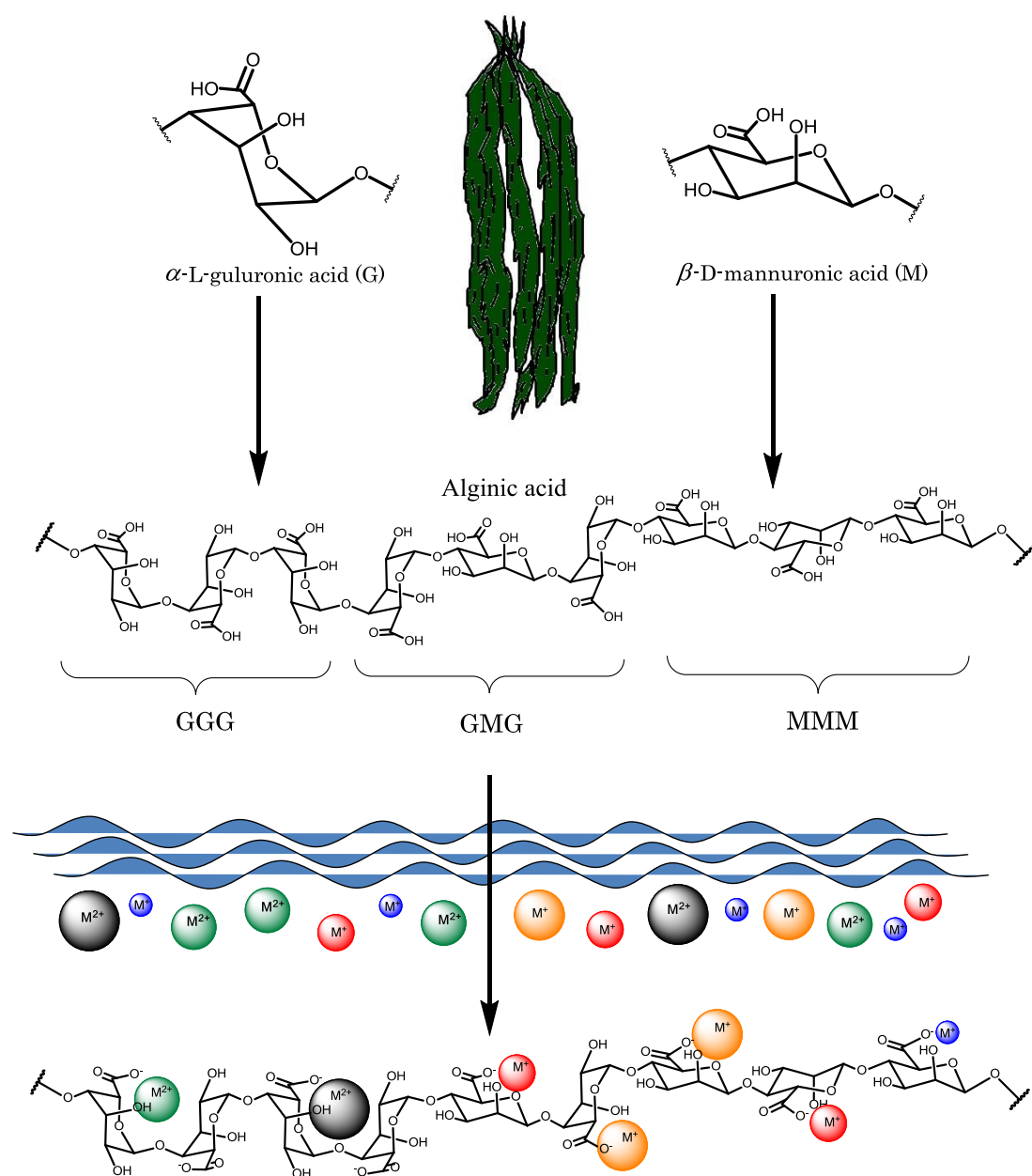


Figure 1: The mode of uptake of various mono- and di-valent metallic ions found in seawater by α -L-guluronic acid and β -D-mannuronic acid, which polymerise to form alginic acid (and the corresponding alginate salts) in large quantities in brown macroalgae [36]

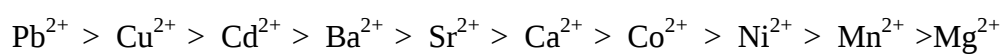


Figure 2: The affinity of alginic acid in *L. digitata* for various divalent cations [47]

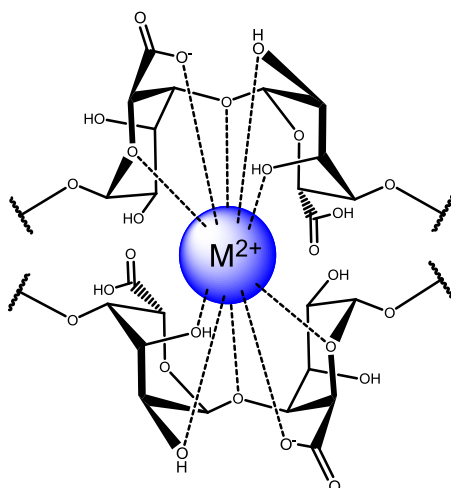


Figure 3: The “egg box” model of divalent cation bonding in alginic acid [46]

Table 1: Partial elemental analysis of H-Alg, Na-Alg and Cu-Alg

	C (wt.%)	H (wt.%)	N (wt.%)	Na (wt.%)	Cu (wt.%)
Alginic acid (H-Alg)	39.94	4.54	0.00	0.39	0.05
Sodium alginate (Na-Alg)	33.95	3.72	0.00	10.60	0.05
Copper (II) alginate (Cu-Alg)	32.29	3.62	0.00	0.03	14.81

Equ. 1

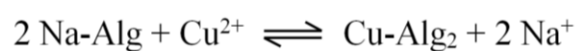


Figure 4: *L. digitata* collection site: Marsden Bay, South Shields, UK

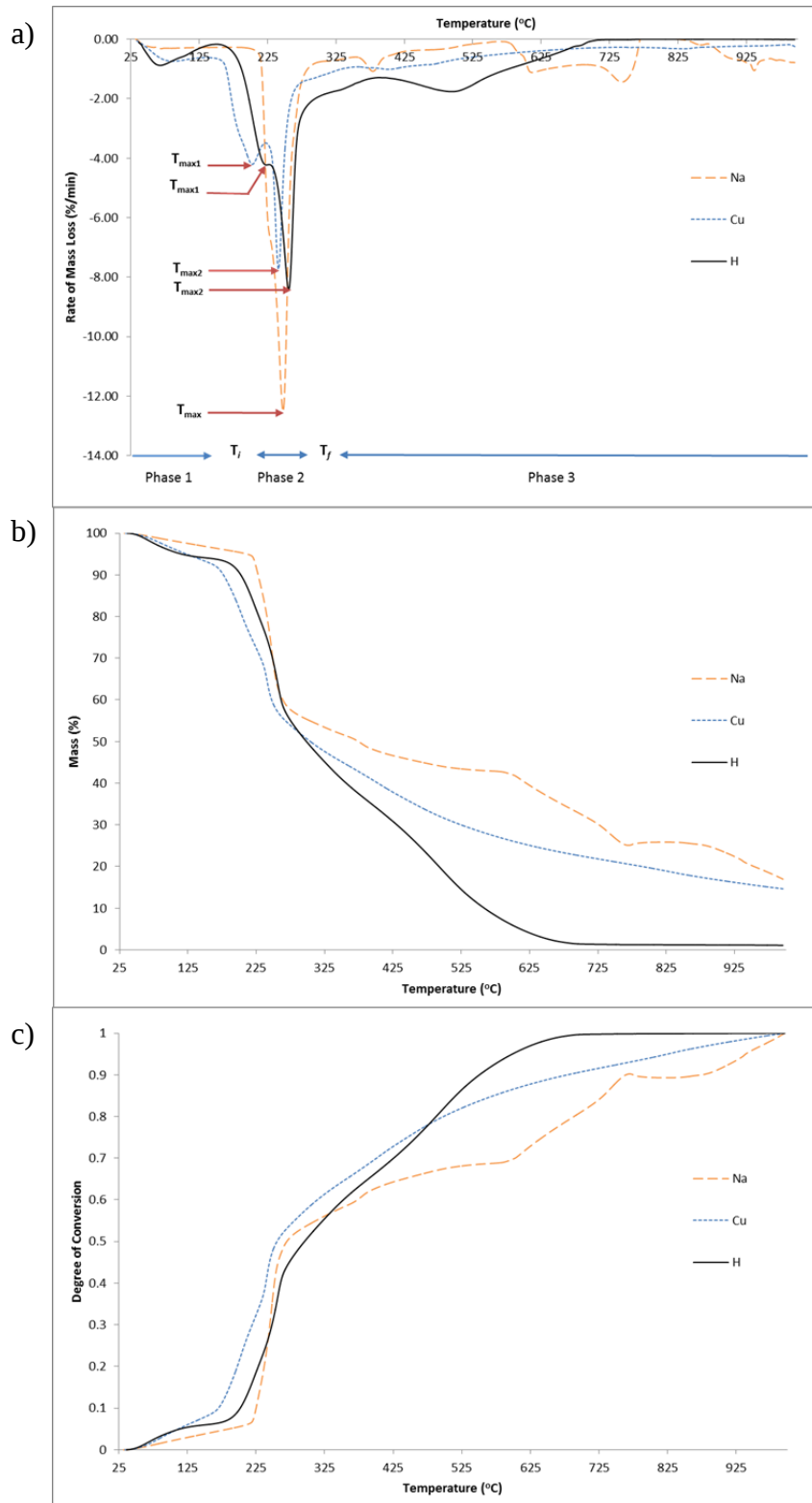


Figure 5: The (a) DTG, (b) TGA and (c) degree of conversion profiles for the thermolysis of H-Alg, Na-Alg and Cu-Alg over the temperature range 25–1000 °C obtained with a heating rate (β) of 10 °C min⁻¹ under N₂

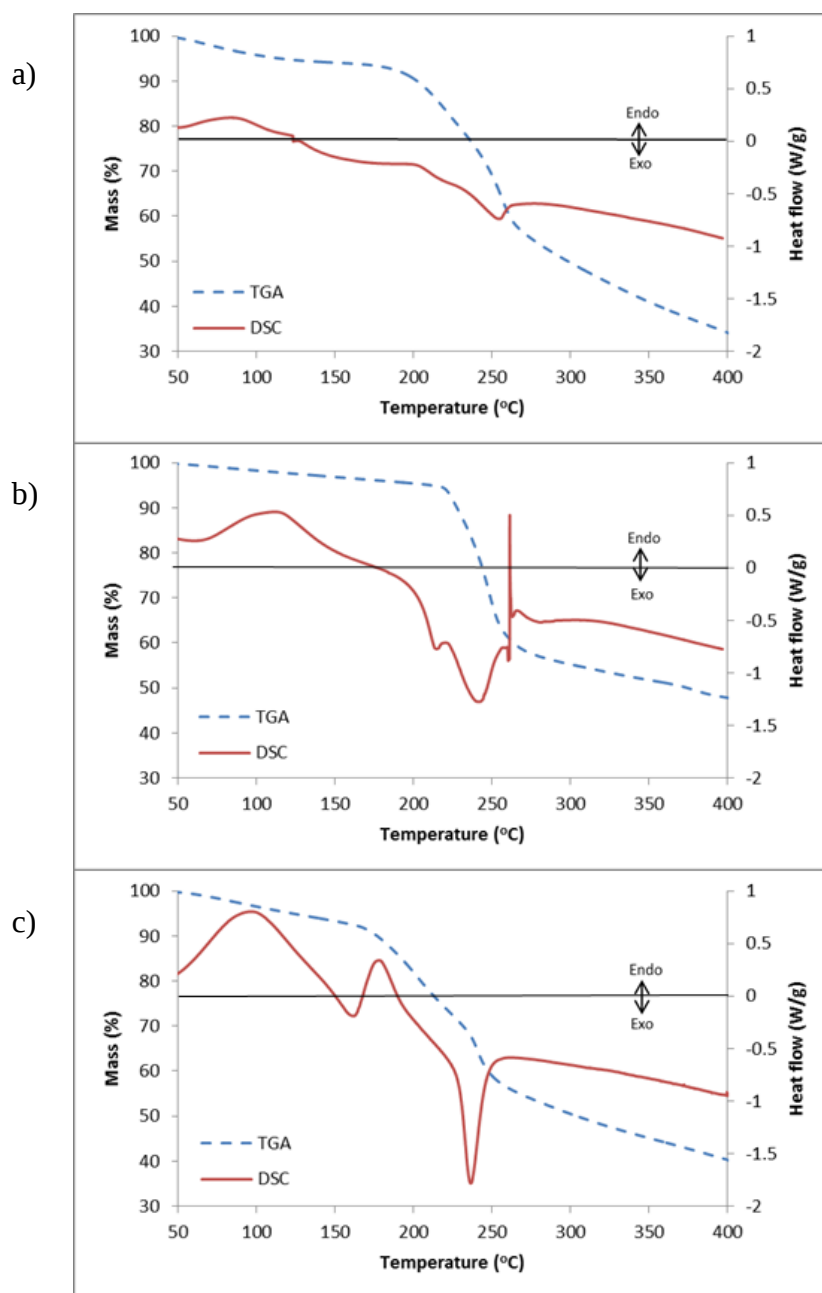


Figure 6: Comparison of TGA and DSC curves for **(a)** H-Alg, **(b)** Na-Alg, and **(c)** Cu-Alg over the temperature range 50 - 400 °C obtained with a heating rate (β) of 10 °C min⁻¹ under N₂

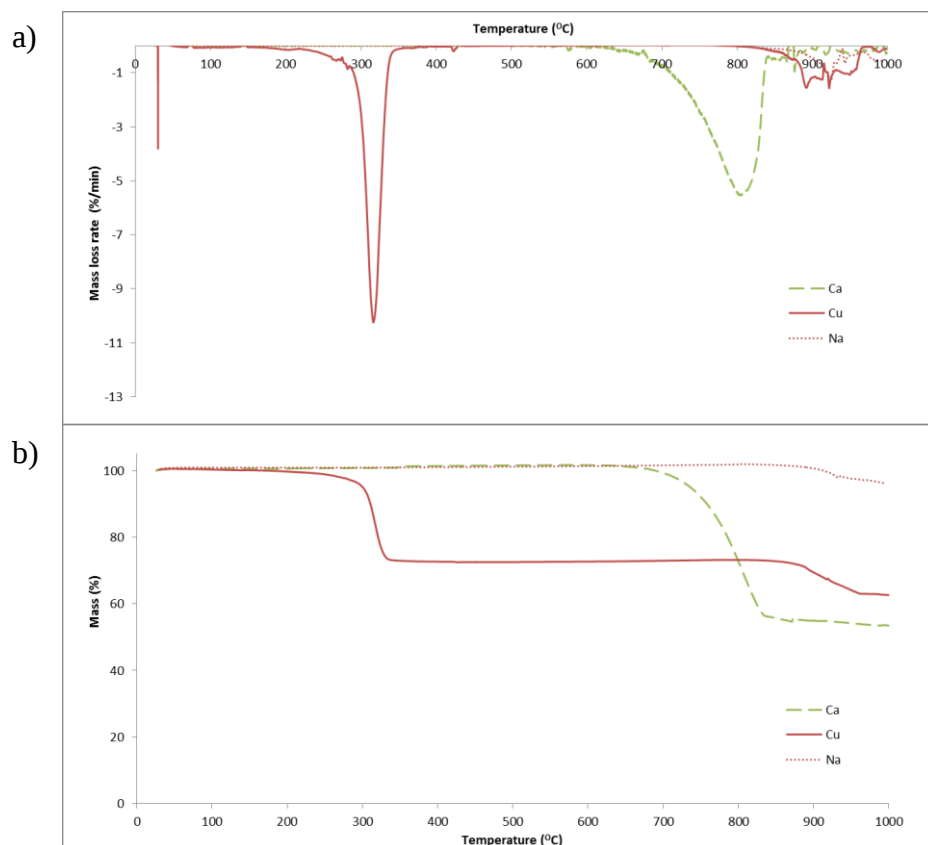


Figure 7: The (a) DTG and (b) TGA profiles for the thermolysis of Na_2CO_3 , CuCO_3 and CaCO_3 over the temperature range 25 - 1000 $^{\circ}\text{C}$ obtained with a heating rate (β) of 10 $^{\circ}\text{C min}^{-1}$ under N_2

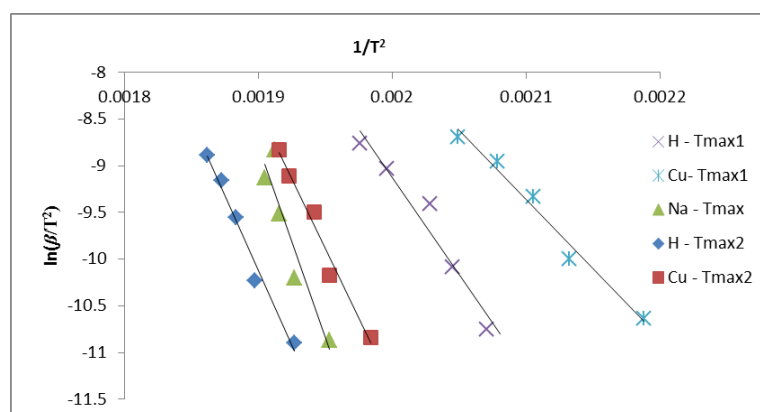


Figure 8: Plot of $\ln(\beta/T^2)$ versus $1/T^2$ at the points of maximum volatilisation of H-Alg, Cu-Alg and Na-Alg, pyrolysed at $\beta = 5, 10, 20, 30$ and 40 $^{\circ}\text{C min}^{-1}$

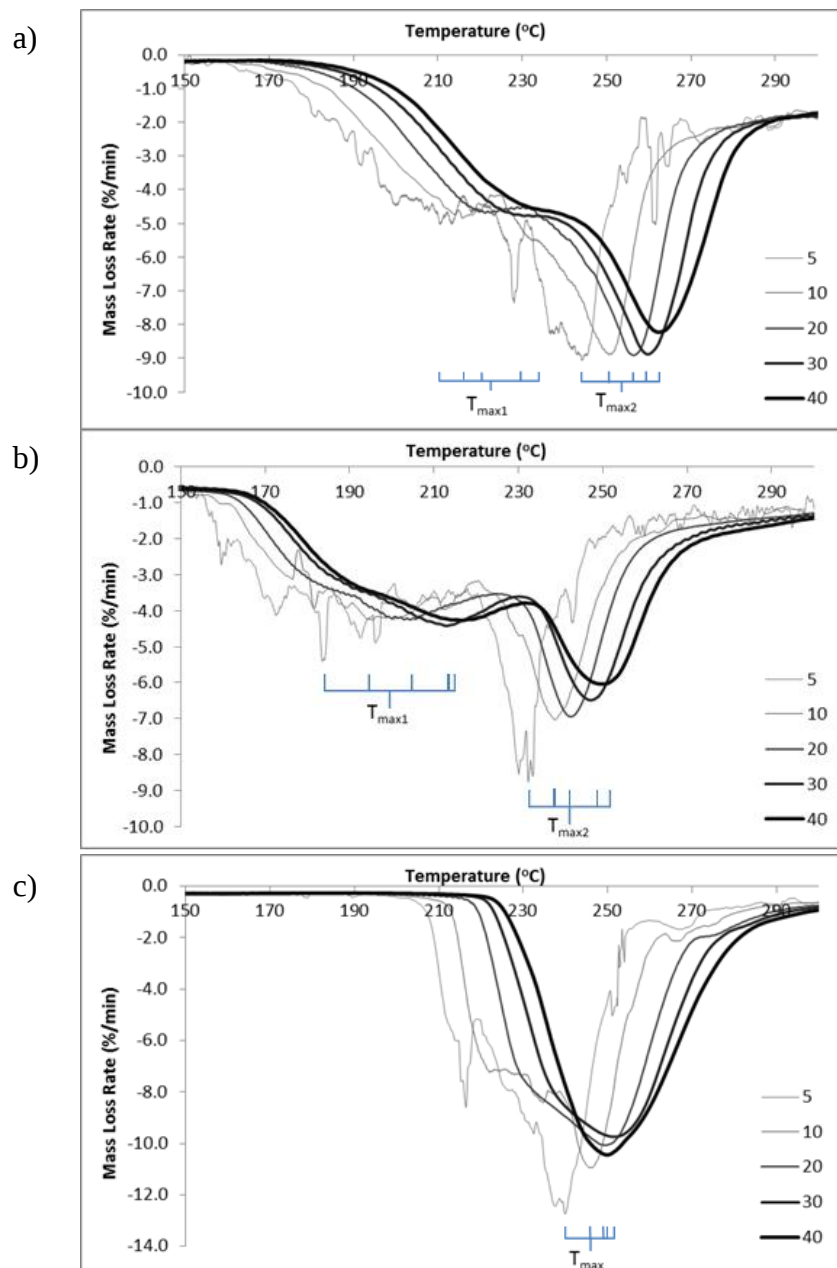


Figure 9: The DTG profiles for the main pyrolysis region of **(a)** H-Alg, **(b)** Cu-Alg and **(c)** Na-Alg at heating rates (β) of 5, 10, 20, 30 and 40 °C min⁻¹ under N₂

Table 2: Key kinetic and thermal parameters in the pyrolysis of H-Alg, Cu-Alg and Na-Alg

Pyrolysis Temperatures (°C)					
	β (°C min ⁻¹)	T_i	T_{max1}	T_{max2}	T_f
H-Alg	5	157	210	246	267
	10	161	216	254	275
	20	168	220	256	278
	30	176	228	261	286
	40	180	233	264	289
	E_a (kJ mol ⁻¹)	-	174	269	-
	$\ln A$	-	36	55	-
	R^2	-	0.95	0.98	-
Cu-Alg	5	143	184	231	261
	10	150	196	239	270
	20	156	202	242	277
	30	162	208	247	287
	40	164	215	249	292
	E_a (kJ mol ⁻¹)	-	123	248	-
	$\ln A$	-	24	52	-
	R^2	-	0.98	0.98	-
Na-Alg	5	204	239	271	
	10	207	246	283	
	20	215	249	286	
	30	221	252	296	
	40	225	250	298	
	E_a (kJ mol ⁻¹)	-	340	-	
	$\ln A$	-	73	-	
	R^2	-	0.88	-	

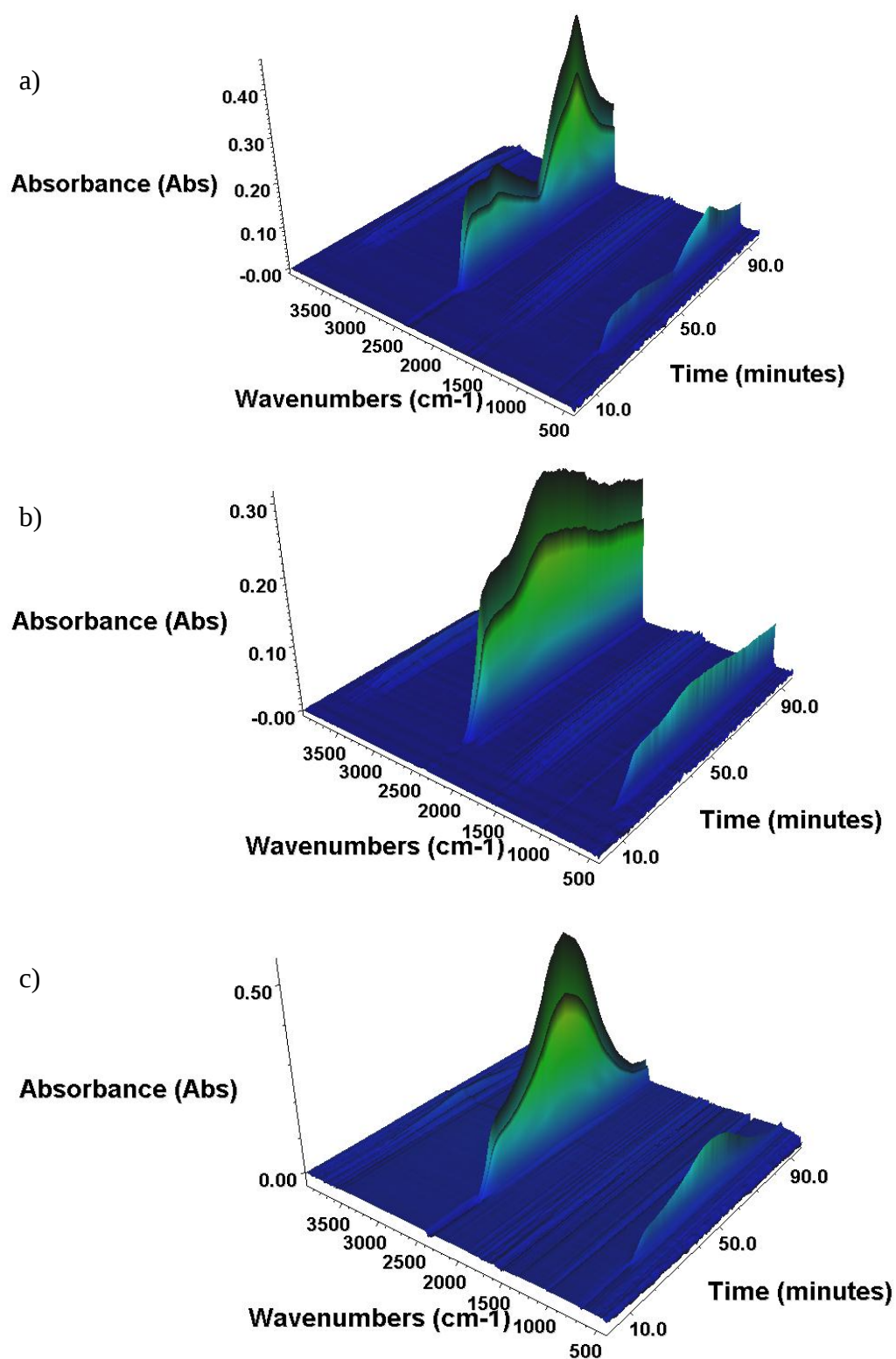


Figure 10: TGA-FTIR profile for the thermolysis of **(a)** Na-Alg, **(b)** Cu-Alg and **(c)** H-Alg over the temperature range 25 - 1000 °C obtained with a heating rate (β) of 10 °C min⁻¹ under N₂

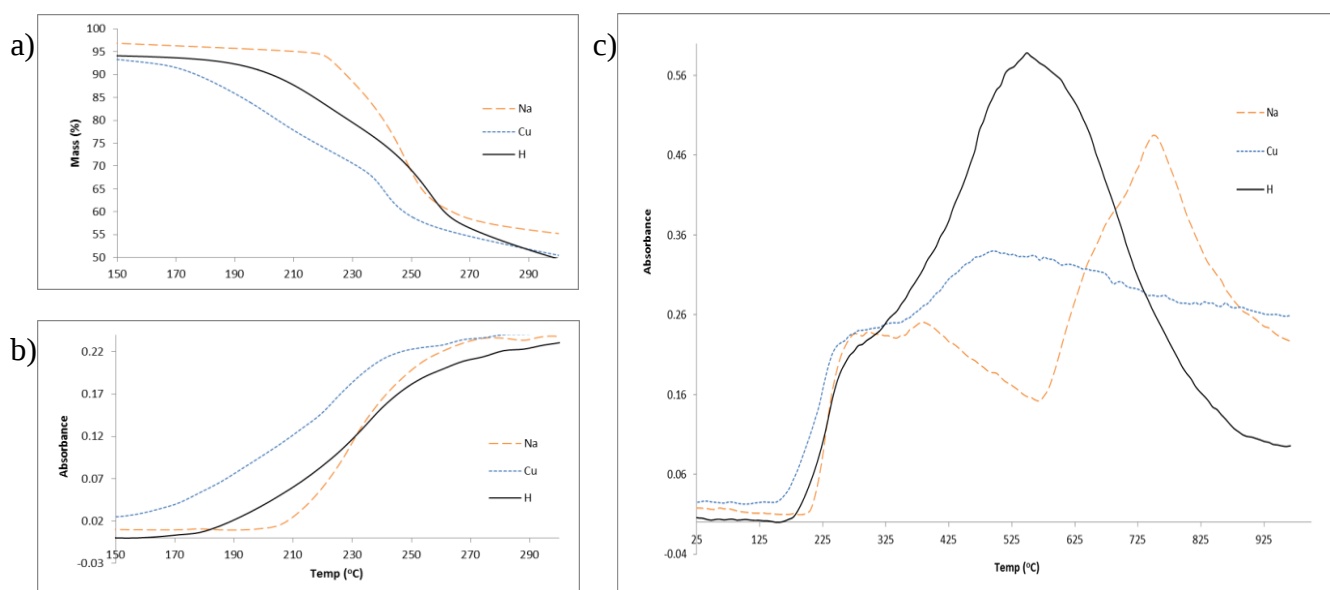


Figure 11: (a) Plot of absorbance at 2360 cm^{-1} versus temperature for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range $150 - 300\text{ }^{\circ}\text{C}$ obtained with a heating rate (β) of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 (b) TGA profile for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range $150 - 300\text{ }^{\circ}\text{C}$ obtained with a heating rate (β) of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 (c) Plot of absorbance at 2360 cm^{-1} versus temperature for the thermolysis of Na-Alg, Cu-Alg and H-Alg over the temperature range $25 - 1000\text{ }^{\circ}\text{C}$ obtained with a heating rate (β) of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2

Table 3: Partial elemental profile of unadulterated *L.digitata* and *L.digitata* treated in a solution of Cu²⁺ ions[‡]

Element*:	Cr	Ba	Li	Mn	Fe	Ni	Zn	Rb	Mo	Ag	Pb	Na	Mg	Al	K	Ca	Sr	Cu	Total	C (wt.%)	H (wt.%)	N (wt.%)
Unadulterated <i>L.digitata</i>																						
(mg / kg _{seaweed})	2	14	1	4	116	1	52	9	0	1	1	42268	13344	345	39787	25002	1727	3	122677	37.6	5.2	1.6
(mmol / kg _{seaweed})	0.04	0.10	0.14	0.07	2.07	0.02	0.80	0.11	0.00	0.01	0.00	1837	556	12.8	1020	625	19.6	0.05	4075			
charge	2+	2+	1+	2+	2+	2+	2+	1+	2+	1+	2+	1+	2+	3+	1+	2+	1+	2+	5285 [†]			
Cu(II)-doped <i>L.digitata</i>																						
(mg / kg _{seaweed})	13	4	0	1	173	10	11	0	1	21	9	3638	35	430	286	159	26	156295	161112	35.6	4.8	1.9
(mmol / kg _{seaweed})	0.25	0.03	0.00	0.02	3.09	0.17	0.17	0.00	0.01	0.19	0.04	158	1.46	15.9	7.33	3.98	0.30	2442	2633			
charge	2+	2+	1+	2+	2+	2+	2+	1+	2+	1+	2+	1+	2+	3+	1+	2+	1+	2+	5116 [†]			

[‡]On a dry basis

*Be, Co, Ga, Cd, Cs, Bi, Tl and V were also detected but below mg/kg levels

[†]The sum of the number of moles of each element multiplied by its charge

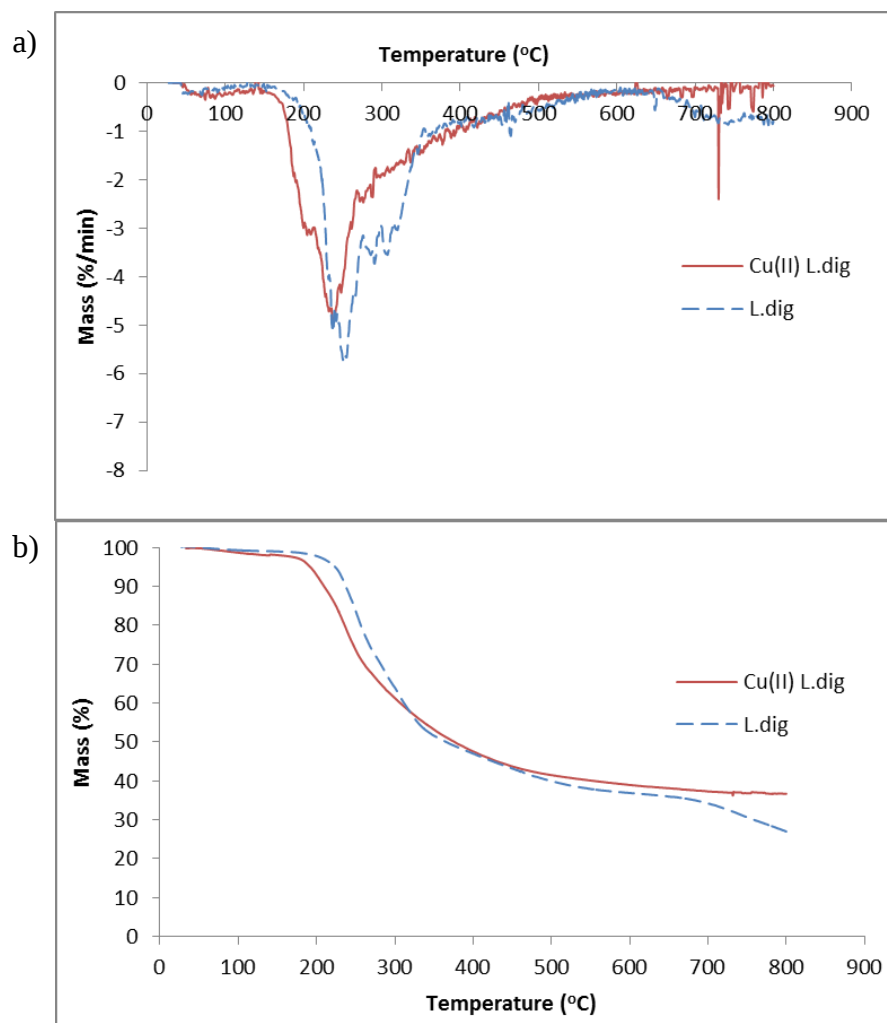


Figure 12: The (a) DTG and (b) TGA profiles for the thermolysis of raw *L. digitata* and *L. digitata* treated in a solution of Cu^{2+} ions in the region 25 - 800 $^{\circ}\text{C}$ with a heating rate (β) of 10 $^{\circ}\text{C min}^{-1}$ under N_2

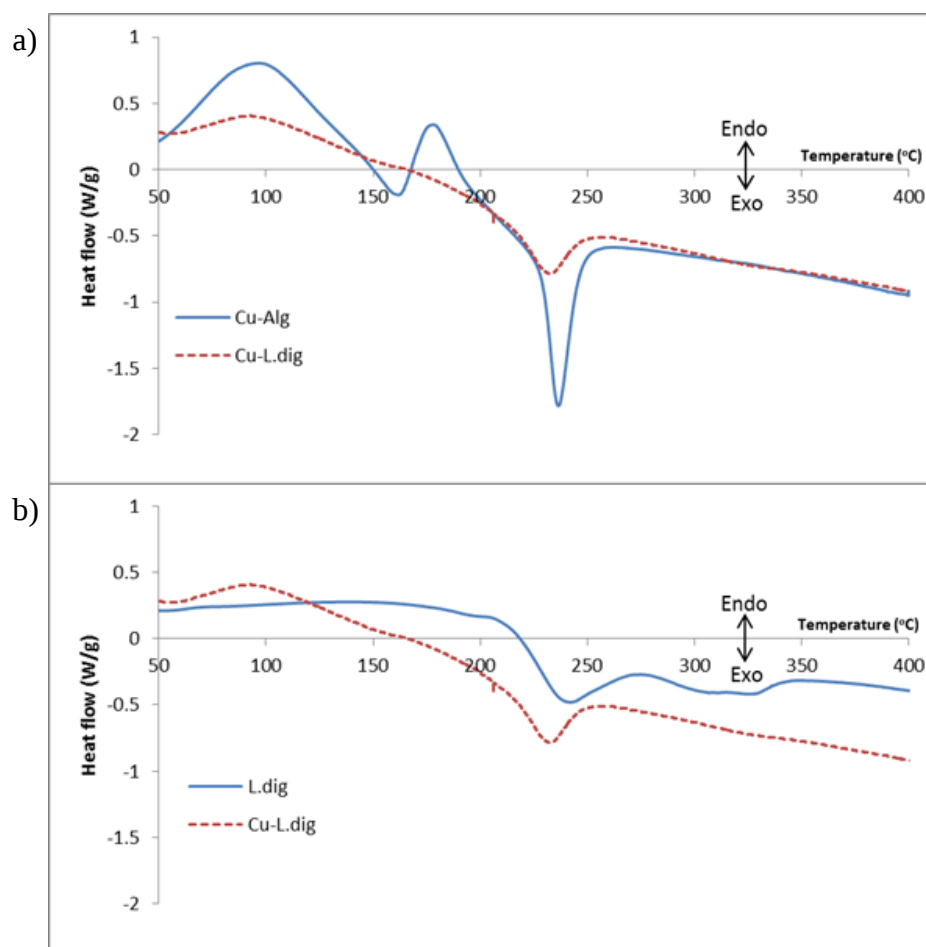


Figure 13: (a) Comparison of DSC curves for copper(II) alginate (Cu-Alg) and copper(II)-doped *L. digitata* (Cu-L.dig) over the temperature range 50 - 400 °C obtained with a heating rate (β) of 10 °C min⁻¹ under N₂ **(b)** Comparison of DSC curves for unadulterated *L. digitata* (L.dig) and copper(II)-doped *L. digitata* (Cu-L.dig) over the temperature range 50 - 400 °C obtained with a heating rate (β) of 10 °C min⁻¹ under N₂