

Heavy Metal Recovery from Industrial Waste with Biosorbent Mesoporous Materials (BioMes)

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ENVIRONMENTAL PROTECTION AGENCY

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Executive Summary

Heavy metals and certain non-heavy metals are highly problematic industrial pollutants in Ireland. Lead, zinc, and copper are particularly problematic, ending up in our groundwater and other fresh water sources.

Ireland has some of the most sustainable, diverse and abundant macroalgae resources in the world. Brown seaweeds have a natural ability to bind metals to naturally occurring polymers within them. This ability of seaweeds to bind pollutant metals presents an opportunity to develop materials from an indigenous Irish resource that can be used for effective environmental remediation.

The class of materials produced from natural sources for this application is called biosorbents. Historically, a major obstacle to producing high-capacity biosorbents of any type has been that they cannot be produced cost-effectively and with a sufficient surface area.

This project presents a method to cheaply produce high-capacity biosorbents from Irish brown seaweeds. We have produced porous biosorbents with a high surface area from a renewable source – *Ascophyllum nodosum* brown macroalgae – by a production method that uses no toxic compounds or non-renewable materials. We have shown that, at the laboratory scale, these biosorbents successfully bind lead, zinc and copper from polluted water.

1 Introduction

Biosorbents are biological source materials that effectively bind certain compounds, such as pollutant metal ions, to their surfaces. Our objective was to produce, from Irish macroalgae, biosorbents with the highest surface area and adsorption capacity yet seen.

Macroalgae, in particular brown algae, have long been known to be among the most effective biosorbents (Haug, 1961; Davis *et al.*, 2003). Ireland has some of the most sustainable, diverse and abundant macroalgae resources in the world (DAFM, 1995; McHugh, 2003; Bruton *et al.*, 2009). The Irish economy relies heavily on pharmaceutical, chemical and technological manufacturing industries. The valuable heavy metals in their waste streams are a problem, both economically and environmentally.

Historically, a major obstacle to producing high-capacity biosorbents of any type has been that they cannot be produced cost-effectively and with sufficient surface area to compete with current man-made sorbent technologies. In the few methods of expansion of biomass for use as biosorbents, the cost arises from the use of supercritical fluids or similarly complex methods (Quignard *et al.*, 2008; Albarelli *et al.*, 2011;

Balu *et al.*, 2012; Alhwaige *et al.*, 2013). Recently, it was shown that it is possible to produce stable mesoporous particles (i.e. particles with pores in the size range of 2–50 nm – pores in the surface of a material increase its surface area) from macroalgae, simply and without expensive processing steps (Dodson *et al.*, 2013). However, no applications of these materials have been demonstrated.

Adapting the aforementioned method, we produced high-capacity biosorbents with a high surface area from the brown macroalgae species *Ascophyllum nodosum* using a cheap and simple process. We call this material BioMes (Biosorbent mesoporous materials). Its efficacy as a biosorbent was tested using sorption experiments with three common and problematic metal ion pollutants: lead, zinc, and copper. This demonstrated the uncomplicated, sustainable production of biosorbents with surface areas and maximum sorption capacities several orders of magnitude above what have been seen in the literature so far. These have a broad application in environmental and industrial waste remediation. The material is an ideal sustainable material.

2 Literature Review

2.1 Biosorption

Biosorbents are biological source materials that effectively bind certain compounds, such as metal ions, to their surfaces. Their most prominent use is in removal of contaminant heavy metal ions from solution. As pollutants, these can be extremely problematic (Naja and Volesky, 2009) and, as evermore rarefied resources, they have growing economic and commercial value (European Commission, 2014). Thus, effective biosorbents have the potential for widespread application in the removal and reclamation of heavy metal pollutants from aqueous waste streams.

The scientific general term for seaweed is macroalgae. Macroalgae, in particular brown algae, have long been known to be among the most effective biosorbents (Davis *et al.*, 2003; Haug, 1961). This is because of their extracellular storage polysaccharides. These are naturally occurring polymers that have evolved within macroalgae, but outside their algal cells (hence “extracellular”), in order to store toxic metal compounds. In nature, these polysaccharides provide a means of holding metal compounds outside the macroalgal cells, preventing the cells from being destroyed by toxic doses of the metals and permitting later controlled usage as needed (Pinto *et al.*, 2003). The predominant extracellular storage polysaccharides in brown algae are alginates, laminarin, mannitol and fucoidan (10–40%, 2–34%, 5–25% and 5–20% of dried mass, respectively, depending on species) (Ross *et al.*, 2009). Cellulose also occurs as 2–20% of dried mass (also species dependent); however, cellulose makes up the inner, rigid fibrillar layer of brown algae (Kreger, 1962; Davis *et al.*, 2003).

2.2 State-of-the-art Methods

The current methods at the industrial scale for removal of heavy metal ions from aqueous waste streams have been established to varying degrees but are not entirely effective. Chemical precipitation (in which a chemical agent is used to solidify the metals and cause them to drop out of solution, usually in the

form of a salt) and coagulation (in which the metals in solution are caught up in a compound that then solidifies the original solution, akin to blood clotting) are methods that work through chemicals that react with heavy metal ions to form insoluble precipitates. The precipitates are recovered by sedimentation or filtration. These methods are well developed and relatively cheap but are ineffective at low metal ion concentrations. Ion-exchange resins are also well established but are expensive. Electrochemical treatments that involve the plating out of metal ions on a cathode surface exist; however, although this technology is well developed, it requires a large initial capital investment, comes with high energy demands and is also ineffective at low metal ion concentrations. The same is also true of electrocoagulation (coagulation brought about by electrical charges). Membrane treatments are another method of aqueous metal ion removal; here, the metal solution is passed through a membrane and the metals ions are concentrated on one side by either excluding their passage through the membrane or permitting their exclusive passage through. Reverse osmosis, electrodialysis, nanofiltration and ultrafiltration are the most established membrane technologies, but these methods are currently underdeveloped. Activated carbons and silicas are the standard industrial particles used for absorption of metal ions. These are effective and well developed but their production has a relatively large environmental impact. Additionally, in the case of activated carbon, depleted sources of coal raw material have resulted in price increases, whereas in the case of silica, it is relatively expensive to produce (Fu and Wang, 2011; Gautam *et al.*, 2015).

In comparison with the above methods, biosorbents have the potential to be highly effective, cheap to produce, renewably sourced, produced with little to no environmental impact and integrated with existing technologies such as membranes, and to remain effective at low metal ion concentrations (Fu and Wang, 2011; Gautam *et al.*, 2015). However, there have been some problems associated with biosorbents, primarily with regard to their sorption capacity. Sorption capacity is the total amount of

objective material that can be bound to a surface. In this case it refers to metal ions being bound to biosorbent particles. A major obstacle to producing high-capacity biosorbents with a high surface area is that they cannot be produced cost-effectively to compete with current man-made sorbent technologies. In the few methods of expansion of biomass for use as biosorbents, the cost arises from the use of supercritical fluids (a method of changing the solvent properties of compounds such as water or CO₂ by placing them under extreme temperatures and pressures) or similarly complex methods (Quignard *et al.*, 2008; Albarelli *et al.*, 2011; Balu *et al.*, 2012; Alhwaige *et al.*, 2013) Recently, it was shown that production of stable mesoporous particles from macroalgae, simply and without expensive processing steps, is possible (Dodson *et al.*, 2013). However, no applications of these materials have been demonstrated to date.

2.3 Sorbate Molecules

Biosorbents are studied for their capacity for a wide range of sorbate molecules. The most pertinent sorbates here are metal ions, which are problematic pollutants industrially, municipally and environmentally.

Biosorbents are highly effective at adsorbing metal ions. They have been used to adsorb lanthanides such as lanthanum, ytterbium and cerium, as well as a host of more common metals such as copper, magnesium, chromium, zinc and gold (Das *et al.*, 2008; Sakamoto *et al.*, 2008; Ahmady-Asbchin *et al.*, 2009; Mata *et al.*, 2009; Vijayaraghavan *et al.*, 2010).

Adsorption of heavy metal pollutants is perceived as a particular specialty of biosorbents. However, the term "heavy metal" has no specific scientific meaning. The most commonly agreed definition of the term is metals and metalloids with an atomic density of greater than 5g/cm³. This encompasses 87 of the known elements. Of these, our study focuses on copper, chromium and zinc. Copper is a common pollutant from industry, especially resulting from logic chip production and mining. It also occurs as a municipal pollutant from

landfill run-off and old water and sewage facility pipes. Zinc is another hugely problematic pollutant and is even more widespread than copper. Chromium is also ubiquitous as a pollutant, especially in road run-off.

Biosorbents produced from macroalgae have been applied to these three metals and have been found to be effective (Sari and Tuzen, 2008; Areco *et al.*, 2012; Akbari *et al.*, 2015; Barquilha *et al.*, 2017). However, the issues around capacity, as already outlined, were still present, preventing their development beyond academic studies.

2.4 Attempts to Increase Biosorbent Efficacy

Historically, there have been successful attempts to increase the surface areas of biosorbents. Supercritical fluids have been used to expand biosorbents produced from banana peels in a process called "exploding", which successfully increased the biosorbent surface area (Albarelli *et al.*, 2011; Comim *et al.*, 2010). However, the technology is prohibitively expensive at the industrial scale and cannot compete economically with materials such as activated carbons and silicas.

Other equally effective methods to increase the biosorbent surface area are radiation (Farooq Umar *et al.*, 2011) and chemical breakdown of cell structures (Lin and Rayson, 1998). These methods are expensive at commercial production scales and environmentally damaging.

Another popular method is to simply state in a publication that a biosorbent inherently has a high surface area. However, this is word play. In reality, such papers are merely presenting biosorbents that typically have an insufficient surface area to be adopted on a large scale.

Finally, a common means of producing sorbents with a high surface area from biomass is to turn that biomass into activated carbon; however, this has the issues associated with activated carbons highlighted in section 2.2.

3 Methods

3.1 Macroalgae Particles

Dodson *et al.* (2013) have demonstrated a short, uncomplicated process to expand brown seaweed particles: take brown seaweed, wash, dry and powder, soak in water, exchange water with ethanol, and vacuum dry. Particles produced by this method from the macroalgae species *Fucus vesiculosus* and *A. nodosum* are reported to have surface areas from 140 to 210 m²/g (typical surface areas before expansion are 0.05–0.1 m²/g) (Dodson *et al.*, 2013).

In our work this method was adopted to expand three brown seaweeds: *A. nodosum*, *Alaria esculenta* and *F. vesiculosus*. Seaweed macroalgae were harvested from three sites off the coast of Cork, Ireland. Samples were dried in air by hanging them in a ventilated room at approx. 25°C for 1 week. A second drying stage was conducted by drying the macroalgae in an oven at approx. 40°C for 24 hours. Dried macroalgae were then broken down in a food processor (Moulinex Multi Moulinette AT711). The dried, processed macroalgae were then ground to a powder in an electric coffee grinder (Krupps 180w 75 ml Coffee Mill F2034238C). The ground macroalgae were then passed through a BS-410 standard sieve, with a mesh size of 150 μm. The sieved macroalgal powder of < 150 μm particle size was then ready for expansion. Expansion by solvent exchange proceeded as described by Dodson *et al.* (2013). Water was used to expand particles initially and then the water was exchanged for ethanol, as ethanol can be more readily evaporated. Some unexpanded particles were set aside to be used for comparative tests to show the effect of expansion. Expansion of the particles was carried out inside a BACOENG 6.8L vacuum chamber kit with a 3 CFM, single-stage, rotary vane vacuum pump and a KGW KF 29-GL-A cold trap. The resulting appearances of the seaweed can be seen in Figure 3.1.

3.2 Metal Solutions

Metal stock solutions of 1000 ppm were prepared from the following metal salts: Cr(NO₃)₃·9H₂O, CuSO₄·5H₂O and ZnSO₄·7H₂O. Calibrations of the inductively



Figure 3.1. Dried seaweed (bottom right), seaweed after blending (bottom left), seaweed after grinding (top left) and seaweed after expansion (top right).

coupled plasma optical emission spectrometer (ICP-OES) were conducted using solutions of 1000, 100, 10, 1, 0.1, 0.01 and 0.001 ppm. These were made by serial dilution of the stock solutions. From the aforementioned stock solutions, working solutions of concentrations of 5, 25, 125, 250, 500 and 1000 ppm were obtained by serial dilution. These values represent the starting concentrations in the adsorption studies and adsorption data shown below.

3.3 Potentiometric Mass Titrations

Potentiometric mass titrations (PMTs) were performed to determine the pH_{pzc} of the sorbent materials. pH_{pzc} is the point of zero charge on a material's surface relative to the pH of the solution and gives an indication of the material's ability to adsorb compounds. This information can also be used to give an indication of what functional groups are on the surface of a material. This method was an adaptation of methods described in the literature (Fiol and Villaescusa, 2009). A 0.03 M aqueous solution of NaNO₃, a 0.1 M aqueous solution of HCl and a 1 M aqueous solution of NaOH

were prepared. Then, 50 ml volumes of the NaNO_3 solution containing 0.0 (blank), 0.2, 0.4 and 0.6 g/L of biosorbent were prepared in 100 ml beakers. This was to ensure that PMTs were conducted at constant ionic strength. Subsequently, three drops of a 1 M NaOH solution was added to each biosorbent solution prior to titration at approx. 25°C , under agitation with a stirrer probe at 250 rpm. These biosorbent solutions were then allowed to settle without agitation. This was done to deprotonate the sorbent surface and adjust the pH to above pH 9.8. To each biosorbent solution, 0.05 ml additions of 0.1 M HCl were then made until 3.0 ml in total was added. Additions were made at approx. 25°C under agitation with a stirrer probe at 250 rpm, after which the solutions were allowed to settle without agitation. The pH of the solutions was then determined. Temperature was controlled using a Stuart SD162 hot plate/stirrer and pH measurements were carried out using a ThermoFisher Scientific Orion Star™ A214 pH/ISE Benchtop Meter, stirring probe, temperature probe and ThermoFisher Scientific Orion™ 8102BNUWP ROSS Ultra™ pH Electrode (see section 4.2).

3.4 Sorption Experiments

Adsorption data were experimentally obtained for three metal ions: chromium (III), copper (II) and zinc (II). Experiments were conducted with starting metal ion concentrations of 5, 25 and 125 mg/L. Each experiment was run in triplicate, giving a total of 27 experiments (three metal ions \times three starting concentrations \times three runs) and nine sets of data (results presented are the average of each set of triplicate results).

Before each experiment, starting metal solutions were adjusted to pH 5.0 (± 0.01), which is below the precipitation pH of all three metals (see section 4.2 for justification). Then, 0.2 g of biosorbent was added to 100 ml of a given metal solution in a 250 ml Erlenmeyer flask. Eleven such prepared flasks were used for each experiment. Flasks were agitated on a rotary shaker (New Brunswick Scientific Excella® E25 Floor Incubator Shaker) at 100 rpm at room temperature. After 5 minutes, one flask was removed and enough of the sample was taken from it to fill two 15 ml centrifuge tubes. These were then spun in a Beckman-Coulter Avanti® J-26 XPI centrifuge at 5000 rpm for

5 minutes to separate the macroalgal solids. The metal concentration in the supernatant liquid was then determined using the ICP-OES. This process was repeated for the remaining flasks after every 17 minutes and 30 seconds, with a total experimental time of 180 minutes. A control sample of the relevant metal solution without biosorbent was also obtained for testing, giving the metal concentration at zero minutes. This permitted quantification of the sorption of metal ions to the biosorbent per unit time. Plots of the solution metal ion concentration versus time were then produced.

3.5 Experimental Data and Kinetic Modelling

The amount of metal ions adsorbed at equilibrium (q_e , mg/g) was calculated using equation 3.1, as described in the literature (Ji *et al.*, 2012; Shamshad *et al.*, 2016):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (3.1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium metal ion concentrations, respectively. The C_e value was taken as the concentration after 180 minutes (see 3.4). V (L) is the volume of the solution and m (mg) is the mass of the adsorbent. C_0 was varied as follows: 5, 25, 125, 250, 500 and 1000 mg/L. For C_0 values of 5, 25 and 125 mg/L, the values of C_e were obtained from the results of the sorption experiments described in section 3.4. For C_0 values of 250, 500 and 1000 mg/L, additional experiments were run as described in section 3.4, except that only a single flask was used and C_e was obtained from the concentration of metal ions in solution after 180 minutes.

Isotherm curves were evaluated using data determined by equation 3.1. Data were fitted to the Langmuir isotherm model. The non-linear expression of the Langmuir isotherm model is illustrated in equation 3.2:

$$q_e = q_{\max} \cdot K_{\text{eq}} \frac{C_e}{1 + K_{\text{eq}} \cdot C_e} \quad (3.2)$$

where q_{\max} (mmol/g) is the maximum biosorption capacity and K_{eq} (mg/L) is the equilibrium constant related to energy or net enthalpy of adsorption.

Linear forms of the isotherm models are widely adopted to determine the isotherm parameters for the

adsorption. Such a linear form was used to determine the fit of our data to the model. This is shown in equation 3.3:

$$\frac{1}{q_e} = \frac{1}{q_{\max} \cdot K_{\text{eq}}} \cdot \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (3.3)$$

where the plot of $1/q_e$ versus $1/C_e$ will produce a line with slope of $1/q_{\max} \cdot K_{\text{eq}}$ and an intercept of $1/q_{\max}$. The values for q_e and C_e are experimentally determined. From this, q_{\max} can be determined as the reciprocal of the intercept. From this, K_{eq} can be determined.

3.6 Analytical Methods

3.6.1 Surface area analysis

Brunauer–Emmett–Teller (BET) surface area (which can simply be considered as being equivalent to surface area for the lay reader), pore diameter, Barrett–Joyner–Halenda (BJH) pore volume (which can be considered as being equivalent to pore volume for the lay reader), adsorption isotherms (graphs of the amounts of metal ions adsorbed on the surface of the biosorbent with varying pressure at constant temperature) and pore size distributions (graph of the number of pores of a given size vs the pore size range) were determined using a Micromeritics Instrument Corporation TriStar II 3020 V1.01 surface area and porosity instrument.

3.6.2 Inductively coupled plasma optical emission spectroscopy

Quantitative analysis of adsorption experiments was conducted using an ICP-OES (PerkinElmer Optima DV 2000). Analyses were run at a variety of wavelengths for each metal using a 1000 ppm standard solution. Solutions contained all metals at each wavelength tested. This was to ensure that no metals were resulting in signals at multiple wavelengths, which may have resulted in false positives. The wavelengths giving the optimum signal-to-noise ratios were chosen to develop calibration curves. From these results, calibration curves were developed by analysing

standard solutions of varying concentrations (outlined in section 3.2) by ICP-OES at the chosen analytical wavelengths. Data from these graphs were used to develop calibration curves by tabulating peak height and corresponding standard solution concentration. Optimum R^2 values for calibrations were obtained for chromium (III) at wavelength 283.563 nm, for copper (II) at wavelength 324.752 nm and for zinc (II) at wavelength 206.200 nm (0.999992, 0.999888 and 0.9997, respectively). For chromium (III) and copper (II), these optimum R^2 values occurred for wavelengths typical of these metals in the literature (Cui *et al.*, 2007). Zinc (II) is conventionally analysed at wavelength 213.857 nm in the literature (Cui *et al.*, 2007; Zhu *et al.*, 2007); however, our calibrations showed a better R^2 value at wavelength 206.200 nm. As such, ICP-OES analyses were calibrated for this wavelength. The calculated R^2 values and the graphs that they were derived from are shown in Figures 3.2–3.4.

3.6.3 Scanning electron microscopy

Images of seaweed particles before and after expansion were obtained using a JEOL model FEI FP 2031/11 Inspect F field emission scanning electron microscope (SEM).

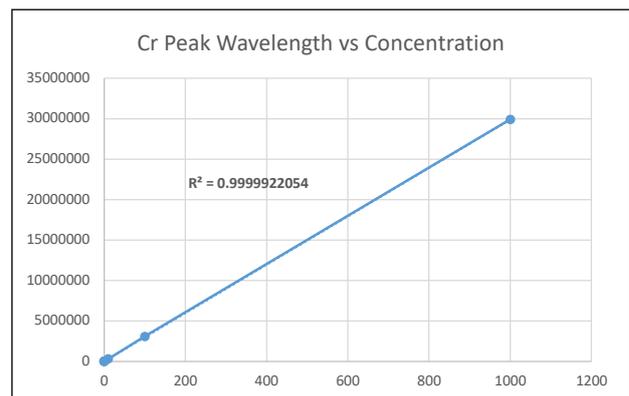


Figure 3.2. ICP-OES calibration curve for chromium at a wavelength of 283.569 nm. $R^2=0.999992$.

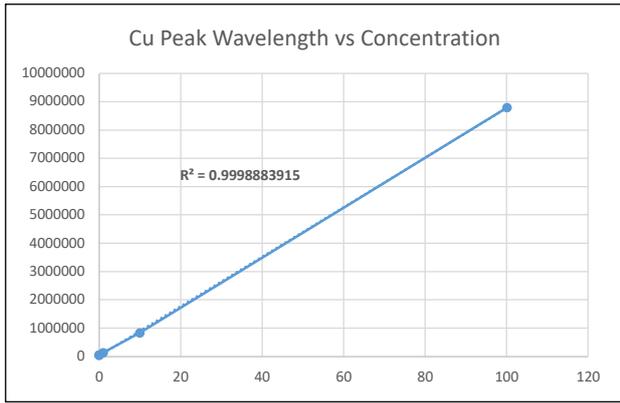


Figure 3.3. ICP-OES calibration curve for copper at a wavelength of 324.752 nm. $R^2=0.999888$.

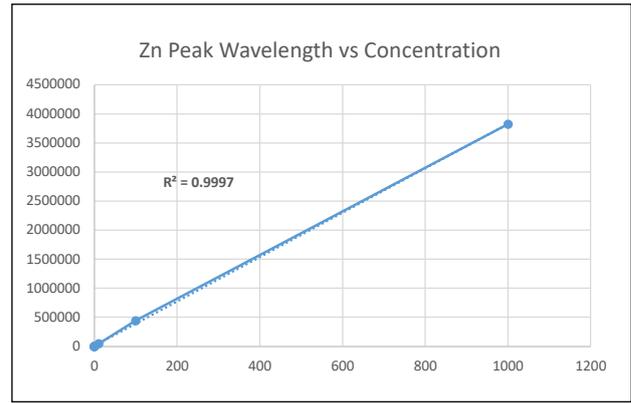


Figure 3.4. ICP-OES calibration curve for zinc at a wavelength of 206.200 nm. $R^2=0.9997$.

4 Results and Discussion

4.1 Macroalgae Particles Production and Characterisation

Expanded and unexpanded macroalgae particles were produced successfully using the methods described in section 2.1. Table 4.1 shows the BET surface area, BJH pore volume and pore diameter data as determined by surface area and porosity analysis for all macroalgae and expanded macroalgae samples. These analyses determined that, on expansion, the largest increase in surface area for the tested species was conferred on *A. nodosum*. Particles of this macroalgae increased in surface area by 4490.0 times the initial area on expansion (BET surface area: before expansion 0.023 m²/g; after expansion 103.270 m²/g). In contrast, expansion of *A. esculenta* and *F. vesiculosus* particles resulted in increases in surface area of 348.3 and 2611.9 times their initial surface areas, respectively.

Of the three species, only *A. esculenta* exhibited any measurable porosity before expansion. However, these were not true pores and are better described as shallow depressions on the surface, with a relatively miniscule overall pore volume of 0.001 cm³/g and a relatively large average pore diameter of 208.870 Å.

After expansion, the *A. nodosum* species exhibited the largest pore volume and pore diameter, at 0.420 cm³/g and 113.236 Å, respectively. Expanded *A. esculenta* (pore volume and pore diameter of 0.295 cm³/g and 75.289 Å, respectively) and *F. vesiculosus* (pore volume and pore diameter were 0.156 cm³/g and 90.357 Å, respectively) had lower values for both measures.

Adsorption isotherms of the expanded particles of all three macroalgae species exhibited a classic mesoporous shape. The adsorption isotherm graph of *A. nodosum* is shown in Figure 4.1. Adsorption isotherm graphs of *A. esculenta* and *F. vesiculosus* are shown in Figures 4.2 and 4.3, respectively.

The pore size distribution of the expanded *A. nodosum* particles is shown in Figure 4.4. The greatest number of pores is in the 100–200 Å pore diameter range. Pore size distributions of *A. esculenta* (Figure 4.5) and *F. vesiculosus* (Figure 4.6) show that the greatest number of pores is in the 50–120 Å and 75–150 Å ranges, respectively.

Figure 4.7 shows SEM images of the *A. nodosum* particles before and after expansion.

A. nodosum has the highest absolute content of polysaccharides of any brown algae species. Additionally, the proportion of alginate is higher in *A. nodosum* than in other brown algae, whereas the proportions of laminarin, mannitol and fucoidan are lower and the proportion of cellulose is approximately the same (Kreger, 1962). Specific proportions vary with season and location. This means that *A. nodosum* contains a wide array of functional groups for binding ions: carboxyl groups in alginate, sulfate groups in fucoidan, methyl groups in cellulose and hydroxyl groups in all but cellulose. This information, along with the previously detailed results of the surface area and porosity analyses showing that *A. nodosum* gained the most in surface area after expansion and had the largest pores of the three tested species, suggests that *A. nodosum* is the optimum species for the production

Table 4.1. BET surface area, BJH pore volume, and pore diameter as determined by surface area and porosity analysis for all macroalgae and expanded macroalgae samples

Macroalgae	BET surface area (m ² /g)	BJH pore volume (cm ³ /g)	Pore diameter (Å)
<i>A. esculenta</i>	0.288	0.001	208.870
<i>A. esculenta</i> (expanded)	100.311	0.295	75.289
<i>A. nodosum</i>	0.023	n/a	n/a
<i>A. nodosum</i> (expanded)	103.270	0.420	113.236
<i>F. vesiculosus</i>	0.016	n/a	n/a
<i>F. vesiculosus</i> (expanded)	41.791	0.156	90.357

of our objective biosorbent. Thus, particles and expanded particles of *A. nodosum* were subjected to the sorption studies detailed below.

4.2 Potentiometric Mass Titrations

Potentiometric mass titrations showed that the pH_{pzc} of the expanded *A. nodosum* particles was 7.6, whereas that of the unexpanded *A. nodosum* particles was 6.6. A pH_{pzc} of 7.6 is far higher than expected for

carboxyl groups and hydroxyl groups in alginic acid (Ahmady-Asbchin *et al.*, 2009; Vijayaraghavan *et al.*, 2010). Ahmady-Asbchin *et al.* (2009) found that brown algae contained at least three kinds of acidic functional groups: carboxyl groups, sulfate groups and hydroxyl groups. While the pH_{pzc} obtained here is higher than is typical for carboxyl and hydroxyl functional groups, it is lower than expected for the sulfate and methyl functional groups (Tamura *et al.*, 1989; Atieh *et al.*, 2010). This suggests that the increase in pH_{pzc} after

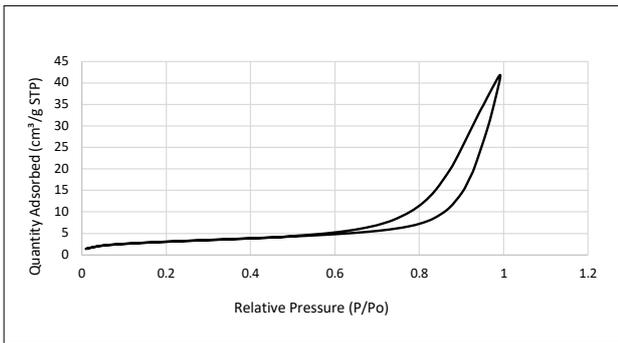


Figure 4.1. Adsorption isotherm for *A. nodosum* expanded.

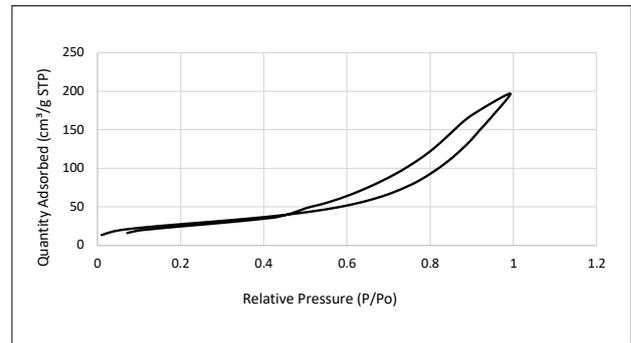


Figure 4.2. Adsorption isotherm for *A. esculenta* expanded.

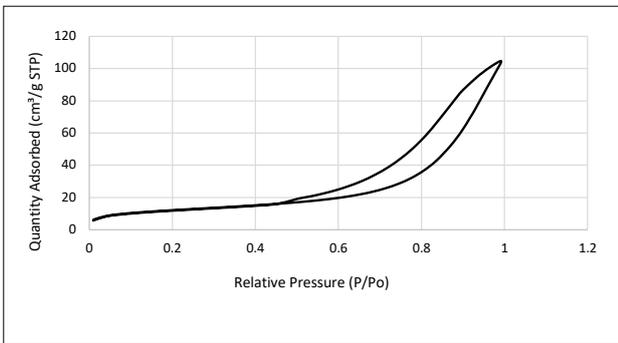


Figure 4.3. Adsorption isotherm for *F. vesiculosus* expanded.

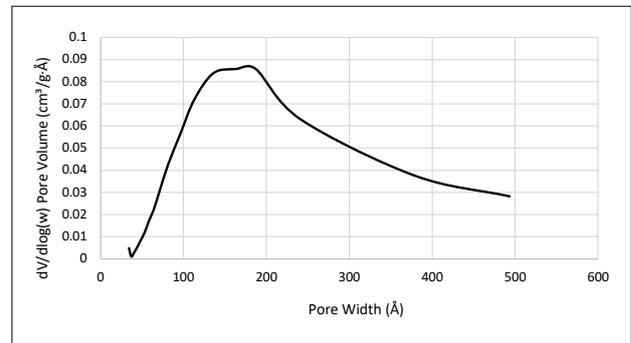


Figure 4.4. Pore size distribution for *A. nodosum* expanded.

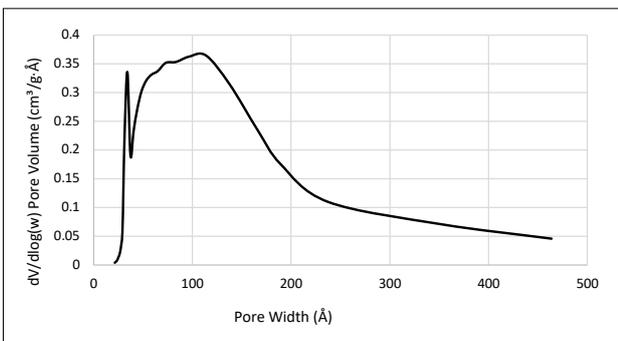


Figure 4.5. Pore size distribution for *A. esculenta* expanded.

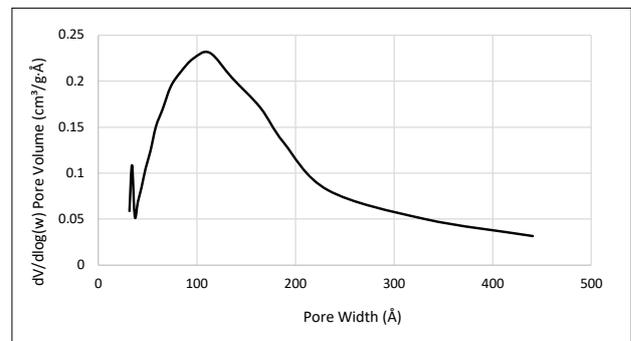


Figure 4.6. Pore size distribution for *F. vesiculosus* expanded.

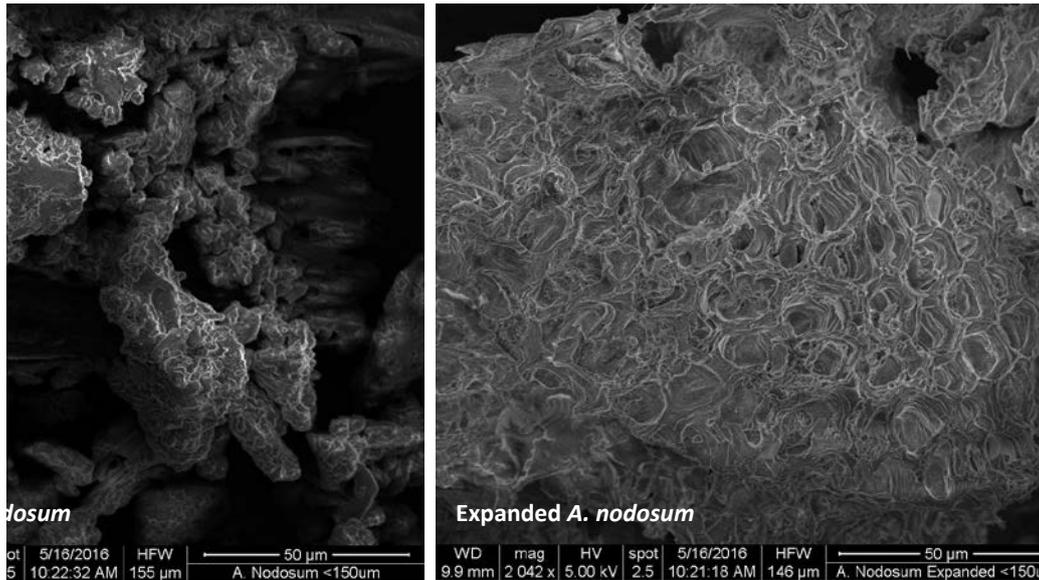


Figure 4.7. SEM images showing unexpanded *A. Nodosum* particles (left) and *A. Nodosum* particles expanded by 4490 times the initial surface area (right).

expansion is the result of the loss of the carboxyl and hydroxyl functional groups. This further suggests that the functional groups remaining are those of fucoidan and/or the cellulose matrix. If this is the case, expansion may result in some loss of the most active biopolymer in the adsorption process – alginate. Additionally, this pH_{pzc} was higher than the precipitation pH in aqueous solution for the metal ions tested. As such, biosorption tests were not conducted at a pH that is optimal for maximum adsorption of each metal. In spite of this, the results showed excellent sorption performances in comparison with the literature (detailed in sections 4.3 and 4.4) and, because the previously highlighted experimental constraints were constant for all experiments, the differences in performance between expanded and unexpanded particles are accurate in absolute terms.

Future work on these materials could focus on retaining more of the functional polysaccharides during the expansion process. Crosslinking is the most probable route to success. The manner of crosslinking must be carefully chosen, however, as the use of toxic crosslinking compounds will reduce the sustainability of the biosorbent production process. If this could be carried out successfully, it may permit sorption

studies to be conducted at optimised pH levels, further boosting the already high sorption capacity of these biosorbents.

4.3 Sorption Studies

Results of experiments monitoring the changes in metal solution concentration over time are shown in Figure 4.8a–f. It is immediately apparent that, in all plots, equilibrium is reached within the first 22.5 minutes. This is quite rapid compared with metal adsorption by other biosorbents made from various macroalgae (Suzuki *et al.*, 2005; Sakamoto *et al.*, 2008; Sari and Tuzen, 2008; Ahmady-Asbchin *et al.*, 2009; Areco *et al.*, 2012) and compared with biosorbents generally (Saeed *et al.*, 2005; Nadeem *et al.*, 2013; Ogbodu *et al.*, 2015). However, there are some reports of similar uptake rates in the literature when using pectin-rich biosorbents (Schiewer and Patil, 2008) and functionalised biosorbents (Ahmad *et al.*, 2015) and when binding certain metal ions to brown macroalgae (Mata *et al.*, 2009). However, in each of these cases, the q_e data obtained are inferior to those observed in this study for the expanded *A. nodosum* particles (Table 4.2).

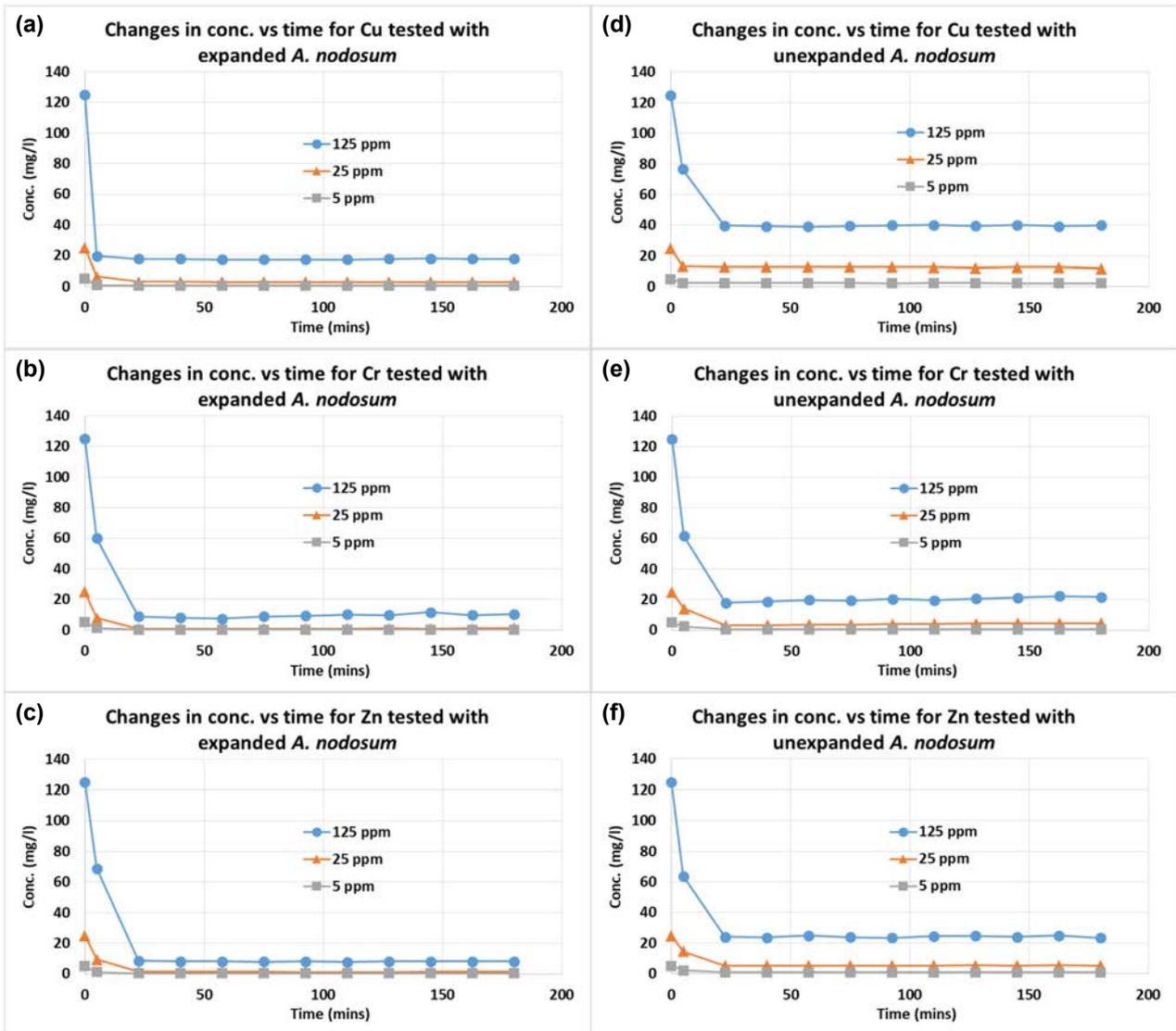


Figure 4.8. Plots of changes in metal solution concentration over time when exposed to expanded particles for (a) copper, (b) chromium and (c) zinc ions and to unexpanded particles for (d) copper, (e) chromium and (f) zinc ions.

Table 4.2. Comparison of equilibrium concentrations of adsorbed metal ions (q_e) for expanded and unexpanded *A. nodosum* particles for each starting concentration of metal (C_0)

C_0 (mg/L)	Chromium		Copper		Zinc	
	Expanded q_e (mmol/g)	Unexpanded q_e (mmol/g)	Expanded q_e (mmol/g)	Unexpanded q_e (mmol/g)	Expanded q_e (mmol/g)	Unexpanded q_e (mmol/g)
5	0.38	0.35	0.35	0.21	0.36	0.31
25	2.21	1.90	1.73	1.03	1.81	1.51
125	10.95	9.86	8.44	4.81	8.93	7.76
250	21.24	16.96	15.55	7.58	16.03	12.52
500	33.84	23.84	22.03	8.55	24.24	16.17
1000	34.86	23.89	21.89	8.81	26.06	16.36

It is also apparent from Figure 4.8 that the expansion process resulted in increased sorption capacity for each metal. The C_e values for copper showed a decrease at all C_0 from exposure to unexpanded *A. nodosum* particles (Figure 4.8d) to expanded particles (Figure 4.8a). The same is observed for chromium (Figure 4.8e and f, respectively) and zinc (Figure 4.8f and c, respectively). These observations are more apparent in the q_e values in Table 4.2.

The expansion process did not result in an increase in adsorption rate. Before and after expansion of the *A. nodosum*, equilibrium was reached within the first 22.5 minutes.

In the following discussion, q_e data for *A. nodosum* particles from all experiments, shown in Table 4.2, are also presented as a percentage of C_0 remaining. These data are shown in Table 4.3.

4.3.1 Chromium

At all C_0 , whether expanded or unexpanded, *A. nodosum* particles exhibited the highest adsorbance capacity for chromium of the metals tested. Regardless of C_0 , once at equilibrium, expanded *A. nodosum* particles adsorbed more chromium than unexpanded *A. nodosum*. Thus, the expansion process increased the adsorption capacity of the *A. nodosum* biosorbent for chromium. The lowest q_e value of chromium for unexpanded *A. nodosum* powder was at $C_0=5$ mg/L; expanded *A. nodosum* particles showed the same result. A general downwards trend in the maximum percentage of C_0 adsorbed with increasing C_0 was seen for both expanded and unexpanded *A. nodosum* particles. A concurrent upwards trend in q_e values was observed

with increasing C_0 . Both expanded and unexpanded particles showed plateauing of q_e values at C_0 values from 500 to 1000 mg/L. In contrast, expanded *A. nodosum* particles showed the same general trend in adsorbance figures as the unexpanded particles, but adsorbance figures were higher for every value of C_0 , showing that expansion resulted in an increase of adsorption capacity. Although the highest adsorption capacities were observed for chromium, for both unexpanded and expanded *A. nodosum* particles, the increases in adsorption capacity for chromium conferred by expansion were the lowest of the three metals tested.

4.3.2 Copper

At all C_0 , whether expanded or unexpanded, *A. nodosum* particles exhibited the lowest adsorbance capacities for copper of the three metals tested. Regardless of C_0 , once equilibrium was reached the expanded *A. nodosum* particles adsorbed more copper than unexpanded *A. nodosum*. This shows that the expansion process increased the adsorption capacity of the *A. nodosum* biosorbent for copper. As for chromium, the lowest q_e value of copper for unexpanded *A. nodosum* powder was seen at $C_0=5$ mg/L, with expanded *A. nodosum* particles showing the same result. Similar trends were seen for copper adsorption testing as for chromium. The results for copper showed a general downwards trend in the maximum percentage of C_0 adsorbed by both expanded and unexpanded *A. nodosum* particles. A concurrent upwards trend in q_e values was observed with increasing C_0 for both expanded and unexpanded *A. nodosum* particles. For both expanded and unexpanded particles, plateauing of

Table 4.3. Comparison of the percentage of starting concentrations of metal ions (C_0) removed at equilibrium

C_0 (mg/L)	Chromium		Copper		Zinc	
	Expanded	Unexpanded	Expanded	Unexpanded	Expanded	Unexpanded
	% C_0 removed					
5	95.60	88.20	88.20	54.20	93.20	80.95
25	95.24	82.08	87.80	52.56	94.60	79.06
125	91.71	82.66	85.79	48.90	93.45	81.19
250	88.35	70.57	79.08	38.56	83.85	65.51
500	70.38	49.58	56.00	21.73	63.40	42.31
1000	36.25	24.85	27.82	11.20	34.08	21.40

q_e values at C_0 values from 500 to 1000 mg/L was seen. In contrast, expanded *A. nodosum* particles showed the same general trend in adsorbance figures as the unexpanded particles, but adsorbance figures were higher for every value of C_0 . This shows that expansion resulted in an increase in adsorption capacity. Although the lowest adsorption capacities were observed for copper, by both unexpanded and expanded *A. nodosum* particles, the increases in adsorption capacity for copper conferred by expansion were the highest of the three metals tested.

4.3.3 Zinc

At all C_0 , whether expanded or unexpanded, *A. nodosum* particles exhibited adsorbance capacities for zinc that were between those for chromium and copper. The results showed that adsorbance capacities were closer to those of chromium (the highest observed) than those of copper (the lowest observed). Regardless of C_0 , once equilibrium was reached, the expanded *A. nodosum* particles adsorbed more zinc than unexpanded *A. nodosum* particles. This shows that the expansion process increased the adsorption capacity of the *A. nodosum* biosorbent for zinc. As with the other metals, the lowest q_e value of zinc for unexpanded *A. nodosum* powder was seen at $C_0=5$ mg/L, with expanded *A. nodosum* particles showing the same result. Similar trends were seen for zinc adsorption testing as for chromium and copper. Results for zinc showed a general downwards trend in the maximum percentage of C_0 adsorbed by both expanded and unexpanded *A. nodosum* particles. A concurrent upwards trend in q_e values was observed with increasing C_0 for both expanded and unexpanded *A. nodosum* particles. In the case of both the expanded and the unexpanded particles, plateauing of q_e values at C_0 values from 500 to 1000 mg/L was observed. In contrast, expanded *A. nodosum* particles showed the same general trend in adsorbance figures as the unexpanded particles, but adsorbance figures were higher for every value of C_0 . This shows that the expansion process resulted in an increase in adsorption capacity of the biosorbent material at every value of C_0 . Adsorption capacities between those of chromium and copper were observed for zinc, for both unexpanded and expanded *A. nodosum* particles, and the increases in adsorption capacity for zinc conferred by expansion were also intermediate of three metals tested.

These trends, exhibiting decreases in the percentage of C_0 removed and a concurrent increase in q_e , with increase in C_0 , are typical of the behaviour of biosorbent materials (Sert *et al.*, 2008; Vijayaraghavan *et al.*, 2010; Nadeem *et al.*, 2013; Calagui *et al.*, 2014; Ogbodu *et al.*, 2015). It has been documented that the affinity of copper for *Ulva lactuca* seaweed is greater than that of zinc (Areco *et al.*, 2012). Our findings show that in the case of *A. nodosum* the affinity is reversed. This may be because of the differences in polysaccharide ratios between green macroalgae, such as *Ulva lactuca*, and brown macroalgae. There is a greater proportion of alginate in brown seaweeds (Davis *et al.*, 2003) and therefore a greater proportion of carboxylic acid functional groups for the adsorption of metals ions. However, the literature indicates that, for brown seaweeds, too, there is a greater affinity for copper than for zinc, for both alginate and fucoidan polysaccharides (Haug, 1961; Davis *et al.*, 2003). Overall, these results show that the expansion process conferred an increase in q_e for every metal tested at every value of C_0 .

Future work will focus on testing a wider range of adsorbate ions on these materials. Work has already begun on lead and lanthanum. Some studies have shown that biosorbents are effective at binding radioactive metal contaminants. This would make for an interesting avenue of research with these expanded biosorbents.

4.4 Biosorption Isotherms and the Langmuir Model

Biosorbent efficacy is commonly judged by sorbate retention. A biosorption isotherm – the plot of q_e versus C_e – is often used to make this judgement. Figure 4.9a and b shows the adsorption isotherms for each metal ion for the expanded and unexpanded *A. nodosum* particles, respectively. All of the isotherms in Figure 4.9a and b can be classified as L-shaped (Giles *et al.*, 1974; Limousin *et al.*, 2007), i.e. the ratio between C_e and q_e decreases as C_0 increases.

The isotherms of the expanded *A. nodosum* particles in Figure 4.9a exhibit an L-shaped isotherm with a strict plateau, with relatively high values of q_e per C_0 . By contrast, the unexpanded particles in Figure 4.9b exhibit an L-shaped isotherm without a strict plateau, demonstrating lower values of q_e per C_0 .

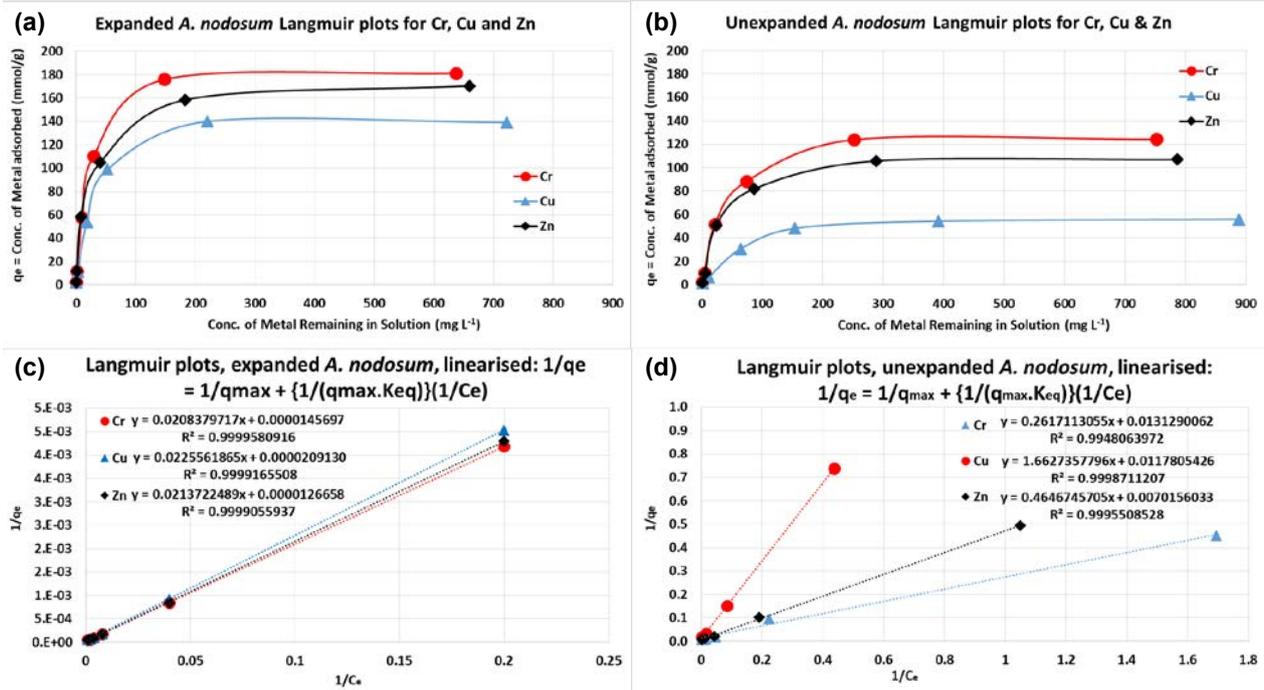


Figure 4.9. Langmuir plots for chromium, copper and zinc adsorption to (a) expanded and (b) unexpanded *A. nodosum* particles. Linearised Langmuir plots of the same data are shown for (c) expanded and (d) unexpanded particles.

The L shape is commonly associated with Langmuir isotherms (Davis *et al.*, 2003; Latour, 2015) and, indeed, the Langmuir isotherm model was found to be the best fit for the experimental data, as shown by the R^2 values displayed in Figure 4.9c and d for the linearised Langmuir plots. However, there are some limitations to the Langmuir isotherm that must be acknowledged. Implicit in its derivation is the assumption that (1) all adsorption sites are equivalent, distinguishable and independent; (2) each adsorption site can bind only one sorbate molecule; (3) adsorbed molecules do not interact with one another in a manner that influences their adsorption behaviour; and (4) the adsorption process must represent a dynamically reversible process (Latour, 2015). At least one of these conditions is typically not met in the case of biosorption. We have seen in the previous sections that there is more than one type of functional group contributing to the biosorption process. Some studies on biosorption have shown that ion exchange is the dominant sorption process occurring, but this comes with its own limitations (Davis *et al.*, 2003). It is possible to incorporate aspects of the ion exchange and Langmuir models into a single model (Davis *et al.*, 2003). However, our study used uncultivated,

wild seaweeds. Thus, it was not possible to quantify the number and variety of functional groups already bound to the surface, nor was it possible to quantify their varying degrees of competition for exchange with sorbate ions. Therefore, adoption of such a model would require even more compromises than are required for the Langmuir model. Even if this were possible, there are still further limitations of the ion-exchange/Langmuir model, which are discussed elsewhere in the literature (Davis *et al.*, 2003). The model is also not broadly applied to biosorption data, making comparison with other studies difficult.

Despite the limitations, the broad application of the Langmuir model in the literature and the excellent R^2 values achieved with our experimental data prompted us to use it as well.

Figure 4.9a and b show that, in all instances, metal ion uptake increased with increasing C_0 and reached saturation at C_0 values between 500 and 1000 mg/L. This represents the maximum amount of metal that the biomass can retain when all bond sites have been occupied. Also clear from Figure 4.9 is that the expanded particles have higher values of q_e than their unexpanded equivalents, as discussed previously in

relation to Table 4.2. Before and after expansion of the *A. nodosum* particles the order of uptake efficacy was zinc < copper < chromium. This is consistent with the literature (Haug, 1961; Davis *et al.*, 2003; Romera *et al.*, 2007; Cardoso *et al.*, 2017)

Table 4.4 shows the K_{eq} and q_{max} values (see section 3.5 for definitions) calculated from the linearised Langmuir plots in Figure 4.9c and d. There is no correlation with the above observed uptake order and K_{eq} or q_{max} values. The highest values of q_{max} , by several orders of magnitude, are observed for the expanded particles. The lowest values of K_{eq} are also observed for these particles, by at least an order of magnitude or more. This is what would be expected given the general observations in the previous sections of the effects of expansion on q_e . However, within the expanded particle tests, the order of q_{max} values is copper < chromium < zinc, whereas the order of K_{eq} values is zinc < chromium < copper. By contrast, within the unexpanded particle tests, the order of q_{max} values is chromium < copper < zinc, whereas the order of K_{eq} values is copper < zinc < chromium. There is no consistent observable trend here.

Comparing the maximum biosorption capacity (q_{max}) values with those seen for metal adsorption to brown macroalgal particles in the literature, the unexpanded *A. nodosum* particles show similar levels as those in other studies when binding metal ions generally and when binding zinc, chromium and copper ions specifically (Romera *et al.*, 2007; Vijayaraghavan *et al.*, 2010; Akbari *et al.*, 2015; Pozdniakova *et al.*, 2015; Barquilha *et al.*, 2017; Cardoso *et al.*, 2017; Castro *et al.*, 2017; Mahmood *et al.*, 2017). Comparing the q_{max} values in the same literature with the q_{max} values obtained for the expanded *A. nodosum* particles, however, shows that the expansion process in this study resulted in a large increase in q_{max} . This was an increase of several orders of magnitude and was far above anything previously reported for macroalgal biosorbents. Given that all other conditions of these experiments are consistent with those in standard biosorption experiments and the only variation is in the surface area of the biosorbent, it can be concluded that this increase in q_{max} value is the result of the expansion of the macroalgae particles.

Table 4.4. K_{eq} and q_{max} values as calculated from linearised plots of Langmuir isotherms

Particles	Metal	q_{max}	K_{eq}
Expanded	Zinc	78952.77	0.000592
Expanded	Chromium	68635.59	0.0007
Expanded	Copper	47817.15	0.000925
Unexpanded	Zinc	142.8571	0.015063
Unexpanded	Copper	84.74576	0.007097
Unexpanded	Chromium	76.33588	0.050057

5 Conclusion

We have produced porous biosorbents with a high surface area from a renewable source – *A. nodosum* brown macroalgae – using a cheap, uncomplicated and sustainable expansion process. This expansion process used a combination of solvent exchange and a simple vacuum chamber to obtain a greater surface area of biosorbent particles. Expansion increased the biosorbent particles by 4490.0 times their original surface area. The pore structure resulting from expansion is mesoporous. The sorption studies of the expanded biosorbents with chromium, copper and zinc showed that the amounts of metal ions adsorbed at equilibrium are superior to those achieved in similar sorption studies in the literature. The expansion process conferred an increase in equilibrium sorption capacity for every metal tested at every starting

metal ion concentration. The biosorbent capacity of both expanded and unexpanded *A. nodosum* was in the order chromium > zinc > copper. Determination of maximum biosorption capacity from Langmuir isotherm models showed large increases for each metal after expansion to capacities far above anything seen in the literature for other biosorbent studies. This is confirmation of the expected outcome of a large expansion in the surface area of such materials and strongly substantiates the objectives of the work. In summary, by application of simple methods of expansion, we have succeeded in producing biosorbents that are far superior in their sorption capacities than any equivalents reported in the literature to date.

6 Recommendations

Future work on BioMes should be focused on four areas of development: (1) finding methods to reduce the amount of polysaccharide lost during the solvent exchange process; (2) testing BioMes on samples of waste streams from municipal and industrial sources; (3) testing multiple platforms for application of BioMes powders; and (4) testing a broader range of sorbate ions.

Reducing the amount of polysaccharides lost during solvent exchange would increase the sorption capacity of the BioMes particles beyond their already high levels. Reducing polysaccharide losses would also minimise the amounts of total organic compounds that are likely to result from the use of the biosorbent in its current state. This could be readily achieved by crosslinking the BioMes particles before or during the solvent exchange phase. This entails making the polymer chains in the sorbent polysaccharides more resistant to solvation during the expansion process, resulting in more of them remaining in the particles after expansion. Crosslinking means literally placing more links between the polymer chains, which renders them more durable. This can be done thermally or by using chemical agents. However, doing so thermally,

i.e. without the use of environmentally problematic crosslinking chemical agents, could prove difficult. This would take the product to the end point of technology readiness level (TRL) 4, as defined by the European Commission (EU, 2014).

Testing on waste municipal and industrial waste streams would move the work onto development of TRLs 5 and 6. Such work would be a repeat of the testing methods described in this report or it could be achieved with analytical methods such as liquid chromatography–mass spectrometry, which would yield a more rapid turnaround time in obtaining quantitative and more reliable data.

Testing on multiple platforms was initially to be conducted as part of this project but the development of the particles to their current state took longer than anticipated. Some preliminary tests on the particles incorporated into a membrane platform were conducted, but the results were either inconclusive or inferior to those seen when BioMes was applied as a simple powder. Other platforms could also be used, such as inline packed columns and inline continuously stirring tank reactors (Figure 6.1), or entirely new application platforms could be engineered. Successful

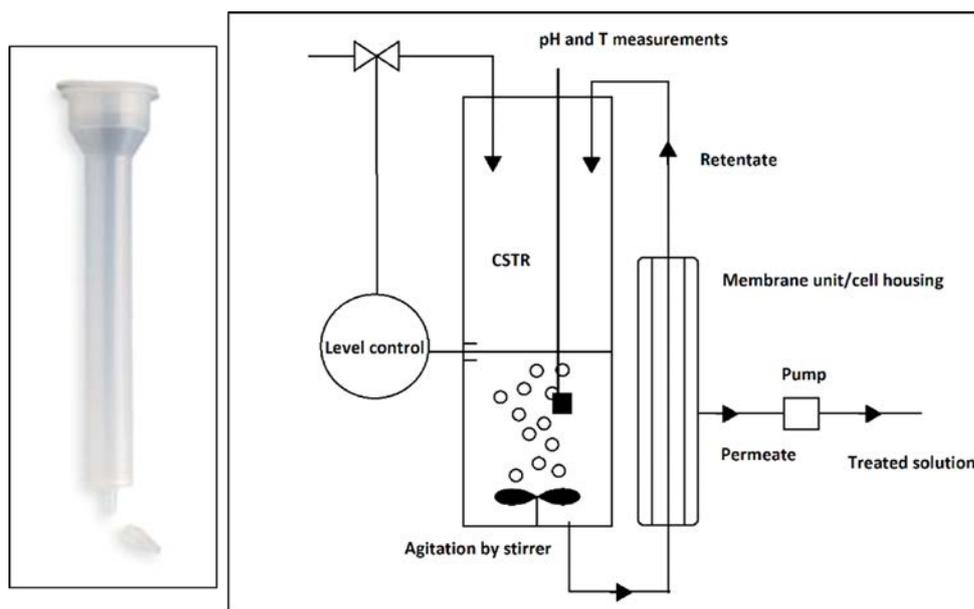


Figure 6.1. A typical inline column (left), which could be packed with biosorbent particles, and a schematic of a continuously stirred-tank reactor (right).

development to this point would take the technology to TRL 7 and to the possibility of commercialisation.

Finally, future work on testing a wider range of sorbate ions on these materials would also be beneficial, expanding the range of potential applications.

Work has already begun on lead and lanthanum. Furthermore, as highlighted in the introduction, most heavy metals can be effectively adsorbed by macroalgal biosorbents. Some studies have shown that biosorbents are effective at binding radioactive metal contaminants.

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Abbreviations

BET	Brunauer–Emmett–Teller
BioMes	Biosorbent mesoporous materials
BJH	Barrett–Joyner–Halenda
C_0	Initial metal ion concentration
C_e	Equilibrium metal ion concentration
ICP-OES	Inductively coupled plasma optical emission spectrometry
K_{eq}	Equilibrium constant related to energy or net enthalpy of adsorption
pH_{pzc}	Point of zero charge on a material's surface relative to the pH of the solution
PMT	Potentiometric mass titration
q_e	Amount of metal ions adsorbed at equilibrium
q_{max}	Maximum biosorption capacity
SEM	Scanning electron microscope
TRL	Technology readiness level

AN GHNÍOMHAIREACTH UM CHAOMHNÚ COMHSHAOIL

Tá an Gníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaoil a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlionta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.

Eolas: Soláthraimid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírthe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bimid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaoil atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaoil inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaoil:

- saoráidí dramhaíola (*m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistriúcháin dramhaíola*);
- gníomhaíochtaí tionsclaíocha ar scála mór (*m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta*);
- an diantalmhaíocht (*m.sh. muca, éanlaith*);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe (*OGM*);
- foinsí radaíochta ianúcháin (*m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha*);
- áiseanna móra stórála peitрил;
- scardadh dramhuisece;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdarás áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhírú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídionn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uisce idirchriosacha agus cósta na hÉireann, agus screamhuisec; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaoil

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (*m.sh. tuairisciú tréimhsiúil ar staid Chomhshaoil na hÉireann agus Tuarascálacha ar Tháscairí*).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis ceaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhar breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainathint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaoil in Éirinn (*m.sh. mórfheananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as tairmí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaoil ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaoil (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosaint agus a bhainistiú.

Múscaill Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord Iáinimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltáí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inní agus le comhairle a chur ar an mBord.

Author: Eoin Flynn

Identifying Pressures

Heavy metals are highly toxic pollutants that bioaccumulate and persist in the environment. Uptake of heavy metals by plants and subsequent accumulation in the food chain can threaten animal and human health. Heavy metals can damage fish in aquatic systems and contaminate groundwater. They are difficult to remove from industrial waste water treatment systems. However, they are a highly valuable resource and are critical to most modern and future electronics technologies.

Over 500 species of seaweed have been identified from Irish waters, a great diversity of species from a small island. Scientists classify seaweeds (algae) based on pigments, with most marine macro-algae being green, brown or red. Seaweeds have been found to have a natural ability to remove heavy metals from water. The (BioMes) materials developed in this project were made from Irish brown seaweeds and can be used to effectively remove heavy metals from waste water.

BioMes materials can be produced sustainably, at low cost, and without using toxic compounds, unlike historical attempts to produce similar materials. Furthermore, they provide a potential means to capture economically valuable heavy metal resources.

Informing Policy

The current intensive use of the world's natural resources is unsustainable. Optimising resource efficiency is critical in the long term to alleviate negative anthropogenic effects on the environment. In addition, these efforts will be key to securing economic growth and jobs for the future.

The Resource-Efficient Europe Initiative is a cornerstone of the Europe 2020 strategy for more effective use of resources and a low-carbon economy. This initiative has been incorporated into Irish governmental strategies. Related to this, in 2014 the European Commission formally identified a list of "critical" raw materials (i.e. materials with a high supply risk and of high economic importance), with heavy metals featuring prominently.

BioMes is a technology that can be used to recover precious resources from waste water in Ireland, using materials made from Irish seaweeds, thereby reducing the pollution that these precious but toxic metals can cause.

The Irish government is aware of the importance of developing the marine economy and of making better use of resources that are available in the Irish sea, such as macro-algae. BioMes technology represents a means of achieving this.

Developing Solutions

Heavy metals and certain non-heavy metals are highly problematic industrial pollutants in Ireland. Lead, zinc and copper are of concern in the environment and can cause contamination in groundwater and other natural water sources.

Heavy metals can bind to natural polymers (polysaccharides) within brown seaweeds, which presents an opportunity to develop materials that can be used for effective environmental remediation and removal of pollutants from waste water.

The type of materials produced from Irish brown seaweeds using the technology outlined in this project are called biosorbents. Historically, a major obstacle to producing high-capacity biosorbents of any type has been that they cannot be produced cost-effectively and with enough surface area to bind sufficient quantities of heavy metals.

This project presents a method to cheaply produce high-capacity and porous biosorbents from a brown macro-algae species (*Ascophyllum nodosum*). This is a renewable material and can be produced without the use of any toxic compounds. We have produced these biosorbents at a laboratory scale for the successful removal of heavy metals such as lead, zinc and copper from water and waste water samples.