DEALGINATED SEAWEED AS A BIOADSORPTION MEDIUM FOR TREATING METAL MINE DRAINAGE: ISSUES SURROUNDING ITS PRE-TREATMENT AND USE IN SMALL SCALE TREATMENT PLANTS IN THE EU LIFE "BIOMAN" PROJECT

S. Hartley[1], N.J.G. Pearce[1], W.T. Perkins[1], E. Dinelli[2], R.G.J. Edyvean[3], G. Priestman[3], L. Sandlands[3] and R. Bachmann[3]

[1]Institute of Geography and Earth Sciences, University of Wales, Aberystwyth, SY23 3DB, UK

[2] Dipartmento di Scienze della Terra e Geologico-ambientali, Università di Bologna, Piazza di Porta San Donato 1, I-40126 Bologna, Italy

[3]School of Process and Chemical Engineering, Mappin Street, University of Sheffield, Sheffield, S1 3JD, UK

Abstract

Dealginated seaweed (DS), a waste product from the alginate industry, has been used as a bioadsorber to remove potentially toxic elements from mine waters during the BIOMAN project. During the project, two different sources of DS were tested, from ISP (International Speciality Products) in Scotland and Algavi in France. The two different DS have very different physical and chemical characteristics. The ISP DS requires less preparation and adsorbs up to 2.4% Zn (w/w) whereas Algavi DS adsorbs only 1.5% Zn (w/w). Unfortunately the ISP DS is no longer available as the processing plant now disposes of the waste via a long-fall pipe into the sea. The Algavi DS requires sieving to remove the 'fines' and then acidifying to neutralise the very alkaline solution that it produces prior to drying to produce granules of the DS that can be used in treatment plants.

Introduction

BIOMAN (BIOadsorption of Metals from Abandoned miNes) was an EU-LIFE Environment funded project to demonstrate the use of dealginated seaweed (DS) as a bioadsorber of potentially toxic metals from abandoned mines. In mid-Wales the drainage waters issue from disused 19^{th} century mines and are often rich in Zn ($\leq$ 42 mg/L), Pb ($\leq$ 2.8 mg/L) and Cd ($\leq$ 100 µg/L), but are low in Fe (< 1mg/L), a result of the dominantly galena/sphalerite mineralisation with very little associated pyrite. The low Fe content in the mine drainage waters means that traditional remediation methods to remove the metals cannot be used, i.e. Fe removal by increasing the pH, or oxidising the Fe to force ochre to precipitate.

The use of waste materials that are low in cost provide an economic alternative to the traditional methods of water treatment (Williams et al., 1998), e.g. seafood processing waste sludge (Lee and Davis, 2001), sewage sludge and paper mill waste (Lister and Line, 2001), discarded automotive tyres (Netzer et al., 1974) and dealginated seaweed (DS).

Dealginated seaweed is a waste product of the alginate industry; about 500,000 t/year of seaweed is harvested and processed in 15 processing plants around the world. The alginate is removed by grinding the dried seaweed, treating it with acid and finally with either NaOH or $Ca(OH)_2$. The alginates are used in the food and pharmaceutical industry. The waste product, dealginated seaweed, is either sold as bulk for cattle feed and fertilisers or disposed of. Dealginated seaweed has been shown to adsorb metals in laboratory scale tests (Willams and Edyvean, 1997; Malik et al., 1999; Romero-Gonzalez et al., 2001), but until now it has never been tested in a field situation.

The DS is predominantly cellulose, which makes up the cell wall material and has been shown to act as a weak cation exchanger, the result of carboxylic acid groups present within the material. There are major advantages using non-viable biomass in mine water remediation, including an increased tolerance of environmental conditions and a lack of nutrient requirements (Williams and Edyvean, 1997). Additionally, DS is low-cost when compared to existing treatment technologies, such as precipitation, ion exchange or electro-chemical winning methods (Williams and Edyvean, 1997).

Dealginated seaweed

1. Sources

Two different sources of DS have been investigated in this project: (1) International Speciality Products (ISP), from a seaweed processing plant in Girvan (Scotland); (2) Algavi (France), from Danisco, a processing company based in Denmark.

The ISP DS was obtained from the treatment of predominantly *Ascophyllum sp.* (knotted wrack) as well as seaweed imported from around the world; whilst the Algavi DS is dominantly *Laminaria sp*. (kelp).

2. Physical and chemical properties of the raw material

The DS samples obtained are very different in appearance and behaviour. The DS from ISP is a granular brown powder whilst that from Algavi is a dusty, grey-green powdery material. The Algavi DS has a grain size distribution dominated by particles <0.1 mm, whereas the ISP DS is much coarser with the majority of the grains >0.1 mm (Fig. 1). The high proportion of fine material in the Algavi DS renders it much less permeable to water and, in its raw state, is not practical to use as a filter medium to treat mine drainage waters.

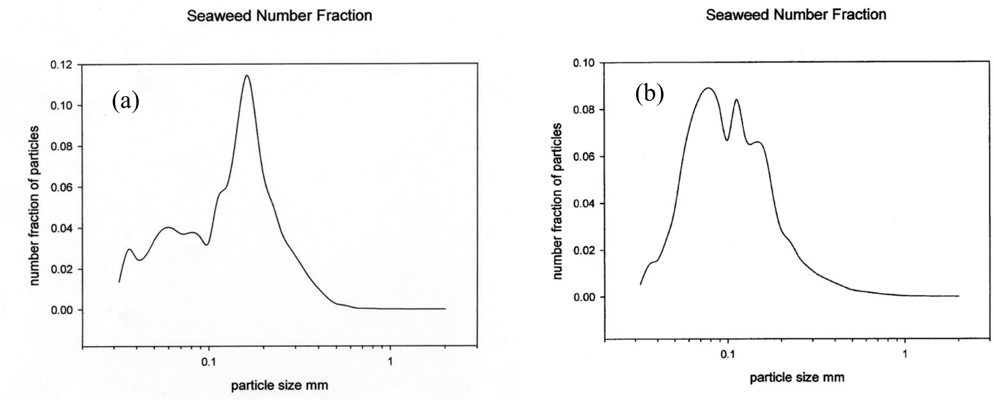

Figure 1. Grain size distribution of (a) ISP and (b) Algavi DS.

A series of laboratory experiments were conducted to determine the physico-chemical properties of the DS. When mixed with water the ISP DS produces a near neutral solution (pH ~ 7.6). In contrast the Algavi DS produces a solution of pH >12 suggesting that the DS is not washed after treatment of the seaweed with alkali.

3. Treatment of Algavi DS

The high pH of the Algavi DS needs to be neutralised and the large quantity of fines needs to be removed before it can be successfully used as a bioadsorber. The fines were removed by sieving through a 180 µm sieve or by "windsifting". The windsifter was designed to separate and collect the DS into fractions <200 µm and >200 µm. This allowed the fines to be retained for use in neutralisation experiments for acid mine drainage (AMD). If the fines could be used for neutralisation it has the advantage that it would adsorb metals from the AMD. Initial experiments using acid mine drainage from Libiola (VMS type Cu-Fe-sulphide mine in north-west Italy) show a dramatic reduction in potentially harmful elements (Table 1).

Table 1. The results of initial tests using dealginated seaweed to neutralise AMD and to reduce the potentially harmful elements.

	Concentrations in Libiola AMD (mg/L)	Concentrations after treatment with DS <200 µm (mg/L)
Fe	550	5
Cu	125	3
Zn	33	2.6
Al	180	5

Although this 'fine' fraction of the Algavi DS produces a strongly alkaline solution there are major issues with "wetting" this material to form a slurry, and thus problems with its use as a neutralising agent for AMD. The powdery nature of the <200 µm fraction, when mixed with water produces a "lumpy" mixture rather than a smooth, pumpable suspension. Additionally, to be effective at raising the pH of AMD to near neutral levels, a large volume of DS fines slurry must be added to cause precipitation of Fe-oxyhydroxides, greatly increasing the volume of precipitate needing disposal.

4. Acidification

Once the fines have been removed from the Algavi DS, the coarse residue had to be treated with dilute HCl to neutralise the effect of the strongly alkaline reaction with water. This treatment converts the acidic groups of the seaweed's polysaccharides to the hydrogen form (Malik et al., 1999) and also removes the excess salts (Na, K, Mg and Ca) (Romero-Gonzalez et al., 2001). This increases the adsorption capacity of the DS.

The Algavi DS also contains about 10% by weight of sand and $CaCO_3$ particles, i.e. shell fragments and coral. These need to be removed because if they are left as part of the DS they consume a large proportion of the acid used in acidifying the DS. The adsorption of Zn by DS containing $CaCO_3$ and by $CaCO_3$-free DS is shown in Figure 2 and shows a dramatic difference. The $CaCO_3$-free DS adsorbs more Zn, which may be because a greater number of adsorption sites have been hydrogenised.

In contrast to the Algavi DS, ISP DS has a restricted grain size distribution, and thus does not require sieving. When mixed with water, the solution it produces is neutral and does not need acidifying. In fact, acidification of the ISP DS is detrimental to the capacity of the DS to adsorb the metals (Fig. 3).

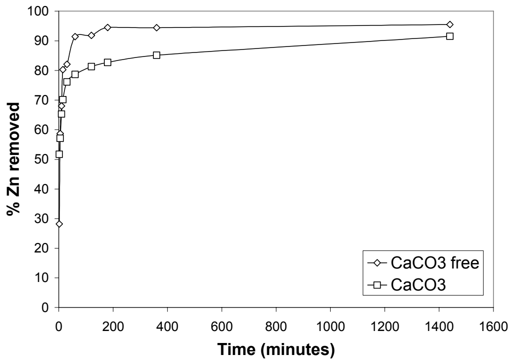

Figure 2. Comparison between the adsorption of Zn between acid washed Algavi dealginated seaweed containing $CaCO_3$ and $CaCO_3$-free. The initial concentration of Zn is ~30 mg/L.

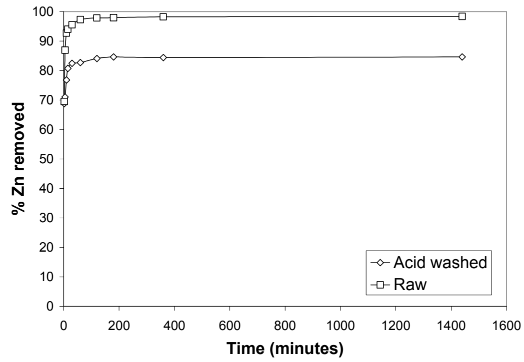

Figure 3. The effect of acid washing on Zn removal from 50 mL of solution by 0.5 g of ISP DS. The initial concentration of Zn is ~35 mg/L.

5. Drying and granulation

Once the fines have been removed from the Algavi DS and it has been acidified, the DS then has to be dried. The DS was oven dried at ~50ºC for 2 to 3 days, with the DS being mixed daily until dry and granulated. When the granulated DS is used in a treatment plant the water flows evenly through the DS allowing the optimum contact time between the DS and the solution. When wet DS was used channelling at the edges of the bed of DS occurred, allowing rapid flow of water through the bed with little or no contact with the DS, and thus no reduction in metal content. For optimum performance, the DS needs to be dried and granulated before use.

6. Adsorption characteristics

The ability of the DS to adsorb metals was tested in parallel treatment plants each containing 2 kg of the two DS. Figure 4 compares the percentage of Zn removed by ISP DS (*Ascophyllum sp.*) and Algavi DS (*Laminaria sp.*) (see Pearce et al., 2007) and shows that the ISP DS removes considerably more Zn than the Algavi DS. The ISP DS removes 48 g Zn in 6600 minutes (2.4% of the DS dry weight) whereas the Algavi only removes 31 g Zn (1.5% of the DS dry weight).

All seaweed and seaweed derived products have been shown to have a high affinity for the removal of metal ions from solution (Willams and Edyvean, 1997), although the seaweed derived materials show a better overall performance than the unprocessed material (Aderhold et al., 1996). Additionally, Williams and Edyvean (1997) determined a considerable variation in the metal removal from solution by different species of seaweed. The variability of different seaweed species to remove metals from solution can also be seen in the DS despite its aggressive chemical treatment. The ability of the Algavi and ISP DS to remove metals is shown in Figure 4 and the difference may be because of the different species used, with Algavi processing *Laminaria sp*. and ISP processing *Ascophyllum sp*.

Conclusions

Dealginated seaweed from ISP and Algavi have both been shown to have excellent potential for bioadsorption, and although only data for Zn is shown here, other metals especially Cd and Pb show similar behaviour (see Pearce et al., 2007 and Perkins et al., 2007).

For use in treatment plants, the DS must be dried and granulated for it to be effective. If left wet, water flows through channels at the edges of the bed of DS, decreasing contact time and thus adsorption of metals.

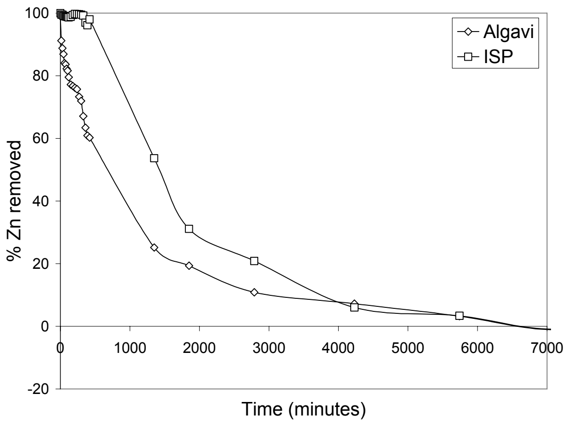

Figure 4. Comparison of Zn removal by 2 kg (dry weight) of Algavi and ISP DS in a parallel treatment plant. The initial concentration of Zn is 30 mg/L.

The ISP DS is the more preferable DS for use in treatment plants as it has a greater capacity to adsorb metals and it requires little or no pre-treatment. Unfortunately, during 2004 the ISP processing plant changed the way it disposed of its waste which is now all pumped out to sea via a long-fall pipe. The Algavi DS is an adequate bioadsorber, although it takes time and materials to prepare the DS for use. The preparation could be made more economic on a very large scale using specialist equipment. It may however be more economic to rinse and dry the wet slurried DS from ISP, if it could be made available. One potential advantage of the Algavi DS is that it provides an alkaline product which could be used to neutralise AMD and remove some of the metals contained within it, although there are problems to be overcome with this.

Acknowledgments

We are grateful to the European Union Life Environment programme for financing this demonstration project (EU Life Environment Project LIFE03ENV/UK/000605).

References

Aderhold D., Williams C.J., Edyvean R.G.F. (1996). The removal of heavy-metal ions by seaweeds and their derivatives. Bioresource Technology 58, 1-6.

Lee S.M., Davis A.P. (2001). Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste sludge. Water Research 35(2), 534-540.

Lister S.K., Line M.A. (2001). Potential utilisation of sewage sludge and paper mill waste for biosorption of metals from polluted waterways. Bioresource Technology 79, 35-39.

Malik D.J., Streat M., Greig J. (1999). Characterisation and evaluation of seaweed-based sorbents for treating toxic metal-bearing solutions. Trans IChemE. 77, Part B, 227-233.

Netzer A., Wilkinson P., Beszedits S. (1974). Removal of trace metals from wastewater by treatment with lime and discarded automotive tires. Water Research 8, 813-817.

Pearce N.J.G., Hartley S., Perkins W.T., Dinelli E., Edyvean R.G.J., Priestman G., Bachmann R., Sandlands L. (2007). Dealginated seaweed for the bioremediation of mine waters in Mid-Wales: results of field trials from the "BIOMAN" EU Life Environment Project. This volume.

Perkins W.T., Hartley S., Pearce N.J.G., Dinelli, E. (2007). Laboratory scale testing of the adsorption character of dealginated seaweed. This volume.

Romero-Gonzalez M.E., Williams C.J., Gardiner P.H.E. (2001). Study of the mechanisms of cadmium biosorption by dealginated seaweed. Environmental Science and Technology 35, 3025-3030.

Williams C.J., Aderhold D., Edyvean R.G.J. (1998). Comparison between biosorbents for the removal of metal ions from aqueous solutions. Water Research 32 (1), 216-224 .

Williams C.J., Edyvean R.G.J. (1997). Optimization of metal adsorption by seaweeds and seaweed derivatives. Trans IChemE. 75, Part B, 19-26.