LABORATORY SCALE TESTING OF THE ADSORPTION CHARACTERISTICS OF DEALGINATED SEAWEED: RESULTS FROM THE BIOMAN PROJECT

W.T. Perkins[1], S. Hartley[1], N.J.G. Pearce[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] Dipartimento 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
In this paper a series of laboratory-scale experiments are described. These experiments have been used to characterise the behaviour of dealginated seaweed, a potential bioadsorber, for mine water remediation. The experiments are divided into two types, batch experiments and column experiments. Batch experiments show that the minimum contact time between the mine water and the adsorber is 10 minutes. In contrast to previous studies this paper shows that pH does not exert a strong control over the adsorption process. Single metal, isotherm, experiments show that dealginated seaweed shows a preferential uptake of Pb over Zn and Cd. Synthetic, multi-element mine water was used to show that the adsorption capacity of the dealginated seaweed was ~4% of the adsorber mass. Dealginated seaweed has the potential to remove toxic metals from mine discharges.

Introduction
The EU LIFE-Environment project BIOMAN aimed to demonstrate the effectiveness of dealginated seaweed as a bioadsorber of metals which are present in water draining from abandoned metal mine sites. Dealginated seaweed is a waste product from the processing of brown seaweed to extract alginate
Published work suggests that dealginated seaweed will adsorb metals from solution and bind them to the solid material (Williams and Edyvean, 1997; Malik et al., 1999; Romero-Gonzalez et al., 2001). Dealginated seaweed shows the potential to treat water with a mixture of metals present (i.e. it is not specific to one metal in solution but is able to adsorb several toxic elements). There have been a number of laboratory studies which have investigated the properties of dealginated seaweed but very few tests of the material for treating mine water. In this paper we describe the evaluation of dealginated seaweed as an adsorber from a series of laboratory scale experiments on both synthetic mixtures of metals and on real mine water.
There are three important and interrelated factors to consider in testing the performance of a bioadsorber: firstly the time that is required for the adsorber to interact with the mine water and remove the metals; secondly the physico-chemical conditions of the mine water and thirdly the concentration/mixture of metals present in solution. The aim is to treat mine waters from a variety of different types of abandoned mines. In order to achieve this goal it is necessary fully to understand the behaviour of the dealginated seaweed in different chemical mixtures.
At the outset of this project the emphasis was placed on mine waters from the mid-Wales orefield (a former Pb-Zn mining region). Two dealginated seaweed materials were evaluated, one from a UK source, the other from Denmark (see Hartley et al., this volume).

Methods
The laboratory scale tests described in this paper were conducted in two stages. In the first stage ‘batch’ experiments were employed whilst in the second stage ‘column’ experiments were used. In batch testing a measured amount of dealginated seaweed is mixed with a measured volume of test solution. The conditions are controlled so that only one physico-chemical characteristic is changed in any one set of tests. The chemistry of the water is then tested to evaluate the effect of the different physico-chemical parameter on the removal of metals from solution. The batch tests consisted of four groups. In the first group the weight of dealginated seaweed and the volume of mine water were kept the same. Water samples were removed from the tests at different time intervals. The aim of this set of tests is to evaluate the length of time necessary for the dealginated seaweed to remain in contact with the water to remove metals from solution. In the second group of tests the weight of dealginated seaweed is kept constant but the volume of mine water is increased. The aim of this set of tests is to indicate the capacity of the adsorber for removing metals from solution. It is also important to consider which elements might be released from the dealginated seaweed. This is typical of an ion exchange process in that one metal is adsorbed from solution and is replaced by a metal which is released from the solid. The results

from this set of tests indicate the maximum capacity of the dealginated seaweed for a given set of conditions and the potential release of elements to the environment. In the third set of tests the mass of dealginated seaweed is increased whilst the length of time the seaweed remains in contact with the water is kept constant. This test is designed to determine the capacity of the dealginated seaweed for removing metals from solution. In the final set of batch experiments the characteristics obtained from the first three tests were used to design a series of experiments to measure the adsorption capability of the dealginated seaweed. In these tests the characteristics such as contact time, water volume and the dealginated seaweed to water ratio are kept constant. The only variable to change is the concentration of the dissolved metals in solution. The results of this series of experiments provided information on the adsorption capacity and behaviour of the dealginated seaweed. These results were used to draw 'isotherms' which will help to define the characteristics of the bioadsorber.
Once the batch tests were completed the column experiments could be designed.
In column testing a known mass of dealginated seaweed is loaded into a vertical glass chromatography column and the test solution is passed through the material. This type of test should imitate the way mine water would interact with dealginated seaweed in a working treatment system deployed into the environment. In the columns the flow of water is controlled by a tap at the base of the column. The length of time the solution takes to pass through the layer of dealginated seaweed, supported on the sinter glass disk, can be controlled by adjusting the flow with the tap in line with the batch experiments completed earlier.

1. Selection of mine water for laboratory scale tests
A number of mine sites were identified as sources for the mine water for these experiments. The Bwlch mine was shown to have high levels of a range of contaminant metals with circum-neutral pH values and low levels of dissolved iron whereas the Cwm Rheidol mine has lower pH and higher iron.
The Bwlch mine represents one of the more challenging iron-free waters in the mid-Wales orefield and as such is a good test solution to indicate the short term behaviour of the dealginated seaweed. The mine water from the Bwlch site has a pH of around 6.5 which makes it an ideal test solution given that previous work suggests that dealginated seaweed should show greater adsorption at pH values close to neutral (i.e. 7). In the batch tests a bulk sample of the Bwlch mine water was used as well as a multi-element synthetic mine water which was produced to resemble, as closely as possible, the toxic metals in the Bwlch water. The multi-element synthetic mixture was made up and the pH adjusted to be 6.5. This synthetic water did not contain the major metal ions (Ca, Mg, Na and K) so that the behaviour of the adsorber with respect to the toxic elements alone could be evaluated without the potential problems of major elements in the water.

Results and Discussion

1. Tests with different contact time between the dealginated seaweed and the mine water
In these tests the mass of dried dealginated seaweed was 0.5 g and the volume of mine water was 50 mL. At time intervals 2, 5, 10, 15, 30, 60, 120, 180, 360 and 1440 minutes samples of mine water were removed. The resulting samples were filtered through Whatman No. 1 filter papers. The solutions were then analysed using ICP-MS and AAS. This series of tests demonstrated several important points about the dealginated seaweed as a bioadsorber. Firstly the material is selective in its absorption of metals showing a greater tendency to adsorb Pb than Zn and Cd. In all of the experiments the major ions Ca, Mg, Na and K are not removed from the mine water solutions whereas the toxic metals Zn, Cd, Pb and Ni are removed. Secondly the pH of the solution does not affect the rate of uptake as strongly as predicted from previous work. Thirdly, in one set of test solutions the dealginated seaweed showed no preference for iron (Fe) in solution. This is again important because the iron has the potential to swamp all of the dealginated seaweed's capacity for adsorbing other metals. The selectivity of the dealginated seaweed is vital to the performance of the filters because major elements such as calcium and magnesium will be present at much higher concentrations than the toxic metals in the mine water. The most important conclusion to come from this set of tests is that efficient removal of metals from solution requires a contact time of at least 10 minutes between the contaminated water and the dealginated seaweed.

2. Tests with different volumes of mine water
In the second series of tests the mass of dealginated seaweed was kept at 0.5 g and mixed with 50, 100, 200, 500 and 1000 mL of the mine waters. The mixtures were agitated for 30 minutes and then a sample of the liquid was removed for analysis. This series of tests showed that the capacity of the dealginated seaweed is largely dictated by the bulk composition of the liquid. This is illustrated by the comparison between the performances of the adsorber in natural mine water when compared with the synthetic mine water. In the synthetic water the test at 1000 mL showed that the 0.5 g of dealginated seaweed was able to remove ~20 mg of Zn from solution which corresponds with an adsorption capacity of ~4% of the mass of the adsorber. When the test was repeated with the natural mine water (which contains both major cations and toxic metals) the calculated adsorption capacity for

Zn is only ~ 2%. Although the dealginated seaweed shows selectivity (as demonstrated in the first series of tests) there is an effect which is related to the matrix of the sample. Furthermore the volume of liquid has a dramatic effect on the ability of the dealginated seaweed to adsorb metals. The same bulk composition mine water was used in each of the tests, yet those tests with larger volumes of water show a greater adsorption of metals. This is somewhat surprising if the adsorption process is a simple physico-chemical process such as ion exchange.

3. Tests with different masses of dealginated seaweed

In the third series of batch tests the volume of mine water was kept at 50 mL and the contact time between the water and the dealginated seaweed was kept at 30 minutes. The only variable in this set of tests was the mass of seaweed added to the test solutions. The masses were 0.1, 0.25, 0.5, 0.75 and 1.0 g. Once the dealginated seaweed had been mixed with the mine water for 30 minutes the solution was filtered through a Whatman No.1 filter paper and the resultant filtrate retained for analysis. The results show that the amount of toxic metal removed from solution is related to the mass of dealginated seaweed and furthermore the amount of the major cations released into the solutions is also related to the mass of dealginated seaweed. This, latter, point is best illustrated when considering the results for the Bwlch synthetic water and the sample from Algavia. This water had no potassium added and thus started with no measurable K in solution. When the relationship between the final concentration of K and the mass of dealginated seaweed added is considered it is found to be linear indicating that the release of K is simply related to the mass of dealginated seaweed used. When the major cations are considered it is shown that the concentration of the element, and therefore the total amount released, has an almost linear relationship with the mass of dealginated seaweed used. Thus any treatment system will contribute major cations to the receiving water course but this is deemed acceptable in the light of the removal of toxic metals.

4. Isotherm experiments: single metal solution

In this series of tests a known mass of dried dealginated seaweed (0.5 g) was mixed with a synthetic solution of a single metal. The metals investigated were those which are present as potentially harmful elements in the mine drainage (zinc, cadmium and lead). The experiment was set up so that the volume of liquid is kept constant (50 mL) but the concentration of the metal in different samples is increased. After a set period of time the solution is separated from the dealginated seaweed residue by filtering through a Whatman No. 1 filter paper. The concentration of the element remaining in solution is then analysed using AAS. The concentration of calcium in the solutions was also determined in addition to the concentration of the element added to the test solutions. If the dealginated seaweed is acting as an ion exchange material then as the test element is adsorbed so another element (or more strictly another ion) must be released/exchanged. In some cases this released ion could be a hydrogen ion in which case the pH of the solution should change during the experiment. Tests showed the pH of the solution did not vary significantly during the experiments. Therefore the exchange process is not releasing hydrogen ions from the dealginated seaweed. When the results of these experiments are plotted on a graph they generate “adsorption isotherms”. Figure 1 presents an isotherm diagram generated from this series experiments. In this graph there is a linear relationship between the concentration in the starting solution and the amount of metal adsorbed by the dealginated seaweed. Linear best-fit relationships between the concentration of an element in solution and the amount of metal adsorbed are typical of ion-exchange media. This is consistent with previous studies which have described ion-exchange properties in dealginated seaweed. The relationship observed between toxic metal adsorption and Ca release is more complex. The results suggest that there are two processes operating in these tests. Firstly, there is a general release of Ca from the dealginated seaweed which gives a concentration in solution of around 50 mg L^{-1} which is equivalent to around 1.2 mM L^{-1}. Secondly, as the toxic elements are adsorbed there is a release of Ca which suggests that Ca ions, attached to the dealginated seaweed, are being exchanged for other metal ions in solution.

5. Column experiments

At the outset of the BIOMAN project it was envisaged that the treatment systems developed would involve the passive flow of contaminated mine water through a bioadsorber. Whilst the exact design of the treatment system was not clear it was obvious that a simple gravity flow system would fulfil the ‘low-technology’ and ‘low-maintenance’ goals of the project. In the second series of laboratory scale tests a set of glass chromatography columns was used to conduct tests of the dealginated seaweed. The columns were of a standard design with a sinter glass disc in the base of the columns to support the dealginated seaweed. This test was designed to be close to the type of system used in the field (see Pearce et al., this volume). The column experiment was set up using the results of the batch tests. The column experiment was designed to keep the mine water in contact with the bed of seaweed for a minimum of 10 minutes. This was achieved by measuring the volume/mass of the bed of dealginated seaweed and then controlling the flow of water through the bed using the 'rotaflow' tap on the outlet of the columns.

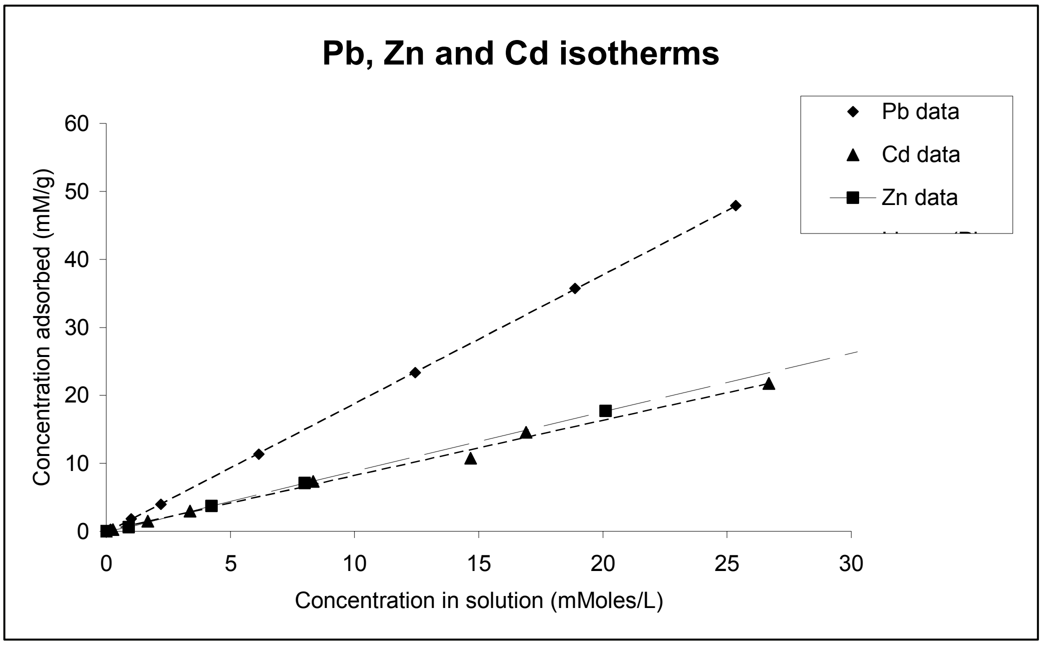

Figure 1. Isotherms generated from the single metal adsorption experiments. The steeper slope of the Pb isotherm shows that the dealginated seaweed has a greater affinity for Pb over Zn and Cd.

Zinc is present in many of the mine waters at concentrations that can be relatively easily measured by AAS. In the column experiments it was decided to concentrate on the removal of zinc from the mine water as this would provide rapid results. Furthermore, the batch experiments had shown that Cd adsorption is very similar to Zn and that Pb was more readily adsorbed than Zn, thus Zn should give a good measure of the performance of the material in a mixed element solution.

In these experiments a known weight/volume of dealginated seaweed was loaded into the chromatography column as a suspension in distilled water. The dealginated seaweed was already equilibrated with water. Once the dealginated seaweed had settled at the base of the column the system was sealed with a reservoir above. The reservoir was filled with Bwlch mine water and the column and reservoir taps were opened to control the flow of water through the bed of dealginated seaweed. The rate of flow was set at 1 ml min^{-1}. All of the mine water passing through the column was collected in 10 mL volumes. In total 660 mL of Bwlch mine water was passed through the column. The collected samples were then analysed for the Zn content, knowing that the concentration of Zn in the Bwlch water was 35 mg L^{-1}. Through the experiment the rate of flow of the Bwlch water decreased and the tap at the base of the column needed to be adjusted to maintain the flow. This decrease in flow has important implications for the field systems, although the restricted nature of column is unlikely to reproduce conditions in a full scale system.

Results of the column tests show that over 23 mg of Zn was adsorbed by 0.5 g of dealginated seaweed.

Conclusions

Laboratory scale tests have shown that dealginated seaweed has the potential to act as a bioadsorber of toxic metals from mine water. The tests define the length of time that the mine water must remain in contact with the material for effective removal of metals (minimum of 10 minutes). The tests show that, contrary to previous studies, the pH of the solution is not critical in adsorption of toxic metals. The experiments demonstrate that the dealginated seaweed is selective in removing toxic elements from mine water whilst showing no affinity for major cations such as Ca, Mg, Na and K. The results of single metal adsorption experiments have been used to define adsorption isotherms which show that dealginated seaweed has a preference for Pb in solution over Zn and Cd. The isotherm experiments also show that dealginated seaweed releases Ca to the water and that this release is enhanced by exchange processes. The results can be used to define operating parameters for the design of field systems which can operate as low maintenance and low-technology solutions to mine pollution problems.

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