# **Desorption of Cadmium and the Reuse of Brown Seaweed Derived Products as Biosorbents**

## W. A. Stirk\* and J. van Staden

Research Centre for Plant Growth and Development, School of Botany and Zoology, University of Natal Pietermaritzburg, P/Bag X01, Scottsville 3209, Republic of South Africa

\* Corresponding author: stirk@nu.ac.za

Dried and ground material of the brown alga *Ecklonia maxima* and the waste product from the manufacture of Kelpak, a seaweed concentrate used in agriculture, have previously been shown to be effective biosorbents of heavy metals. The recovery of bound cadmium and the subsequent reuse of the biosorbents were investigated. Acids (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) and the chloride salts (NaCl and CaCl<sub>2</sub>) were more effective at desorbing cadmium ions than the carbonate salts (NaHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>) and the chelator Na<sub>2</sub>EDTA. The optimum concentration of the acids for desorption was between 0.01 M–0.1 M. Depending on the acid and concentration used for desorption, optimum time for desorption ranged from 30 min to 2 h. The sorbent derived from ground *Ecklonia maxima* could be used for more than four adsorption-desorption cycles whereas the sorbent derived from the Kelpak Waste could only be used effectively for up to three adsorption-desorption cycles.

## Introduction

Cadmium with lead and mercury, is rated as one of the top three metals most hazardous to man and the environment. Whereas the use of lead and mercury are declining, cadmium is increasingly being used in industrial processes (Aldor *et al.* 1995). Existing technologies used in heavy metal remediation include precipitation, filtration, ion exchange, electrolysis, membrane processes and evaporative recovery. These are expensive and have operational problems such as sensitivity to acids and salts and fouling (Aderhold *et al.* 1996). Thus, there is a great need for an inexpensive, rapid and easy to operate process for the removal of heavy metals from industrial effluent.

Biosorption is an inexpensive and efficient method to remove metal ions from solution and has application in controlling industrial effluents. Biosorption is the use of both plant- and animal-derived material to sequester metal ions from solution. Metal sequestration involves a number of mechanisms including ion exchange, chelation, adsorption by physical forces and ion entrapment. The sorbent may be living, and uptake would include both passive and active methods, or non-living where only passive uptake would occur.

Sorbents derived from dried and ground *Ecklonia maxima* (Osbeck) Papenf. and 'Kelpak Waste', are effective sorbents of copper, zinc and cadmium. 'Kelpak' is a commercial seaweed concentrate used as a growth stimulant in agriculture. It is made from *Ecklonia maxima* using a 'cell burst process', which relies on changes in pressure to rupture the cell walls with no chemicals or heat being applied. The waste consists mainly of ruptured cell walls. Metal adsorbance by the

Kelpak Waste was equal or superior to that of the sorbent made from ground *Ecklonia maxima* when tested over a range of concentrations (0–100 mg L<sup>-1</sup>) and for different lengths of time (0–24 h) (Stirk and van Staden 2000). The Kelpak Waste is abundant and inexpensive with between 350–400 tonnes being generated annually. Along with its good adsorption abilities, its potential for use in waste water remediation is promising. If the bound metals could be recovered from the sorbent and the sorbent regenerated and reused, it would further increase its cost effectiveness. One of the many advantages of using biosorbents over more conventional processes is the greatly improved recovery of the bound heavy metal ions from the biomass (Wilde and Benemann 1993).

In this study we determined which eluents are the most effective at desorbing cadmium from the seaweed-derived sorbents and optimized the desorption process. This included regeneration and reuse of the sorbent for successive adsorption-desorption cycles.

# **Materials and Methods**

Ecklonia maxima was collected from the west coast of South Africa, dried and ground to 0.5–1.0 mm. Kelpak Waste was obtained from the Kelpak factory in Simonstown, South Africa. As the Kelpak Waste was a moist sludge, the wet:dry weight ratio was determined.

A stock solution of 100 mg L<sup>-1</sup> 3CdSO<sub>4</sub>.8H<sub>2</sub>O was prepared using deionized distilled water. For all experiments, cadmium solutions of 10 mg L<sup>-1</sup> at a pH of 4.5 were prepared. Deionized distilled water was used throughout the experiments.

#### **Experimental design**

Adsorption Cycle 1: The sorbent (0.5 g dry weight) was added to 50 mL of 10 mg L<sup>-1</sup> cadmium solution and left on an orbital shaker at 100 rpm for 3 h. The pH was monitored at hourly intervals and adjusted using NaOH or HCl to pH  $4.5\pm0.5$  where necessary. After 3 h, 15 mL solution was removed and the final ion concentration measured using an Atomic Absorption Spectrophotometer (Varian AA-1275 series) in an air/acetylene flame. The remaining solution was filtered off from the sorbent and the sorbent rinsed with deionised distilled water. *Ecklonia maxima* was filtered using a glass filter and rinsed twice with 25 mL water. The Kelpak waste was centrifuged at 1.5 U min<sup>-1</sup> for 5 min, and then centrifuged twice more with 25 mL water.

Desorption Cycle: The sorbent, now loaded with cadmium, was added to 50 mL of the desorption eluent and left on an orbital shaker at 100 rpm. The solid to liquid ratio (S/L) was kept constant for all experiments at 0.5 g 50 mL<sup>-1</sup> (10 g L<sup>-1</sup>). After 2 h, 15 mL of the eluent was removed and the final ion concentration measured. The sorbent was then filtered and rinsed as previously described.

Adsorption Cycle 2: The same sorbent was subsequently added to  $50\,\mathrm{mL}$  cadmium solution ( $10\,\mathrm{mg}\,\mathrm{L}^{-1}$  at pH 4.5) and left on an orbital shaker set at  $100\,\mathrm{rpm}$  for 3 h. The pH was adjusted at hourly intervals to pH  $4.5\pm0.5$ . After 3 h,  $15\,\mathrm{mL}$  of solution was removed and the final ion concentration determined.

There were 3 replicates for each treatment. The desorption potential of the eluents was expressed as % recovery of the initial biosorbent loading. The effect of the desorption eluent on subsequent adsorption was determined using the metal uptake parameter 'q' which was calculated as:

$$q = (C_i - C_f) V/s$$

where  $C_i$  and  $C_f$  are the initial and final cadmium concentration in solution (mg L<sup>-1</sup>), V is the volume of the solution (L) and s is the dry weight of the sorbent biomass (g) (Aldor *et al.* 1995).

Experiment 1: Determining the desorption potential of different eluents. Acids, salts and a chelator were tested for their desorption potential. The four acids were HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH, the four salts were NaHCO<sub>3</sub>, NaCl, CaCl<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub>. Na<sub>2</sub>EDTA was the chelator applied during the desorption cycle. Deionised distilled water was used as a control. Each desorption eluent was applied at two concentrations – 0.1 M and 1 M for 2 h.

Experiment 2: Optimizing the concentration of the desorption eluents. Three acids, HCl, HNO $_3$  and H $_2$ SO $_4$ , were applied during the desorption cycle at 0.001 M, 0.01 M, 0.1 M and 1 M respectively for 2 h. Water was used as a control.

Experiment 3: Determining the shortest time required for maximum desorption.  $0.01\,M\,H_2SO_4$  and

0.1 M HCl were applied for 0, 5, 15, 30, 60 and 120 min for the desorption cycle.

Experiment 4: Determining the number of adsorption-desorption cycles for which the sorbent is effective. The same sorbent material was used repeatedly for a number of adsorption-desorption cycles where 0.001 M H<sub>2</sub>SO<sub>4</sub> was applied for 120 min and 0.1 M HCl was applied for 30 min for four successive cycles. Desorption was determined as a % of cadmium loaded in the preceding adsorption cycle.

#### Results

Experiment 1: Determining the desorption potential of different eluents. The three acids, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, proved effective desorption eluents at both 0.1 M and 1 M for *Ecklonia maxima* and the Kelpak Waste with over 80 % recovery being achieved. The two chloride salts, NaCl and CaCl<sub>2</sub> also gave good recovery of cadmium, especially at 1 M, but caused discolouration of the solution. The fourth acid tested, CH<sub>3</sub>COOH, the chelator, the carbonate salts, NaH-CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> and the water control were not effective at recovering the ions from the sorbent (Fig. 1A and B).

Subsequent adsorption of cadmium (Adsorption Cycle 2) by *Ecklonia maxima* improved compared to initial adsorption (Cycle 1) after exposure to all the desorption eluents with the exception of 1 M NaH-CO<sub>3</sub> and CaCl<sub>2</sub> and 0.1 M and 1 M K<sub>2</sub>CO<sub>3</sub> (Fig. 1C). The Kelpak Waste was more sensitive to the desorption eluents. All the salts and the chelator caused a large reduction in subsequent adsorption when applied at both 0.1 M and 1 M. The acids, when applied at 1 M, also caused a reduction in adsorption during Cycle 2 (Fig. 1D). The cadmium uptake (q) for Adsorption Cycle 2 and the pH in the desorption eluent after 2 h are shown in Table I.

Experiment 2: Optimizing the concentration of the desorption eluents. As in the previous experiment, the three acids, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, when applied at 0.1 M and 1 M achieved over 80 % recovery of the cadmium ions for both *Ecklonia maxima* and the Kelpak Waste. When H<sub>2</sub>SO<sub>4</sub> was applied at the lower concentration of 0.01 M, it also proved effective with over 80 % recovery being measured for both sorbents. All the other lower concentrations gave very poor recovery results (Fig. 2A and B).

Subsequent cadmium adsorption (Cycle 2) was enhanced in all instances, except for 1 M H<sub>2</sub>SO<sub>4</sub>, for *Ecklonia maxima* (Fig. 2C). Adsorption was enhanced after exposure to 0.001 M–0.1 M but decreased compared to adsorption in Cycle 1 after exposure to 1 M of the three desorption acids for the Kelpak Waste (Fig. 2D). The cadmium uptake (q) for Adsorption Cycle 2 is shown in Table II.

Experiment 3: Determining the shortest time required for maximum desorption. The length of time the sorbent is exposed to the desorption eluent affects

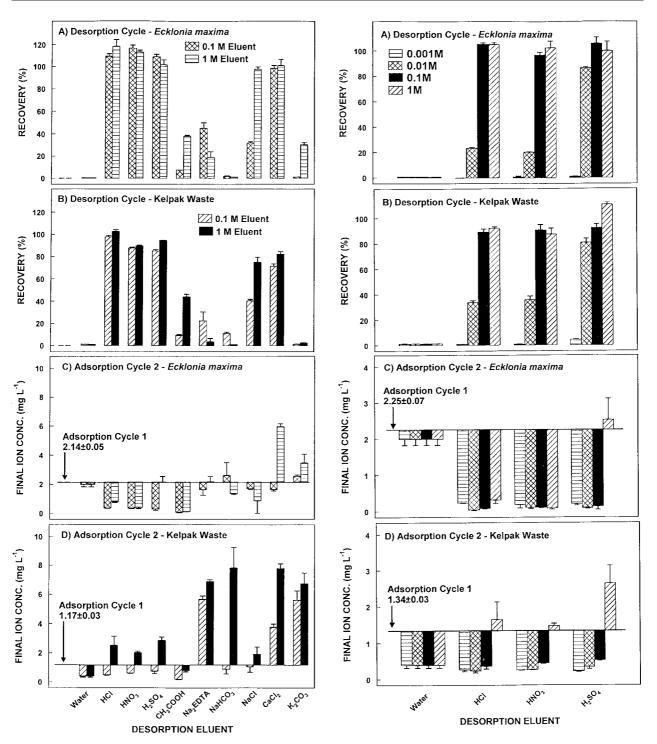


Fig. 1. Effect of different eluents on the desorption of cadmium and subsequent reuse of the sorbent. Desorption from A) *Ecklonia maxima* and B) Kelpak Waste. Cadmium adsorption subsequent to desorption (Cycle 2) in C) *Ecklonia maxima* and D) Kelpak Waste. The adsorption results from Cycle 1 are also indicated.

the amount of ions recovered. Maximum recovery of the cadmium ions was achieved only after exposure for 1–2 h to  $0.01\,M\,H_2SO_4$  and after 30 min to  $0.1\,M\,HCl$  (Fig. 3A and B). The length of time the sorbent was exposed to the desorption acid had no effect on subsequent adsorption with similar adsorption results

Fig. 2. Effect of different concentrations of acids on the desorption of cadmium and the reuse of the sorbent. Desorption from A) *Ecklonia maxima* and B) Kelpak Waste. Cadmium adsorption subsequent to desorption (Cycle 2) in C) *Ecklonia maxima* and D) Kelpak Waste. The adsorption results from Cycle 1 are also indicated.

being achieved for all treatments (Fig. 3C and D). The cadmium uptake (q) for Adsorption Cycle 2 is shown in Table III.

Experiment 4: Determining the number of adsorption-desorption cycles for which the sorbent is effective. Desorption using 0.01 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HCl

Table I. Cadmium uptake (q) for the sorbents made from *Ecklonia maxima* and Kelpak Waste after exposure to ten desorption eluents for 2 h.

Sorbent	DE	0.1 M		1 M		
		pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )	pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )	
E. maxima	Water	4.90	$0.71 \pm 0.02$	_	_	
	HCl	1.38	$0.85 \pm 0.00$	0.92	$0.81 \pm 0.01$	
	$HNO_3$	1.48	$0.89 \pm 0.00$	1.00	$0.88 \pm 0.01$	
	$H_2SO_4$	1.80	$0.86 \pm 0.01$	1.42	$0.67 \pm 0.04$	
	CH <sub>3</sub> COOH	2.95	$0.92 \pm 0.00$	2.55	$0.91 \pm 0.00$	
	Na <sub>2</sub> EDTA	4.25	$0.76 \pm 0.04$	4.53	$0.70 \pm 0.03$	
	Na <sub>2</sub> HCO <sub>3</sub>	8.52	$0.66 \pm 0.09$	8.60	$0.78 \pm 0.02$	
	NaCl	3.72	$0.72 \pm 0.01$	4.53	$0.80 \pm 0.01$	
	CaCl <sub>2</sub>	3.87	$0.73 \pm 0.01$	3.65	$0.29 \pm 0.02$	
	$K_2CO_3$	10.45	$\boldsymbol{0.66 \pm 0.01}$	11.10	$0.57 \pm 0.06$	
Kelpak Waste	Water	4.95	$0.89 \pm 0.01$	_	_	
•	HCl	1.73	$0.87 \pm 0.00$	1.13	$0.67 \pm 0.06$	
	$HNO_3$	1.78	$0.88 \pm 0.00$	1.28	$0.74 \pm 0.01$	
	$H_2SO_4$	1.38	$0.85 \pm 0.02$	1.15	$0.74 \pm 0.02$	
	$CH_3COOH$	3.13	$0.89 \pm 0.00$	2.67	$0.83 \pm 0.01$	
	Na <sub>2</sub> EDTA	4.27	$0.39 \pm 0.03$	4.53	$0.33 \pm 0.01$	
	NaHCO <sub>3</sub>	8.37	$0.82 \pm 0.03$	8.55	$0.13 \pm 0.01$	
	NaCl	3.25	$\boldsymbol{0.81 \pm 0.00}$	4.33	$0.73 \pm 0.05$	
	CaCl <sub>2</sub>	3.32	$0.65 \pm 0.02$	3.90	$0.24 \pm 0.03$	
	$K_2CO_3$	10.50	$\boldsymbol{0.39 \pm 0.06}$	11.20	$0.27 \pm 0.00$	

Values highlighted in bold indicate a significant decrease in  $q_2$  (metal uptake in Adsorption Cycle 2) compared to  $q_1$  (metal uptake in Adsorption Cycle 1) where  $q_1$  for *Ecklonia maxima* = 0.71  $\pm$  0.01 and for Kelpak Waste = 0.83  $\pm$  0.01. The pH of the desorption eluent (DE) after the 2 h desorption cycle is also included.

Table II. Cadmium uptake (q) for the sorbents made from  $Ecklonia\ maxima$  and Kelpak Waste after exposure to three acids at four concentrations for 2 h.

DE Conc	Conc.	Ecklonia ma	Ecklonia maxima		Kelpak Waste		
		pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )	pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )		
Water	_	4.90	$0.71 \pm 0.02$	4.95	$0.89 \pm 0.01$		
HCl	0.001 M	4.03	$0.94 \pm 0.00$	3.95	$0.93 \pm 0.00$		
	$0.01\mathrm{M}$	2.53	$0.96 \pm 0.00$	2.53	$0.93 \pm 0.00$		
	$0.1\mathrm{M}$	1.78	$0.93 \pm 0.01$	1.95	$0.92 \pm 0.01$		
	1 M	1.40	$0.89 \pm 0.01$	1.30	$\boldsymbol{0.79 \pm 0.05}$		
$HNO_3$	$0.001{ m M}$	3.67	$0.91 \pm 0.01$	3.62	$0.90 \pm 0.00$		
	$0.01\mathrm{M}$	2.72	$0.92 \pm 0.00$	2.32	$0.90 \pm 0.00$		
	$0.1\mathrm{M}$	1.98	$0.92 \pm 0.00$	1.82	$0.88 \pm 0.01$		
	1 M	1.55	$0.96 \pm 0.00$	1.43	$0.79 \pm 0.01$		
$H_2SO_4$	0.001 M	2.80	$0.90 \pm 0.00$	3.08	$0.92 \pm 0.00$		
- '	$0.01\mathrm{M}$	2.22	$0.96 \pm 0.00$	2.18	$0.91 \pm 0.01$		
	$0.1\mathrm{M}$	1.93	$0.96 \pm 0.00$	1.97	$0.87 \pm 0.00$		
	1 M	1.10	$\boldsymbol{0.67 \pm 0.06}$	1.63	$0.66 \pm 0.05$		

Values highlighted in bold indicate a significant decrease in  $q_2$  (metal uptake in Adsorption Cycle 2) compared to  $q_1$  (metal uptake in Adsorption Cycle 1) where  $q_1$  for *Ecklonia maxima* =  $0.71 \pm 0.01$  and for Kelpak Waste =  $0.81 \pm 0.01$ . The pH of the desorption eluent (DE) after the 2h desorption cycle is also included.

did not vary over successive desorption cycles for both *Ecklonia maxima* and Kelpak Waste sorbent (Fig. 4A and B). As found previously, there was increased ad-

sorption of cadmium in Adsorption Cycle 2 compared to Adsorption Cycle 1 for both *Ecklonia maxima* and Kelpak Waste sorbents after exposure to the two acid

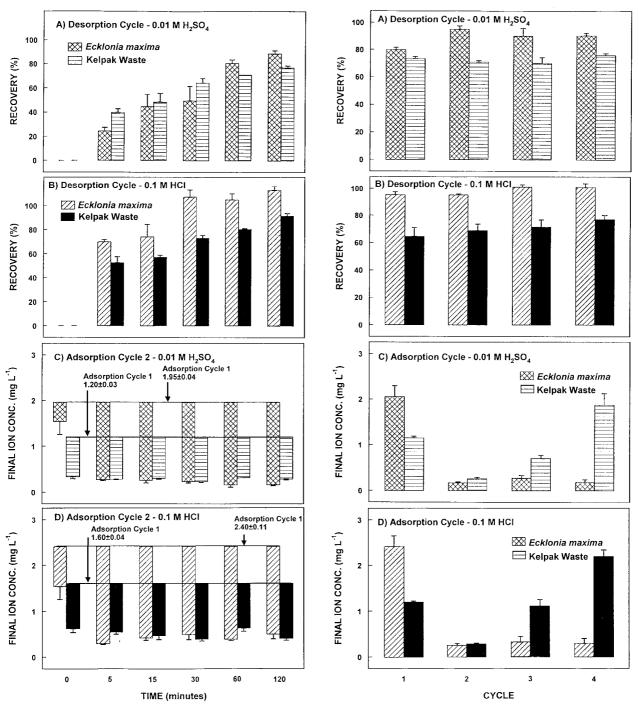


Fig. 3. The effect of length of time of the desorption cycle on recovery of cadmium ions. Desorption using A) 0.01 M  $H_2SO_4$  and B) 0.1 M HCl. Cadmium adsorption subsequent to desorption (Cycle 2) using C) 0.01 M  $H_2SO_4$  and D) 0.1 M HCl. The adsorption results from Cycle 1 are also indicated.

Fig. 4. The effect of a number of successive adsorption-desorption cycles on the two sorbents. Desorption using A) 0.01 M  $H_2SO_4$  for 2 h and B) 0.01 M HCl for 30 min. Cadmium adsorption after exposure to C) 0.01 M  $H_2SO_4$  for 2 h and D) 0.01 M HCl for 30 min.

desorption eluents. Adsorption did not vary for subsequent adsorption cycles (Cycles 3 and 4) for *Ecklonia maxima*. However, there was a significant decrease in the binding capacity for each successive adsorption cycle for the Kelpak Waste (Fig. 4C and D). The cadmium uptake (q) for each adsorption cycle is shown in Table IV.

# Discussion

Effective desorption eluents can be proton exchangers, complexing agents or contain competing ions. The mineral acids are the most commonly used desorption eluents and are considered to be proton exchanging agents. The acids HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>

Table III. Cadmium uptake (q) for the sorbents made from A	Ecklonia maxima and Kelpak	Waste after exposure to 0.01 M
H <sub>2</sub> SO <sub>4</sub> and 0.1 M HCl for various lengths of time.		

Sorbent	Time	0.01 M H <sub>2</sub> SO <sub>4</sub>		0.1 M HCl		
		pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )	pH (DE)	q <sub>2</sub> (mg g <sup>-1</sup> )	
E. maxima	0 min	_	$0.77 \pm 0.03$	_	$0.73 \pm 0.05$	
	5 min	2.28	$0.90 \pm 0.00$	2.08	$0.85 \pm 0.00$	
	15 min	2.27	$0.90 \pm 0.01$	2.10	$0.84 \pm 0.01$	
	30 min	2.33	$0.90 \pm 0.01$	2.10	$0.84 \pm 0.01$	
	60 min	2.57	$0.91 \pm 0.00$	2.62	$0.85 \pm 0.01$	
	120 min	2.52	$0.91 \pm 0.00$	2.77	$0.83 \pm 0.01$	
Kelpak Waste	0 min	_	$0.86 \pm 0.00$	_	$0.83 \pm 0.01$	
•	5 min	2.37	$0.91 \pm 0.00$	1.88	$0.83 \pm 0.00$	
	15 min	2.4	$0.88 \pm 0.01$	1.75	$0.84 \pm 0.01$	
	30 min	2.4	$0.87 \pm 0.00$	1.73	$0.85 \pm 0.00$	
	60 min	2.4	$0.86 \pm 0.01$	1.80	$0.82 \pm 0.01$	
	120 min	2.45	$0.90 \pm 0.00$	1.67	$0.85 \pm 0.00$	

There were no significant decreases in  $q_2$  (metal uptake in Adsorption Cycle 2) compared to  $q_1$  (metal uptake in Adsorption Cycle 1) where  $q_1$  for *Ecklonia maxima* = 0.73 ± 0.01 and 0.64 ± 0.01 and for Kelpak Waste = 0.79 ± 0.01 and 0.73 ± 0.01 respectively. The pH of the desorption eluent (DE) after the 2 h desorption cycle is also included.

Table IV. Cadmium uptake (q) for the sorbents made from *Ecklonia maxima* and Kelpak Waste after exposure to 0.01 M H<sub>2</sub>SO<sub>4</sub> for 2 h and 0.1 M HCl for 30 min for 4 successive adsorption-desorption cycles.

Sorbent	Cycle	0.01 M H <sub>2</sub> SO <sub>4</sub>		0.1 M HCl		
		pH (DE)	q (mg g <sup>-1</sup> )	pH (DE)	q (mg g <sup>-1</sup> )	
E. maxima	1	2.32	$0.73 \pm 0.02$	1.77	$0.65 \pm 0.02$	
	2	2.23	$0.92 \pm 0.00$	1.77	$0.86 \pm 0.00$	
	3	2.12	$0.92 \pm 0.01$	1.70	$0.85 \pm 0.01$	
	4	2.25	$0.93 \pm 0.01$	1.75	$0.86 \pm 0.01$	
Kelpak Waste	1	2.35	$0.82 \pm 0.01$	1.78	$0.77 \pm 0.00$	
•	2	2.35	$0.91 \pm 0.00$	1.77	$0.86 \pm 0.00$	
	3	2.20	$0.86 \pm 0.01$	1.67	$0.78 \pm 0.01$	
	4	2.27	$0.76 \pm 0.06$	1.80	$0.67 \pm 0.01$	

The pH of the desorption eluent (DE) after each desorption cycle is also included.

are also able to dissolve cadmium to form the soluble salts CdCl<sub>2</sub>, CdSO<sub>4</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> respectively. Cadmium can also form complexes with bicarbonate, carbonate, chloride and sulfate while calcium, sodium and potassium also participate in ion exchange so that these salts and anions have potential as desorption agents. (Aldor *et al.* 1995). Both 0.10N EDTA and 0.11N HCl are able to desorb copper from packed columns of *Sargassum kjellmanianum* Yendo with over 99.5 % recovery being recorded (Zhou *et al.* 1998). The authors claim that the columns could be regenerated and reused although no results were presented to support this.

A critical factor in the desorption of metal ions is the pH which influences the mechanisms of proton exchange. Aldor *et al.* (1995) found that cadmium desorption only occurred below pH 3.0 and was most

effective when below pH 2.1 for Sargassum fluitans Børg. This could explain the poor desorption ability of CH<sub>3</sub>COOH in the current study compared to the other three acids investigated. The CH<sub>3</sub>COOH lowered the pH to between 2.55-3.13 when applied to both cadmium-loaded sorbents while the other acids all lowered the pH to below 1.8 (Table I). The more dilute concentrations of HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> also had a higher pH and poorer desorption (Table II). The two carbonate salts (NaHCO3 and K2CO3) caused very alkaline conditions (above pH 8.3) on contact with the biosorbents (Table I). The poor desorption of these two salts indicates that the cadmium carbonate complex formed was not strong enough to destabilize the biosorbent-metal complex at these high pH values (Aldor et al. 1995).

Aldor et al. (1995) working with cross-linked Sar-

gassum fluitans found that the three acids HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, the chelator Na<sub>2</sub>EDTA and CaCl<sub>2</sub> salt were the most effective desorption eluents for cadmium recovery. However, the high cost of the chelator and salt and the unspecified damage to the biosorbent material by HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> caused these eluents to be eliminated as possible desorbing agents. They concluded that HCl had the most potential as a desorbing agent. Desorption from waste water sludges which consist mainly of microbial biomasses was possible using 0.2 N H<sub>2</sub>SO<sub>4</sub> and HCl and 0.4 N CH<sub>3</sub>COOH (Bux et al. 1995, 1996) while H<sub>2</sub>SO<sub>4</sub> affected above 96 % recovery of zinc ions from a column packed with the aquatic fern Azolla filiculoides Lam., and HCl affected above 85 % recovery (Zhao et al. 1999).

This study also indicated that an acid is the most effective desorbing eluent to use for the two *Ecklonia maxima* derived sorbents. The acids gave a high % recovery and improved adsorption in Cycle 2. The salts and chelator either gave poor ion recovery or the chloride salts, which affected over 75 % recovery when applied at 0.1 M, caused a discolouration in the water due to leaking of unspecified compounds. This resulted in damage to the sorbents and adversely affected subsequent adsorption.

Another important criterion is the length of time of the desorption cycle. For industrial application, the shorter the desorption cycle, the sooner the sorbent can be reused and the quicker the waste water can be processed. The length of time of the desorption cycle does influence the amount of ions recovered until an equilibrium is reached. In this respect, use of 0.1 MHCl is more advantageous than using 0.01 M H<sub>2</sub>SO<sub>4</sub> as an equilibrium is achieved after 30 min with HCl and only after 2h with H<sub>2</sub>SO<sub>4</sub>. The length of time of the desorption cycle does not influence the subsequent adsorption in Cycle 2. Aldor et al. (1995) also found that desorption equilibrium was reached in less than 2 h for Sargassum fluitans in batch culture. In a 8.9 cm long column packed with copper-loaded Sargassum kjellmanianum, 99.5 % recovery was achieved after only 50 mL of 0.11N HCl or 0.010N EDTA were applied (Zhou et al. 1998) while columns of zinc-loaded Azolla filiculoides where desorbed with application of 120 mL 0.2N H<sub>2</sub>SO<sub>4</sub> and HCl (Zhao et al. 1999). Bux et al. (1996) found that desorption occurred immediately and equilibrium was established within 10 min from microbial sludges.

An important consideration is the regeneration of the biosorbent material for subsequent reuse. In this respect, the performance of the Kelpak Waste was

disappointing with metal binding capacity decreasing after three desorption cycles. It was not possible to use lower acid concentrations which are likely to cause less structural damage as they do not show good recovery. The performance of the dried *Ecklonia maxima* was promising with no deterioration in its metal binding capacity being recorded after 4 desorption cycles. The fern Azolla filiculoides could be regenerated for up to 6 cycles with adsorption being only slightly lower than for Cycle 1 (Zhao et al. 1999). Similarly, both crosslinked Sargassum fluitans and Ascophyllum nodosum (L.) LeJolis can be used for a number of adsorptiondesorption cycles. These were cross-linked using formaldehyde and HCl (Aldor et al. 1995). When Ascophyllum nodosum was not reinforced by cross-linking, acid desorption significantly reduced its metal binding capacity. This indicates that biomass cross-linking can increase the resistance of the algal biomass to acidic desorption eluents (Aldor et al. 1995). If the Kelpak Waste is to be developed for industrial remediation of waste water, a cross-linking reinforcement should be considered to improve its effectiveness over a number of cycles.

The Kelpak waste has potential to be used in industrial waste water remediation. It can effectively sequester a range of metal ion from both high and low initial ion concentration (Stirk and van Staden 2000) and is readily available and inexpensive being a by-product from the manufacture of the seaweed concentrate Kelpak. It is also cost effective in that the bound metals can easily be recovered with HCl having the most potential as a desorbing agent. The main drawback is the structural damage caused by the desorbing acid. This limits the use of the Kelpak Waste sorbent to a maximum of three desorbing cycles unless it can be reinforced by cross-linking (Aldor et al. 1995). The cost and effectiveness of cross-linking versus the abundance of the sorbent would have to be taken into consideration. In this regard, the Ecklonia maxima sorbent was more effective as subsequent adsorption was not affected by the desorption acid. However, initial adsorption was not as good compared to the Kelpak Waste sorbent (Stirk and van Staden 2000) and it would have to be harvested from the ocean, increasing its initial cost.

# Acknowledgements

The University of Natal Research Fund is thanked for financial assistance.

Accepted 12 July 2001.

# References

Aderhold, D., C. J. Williams and R. G. J. Edyvean. 1996. The removal of heavy metal ions by seaweeds and their derivatives. *Biores. Technol.* 58: 1–6.

Aldor, I., E. Fourest and B. Volesky. 1995. Desorption of cadmium from algal biosorbent. *Can. J. Chem. Engin.* 73: 516–522.

- Bux, F., F. M. Swalaha and H. C. Kasan. 1995. Assessment of acids as desorbents of metal ions bound to sludge surfaces. *Water S. A. 21*: 319–324.
- Bux, F., D. Naidoo and H. C. Kasan.1996. Laboratory-scale biosorption and desorption of metal ions using waste sludges and selected acids. S. A. J. Sci. 92: 527–529.
- Stirk, W. A. and J. van Staden. 2000. Removal of heavy metals from solution using dried brown seaweed material. *Bot. Mar.* 43: 467–473.
- Wilde, E. W. and J. R. Benemann. 1993. Bioremoval of heavy metals by the use of microalgae. *Biotech. Adv. 11*: 781–812.
- Zhao, M., J. R. Duncan and R. P. van Hille. 1999. Removal and recovery of zinc from solution and electroplating effluent using *Azolla filiculoides*. *Wat. Res.* 33: 1516–1522.
- Zhou, J.L., P.L. Huang and R. G. Lin. 1998. Sorption and desorption of Cu and Cd by macroalgae and microalgae. *Environ. Pollut.* 101: 67–75.