

OD1) Biosorption and Desorption of Chromium by Ca-loaded *Laminaria Japonica* Biomass

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1. Introduction

The metal ion binding mechanism in biosorption may involve different processes such as complexation, coordination, electrostatic attraction, or microprecipitation whereby ion exchange plays a major role in the binding of metal ions by algal biomass [1]. In the case of biosorption of heavy metals by brown algal biomass, the mechanisms can be viewed as being extracellular or occurring discretely at the cell wall [2]. The order *Laminariales* are the most important groups of algae to the field of biosorption because of the abundance of their cell wall matrix polysaccharides and extracellular polymers. The alginate polysaccharides are mainly responsible for the natural ion-exchange capacity of the brown algae. Its unique macromolecular structure gives rise to selective metal binding whose mechanism is commonly represented as "egg-box" model. Although *L. Japonica* reveals a high adsorption capacity of heavy metals and almost 99% of heavy metal elution by means of acids, the percentage of Cr ion desorption is very low.

2. Materials and method

Sorption Experiments

Previous investigations [3] showed that Ca-loaded biomass is more suitable for Cr ion sorption. Raw *L. japonica* was collected and sun-dried on the beach near Kijang, East Coast of Korea. Pretreatment may be in terms of hardening the cell wall structure through increasing the negative charge on the cell surface by NaOH treatment, or opening of the available sites for the adsorption by acid treatment, and enhancing ion exchange by Ca^{2+} solution treatment. Dry raw biomass was treated by soaking in 1 N CaCl_2 solution in flask shaken gently on an orbital shaker. Ca-loaded *Laminaria Japonica* was washed with 0.1N HNO_3 for 8 hours to remove Ca^{2+} ion and then rinsed with distilled water. The amount of binding sites was supposed to be 1.8 mmol/g for Ca-loaded biomass and 2.1 mmol/g for Ca-alginate beads (with same treatment method). The Cr solutions of desired concentrations were prepared by dissolving $\text{Cr}(\text{NO}_3)_3$ in distilled deionized water to desired initial concentrations. All sorption experiments were

performed by suspending 100 mg of biomass in 100 ml of the metal-bearing solution and shaking on an orbital shaker for 8 hours. 0.1 N HCl and 0.1 N NaOH were used for pH 4.5 adjustment. At the end of experiment each sample was filtered by 0.18 μm Millipore membrane and the filtrate was analyzed by atomic adsorption flame emission spectrophotometer (Shimadzu AA 6200) for the equilibrium metal content. The metal uptake was calculated as $q(\text{mg/g})$ (Eq. 1)

$$q = \frac{V \cdot (C_i - C_e)}{M} \quad (1)$$

where C_i and C_e are the initial and final (equilibrium) metal concentration in the solution, respectively (mg/L), V is the solution volume (L), and M is the initial mass of the used biosorbent (g).

Desorption Experiments

Desorption experiments were performed (a) in 250 ml Erlenmeyer flasks with 100 ml of working volume. The Aqua Regia ($3\text{HCl} + \text{HNO}_3$), 0.1 N HNO_3 , 1 N NaOH, 0.5 M H_2SO_4 solutions were used as eluants; (b) heating under 700°C in electric furnace for 5 hours. The contact time was 1 hour, 8 hours, 10 days and 25 days respectively, which was long enough to reach equilibrium. The flasks were agitated on a shaker at 200 and room temperature. Samples for analysis of Cr(III) concentrations were intermittently removed from the flasks and appropriately diluted. Also Cr-loaded biomass was treated at 700°C in a furnace during 5 hours. The ash was analyzed by SEM (Scanning Electron Microscope Hitachi S-3000N). At the end of each desorption experiment the samples were filtered using Whatman No. 1 and the filtrate was analyzed by AAS. The metal uptake was calculated from the desorption experiments results as q (mg/g) (Eq. 2)

$$q = \frac{V \cdot C_f}{M} \quad (2)$$

where C_f is the final eluted metal concentration in solution (mg/L), V is the solution volume (L), and M is the initial mass of the used biosorbent (g).

3. Results and Discussion

Chromium Sorption Experiments

The adsorption of metals by different types of algae was observed to be a reversible phenomenon and could be represented by Langmuir adsorption isotherm. Langmuir isotherm equation is based on monolayer sorption onto a surface with finite number of identical sites, which are homogeneously distributed over the sorbent surface and is given by Eq. 3

$$\frac{C_e}{q} = \frac{C_e}{q_{\max}} + \frac{1}{(K \cdot q_{\max})} \quad (3)$$

where q_{\max} and K are Langmuir constants denoting maximum adsorption capacity and the affinity of binding sites ($k_{\text{adsorption}}/k_{\text{desorption}}$), respectively. These constants can be determined from the $1/C_e$ versus $1/q$. Results calculating by eq. 3 are represented in Fig. 1. Langmuir constants q_{\max} and K are calculating from the linear type of Langmuir isotherm and represented in Table 1. Ca-alginate beads showed lower sorption capacity than Ca-loaded *L. Japonica*. The explanation may lay to the fact that the presence of fucoidan in *Laminaria* specie structure provides additional binding sites. The sulfonic acid of fucoidan may also bind Cr; although sulfonic acid groups typically play a secondary role, when metal binding takes place at low pH their adsorption capacity increases [2]. The total binding sites for Cr as determined do not quantitatively correlate with the total Ca ions - 1.8mmol/g in Ca-loaded *Laminaria Japonica*. We suggest that in the biomass alginate is cross-linked with protein at the interface which makes the alginate-fucoidan matrix structure very dense. In such a dense structure, some sites might not be reachable by Cr ions. The initial concentration of Cr(III) was varied from 10 to 100 and from 100 to 800 mg/L while the pH and temperature were maintained to 4.5 and 25°C respectively. The uptake percentage was increased as the initial Cr(III) concentration increased up to 50 mg/L but further increase in concentration removal was decreased. The maximum percentage removal was observed 78.6% with CaCl_2 treated biomass at 50mg/L concentration. This may be due to the fact that the sites available for sorption on surfaces of algal cell get saturated, preventing further metal ion adsorption.

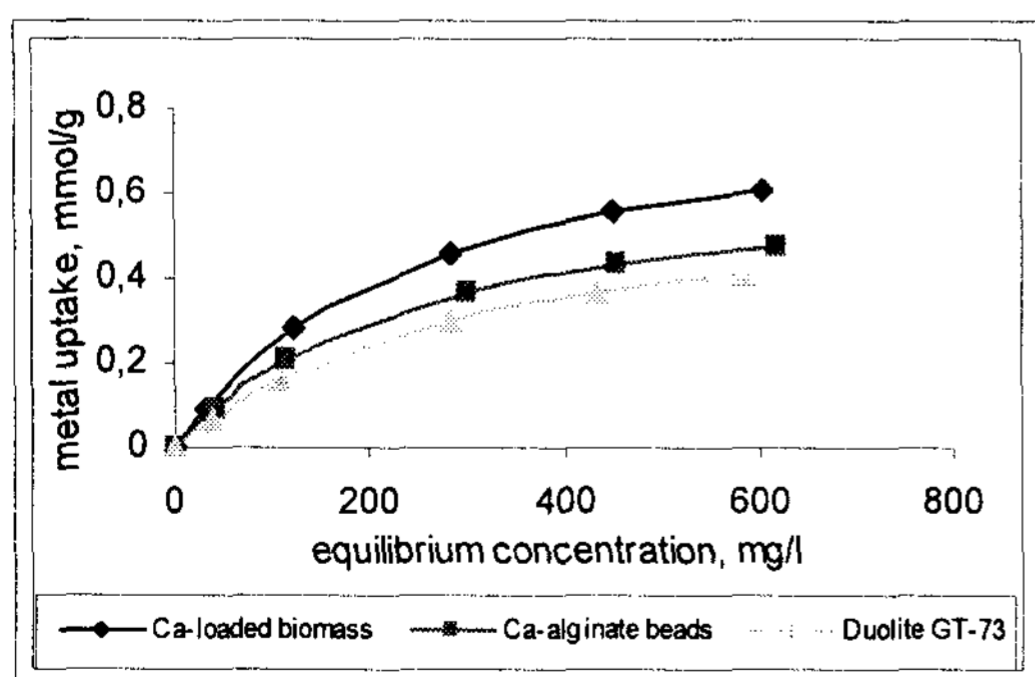


Fig. 1. Cr(III) uptake for Ca-loaded *L. Japonica* biomass at pH 4.5 and for Ca-alginate beads

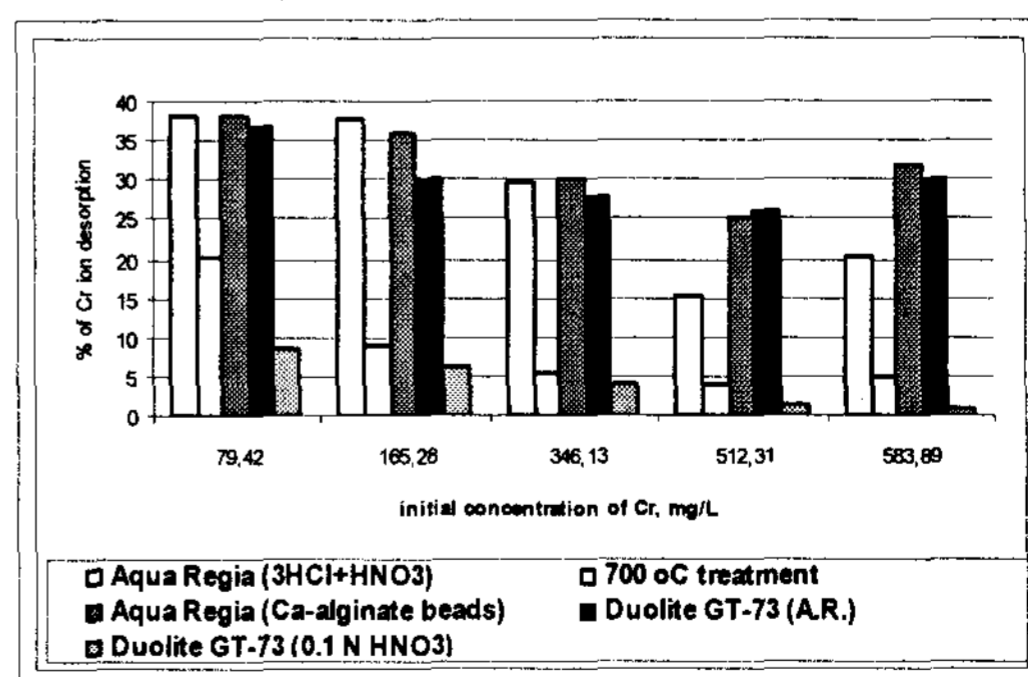


Fig. 2. Weight % of Cr ion desorption using 0.1N HNO_3 , Aqua Regia and 700°C treatment (Ca-loaded Biomass and Ca-alginate Beads)

Table 1. Langmuir constants for different sorption systems.

System	Q _{max} , mmol/g	K, (l/mmol)
Ca-loaded biomass	0.668	0.004
Ca-alginate beads	0.667	0.004
Duolite GT-73	0.642	0.003

Effect of pH on Adsorption

It is well known that Cr³⁺ cations in water can undergo hydrolysis and complexation reactions, the extent of which depend primarily on the total Cr(III) concentration:



The value of the equilibrium constant of reaction (4) has been reported by Hunt (1965) to be $K_h = 10^{-3.82}$ yielding a pK_h of 3.82. This means that at pH=3.8, approximately 50% of the overall Cr(III) content of the system will be in the Cr(OH)²⁺ form. During the bio-sorption process every hour pH measuring was made. At the beginning of experiment the pH was adjusted at 4.5 value. In 2 hours pH control was made by means of 0.1 N NaOH or 0.1 N HNO₃. The results are shown at Fig.4.

Scanning Electron Microscope Results Scanning Electron Microscope (Hitachi S-3000N) was used for analysing the biomass structure and its composition. Surface of biomass sorbed Cr, treated with HNO₃, Aqua Regia and 700°C are shown in Fig. 5. The biomass composition of Cr sorbed, HNO₃, Aqua Regia and 700°C treatment and Ca-alginate beads composition are shown in Table 2 and Table 3, respectively.

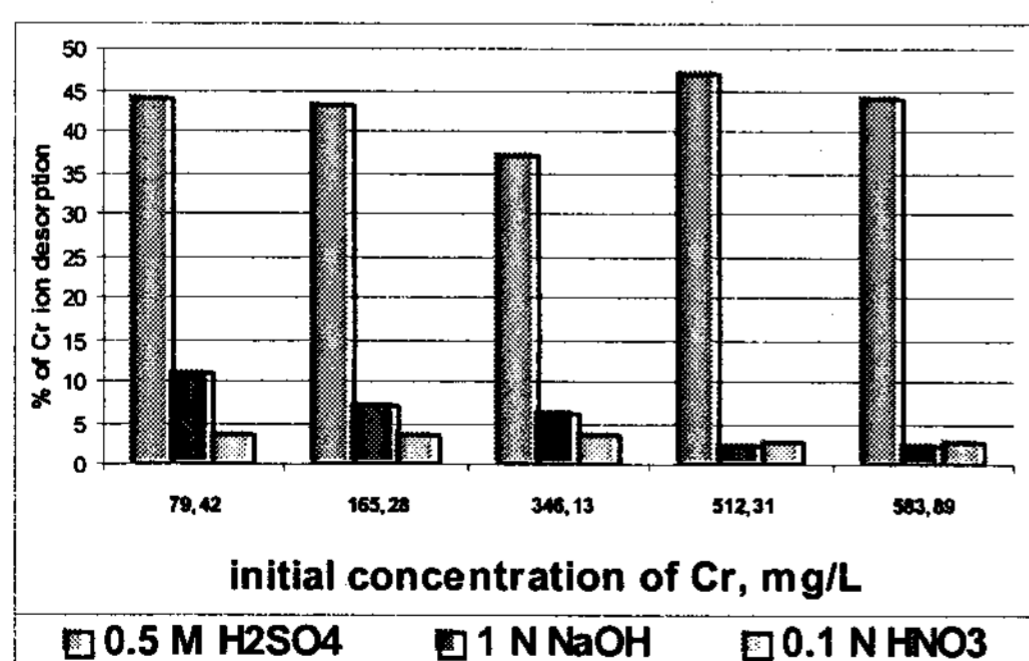


Fig. 3. Weight % of Cr ion desorption using 0.1N HNO₃, 1 N NaOH and 0.5 M H₂SO₄ (Ca-loaded Biomass)

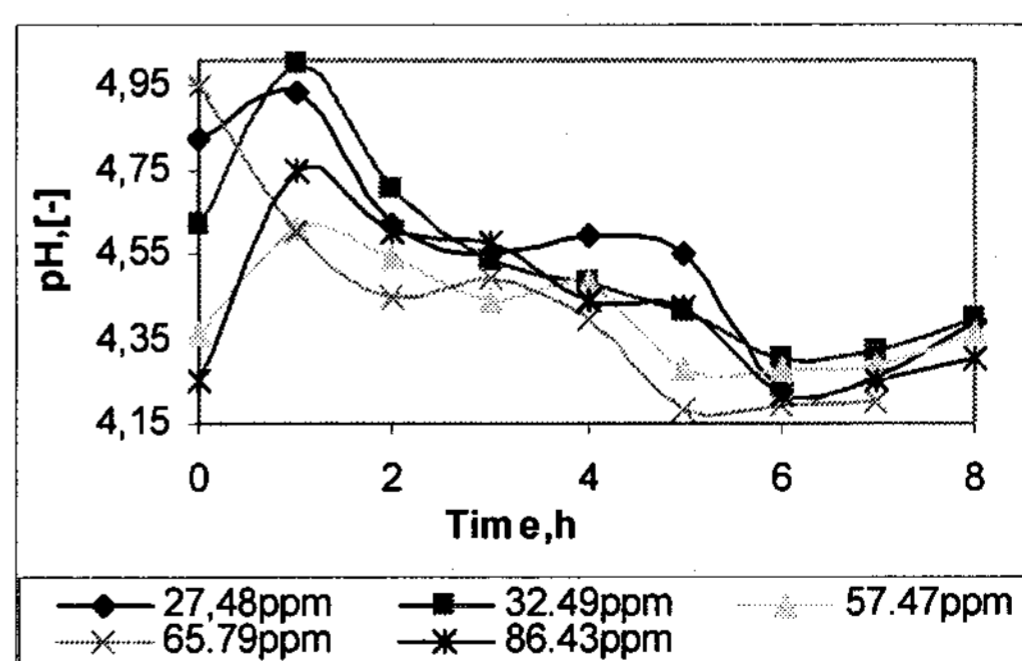


Fig. 4. pH measuring during Ca-loaded biomass sorption process (10-100 ppm)

Table 2. The biomass composition after Cr sorption, HNO₃, Aqua Regia and 700°C treatment

	Cr sorption		HNO ₃ treatment		Aqua Regia treatment		700°C treatment	
	Wt. %	Atomic %	Wt. %	Atomic %	Wt. %	Atomic %	Wt. %	Atomic %
C	37.37	48.37	39.20	49.41	55.79	66.13	6.49	12.27
O	48.87	47.48	48.83	46.94	33.47	29.78	46.09	66.30
Ca	0.38	0.15	0.39	0.15	0.09	0.03	2.91	1.66
Cr	13.38	4.00	11.58	3.50	1.71	0.47	44.51	19.77
Cl	-	-	-	-	8.94	3.59	-	-

Table 3. The Ca-alginate beads composition after Cr sorption, HNO₃ and Aqua Regia

	Before Cr sorption		Cr sorption		Aqua Regia treatment	
	Wt. %	Atomic %	Wt. %	Atomic %	Wt. %	Atomic %
C	33.00	33.99	28.54	42.41	51.96	62.00
O	45.23	49.16	41.82	46.39	39.15	35.055
Ca	23.87	13.24	1.28	0.59	1.36	0.49
Cr	0	0	27.31	10.07	4.64	1.28
Cl	7.90	3.61	1.05	0.55	2.89	1.17

Desorption experiments

Desorption results of Ca-loaded biomass, Ca-alginate beads and industrial Duolite GT-73 by means of 0.1 N HNO₃, Aqua Regia and 700°C treatment are represented in Fig. 2 and Fig. 3. As seen in figures, the Cr bound on the biomass was desorbed by various eluants, and the desorption behavior was dependent on the characteristics of the eluant used. Almost 5% of Cr desorption was obtained using 0.1 N HNO₃ as an eluent. This low percentage of desorption reveals the stable Cr-alginate complex to be formed in the biomass during the adsorption. Bai et al. [4] reported that a highly alkaline pH (8 - 10) was least favorable for Cr adsorption by biomass. Such conditions enhanced the weakening of adsorption forces and thus facilitated elution of bound Cr ions and its release into the aqueous system. In case of fungal biomass Park et al. [5] and [6] reported that 1N NaOH desorbed both Cr(III) and Cr(VI) from *A. niger* biomass in 90%. But in case of *Laminaria Japonica* biomass Cr ion release from algal biomass was just in 11%. We suggest to toughen eluating conditions to make Cr ion release from biomass believing that highly alkaline pH is more favorable for Cr ion desorption. To ruin stable Cr-alginate complex the high temperature treating was used. After 5 hours of 700 °C bi-

biomass treating 90% weight loss of biomass was indicated. Experiment was carried out in the presence of ambient air. The furnace cell is not an isolated cell, which allows oxygen of ambient air to react with the products of biomass combustion. After 700°C biomass treatment almost 90%wt. of Carbon binds are broken during burning the biomass into ash. According to the Table 2, 44% of Cr still remains in biomass while the biomass weight after high temperature treating was decreased 10 times. Moreover after 700°C biomass treating there occurs Cr weight loss in the biomass. Almost 83% of Cr ions seem to disappear after biomass burning down. The explanation lays on the fact that at temperatures in excess of about 1000°C, Cr forms a volatile oxide with the oxygen of the air. So only 16% of Cr ions remain in burned biomass which can be easily eluted by any acid eluent. The Aqua Regia treatment method reveals high desorption capacity – almost 38% of Cr ion release from biomass. But this strong oxidation agent may injure biomass structure making it incapable of continuous Cr sorption and also almost 9% wt. of Chlorine ion remain bonded in biomass in complex form. Previous investigations with fungal biomass [7] showed that 25 days of contact time was required for complete elution of the Cr(III) by the 0.5 M H₂SO₄ eluant. In case of algal biomass this eluant proved to be a most effective elutant than others, with more than 45% Cr being desorbed into the solution. The explanation of this low Cr ion release from biomass we may give is very dense Cr-linked alginate-fucoidan matrix structure, therefore some sites might not be reachable by eluant ions.

4. Conclusions

The obtained results showed that the pretreated brown seaweed biomass selectively adsorbed Cr ions. Scanning Electron Microscope detected large surface area and a high Cr sorption capacity of *L. Japonica* biomass – almost 48% of its dry weight at pH 4.5 in comparison with Ca-alginate beads and industrial Duolite GT-73. The reason we may

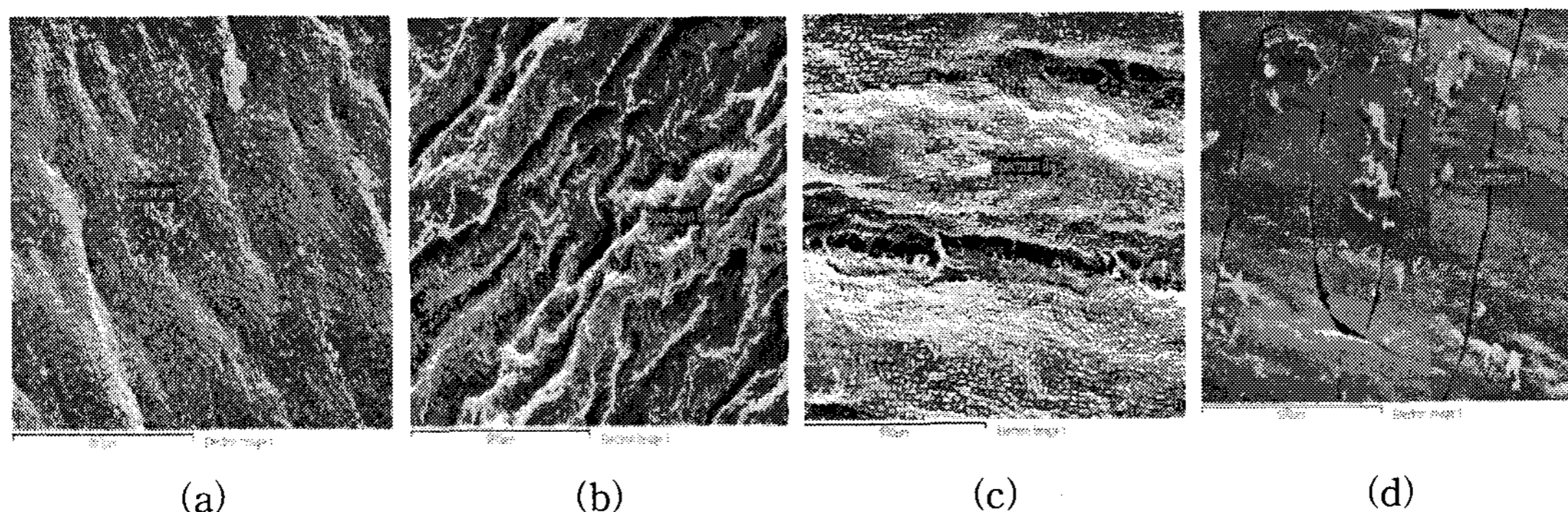


Fig. 5. Surface of biomass sorbed Cr(a), treated with HNO₃(b), Aqua Regia (c) and treated at 700°C (d).

suggest is the presence of fucoidan in the brown algae, which also is capable of heavy metal adsorption. Only 5% of Cr desorption was obtained by using 0.1 N HNO₃ and 1 N NaOH as an eluent. This low percentage of desorption reveals the stable Cr-alginate complex to be formed in the biomass. To ruin this strong bond the high temperature treating was used. The Aqua Regia treatment method reveals high desorption capacity - almost 38% of Cr ion release from biomass. Also 0.5 M H₂SO₄ solution elute Cr ion from algal biomass with 47%, but in both cases the biomass was injured by those oxidation agents.

References

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