Column study on Cr(VI)-reduction using the brown seaweed *Ecklonia* biomass

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Abstract

The potential use of the brown seaweed, *Ecklonia*, biomass as a bioreductant for reducing Cr(VI) was examined in a continuous packed-bed column. The effects of the operating parameters, such as influent Cr(VI) concentration, influent pH, biomass concentration, flow rate and temperature, on the Cr(VI) reduction were investigated. Increases in the influent Cr(VI) concentration and flow rate or a decrease in the biomass concentration inside the column led to a higher breakthrough of the Cr(VI) ions in the effluent. Particularly, the influent pH and temperature most significantly affected on the breakthrough curve of Cr(VI); a decrease in the influent pH or an increase in the temperature enhanced the Cr(VI) reduction in the column. For process application, a non-parametric model using neural network was used to predict the breakthrough curves of the column. Finally, the potential of the column packed with *Ecklonia* biomass for Cr(VI) detoxification was demonstrated.
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1. Introduction

Environmental pollution due to technological development is one of the most significant problems of this century. Chromium has widely used in electroplating, leather tanning, metal finishing and chromate preparation industries. Thus, wastewaters produced from these industries contain both trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). It is interesting to note that these two forms of chromium exhibit very different toxicities and mobilities. Cr(VI) usually occurs as highly soluble and toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$) and is a suspected carcinogen and mutagen [1]. In contrast, Cr(III) is relatively insoluble over pH 5 in aqueous systems and exhibits little or no toxicity than Cr(VI) [2]. Thus, the discharge of Cr(VI) into surface water is regulated to below 0.05 mg L^{-1} by the U.S. EPA [3].

Conventional methods for removing Cr(VI) ions from wastewaters include chemical reduction, electrochemical treatment, ion exchange and evaporative recovery. Such processes may be ineffective or extremely expensive when initial Cr(VI) concentrations are below tens of mg L^{-1}; thus, industry has begun to seek alternative ways of treating Cr(VI) wastewaters. Some researchers have proposed that Cr(VI) wastewaters can be treated by detoxification using living cell, such as *Pseudomonas putida* [4] and *Bacillus* sp. [5]. However, there are also some problems associated with the use of living cells, such as cell death due to Cr(VI) toxicity, supply of nutrients, complex facilities and separation of the liquid treated. To compete with conventional procedures, new methods must be economically viable as well as successful in contaminant removal. Biosorption, using biological materials, has known as an alternative process for the removal of heavy metals from aqueous

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solutions, as this novel approach is effective and cheap [6,7]. Because of these advantages, there has been extensive research exploring appropriate biosorbents that are able to effectively remove Cr(VI) [8–11].

Recently, the removal mechanism of Cr(VI) by brown seaweed, *Ecklonia*, biomass from aqueous phase was clarified, which differed from existing reports; the Cr(VI) was completely reduced to Cr(III) by contact with the biomass below pH 5, and Cr(III) appeared in the aqueous phase or partly bound onto the biomass [12–17]. Due to the consumption of protons during the Cr(VI) reduction, the reduction rate of Cr(VI) increased with decrease of the solution pH. The electrons required for the Cr(VI) reduction were supplied from the organic compounds presented in the biomass, resulting in oxidation of the biomass. It is meaningful to note that 223 g of the *Ecklonia* biomass was required for the complete reduction of 1 mol of Cr(VI), while 834 g of $FeSO_4 \cdot 7H_2O$, which is a common Cr(VI) reductant, is required. Based on these results, the abundant and inexpensive *Ecklonia* biomass can be proposed for use in the conversion of toxic Cr(VI) into the less or no toxic Cr(III).

In process application, the most effective apparatus for continuous operation is a column reactor, much like that used for ion exchange. Thus, many researchers have used a column packed with various biomasses capable of removing heavy metals [10,11,18–20]. Meanwhile, many mathematical models have been used to study column systems, and their dynamic behavior has also been well established [19,20]. All these models have been mainly originated from research on activated carbon sorption, ion exchange or chromatographic applications. However, in the case of Cr(VI) removal in the column, a few studies have been reported, but no theoretical model has been proposed to predict the experimental breakthrough data [10,11]. Since the removal mechanism of Cr(VI) by the *Ecklonia* biomass is different to that of cationic heavy metals, such as Pb(II) and Cd(II), all mathematical models reported to date do not describe the dynamic behavior of Cr(VI) removal in a column packed with the biomass.

As a continuation of our previous works [12–16], the use of *Ecklonia* biomass for the continuous detoxification of Cr(VI) is reported in this study. The effects of some operating parameters, such as influent Cr(VI) concentration, influent solution pH, biomass concentration, flow rate and temperature, were examined on the Cr(VI)-reduction performance in the column. In addition, a neural network was used to model breakthrough curves for the column. Finally, the potential of the column packed with *Ecklonia* biomass for Cr(VI) detoxification was demonstrated.

2. Materials and methods

2.1. Preparation of the biomass

The brown seaweed, *Ecklonia* sp., was collected along the seashore of Pohang, South Korea [21]. After swelling and rinsing with deionized-distilled water, the sun-dried biomass was cut into approximately 0.5 cm sized pieces. The cut biomass was treated with a $1 \, mol \, L^{-1} \, H_2SO_4$ solution for 24 h, which replaced the natural mix of ionic species with protons and sulfates. The acid-treated biomass was washed several times with deionized-distilled water and then dried at 100 °C for 24 h. The dried biomass was stored in a desiccator and used for column experiments.

2.2. Reagents

The Cr(VI) solution was prepared by dissolving analytical grade $K_2Cr_2O_7$ (Kanto) in deionized-distilled water, with pH adjustment to the desired values using concentrated H_2SO_4 solution. Potassium permanganate solution was prepared by dissolving 1.0 g $KMnO_4$ in 25 mL deionized-distilled water. Diphenylcarbazide solution was prepared by dissolving 250 mg of 1,5-diphenylcarbazide in 50 mL of HPLC-grade acetone, which was stored in a brown bottle.

2.3. Continuous reactor system

Continuous reactor used in this study consists of a 53 cm long and 3 cm internal diameter glass column, i.e., total volume of it is 375 mL. The column was densely packed with a known amount (52.5 or 26.3 g) of dried biomass. The process was operated in an up-flow mode, and set at constant temperature with the aid of a water bath. The flow rate was regulated with a variable speed pump, with a Masterflex L/S digital drive having an error below 0.5%. A damper was used to minimize the liquid fluctuation due to the mechanical movement of a pump head.

2.4. Reactor operation

To stabilize the reactor system before a run, deionized-distilled water, adjusted to the desired pH (2 or 3), was allowed to flow into the column packed with biomass for 24 h, at a flow rate of 10 mL min^{-1}. Thereafter, synthetic Cr(VI) wastewater was allowed to flow into the column. Intermittently, 10 mL of the effluent was sampled to measure the effluent pH, Cr(VI) and total Cr concentrations. After each column operation, packed-biomass was vacated from the column, and fresh dried biomass was packed and used for another operation. All experiments were performed without any buffer solution to avoid the addition of any external electrolytes, which may influence the biosorption process. The influent compositions and operating conditions of column are listed in Table 1. To quantify the removal capacity

Table 1
Operating conditions of the column reactor[a]

	[Cr(VI)] (mg L^{-1})	[B] (g L^{-1})	pH (−)	Q (mL min^{-1})	Temperature (°C)
Run 1	100	140	2.00	10	25
Run 2	200	140	2.00	10	25
Run 3	100	70	2.00	10	25
Run 4	100	140	3.00	10	25
Run 5	100	140	2.00	20	25
Run 6	100	140	2.00	10	45

[a] [B] and Q represent the concentration of biomass packed within the column and flow rate of influent, respectively.

of each column under given operating condition, the concept of bed number was used instead of operating time or volume, and it was calculated as follows:

$$\text{bed number} = \frac{\text{flow rate} \times \text{operating time}}{\text{total volume of column}} \quad (1)$$

Meanwhile, the accumulated amount of total Cr bound onto the biomass during each run was calculated as follows:

$$\text{uptake of total Cr} = \frac{\int_0^t \begin{array}{c}\text{difference between influent and}\\ \text{efflent concentrations of total Cr}\end{array}}{\text{dosage of biomass}} \quad (2)$$

2.5. Analytical methods

The concentration of Cr(VI) in the liquid samples was determined colorimetrically by the reaction with 1,5-diphenylcarbazide in acid solution. The absorbance of the resulting red–violet sample was measured at 540 nm using a spectrophotometer (Spectronic 21, Milton Roy Co.). To determine the total concentration of chromium, all the chromium was converted into the hexavalent state by oxidation with potassium permanganate at high temperature (120–130 °C). Thereafter, the oxidized chromium was analyzed by the above-mentioned method for Cr(VI) analysis. Since chromium in solution is mostly in the hexavalent or trivalent states, the concentration of Cr(III) can be obtained from the difference in concentration between the total and hexavalent chromium. The analytical method of chromium is detailed in standard methods [22].

After filtering and diluting the effluent samples, the soluble total organic carbon (TOC) and inorganic carbon (IC) concentrations were analyzed by using a TOC/IC analyzer (Shimadzu TOC 5000 A).

2.6. Neural network modeling

Neural network has been proved to be able to model non-linear systems, and successfully applied to various non-linear process models [23,24]. Recently, the use of neural network has gained popularity for modeling biological wastewater treatment processes [25,26]. Neural network can map a set of input patterns onto a corresponding set of output patterns after a series of past process data from a given system have been acquired. Moreover, neural network has a distinctive ability to learn nonlinear functional relationships without the requirement for structural knowledge of the process to be modeled.

A variety of neural network architectures and training algorithms have been proposed and used to model non-linear systems. However, there no guidelines exist for choosing network architectures for the optimal solution of a given problem. A feed-forward back-propagation neural network (FBNN) was employed for our purpose, which has been successfully applied in modeling a wide range of non-linear systems, especially chemical/biological engineering processes. A typical FBNN structure consists of one input layer, one (or multiple) hidden layer(s) and one output layer. Each layer could have a number of nodes (processing elements), which are connected linearly by
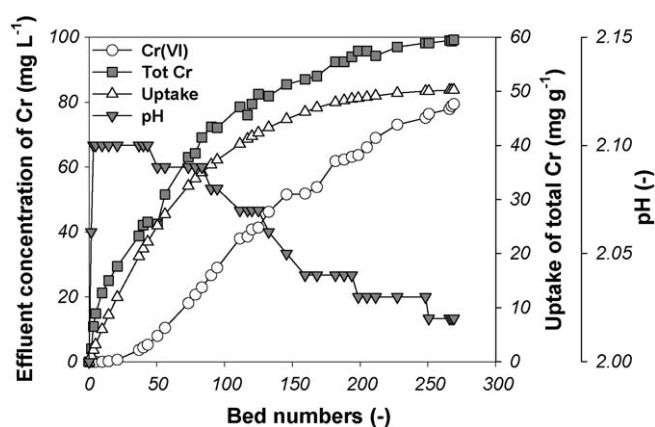

Fig. 1. Breakthrough curves for Cr(VI) removal under the conditions used in Run 1.

weights to the nodes in the neighboring layers. The training process adjusts weights to minimize the error between the measured output and the output produced by the network. Through this adjustment, the neural network learns the input–output behaviors of the system.

3. Results and discussion

3.1. Reduction of Cr(VI) into Cr(III) during continuous column operation

To examine the characteristics of Cr(VI) removal in the column packed with the *Ecklonia* biomass, the effluent profiles of pH, Cr(VI) and total Cr concentrations were investigated under the operating conditions used in Run 1 (Fig. 1). The effluent Cr(VI) concentration was below 0.1 mg L^{-1} for the first 15 beds, and then sigmoidly increased to 79.4 mg L^{-1} by the 274th beds. The total Cr concentration rapidly increased in the effluent, finally reached that of the influent level. The difference between the total Cr and Cr(VI) concentrations indicated that the Cr(VI) was reduced to Cr(III) by contact with the biomass packed inside the column. Meanwhile, the pattern of the total Cr concentration in the effluent indicated that a part of the total Cr had been adsorbed onto the biomass while passing through the column. A previous study using an X-ray photoelectron spectroscopy (XPS) showed that the chromium bound onto the *Ecklonia* biomass was not the hexavalent, but the trivalent form [12]. These results lead to the conclusion that the *Ecklonia* biomass could completely reduce the Cr(VI) into Cr(III), and the reduced-Cr(III) could be bound onto the biomass or exist as organic-complexed forms in the aqueous phase. However, as the operation of the column proceeded, the accumulated amount of chromium bound onto the biomass increased and reached 50.2 mg g^{-1} by the 274th beds (Fig. 1). It must be noted that trivalent chromium ions (Cr^{3+} and CrOH^{2+}) are barely adsorbed to the biomass below pH 2, due to the complete protonation of the functional group which are responsible for binding of cationic metals, i.e. the carboxyl group having a pK_H value of 4.6 [8,21]. Thus, it can be assumed that binding of the reduced-Cr(III) might
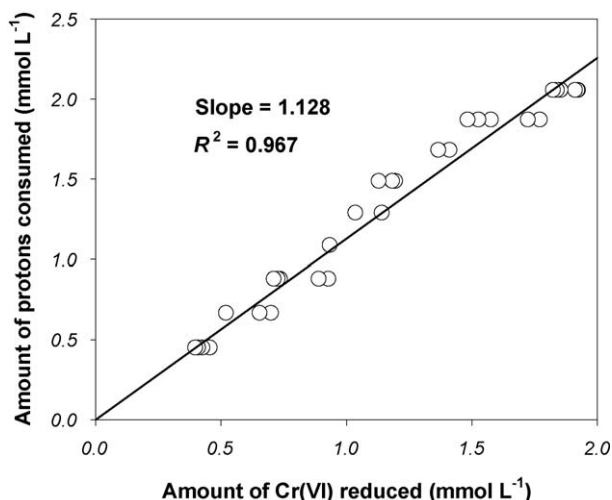
Fig. 2. Relation of proton consumption to Cr(VI) removal.

Fig. 4. Breakthrough curves for Cr(VI) removal under the conditions used in Run 2.

be different to that of trivalent chromium ions, with the former being stronger than the latter.

Monitoring of the effluent pH during the column operation showed an abrupt increase in the solution pH, from 2.00 to 2.10, for the initial three beds, but this maintained at 2.10 until the 30th bed (Fig. 1). However, as the Cr(VI)-reduction performance of the column decreased, the effluent pH also decreased, since protons was consumed during Cr(VI) reduction [12]. Fig. 2 shows the relation between Cr(VI) reduction and proton consumption. The reduction in the protons in the aqueous phase was proportional to the amount of Cr(VI) reduced; almost 1.13 mol of protons were consumed for the reduction of 1 mol of Cr(VI), which was similar to that obtained from the batch experiment, i.e. 1.15 ($\pm$0.02) mol of protons per mol of Cr(VI) [12].

Three moles of electrons are required for the reduction of 1 mol of Cr(VI) into Cr(III). In our system, the electrons were supplied from the biomass, resulting in the oxidation of the organic compounds present in the biomass. Therefore, as the column operation proceeded, the Cr(VI)-reduction performance of the column decreased due to the loss of available electrons present in the biomass. Fig. 3 represents the dynamics of the soluble total organic carbon (TOC) and inorganic carbon (IC) in the
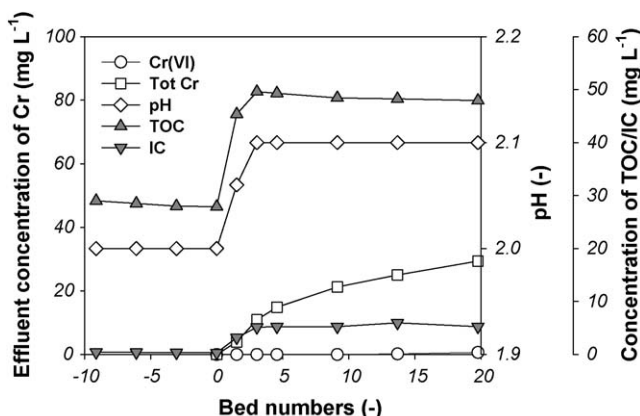

Fig. 3. Dynamics of TOC/IC in the effluent before and after the influx of Cr(VI) into the column.
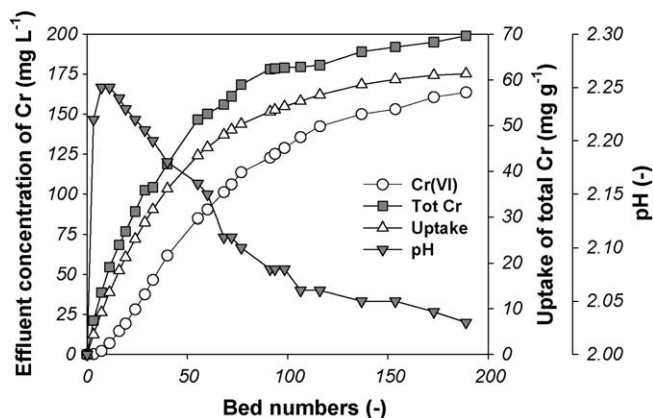
effluent before and after the influx of Cr(VI) into the column. The column was stabilized by passing Cr(VI)-free water, adjusted to pH 2; the effluent pH, TOC and IC concentrations were almost constant before the Cr(VI) influx. However, after flowing Cr(VI) into the column, the TOC and IC concentrations in the effluent were significantly increased. The increase of soluble organic carbons in the effluent implied that the oxidation of the biomass by Cr(VI) resulted in the partial release of soluble organic compounds. Particularly, the appearance of inorganic carbons (e.g., dissolved CO_2 and HCO_3^-) in the effluent suggested that parts of the organic carbon of the biomass were completely oxidized into CO_2. Furthermore, the surface of the biomass was observed to be seriously damaged after contact with Cr(VI).

3.2. Effects of various operating parameters on column performance

3.2.1. Effect of influent Cr(VI) concentration

To evaluate the effect of the influent Cr(VI) concentration on its reduction in the column, the concentration of it was increased from 100 to 200 mg L^{-1} under the same operating condition. Fig. 4 shows the breakthrough curve dynamics obtained from Run 2. Compared with the results obtained in Run 1, the change in the influent Cr(VI) concentration significantly affected the breakthrough curves. As expected, the higher the influent Cr(VI) concentration, the faster the breakthrough of effluent Cr(VI). The pH was found to increase from 2.00 to 2.25 during the initial seven beds, but decreased to 2.03 thereafter, implying that the increase in the influent Cr(VI) concentration caused more proton consumption. Meanwhile, the accumulated amount of chromium bound onto the biomass reached to 61.3 mg g^{-1} after 189 beds.

3.2.2. Effect of biomass concentration

Fig. 5 shows the breakthrough curve dynamics obtained from Run 3, where the biomass concentration was decreased from 140 to 70 g L^{-1}. With the reduction of Cr(VI), the decrease in biomass concentration caused decreases in the Cr(VI) and total Cr removal efficiencies by the column, due to the lack of the
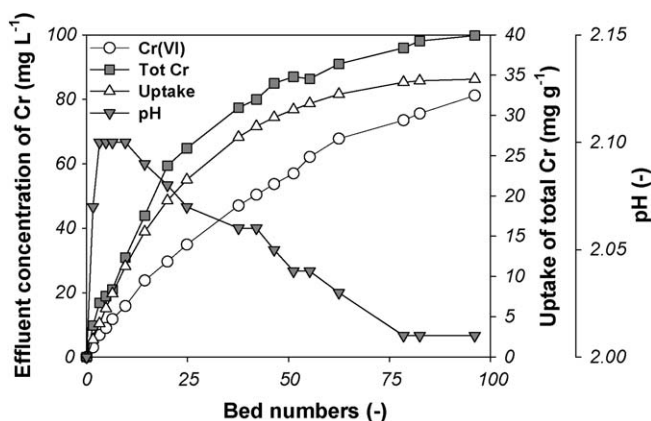
Fig. 5. Breakthrough curves for Cr(VI) removal under the conditions used in Run 3.

Fig. 7. Breakthrough curves for Cr(VI) removal under the conditions used in Run 5.

electrons required for Cr(VI) reduction and the functional groups responsible for chromium binding.

3.2.3. Effect of influent pH

The most important single parameter influencing the Cr(VI) reduction was the solution pH [12,14,15]. The batch experimental results showed that the reduction rate of Cr(VI) from aqueous solution increased with decreasing pH, due to the consumption of protons during Cr(VI) reduction. As expected, the higher the influent pH, the poorer the Cr(VI)-reduction efficiency (Fig. 6). Particularly, the shape of the breakthrough curve of Cr(VI) in the effluent was different to those for the other runs. There was an abrupt increase in the effluent Cr(VI) concentration during the initial beds, but a gradual increase thereafter. The insignificant difference between the total Cr and Cr(VI) concentrations indicated that most of the reduced-Cr(III) was bound onto the biomass. It is well known that cationic metal ions can easily adsorb to biosorbents at higher pHs [21]. There was also an abrupt increase in the effluent pH, from 3.00 to 3.88, during the initial 15 beds, followed by a gradual decrease, to 3.38, after 138 beds. It is worth to note that the amount of protons consumed was smaller than in Run1, i.e. 0.63 mol of protons per mol of Cr(VI). This was due to the significant buffering behavior of the
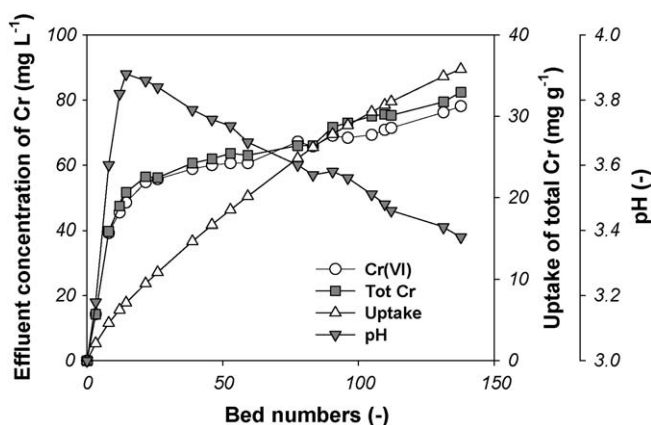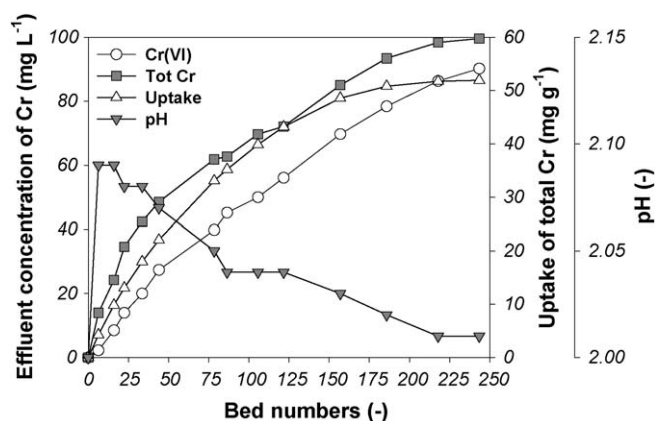
biomass inside the column. Fortunately, chromate wastewaters are generally acidic (below pH 3), so the buffering behavior of the *Ecklonia* biomass is advantageous, as it may avoid the need for adjustment of the solution pH by the addition of acids.

3.2.4. Effect of flow rate

The flow rate was changed from 10 to 20 mL min^{-1}, while maintaining the influent Cr(VI) concentration constantly at 100 mg L^{-1}. The plots of the effluent Cr(VI) and total Cr concentrations versus bed numbers are given in Fig. 7. The breakthrough curves of Cr(VI) became steeper and the breakpoint time decreased with increasing flow rate. Earlier saturation and a lower Cr(VI)-reduction efficiency were observed in Run 5. The two main reasons for this behavior were the insufficient reaction time inside the column and the diffusion limitation of the Cr(VI) ions onto the surface of the biomass. However, the accumulated amount of chromium bound onto the biomass was almost equal to that in Run 1.

3.2.5. Effect of temperature

The effect of temperature on Cr(VI) reduction was also examined in the column. As shown in Fig. 8, higher temperatures gave a gentler breakthrough curve in relation to the effluent Cr(VI)
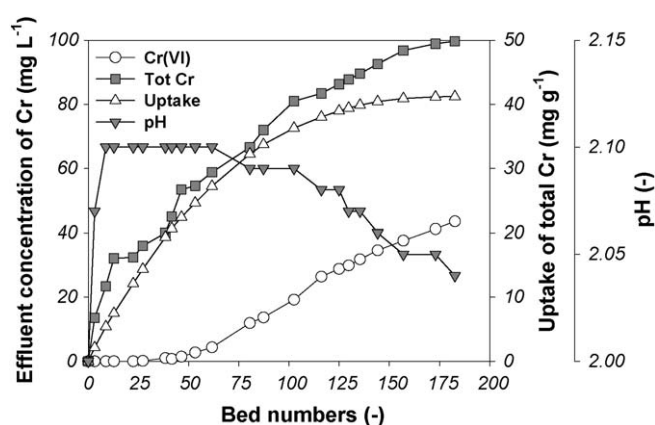

Fig. 6. Breakthrough curves for Cr(VI) removal under the conditions used in Run 4.
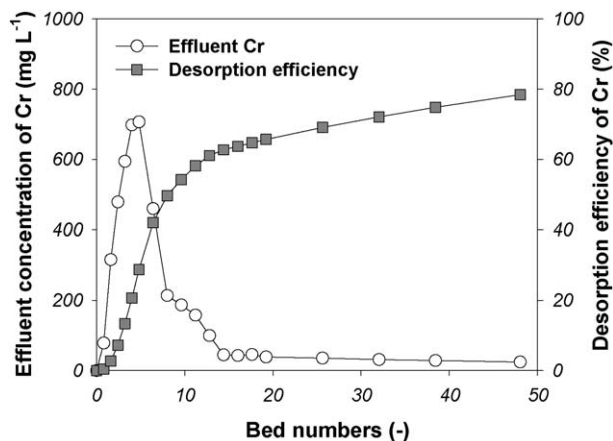

Fig. 8. Breakthrough curves for Cr(VI) removal under the conditions used in Run 6.

Fig. 9. Regeneration of the chromium loaded biomass using $1 \, mol \, L^{-1} \, H_2SO_4$ solution at a flow rate of $10 \, mL \, min^{-1}$.

concentration. This result was supported by previous batch experiment [12]. In general, increase in temperature increases the rate of a redox reaction [27]. The difference between the effluent total Cr and Cr(VI) concentrations was larger than that in Run 1, implying that more reduced-Cr(III) flowed out of the column without adsorption to the biomass. Indeed, the accumulated amount of chromium bound onto the biomass was only $41.2 \, mg \, g^{-1}$, which was smaller than the $50.2 \, mg \, g^{-1}$ in Run 1.

3.3. Chromium recovery from the column and reuse of the biomass

A suitable method for chromium removal/recovery from the biomass and reuse of the biomass is just as important as its accumulation from chromium wastewaters. The removal/recovery of chromium from the biomass was achieved using $1 \, mol \, L^{-1}$ H_2SO_4 solution. The desorption profile presented in Fig. 9, exhibited a sharp increase in trivalent chromium at the beginning of acid elution, suggesting that the chromium in the influent could be greatly concentrated by its biosorption inside the column. However, the desorption efficiency of chromium only reached to 78% after 48 beds. These results imply that chromium could not be completely removed or recovered from the biomass by flushing with acids. In general, the rate and efficiency of chromium desorption by acids were lower than those for divalent metal ions, such as Cd(II), Ni(II), Zn(II) and Pb(II) [8]. The poor rate and efficiency of chromium desorption by acids might be due to the physical or chemical properties of chromium binding, but little information with regard to these is available. Thus, there is a need for detailed study on chromium desorption from biosorbents.

Meanwhile, the column regenerated by acid flushing was subsequently operated with Cr(VI) containing solution, but showed poor Cr(VI)-reduction efficiency due to the remarkable exhaustion of the electrons present in the biomass. Therefore, chromium recovery using acid flushing might be ineffective, as the Cr(VI)-reduction performance of the column could not be regenerated, but a by-product, i.e. a very acidic solution con-

taining hundreds $mg \, L^{-1}$ of Cr(III), was produced, which would require additional treatment.

As an alternative for treating the chromium-laden seaweed biomass, Aravindhan et al. tested its application as a reductant in the preparation of a basic chromium sulfate (BCS) tanning agent [28,29]. The seaweed contains organic compounds, such as carbohydrates and proteins, and hence it can act as an excellent reductant. Furthermore, the chromium present in the seaweed biomass does not require separation since the end product is the trivalent form and the produced BCS can be successfully used as a tanning agent [28,29]. Meanwhile, the chromium-laden biomass may be burned, as the incineration of the seaweed biomass is energetically and economically attractive. As a result, the polluted wastes may be obtained in a highly concentrated form, with the costs of final storage greatly reduced.

3.4. Modeling of Cr(VI) reduction in the column: neural network modeling

As can be assumed, the theoretical modeling of Cr(VI) reduction in a column is very difficult, since the reduction mechanism of Cr(VI) by *Ecklonia* biomass is very complex, and remains to be fully elucidated [14]. There is a redox reaction between Cr(VI) and the biomass, a cationic adsorption of the reduced-Cr(III) and a change in the solution pH during Cr(VI) reduction. Above all, the heterogeneity of the biomass and the non-ideal dispersion of Cr(VI) ions inside the column make theoretical modeling more complex and less predictable than experimental data. In fact, derivation from the theoretical model describing the trends of Cr(VI) reduction in the column were shown to be extremely complicated, and the model was associated with partial differential equations, which were unsolvable and numerically unstable. Thus, the employment of this model for the control and optimization of the column was not feasible (data not shown).

In the approach of the present model, a FBNN model was applied to describe and predict the behavior of Cr(VI) reduction in the column. This approach is justified due to the difficulty and lack of agreement in representing the general chemistry and heterogeneous nature of the organic compounds, particularly the specific moieties involved in Cr(VI) reduction. Previous experimental results have shown the effects of the operating parameters, such as the influent Cr(VI) concentration, biomass concentration, influent pH, flow rate and temperature. Consequently, these five independent parameters, as well as the bed number, were included in the input layer to map the Cr(VI) concentration in the output layer for the column. A training set of 127 experimental data sets were selected to develop the model. The optimal neural network configuration was chosen by varying the number of hidden layers and the number of nodes within, based on the cross validation technique. The best network structure was determined as two hidden layers, with five nodes within, with three nodes in the second hidden layer. The optimized structure of the network used in the present study for describing the dynamics of Cr(VI) in the effluent is shown in Fig. 10. The hyperbolic tangent functions in the hidden layers and a linear function in the output layer gave the best performance in the
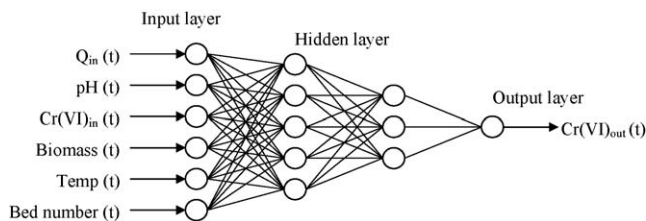
Fig. 10. Neural network architecture used for modeling the breakthrough curves.

training process, so were chosen as the activation functions:

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \qquad (5)$$

A generalized delta-rule, with a momentum and adaptive learning rate, was used for the training process, with the aid of MATLAB [30]. The performance of the neural network simulation was evaluated in terms of the root mean square error (RMSE) criterion. The RMSE performance index was defined as

$$\text{RMSE} = \sqrt{\frac{\sum (\hat{y} - y)^2}{n}} \qquad (6)$$

where y is the measured values, $\hat{y}$ the corresponding predicted values and n is the number of samples. The global quality of the trained network was tested by comparing the predicted and experimental values of an additional data set. The developed network model was thus examined for its ability to predict the response of experimental data not forming part of the training program. Fig. 11 shows the results obtained by the neural network simulation for both the training and tested data sets. The Cr(VI) concentrations were precisely predicted for the training data sets. The neural network simulation was also capable of satisfactorily estimating the Cr(VI) dynamics of the tested data sets. The RMSE for the training and tested data sets were 2.523 and 3.20, respectively. This result indicates that a neural network is a useful tool for accurate and cost-effective modeling of
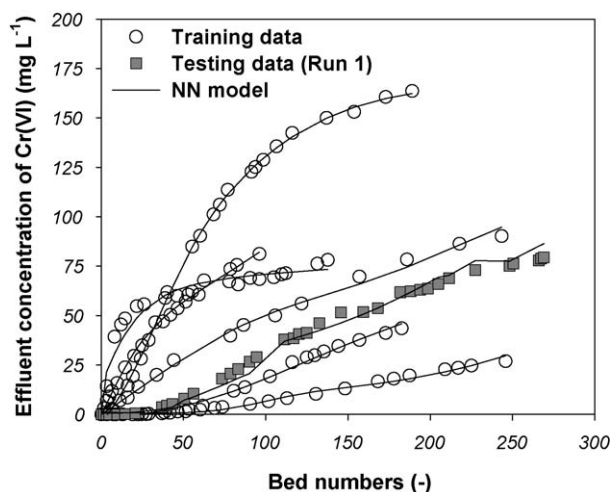
biological processes in the absence of other reasonably accurate process models.

4. Conclusions

In this work, a detailed experiment on the Cr(VI) reduction by the *Ecklonia* biomass in a column has been presented. Various experimental conditions were tested in order to investigate the influence of the main operating parameters on the breakthrough curves. As expected, increases in the influent Cr(VI) concentration and flow rate, or a decrease of the biomass concentration inside the column, led to a higher breakthrough of the Cr(VI) ions in the effluent. Particularly, the influent pH and temperature most significantly affected the Cr(VI) breakthrough curve; a decrease in the influent pH or an increase in the temperature enhanced the Cr(VI) reduction by the column. Given these results, it is meaningful to note that chromate wastewaters, particularly those produced from electroplating facilities, are acidic and warm.

For application of a process, a non-parametric model, using neural network, was tested to model the breakthrough curves of the column, which successfully predicted the experimental data. Therefore, the developed model may be used to predict the design and performance of a column process for Cr(VI) detoxification.

In conclusion, *Ecklonia* biomass can be used to convert toxic Cr(VI) to the less or no toxic Cr(III). The main advantages of using this biomass are the substantially lower cost of the material and its economic feasibility. Furthermore, the use of dead *Ecklonia* biomass is more advantageous for chromate wastewater treatment, as it is not affected by toxic Cr(VI), does not require a continuous supply of nutrients and is easily separated from the treated water after biosorption due to its macro structure. In addition, the chromium-laden biomass may be reused as a tanning agent.

Fig. 11. Predicted and experimental breakthrough curves of Cr(VI) in the effluent.

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