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Biological and chemical removal of Cr(VI) from waste water: Cost and benefit analysis

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Abstract

The objective of the present study is cost and benefit analysis of biological and chemical removal of hexavalent chromium [Cr(VI)] ions. Cost and benefit analysis were done with refer to two separate studies on removal of Cr(VI), one of heavy metals with a crucial role concerning increase in environmental pollution and disturbance of ecological balance, through biological adsorption and chemical ion-exchange.

Methods of biological and chemical removal were compared with regard to their cost and percentage in chrome removal. According to the result of the comparison, cost per unit in chemical removal was calculated €0.24 and the ratio of chrome removal was 99.68%, whereas those of biological removal were €0.14 and 59.3%. Therefore, it was seen that cost per unit in chemical removal and chrome removal ratio were higher than those of biological removal method. In the current study where chrome removal is seen as immeasurable benefit in terms of human health and the environment, percentages of chrome removal were taken as measurable benefit and cost per unit of the chemicals as measurable cost.

Keywords: Cost and benefit analysis; Heavy metal; Chrome; Adsorption; Ion-exchange

1. Introduction

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. The presence of these metals in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. Among these heavy metals, copper, chromium and zinc ingestion beyond permissible quantities causes various chronic disorders in human beings. It is well known that heavy metals can damage nerves, liver and bones and they block functional groups of essential enzymes [1–4].

Chromium is a toxic metal of widespread use. Of its two most common and stable oxidation states, trivalent and hexavalent. Hexavalent chromium [Cr(VI)] species are known to be much more dangerous than trivalent chromium Cr(III) species. Chromium(III) occurs naturally and is an essential nutrient that helps the body to use sugar, protein and fat. An intake of 50–200 mg of chromium(III) per day is recommended for adults. Chromium(VI) rarely occurs naturally, but is usually produced from anthropogenic sources. The International Agency for Research on Cancer (IARC) has determined that chromium(VI) is carcinogenic to humans. EPA has set the maximum level of total chromium allowed in drinking water at 100 mg/L. The remediation of chromium(VI) contaminated industrial effluents is gaining great interest due to limitations on potable water supplies [5]. Extensive use of chromium in many industries such as electroplating, steel productions, wood preservation and leather tanning results in releasing chromium containing effluents to the environment making it a serious pollutant and a severe threat to the ecological system [6,7]. Sorption is one of the more popular methods for the removal of chromium from the wastewaters. The solid adsorbent surface adsorbs the pollutants from the effluent with the quantity of the removed pollutant depending on the adsorption capacity of the sorbent [8]. The conventional methods described above for removing chromium species from effluents are restricted because of technical or economical constrains. Therefore, recent studies have concentrated on the development of low cost processes and the use of microorganisms has received

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much more attention in recent years since they carry wide range of binding sites for heavy metal ions [9].

Three main strategies can be considered for Cr(VI) removal from wastewaters: (i) reduction of hexavalent chromium to trivalent with subsequent immobilization as the hydroxide [10], (ii) sorption onto various materials, including ion-exchange and biosorption [11–16] and recently also (iii) membrane filtration. This latter has attracted increasing attention [17–19].

Cost and benefit analysis is the most common method used in decision making and determination of criteria to protect the environment, foreseeing possible environmental effects in application process of both biological and chemical methods.

Cost and benefit analysis is estimation of benefit from a project during its economic life time and expected cost followed by comparison of them referring to a certain year [20–23]. For approval of project implementation, this ratio must be 1 or higher than 1 [20,21,24].

In this study, cost and benefit analysis of biological and chemical removal of hexavalent chromium [Cr(VI)] ions were done. Cost and benefit analysis were done with refer to two separate studies, thesis studied by Şahin [25] and Kara on removal of Cr(VI) [26]. First one, Master of Science thesis was prepared by Kara in the Institute for Graduate Studies in Pure and Applied Science of Ondokuz Mayıs University in 1993. Second one is also Master of Science thesis which was prepared by Şahin in the Institute for Graduate Studies in Pure and Applied Science of Niğde University in 2003. Adsorption results obtained by the studies were compared due to their costs and benefits. For these purposes, each study was analyzed for its cost per unit and compared its social benefit. When social benefit was discussed, measurable and immeasurable benefits of both methods were determined. For determining of measurable benefits, Cr(VI) removal performances of both methods were compared. For determining of immeasurable benefits, Cr(VI) effects on human health were discussed.

2. Material and method

2.1. Material

In the present study, the study referred to and taken as a biological adsorption of Cr(VI) by using *Bacillus thuringiensis* T01001 stereotype which has been taken from University of Ankara, Department of Food Science and Technology (Ankara, Turkey). The strain was grown and maintained on both nutrient broth and nutrient agar. Cells were inoculated on nutrient agar plates by scratching and were left overnight at 60 °C in the incubator. Vegetative cell cultures were collected from petri dishes by the aid of serum physiologic and were harvested by means of centrifugation at 13,000 rpm for 5 min, then were washed twice with serum physiologic. Then the pellets of stock vegetative cell were put in petri dishes and dried at 60 °C for 24 h. However, to obtain spore–crystal mixture the petri dishes were kept for 15 days at room temperature after incubation. Then the same procedure was followed as that for vegetative cell. The pellets of spore–crystal mixtures were dried at 60 °C for 24 h. Biosorption of Cr(VI) has been studied from aqueous solution by using dried vegetative cell, mixture spore and crystal of the bacteria. Effects of pH, initial metal concentration and temperature have been tested [25]. Another study referred to was a chemical method and it had the title of "Cr(VI) Removal from Waste Water". In this study, Amberlite IRA-904 and IR-120 Plus resins have been used. Effect of mixing time, pH, concentration, anions (F^-, Cl^-) and regeneration have been tested in batch system [26]. Used chemical in both studies have been analytical grade.

The concentration of unadsorbed chromium(VI) ions in the solution was determined spectrophotometrically at 540 nm using 1,5-diphenyl carbazide as the complexing agent. The sample of 1 mL containing free chromium(VI) ions was mixed with 3.3 mL of 0.2 M H_2SO_4 and 1 mL of 1,5-diphenyl carbazide solution which was prepared by dissolving 0.25 g of 1,5-diphenyl carbazide in 100 mL of absolute alcohol. After 10 min, the pink-violet coloured solution was analyzed for the chromium(VI) ions [27].

2.2. Method

In the present study, a cost and benefit analysis of Cr(VI) removal due to biological removal by *B. thuringiensis* [25] and chemical removal by ion-exchanger Amberlite IRA-904 and IR-120 Plus [26] was done, using the Standard Mishan cost and benefit analysis method [20]. The cost and benefit analysis was completed in three stages: determination of costs and benefits, measurement of costs and benefits, assessment of costs and benefits. During the cost analysis, costs of chemical input in biological adsorption and chemical ion-exchange were taken as measurable direct cost and chrome removal ratios as measurable direct benefit. Through the data (1),

$$\frac{B}{C} = \frac{\sum_{t=0}^{n} B_t}{\sum_{t=0}^{n} C_t} > 1 \tag{1}$$

where B is the benefit, C the cost, B_t the benefit of any time interval and C_t is the cost of any time interval.

The formula above was used to estimate cost and benefit ratios [20,24]. As a result, bacteria and resin form with high net benefit was determined, calculating values with B/C ratio higher than 1. An assessment was made in terms of minimum-cost-maximum benefit, minimum cost-minimum benefit, and maximum cost-maximum benefit for organizations of chrome removal using these methods.

Factors leading to a decrease in cost or an increase in benefit were assessed in the context of cost–benefit analysis for organizations of Cr(VI) removal using ion-exchange method. Net social benefit was determined using the following formula:

$$\mathrm{NSB} = \mathrm{DP} - \mathrm{IC}$$

where NSB is the net social benefit, DP the desired payment and IC is the indemnified cost.

In both of the methods, chrome removal, the immeasurable indirect benefit in terms of human health and the environment, was taken as data and assessed regarding obligations of organizations and quantitative data were presented orally.

Table 1
Langmuir and Freundlich isotherm parameters

	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$ (mg/g)	b (L/mg)	R^2	K_F	n	R^2
Cell form						
Vegetative	83.33	7.92×10^{-3}	0.97	0.15	1.68	0.98
Spore–crystal mixture	72.99	2.36×10^{-2}	0.98	0.69	2.45	0.99
Resin type						
Amberlite IRA-904	30.58	0.163	0.92	5.82	2.26	0.96
Mixture	31.06	0.184	0.85	7.77	3.48	0.95

3. Results

Rapid industrialization and increasing urbanization including technological advancement grossly contaminating our environment by discharging the heavy metals in the effluents causing health hazards. Among all heavy metals, copper, chromium and zinc ingestion beyond permissible quantities causes various chronic disorders in human beings [28]. Potable waters containing more than 0.05 mg/L of chromium is considered to be toxic [29]. Adsorption technology enables one to use several adsorbents for removal of heavy-metal ion from wastewater [30]. In this study, we have planned to compare two separate studies [25,26] according to their cost and benefit parameters. For this purpose, we calculated the costs of chemical reagents, nutrients and biological components. We considered also effect of regeneration of resin and *B. thuringiensis* cells. After that, benefit analyses of all components were done. The origin of this study is that determination of method which is more effective to treat wastewater. Also, cost and benefit analysis were done to determine the method which is more applicable for industrial Cr(VI) removal from wastewater.

3.1. Adsorption isotherms

Two important physico-chemical aspects for evaluation of the adsorption process as a unit operation are the kinetics and the equilibria of adsorption. Modelling of the equilibrium data has been done using the Langmuir and Freundlich isotherms for both biological and chemical removal of Cr(VI) ions [31]. The Langmuir and Freundlich isotherms are represented as follows Eqs. (2) and (3), respectively.

$$\frac{1}{q_e} = \left(\frac{1}{q_{\max}}\right) + \left(\frac{1}{q_{\max} b}\right)\left(\frac{1}{C_e}\right) \tag{2}$$

$$\ln q_e = \frac{1}{n}(\ln C_e) + \ln K_F \tag{3}$$

where $q_{\max}$ is the maximum adsorption capacity (mg/g), q_e the experimental amount of Cr(VI) ion adsorbed at equilibrium (mg/g), C_e the concentartion of Cr(VI) ion in solution at equilibrium (mg/L), b the Langmuir isotherm constant, K_F the Freundlich constant and n is the Freundlich exponent. $1/n$ is a measure of the surface heterogeneity ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. Langmuir and Freundlich parameters of adsorption systems are summarized in Table 1 [25,26].

A cost and benefit analysis was done concerning biological adsorption and chemical ion-exchange method in batch systems for removal of Cr(VI). In industrial waste water and the data are presented in following tables.

Cost per unit corresponding to the ones in both vegetative cell and endospor for biological removal of Cr(VI) is €0.14 (Table 2). When compared in terms of benefit, benefit of Cr(VI) removal through vegetative cell was 33.2%, the original amount of which was 64.3 mg/L, whereas benefit of chrome removal through endospor was 54.3%, the original amount of which was 54.3 mg/L. In both of the studies, amount of microorganisms was 0.2 mg/L.

Cost per unit corresponding to the one in ion-exchange for removal of chrome is €0.095 and €0.092, respectively when 0.1% Amberlite and 0.1% mixed resin is used (Table 3). For 0.1% Amberlite the original amount of chrome was 50.20 mg/L

Table 2
Amounts of chemical input used for measurement of removal and cost per unit in chemical removal of Cr(VI)

Chemicals	Vegetative cell		Mixture (endospor crystal endotoxine)	
	Amount of chemical substance (g or L)	Current cost (€)	Amount of chemical substance (g or L)	Current cost (€)
Nutrient agar	0.60 g	0.064	0.60 g	0.064
Nutrient broth	0.26 g	0.064	0.26 g	0.064
Serum physiologic	0.18 g	0.001	0.18 g	0.001
Sulfuric acid (H_2SO_4)	0.071 L	0.0003	0.071 L	0.0003
Ethanol	0.001 L	0.0078	0.001 L	0.0078
1,5-Diphenyl carbazide	0.0025 g	0.004	0.0025 g	0.004
Total cost (€)		0.14		0.14

Table 3
Chemical input used for removal of Cr(VI) concerning 0.1 g amberlite and mixed resin and for measurement of removal and cost per unit

Chemical input	Amberlite IRA 904		Mixed resin	
	Amount of chemical substance (g or L)	Current cost (€)	Amount of chemical substance (g or L)	Current cost (€)
Amount of resin	0.1 g	0.0013	0.1 g	0.0098
1,5,-Diphenyl carbazide	0.01 g	0.022	0.01 g	0.022
Asetone	0.002 L	0.0092	0.002 L	0.0092
Sulfuric acid (H_2SO_4)	0.0108 L	0.050	0.0108 L	0.050
Total cost (€)		0.095		0.092

Table 4
Chemical input used for removal of Cr(VI) concerning 1.5 g Amberlite and Mixed Resin and for measurement of removal and cost per unit

Chemical input	Amberlite IRA 904		Mixed Resin	
	Amount of chemical substance (g or L)	Current cost (€)	Amount of chemical substance (g or L)	Current cost (€)
Amount of resin	1.5 g	0.19	1.5 g	0.15
1,5-Diphenyl carbazide	0.01 g	0.022	0.01 g	0.022
Asetone	0.002 L	0.0092	0.002 L	0.0092
Sulfuric acid (H_2SO_4)	0.0108 L	0.051	0.0108 L	0.051
Total cost (€)		0.27		0.24

and chrome removal amount was 51.85%, for 0.1% mixed resin the original amount of chrome was 50.04 mg/L and chrome removal amount was 63.02%.

Cost per unit in ion-exchange for removal of Cr(VI) is 0.27% and €0.24, respectively when 1.5% Amberlite and 1.5% mixed resin is used (Table 4). It was seen that Cr(VI) removal ratios were 99.62 and 99.69%, respectively. For 1.5% Amberlite the original amount of Cr(VI) was 50.20 mg/L, for 1.5% mixed resin the original amount of Cr(VI) was 50.04.

Costs per unit for regenerators of various concentration levels used in resin regeneration and ratios for removal of Cr(VI) for resins after regeneration were calculated (Table 5).

Best removal of Cr(VI) ratios of biological and chemical methods used in removal of Cr(VI) and costs per unit are presented in Table 6. In biological method, the highest ratio of Cr(VI) removal is 59.3% for endospor and it is 99.69% for 1.5% mixed resin in chemical method.

4. Discussion

A cost–benefit analysis was done for vegetative cell and endospor, which are two different forms of *B. thuringiensis* used in biological adsorption (Table 2). For the two bacteria forms, Cr(VI) removal ratios were taken as measurable benefit

Table 5
Cost per unit for regenerators of various concentration levels used in regeneration and ratios for removal of Cr(VI) for resins after regeneration

Regenerator	Amberlite IRA 904			Mixed Resin		
	Cost per unit for regenerator (€)	The original amount of Cr(VI) (Co mg/L)	Cr(VI) removal (%)	Cost per unit for regenerator (€)	The original amount of Cr(VI) (Co mg/L)	Cr(VI) removal (%)
NaOH (1N)	50.20	50.20	51.85	50.20	50.28	99.51
NaOH (0.1N)	0.0031	50.20	74.74	0.0031	50.28	85.22
KCl (0.1N)	0.012	50.20	86.84	0.012	50.28	99.68
NaCl (0.1N)	0.0041	50.20	91.45	0.0041	50.28	99.64

Table 6
Cost per unit corresponding to best removal of Cr(VI) ratios of biological and chemical methods used in removal of Cr(VI)

	Biological method		Chemical method	
	Vegetative cell	Endospor crystal endotoxine	Amberlite IRA 904	Mixed resin
Amount of microorganisms	0.2	0.2	–	–
Amount of resin (g/100 mL)	–	–	1.5	1.5
The original amount of Cr(VI) (mg/L)	37.4	34.7	0.20	50.04
Cr(VI) removal ratio (%)	38.3	59.3	99.62	99.69
Total cost (€)	0.14	0.14	0.27	0.24

and chemical substances were taken as measurable cost per unit. Given the fact that Cr(VI) removal per liter is 0.00005 kg/day (50 mg/L) on average in a year, using vegetative cell and endospor, Cr(VI) removal is 0.01825 kg/year in a year. According to the data, cost of annual chemical input is €51.1. The ratio of benefit/cost (*B*/*C*) for only chemical input is 0.65 (32.3/51.1) for vegetative cell and 1.1 (54.3/51.1) for endospor.

A cost–benefit analysis was done for two different forms of resin individually used in ion-exchange. Total cost and ratios of Cr(VI) removal per unit for 0.1% Amberlite IRA 904 and 0.1% mixed resin (Amberlite IRA 904 and Amberlite IR 120 Plus) were calculated. The same ratios were calculated for 1.5% Amberlite and 1.5% mixed resin (Table 4).

Cost of chemical input for Cr(VI) removal of 0.01825 kg/year, which is for 0.1% Amberlite (cost per unit) is €34.68 on laboratory scale. The *B*/*C* ratio for 0.1% Amberlite is 1.49 (51.85/34.68).

Cost of chemical input for Cr(VI) removal for 0.1% mixed resin (cost per unit) is €33.58 on laboratory scale. The *B*/*C* ratio is 1.87 (63.02/33.58).

The *B*/*C* ratio for the two resin forms is higher than 1. In that case, Cr(VI) removal is possible through the use of the two resins. However, since the *B*/*C* ratio is higher in mixed resin, this one should be preferable.

Cost per unit corresponding to the one on laboratory scale for 1.5% Amberlite concerning annual Cr(VI) removal is €98.55 and cost per unit is €87.6 when 1.5% mixed resin is used. The *B*/*C* ratio for 1.5% Amberlite is 1.0 (99.62/98.55) and is 1.13 (99.69/87.6) for 1.5% mixed resin.

The *B*/*C* ratio for the two resin forms is 1 or higher than 1. Organizations should prefer Cr(VI) removal through mixed resin when it aims at low cost but high benefit.

That resin can be regenerated makes it superior to other chemical methods. At the same time, when chemical input is considered cost of resin decreases. Annual Cr(VI) removal calculated with cost per unit requires 547.5 g Amberlite and mixed resin. Annual cost per unit for 547.5 g Amberlite to be used in a year is €69.35, whereas annual cost for mixed resin is €54.75. Given an organization using the chemical method for Cr(VI) removal, €69.35 and €54.75 are annual desired amounts for that organization. Since regeneration is completed through 3 g Amberlite and 2.5 g mixed resin, 182.5 g Amberlite (547.5/3) and 219 g mixed resin (547.5/2.5) are used regenerated. In that case, the organization pays €23.12 for 182.5 g Amberlite and €21.90 for 219 g mixed resin. The difference in between is customer excess for the organization and the cost will be net social benefit for the organization. Net social benefit is NSB = 69.35 − 23.12 = €46.23 for Amberlite and NSB = 54.75 − 21.90 = €32.85 for mixed resin.

Best regenerator for Amberlite is 0.1N NaCl (Table 4). Annually 182.5 g Amberlite is regenerated, therefore 35.59 g NaCl is used in regeneration and cost per unit is €0.25. It is an additional cost of €0.25 for the organization. However, the organization can afford that cost in order to provide the net social benefit of €46.23 through regeneration of resin. Best regenerator for mixed resin is 0.1N KCl (Table 5). Annually 219 g resin is regenerated. Therefore, 65.26 g KCl is used and the annual cost is €1.06. It is an additional cost of €1.06 for the organization. However, the organization can afford that cost in order to provide the net social benefit of €32.85 through regeneration of resin. In that case, total net social benefit for the organization is:

$$\text{For Amberlite}\quad \sum \text{NSB} = 69.35 - (23.12 + 0.25),$$

$$\sum \text{NSB} = €45.98$$

$$\text{For mixed resin}\quad \sum \text{NSB} = 54.75 - (21.90 - 1.06),$$

$$\sum \text{NSB} = €31.79$$

As long as the organization uses regeneration step, its total net social benefit will be increased as €45.98 for Amberlite and €31.79 for mixed resin, respectively.

The highest ratio is through endospor in biological Cr(VI) removal and through 1.5% mixed resin in chemical removal (Table 6).

Net social benefit for the organization is high quality of refining in water and re-use of water. The data here will provide the organization with profit since it decreases the denominator in the ratio of benefit/cost. Therefore, it will be immeasurable indirect social benefit fort he organization.

Although ion-exchange has a high cost, it provides high benefit in Cr(VI) removal. However, value of refining water in use is higher than those in other chemical refining systems but lower than those in biological methods.

When biological adsorption technique is used by industrial organizations that release Cr(VI) in waste water, the financial benefit fort he organization is Cr(VI) removal at a low cost through low costs of process and investment. Environmental benefit is Cr(VI) removal in waste water without any damage to ecosystem. Another environmental benefit is high quality of refining and use of refined water for different purposes. As a result of the environmental and financial benefits by industrial organizations, the organization will take measures to protect the environment and make a profit at a low environmental cost. Also, the organization will fulfill its social responsibility concerning the environment.

“To what extent can you risk your health?” If a person loses his health while getting the advantage of a benefit provided by an organization, especially if he dies then the benefit is useless. This benefit will increase in health expenses for that person and a decrease in life quality because of the treatment process. Also, loss of working power in long or short run, increases in personal expenses and decreases in salary/wages will function as costs for benefit/cost ratio and be included in measurable costs. A decrease in life quality and life standard because of sociological or psychological problems in treatment process does not have a measurable cost. The contribution of a waste water refining plant to human health does not have a measurable value. Industrial organizations fulfill their social responsibilities concerning health of people and the society by establishing such systems.

5. Conclusions

According to the data obtained by the analysis, costs of Cr(VI) removal through biological adsorption and Cr(VI) removal ratios are lower than those of ion-exchange. Chemical sorption method has high benefits at high costs. Besides, various chemicals included in refining water lead to a decrease in quality. Although biological adsorption has a low Cr(VI) removal ratio, biological methods at low costs are preferable; because it contributes to the environment much. Also, the quality of refining water is high and it can be used for irrigation. It is now thought that biological adsorption, which is not being used yet, is promising for Cr(VI) removal at low concentrations in waste water and will have a potential application field in the future.

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