Hindawi Publishing Corporation
Journal of Chemistry
Volume 2013, Article ID 158167, 7 pages
http://dx.doi.org/10.1155/2013/158167

Research Article

Removal and Recovery of Chromium from Solutions Simulating Tannery Wastewater by Strong Acid Cation Exchanger

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Received 6 December 2012; Accepted 20 January 2013

Academic Editor: Alberto Ritieni

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The process in this study was conducted on removal of chromium(III) in a solution simulating a typical spent chrome tanning bath by the resin having matrix of styrene-divinylbenzene-based macroporous sulphonate, Amberjet 1200Na. The column experiments were carried out with the bed volumes of the resin as 751 mL and 1016 mL for different installation systems of the laboratory-scale pilot plant. The feeding solutions in the bed volumes of 200 and 190 were used for each installation system. The regeneration behaviour of the resin was determined by using reverse regeneration procedure with the solution of hydrogen peroxide in alkaline. The regeneration kinetics of the exhausted resin was examined with a range of the solutions having different concentration series of the alkaline hydrogen peroxide. The solutions of the basic chromium sulphate were recycled for each installation system following the regeneration cycles. The chromium ions in effluent were quantitatively eluted, and satisfactory removal of chromium(III) and recovery of chromium(VI) were achieved.

In memory of Wolfgang H. Höll

1. Introduction

Tannery industry plays an important role with respect to environmental pollution due to the disposal of large volumes of solutions of tanning baths. The discharge of chromium rich tannery effluent is a serious threat for environment with high concentrations of organic and inorganic components that they create risk to human health and environmental aspects [1]. The minimization of wastes and the applications for reusing procedures are, therefore, highly important in tannery industry [2]. The chromium(III) compounds are mainly toxic components of tannery wastewater, and they are used in various industries such as metallurgy, production of pigments, electroplating, and leather tanning [3] by applications for conservation/stabilisation of proteins of animal hides. Consequently, tannery wastewaters contain large quantities of chromium; a major potential contributor has existed for chromium pollution in the environment.

Trivalent chromium is an essential trace element and hazardous at relatively high doses interest in respiration [4]. The chromium is relatively stable and slowly oxidised to the much more toxic hexavalent chromium. Therefore elimination of hexavalent chromium has gained much more interest.

During tanning procedure chromium is used as basic chromium(III) sulphate compound, and most of the chromium is absorbed by means of hides, and the remaining part, therefore, occurs in the wastewater. The several processes have been studied and developed for treatment of chromium-bearing wastewaters. The precipitation methods by means of lime are conventional procedures to remove chromium(III) as $Cr(OH)_3$ under the neutral or basic conditions [5], and the elimination of chromium hydroxide is efficient due to its low solubility. The further investigated methods have included ion exchange, reverse osmosis, liquid-liquid extraction, liquid membranes, and foam

separation [6, 7]. Cetin et al. present a study on the exchange of Cr(III) species from both $CrCl_3$ and basic chromium sulphate solutions with strong acid ion exchangers [8].

The ion exchange methods have provided an efficient removal and recovery of chromium from liquid effluents. The different laboratory-scale processes have been designed to recover Cr(III) and Cr(VI) ions from electroplating industry wastewater after separation methods. During the predominant valency, Cr(VI) ions are retained on a strongly basic resin, Dowex IX8, and the original and reduced Cr(III) in the solution has been recovered by using weak acid cation exchanger, Amberlite IRC 50 [9]. Some procedures are based on solid phase extraction methods by using chelating resins such as Amberlite XAD1180 [10] and Dowex M 4195 [11]. These methods have been applied for determination of Cr(III), Cr(VI), and total chromium in environmental samples by means of oxidation of Cr(III) to Cr(VI). A study is presented on biosorption characteristics of Cd(II) and Cr(III) ions from aqueous solution by using the moss biomass [12]. The optimum biosorption conditions and maximum biosorption capacity of biomass have been determined by taking place of chemical ion exchange. Petruzzelli and coworkers have investigated some processes based on ion exchange for removal and recovery of Cr(III) from tannery wastes by weak electrolyte carboxylic resin [13–15]. These processes are able to remove chromium from the liquid effluent followed recovery with a regeneration step. A process has been developed with an application of strong acid cation exchangers by Akcin et al. [16]. The investigations including chelating and strong acid cation exchanger resins have been presented. Kocaoba and Akcin have studied sorption onto various cation exchangers from basic chromium sulphate solutions [17, 18]. The regeneration procedure of trivalent chromium with alkali peroxides has been presented by means of oxidation of the chromic species to anionic chromate with the aim of improving the regeneration efficiency of the resin [19].

The objective of this work is the removal of chromium from solutions simulating tannery wastewater with a strong acid cation exchanger, Amberjet 1200Na, by using multisorption and regeneration cycles. This study also presents improving the efficiency of the regeneration by using regenerant solutions at different initial concentrations of hydrogen peroxide in alkali media and kinetics of the oxidative regeneration.

2. Experimental

2.1. Materials for Column Studies. The strong acid cation exchanger resin, Amberjet 1200Na, was used for column studies and also batch experiments for kinetic of regeneration. The resin was conditioned with the solution of 0.5 M sulphuric acid. Table 1(a) shows the main physicochemical properties of the resin investigated [20], whereas Table 1(b) shows the pH and the initial chromium(III) concentrations of the solutions simulating tannery wastewaters. The analytical reagent grade basic chromium sulphate Merck (Darmstadt, Germany) and bidistilled pure water were used throughout the experiments. The solutions of the basic chromium sulphate bearing chromium(III) in the concentrations of 83 mg/L and 117 mg/L were used as feeding solutions for exhaustion procedures of different installation systems. The liquid phase was taken for each hour to determine concentration of the chromium in influent by an automatic sampler during exhaustion. The pH values of the solutions simulating tannery wastewaters were measured by a pH meter with a model of knick 704. The sample solutions were filtered by millipore filters having size pore of 0.45 μm and acidified with concentrated nitric acid solution before measurement. The exhaustion and regeneration of the column were carried out at flow rates, respectively, of 10 BV/h and 2 BV/h. The upflowing elution for exhaustion and downflowing elution for regeneration were run to minimize problems in the column able to change flow rate in the presence of the gase bubbles of oxygen consisting of disproportionation reaction of the hydrogen peroxide in alkaline media.

Table 1: Manufacturer data of the resin (Rohm and Haas 1998 [20]).

(a) The properties of the resin, Amberjet 1200Na

Matrix	Styrene divinylbenzene copolymer
Functional groups	Sulfonic acid
Physical form	Insoluble, amber beads
Ionic form as shipped	Sodium
Total exchange capacity	2.0 meq/mL minimum (Na^+ form)
Moisture holding capacity	43 to 47% (Na^+ form)
Shipping weight	53 lbs/ft^3
Harmonic mean size	0.57 to 0.67 mm
Uniformity coefficient	1.2 maximum
Maximum reversible swelling	Approximately 10% (from Na^{+4} form to hydrogen)

(b) Suggested operating conditions of the resin

pH range	0 to 14		
Maximum operating temperature	250°F		
Minimum bed depth	24 inch minimum		
Service flow rate	1 to 6 gpm/ft^3		
Maximum service velocity	25 gpm/ft^2		
Regenerants (100%)	NaCl	HCl	H_2SO_4
Flow rate (gpm/ft^3)	2 to 8	2 to 5	2 to 20
Concentration (%)	10	4 to 10	1 to 8
Level (lbs/ft^3)	3 to 15	2 to 8	2.5 to 12.5
Minimum contact time	20 minutes		
Slow rinse	15 gal/ft^3 at regeneration flow rate		
Fast rinse	8 to 22 gal/ft^3 at service flow rate		

2.2. Materials for Regeneration Studies. A laboratory-scale device has been used for experiments on kinetic of the regeneration. The installation is consisted of a vessel containing 2.0 L of the regenerant solution, a basket of the resin at the

Table 2: The composition of the regenerant solutions.

The series of experiment	The concentration of NaOH (mol/L)	The concentration of H_2O_2 (mol/L)
1	0.1	0.1
		0.2
		0.3
2	0.2	0.1
		0.2
		0.3
3	0.4	0.1
		0.2
		0.3
		0.4

diameter of 10 cm to store resin material, and a mechanical stirrer rotating with a constant rate which is adopted to the basket of resin.

The regeneration of the exhausted resin was realised with the solutions of 0.3 M H_2O_2 and 0.2 M NaOH followed by sulphuric acid solution in the concentration of 0.5 M throughout the experiments.

The batch experiments are carried out to determine the efficiency of the regeneration. The sample of 100 g of the resin in hydrogen form was put into a small column and was exhausted with 1 liter of the solution of basic chromium sulphate in the concentration of 500 ppm. The exhausted resin was centrifuged at 5000 rpm for 20 minute before weighing. The 2.0 g of the exhausted resin was taken to the basket of the resin and was placed into the vessel of reaction containing the solution of the alkaline hydrogen peroxide in the volume of 2.0 L. The basket stirrer was moved in the regenerant solution for one hour, while the stirrer worked at 200 rev./min. This procedure was repeated by using a series of different concentrations of solutions of H_2O_2 and NaOH. The samples of 500 μL were taken from the solution of regenerant to measure concentration of the chromium for each 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 50 min, and 60 min. The samples were diluted to 20 mL and were acidified by means of solution of nitric acid. The concentrations of chromium were determined by an atomic absorption spectrophotometer with a model of Varian Spectra 300 and air-acetylene flame. Table 2 shows the composition of regenerant solutions by the concentrations of sodium hydroxide and hydrogen peroxide.

2.3. Materials for Pilot Plants. The different laboratory-scale pilot plants mentioned as installation I and II were designed to operate the equivalent exhaustion, regeneration performance obtained in the laboratory investigations. The plants are made of ion exchanger columns, reservoirs for feeding, dosage pumps, automatic samplers, and a pH controlling system with a pH control unit and a pH electrode. Table 3 shows the characteristics of the pilot plants. The several exhaustion and regeneration cycles were run with satisfactory performances for both systems.

Table 3: The characteristics of the pilot plants.

	Installation I	Installation II
Column height (m)	30.00×10^{-2}	19.40×10^{-2}
Column diameter (m)	6.70×10^{-2}	10.00×10^{-2}
Bed height (m)	21.31×10^{-2}	12.94×10^{-2}
Resin bed volume (mL)	751	1016
Exhaustion flow rate (BV/h)	10	10
Regeneration flow rate (BV/h)	2	2
Effluent volume (BV)	200	183
Removal of chromium (%)	98.70	89.24
Recovery of chromium (%)	81.56	92.50

3. Results and Discussion

3.1. Method for Elimination and Recovery of Chromium(III). The ion exchange process is based on a strong acid cation exchanger resin, Amberjet 1200Na, for setting exhaustion-regeneration behaviour of the resin. The resin matrix was converted to the H^+ form from Na^+ according to the following reaction as the exhaustion step was operated on H^+ form:

$$\overline{R\text{–}SO_3{}^-Na^+} + H^+ + H_2SO_4 \longrightarrow \overline{R\text{–}SO_3{}^-H^+} + Na^+ + HSO_4{}^- \quad (1)$$

The pH range of the effluent was about 3.00 to avoid precipitation of the chromium hydroxides onto resin.

The exchange reaction of chromium(III) ions can be summarized as follows:

$$\overline{R\text{–}\left(SO_3{}^-H^+\right)_3} + Cr^{3+} \longrightarrow \overline{R\text{–}\left(SO_3{}^-\right)_3Cr^{3+}} + 3H^+ \quad (2)$$

The chromium(III) species have an efficient displacement with oxidation of trivalent to hexavalent although trivalent chromium has a strong preference to resin. Therefore, the chromic species were oxidated by using alkaline hydrogen peroxide solution with the aim of regeneration of the resin.

The reaction of oxidation was carried out with the solutions of 0.2 M of NaOH and 0.3 M of H_2O_2 according to the following reaction:

$$\overline{2R\text{–}\left(SO_3{}^-\right)_3Cr^{3+}} + 10NaOH + 3H_2O_2 \longrightarrow \overline{2R\text{–}\left(SO_3{}^-Na^+\right)_3} + 2Na_2CrO_4 + 8H_2O \quad (3)$$

Another redox reaction has occurred with the disproportionation of the hydrogen peroxide solution in alkaline media:

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \quad (4)$$

This reaction may be significant only when H_2O_2 is used in excess over the stoichiometric value. The stoichiometric value of hydrogen peroxide was calculated for installation I and installation II, respectively, as 0.360 mol and 0.664 mol.

3.2. Optimization of the Regeneration Efficiency. The regeneration efficiency of the resin was investigated with the aim

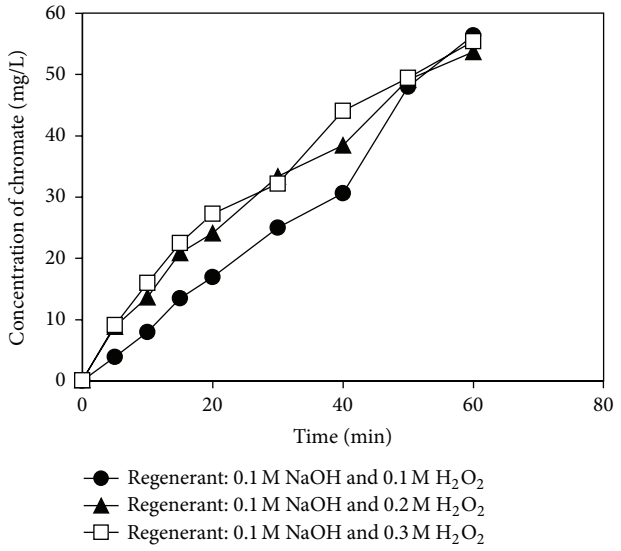


Figure 1: The regeneration efficiency depends on the amount of regenerant solutions. (The amount of exhausted resin: 2.0 g; the speed of the stirrer; 200 rev./min; the volume of regenerant solution is 2.0 L) (serie I).

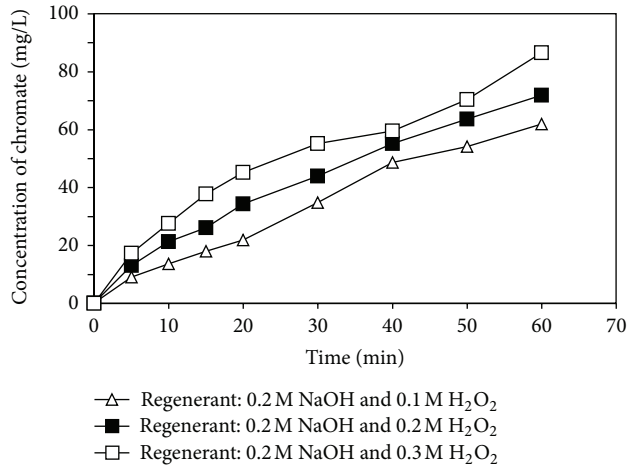


Figure 2: The regeneration efficiency depends on the amount of regenerant solutions. (The amount of exhausted resin; 2.0 g; the speed of the stirrer; 200 rev./min; the volume of regenerant solution is 2.0 L) (serie II).

of developing the displacement of chromium(III) ions from the resin, Amberjet 1200Na. The efficiency of regeneration for exhausted resin was determined by using regenerant solutions in different concentrations. The regeneration allows an effective displacement of chromium(III) species from the exchanger. Although the performance of the regeneration has been more effective by using higher concentration of hydrogen peroxide and sodium hydroxide solutions on the other hand the resin matrix has had oxidation with increasing concentrations of hydrogen peroxide. The oxidation of the resin has occurred in the concentration of H_2O_2 of more than 0.3 M, and it was observed by changing the colour of the resin from brown to yellow. Therefore, the concentration of the hydrogen peroxide has to be limited to about 0.3 mol/L to avoid substantial oxidation of the exchanger matrix.

Figures 1, 2, and 3 show the regeneration efficiency to be applied with solutions of 0.3 M of H_2O_2 and 0.2 M of NaOH depending on different kind of regenerant solutions.

4. Exhaustion/Regeneration Behaviour of the Resin

The experiments with the resin of Amberjet 1200Na are based on different installation systems of the laboratory-scale pilot plants. The height and the diameter of the ion exchange columns were, respectively, 30.00×10^{-2} m; 6.70×10^{-2} m and 19.40×10^{-2} m; 10.00×10^{-2} m for installation systems I and II. The columns have been filled with the volumes of the resin as, respectively, 751 mL and 1016 mL for both systems. While the chromium(III) concentrations of the feeding solutions were 83 mg/L (pH: 2.97) and 117 mg/L (pH: 2.98) for systems, respectively, as installation I and installation II the chromium

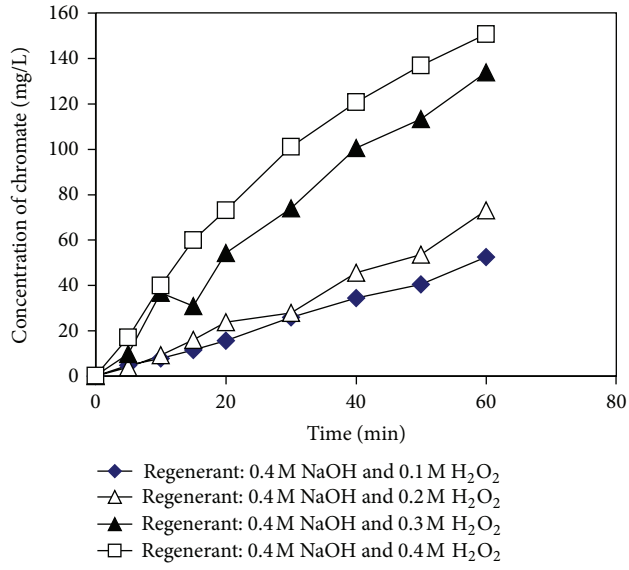


Figure 3: The regeneration efficiency depends on the amount of regenerant solutions. (The amount of exhausted resin; 2.0 g; the speed of the stirrer; 200 rev./min; the volume of regenerant solution is 2.0 L) (serie III).

concentrations in influent were in the range of 10–20 mg/L. The volumes of the feeding solutions were 150 L and 193 L for the first cycle of both systems. A few exhaustion and regeneration cycles were run with satisfactory performance for the systems of installations.

Figures 4(a) and 4(b) show the typical exhaustion breakthrough and regeneration curves for the first cycle with the system of installation I.

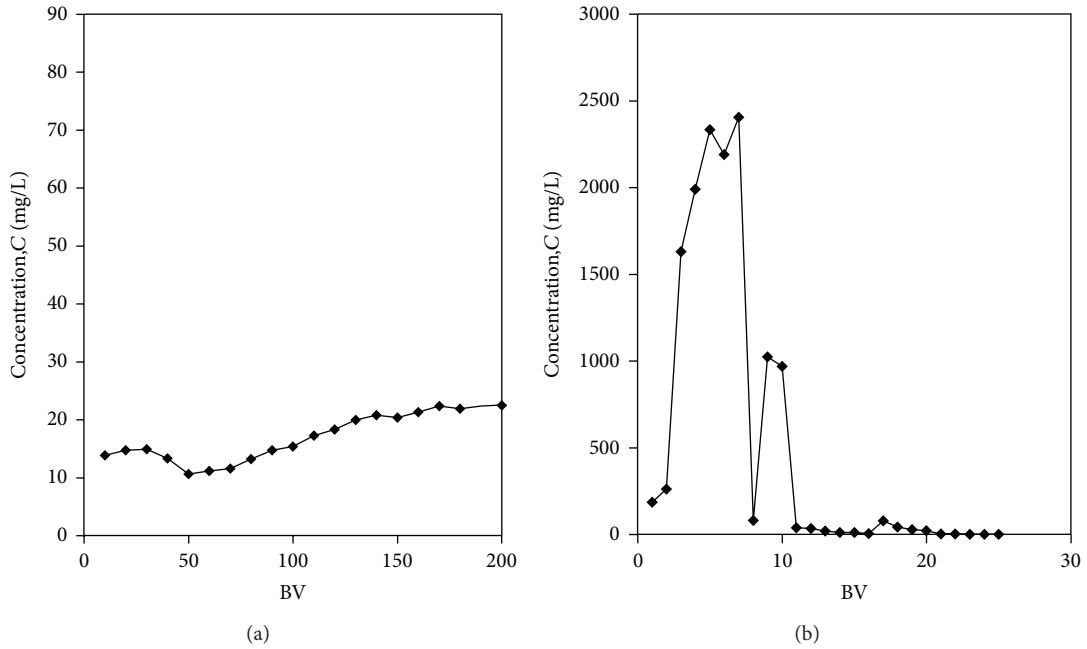


Figure 4: (a) The exhaustion breakthrough curve (first cycle). Initial chromium(III) concentration: 83 mg/L; pH: 2.97 (installation I). (b) The regeneration curve (first cycle). Regenerant solution: 0.3 M H_2O_2; 0.2 M NaOH (installation I).

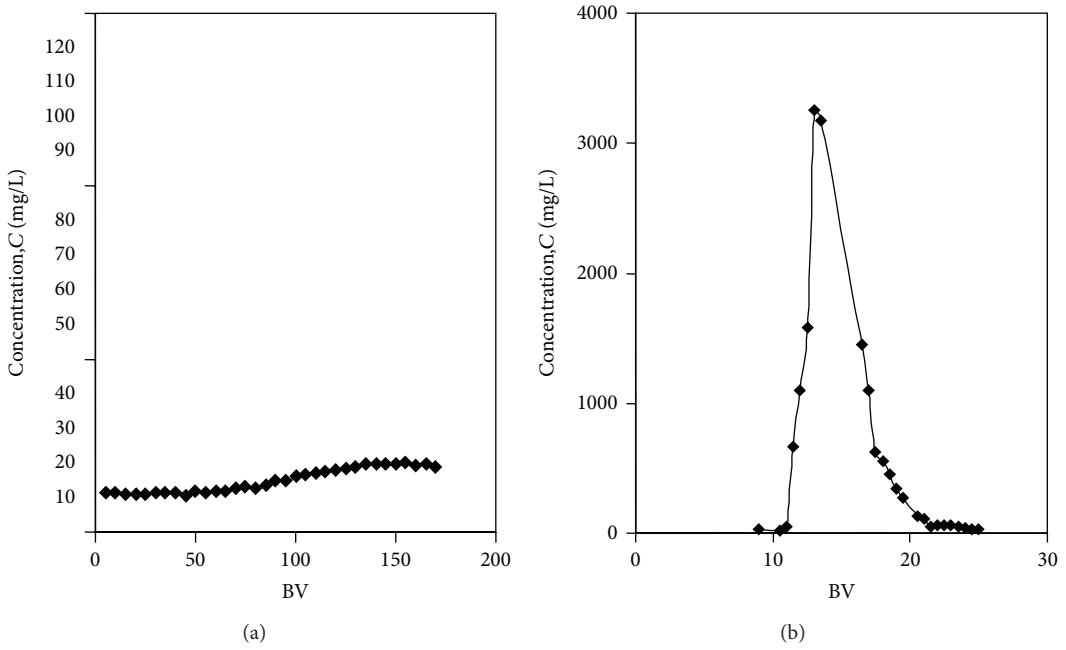


Figure 5: (a) The exhaustion breakthrough curve (first cycle). Initial chromium(III) concentration: 117 mg/L; pH: 2.98 (installation II). (b) The regeneration curve (first cycle). Regenerant solution: 0.3 M H_2O_2; 0.2 M NaOH (installation II).

Figures 5(a) and 5(b) show the typical exhaustion breakthrough and regeneration curves for the first cycle with the system of installation II.

5. Conclusion

The process is based on an ion exchange by using a strong acid cation exchanger resin, Amberjet 1200Na. The resin of Amberjet 1200Na has a uniform particle size and high quality for water treatment applications. The resin allows elimination of chromium(III) ions from synthetic wastewater of tannery and oxidative regeneration with hydrogen peroxide in alkaline media. The equivalent exhaustion and regeneration performances are obtained for laboratory investigation. The regeneration efficiency of the resin has been improved by optimisation of the amounts of the hydrogen peroxide and

sodium hydroxide solutions. The high concentrations of the hydrogen peroxide over 0.4 M have caused the oxidation of the resin material as hydrogen peroxide can react with organic constituents of the resin. As NaOH plays a significant role in regeneration performance of the resin as an alkylating agent, the amount of the NaOH was optimised with kinetic experiments by using a series of the different concentrations between 0.1 M and 0.4 M. There has been a study in the literature on performance of the regeneration depending on the effect of the amount of sodium hydroxide [18]. According to the study regeneration efficiency of the resin has reduced by increasing the amount of the sodium hydroxide to be 0.5 M. Therefore the solution of the 0.2 M of NaOH was used for regeneration, and a quantitative regeneration of chromium(III) ions has been obtained with the solutions of 0.3 M of H_2O_2 and 0.2 M of NaOH. The chromate ions in influent can be reused for production of tannery by recycling after reduction to Cr(III).

The results have shown that while average efficiencies of the removal of chromium(III) ions were 98.70% and 89.24% the average efficiencies of the recovery were 81.56% and 92.50% with laboratory-scale pilot plants, respectively, with installations I and II. The experiments have demonstrated that strong acid cation exchanger, Amberjet 1200Na, can be applied successfully for elimination and recovery of chromium(III) ions from solutions simulating tannery wastewaters regarding chromium(III) concentration. The best performances have been occupied in the literature with more number of exhaustion and regeneration cycles between 10 and 30 by using the solutions of regenerant in similar concentration [13, 21]. In this study the successful efficiencies of the chromium removal and recovery have been reached in the case of existence of less number of cycles by using the resin of Amberjet 1200Na having uniform particle size.

Acknowledgments

This work was supported by a cooperation project between Turkey and Germany (Tübitak & Jülich Research Centre; Project no: 101I051). The authors thank Öznur Alp for her contribution in this study.

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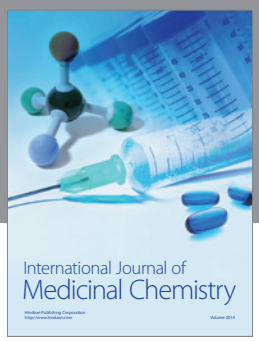
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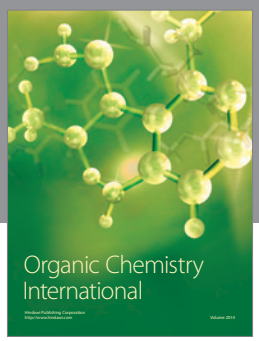
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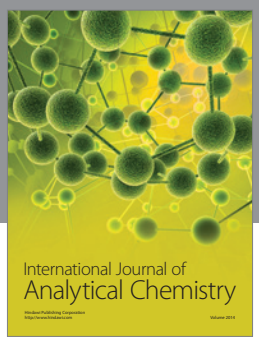
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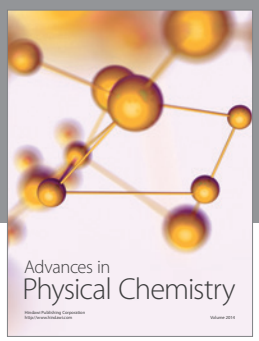
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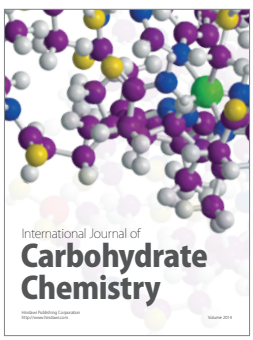


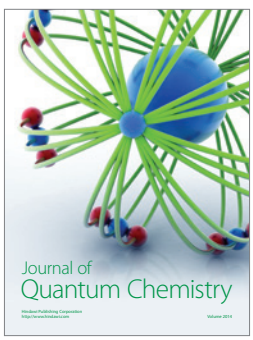












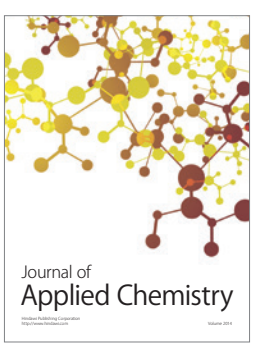


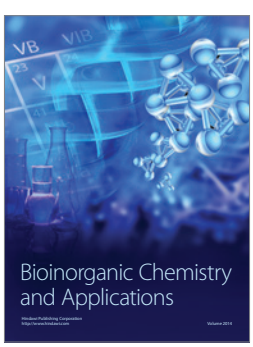




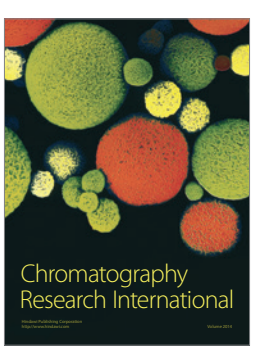




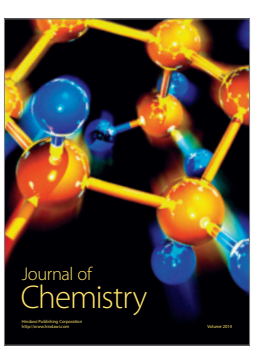














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