Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.963685

56 (2015) 2917–2924
December

Taylor & Francis
Taylor & Francis Group

Selective removal of chromate using hybrid anion exchanger

Medhat Mohamed El-Moselhy[a,b,*], Othman M. Hakami[b]

[a] *Faculty of Science, Chemistry Department, Al-Azhar University, Nasr City, Cairo, Egypt, Tel. +20 1006292802, +20 966595023670; email: medhatmohamed@yahoo.com (M.M. El-Moselhy)*
[b] *Faculty of Science, Chemistry Department, Jazan university, Jazan, Saudi Arabia, Tel. +966 564333764; email: omhakami@jazanu.edu.sa (O.M. Hakami)*

Received 23 February 2014; Accepted 1 September 2014

ABSTRACT

Adsorption and preconcentration of chromate species from water and wastewater were investigated using carminic acid modified anion exchanger (IRA 900). The existence of some oxyanions which might have a competing effect on chromate removal such as MoO_4^{2-}, SO_4^{2-}, SeO_4^{2-}, and AsO_4^{2-} was investigated beside the influence of pH. Adsorption reached equilibrium within 30 min and was independent of initial concentration of chromate oxyanions. Studies were performed at different pH values to find the pH at which maximum adsorption occurred and was determined to be at a pH between 4.0 and 4.5. The Langmuir adsorption capacity (q_{max}) was found to be 19.27 mg Cr(VI)/g of the adsorbent. The results showed that modification of IRA 900 with carminic acid is suitable for the removal of Cr (VI), as chromate, from water and wastewater samples. The obtained material was subjected to efficient regeneration.

Keywords: IRA900; IRA900 modification; Cr(VI) removal; Preconcentration

1. Introduction

Chromate (CrO_4^{2-}) is an anionic contaminant often associated with industrial and power generation wastes that are disposed to the land surface. In domestic waters, chromate is a regulated constituent (US Environmental Protection Agency, 1986) because it may be toxic to man and other organisms. Chromium water pollution is of considerable concern, as this metal has widespread use in electroplating, leather tanning, metal finishing, nuclear power plants, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr(III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent form [1–4] and is toxic to microorganism plants, animals, and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (US Department of Health and Human Services, 1991) [5–8]. The tanning process is one of the largest polluters of chromium throughout the world. Most of the tanneries in India adopt the chromium tanning process because of its processing speed, low costs, light color of leather, and greater stability of the resulting leather. In the chromium tanning process, the leather takes up only 60–80% of the applied chromium, and the rest is usually discharged into the sewage system, causing serious environmental impact.

Chromium ion in liquid tanning wastes occurs mainly in the trivalent form, which is further oxidized to the hexavalent Cr(VI) form, due to the presence of organics. The maximum levels permitted in wastewater

---

*Corresponding author.

are 5 mg/L for Cr(III) and 0.05 mg/L for Cr(IV) [8–16]. With this limit, it is essential for industries to treat their effluents to reduce the chromium to acceptable levels. Due to more stringent environmental regulations nowadays, the mineral processing plants and metal-finishing industries are facing the difficult problem of the disposal of the chromium-laden wastewater that they produce in huge quantities.

Chromium metal ions are usually removed by precipitation, although ion exchange and adsorption [17–24] are also used. The hydroxides of heavy metals are usually insoluble, so lime is used commonly for precipitating them. The most important factor in the precipitation of heavy metal is the valence state of the metal in water. Chromate CrO_4^{2-}, hexavalent form of chromium, is considerably more soluble than its trivalent form, Cr(III). In this case, the chromate, in which chromium is present as Cr(VI), must be reduced, usually with SO_2 available from sodium metabisulfite at low pH levels for the removal of chromium as Cr(III) by the precipitation process. Another aspect of the precipitation process is the zeta potential of the initial heavy metal colloidal precipitate. In many plants where heavy metals are being removed, a principal problem in reaching the desired effluent limits is the colloidal state of precipitated materials—they have not been neutralized, coagulated, and flocculated properly. A final aspect of heavy metals is the possible formation of complex ions, which is common when dealing with wastewaters containing ammonia, fluoride, or cyanide ions along with heavy metals. Because of these important aspects in the precipitation of heavy metals, there is no way to predict the best solution of a specific problem without undergoing a series of bench tests to evaluate the alternative available [25,26].

At lower concentration of chromate in wastewater, the use of ion exchange process represents a good way for the achievement of chromate removal [27–29]. Furthermore, the reductions of chromate using either electrochemical techniques or biotechniques are also used in the process of treatment [30–38].

Carminic acid represents an example for polyol organic dyes, which have the ability to form surface complexes with oxyanions in the lower pH range. This is due to the large number of hydroxyl groups that are positively charged at a low pH level and can attract negatively charged oxyanions. When using these hydroxylated compounds, there is no chance for the competing effect of other competing oxyanions, such as CrO_4^{2-}, MoO_4^{2-}, SO_4^{2-}, SeO_4^{2-}, and AsO_4^{2-}, to occur.

In this work, carminic acid was loaded onto IRA 900 resin (strong base anion exchanger with the quaternary ammonium functional group) and the obtained material was dried at room temperature. The prepared resin was used for the removal of chromate oxyanions from synthetic and real wastewater samples. Removal occurs because carminic acid has hydroxyl groups that are replaceable by metal and oxygen atoms that can form stable complexes. The aim of this work was to evaluate the potential applicability of removing Cr(IV) in the form of chromate from leachate wastewater samples.

2. Materials and methods

2.1. Instrumentation

2.1.1. Determination of oxyanions

Determination of the Cr and other competing oxyanions, such as As and Se, was carried out using a Perkin Elmer atomic absorption spectrophotometer (AAS) with graphite furnace accessories (Model SIMAA 6000) and an electrodeless discharge lamp. *Determination of Mo(VI) in wastewater samples*: a mixture of 0.1 mL of 1×10^{-3} mol/L bromopyrogallol red and 1.5 mL of 1×10^{-3} mol/L cetyltrimethylammonium bromide were added to 2.5 mL of wastewater samples. Using HCl, the pH of the solution was adjusted to 1.0, and the solution was diluted to 5 mL with deionized water. The absorbance of the solution was measured at $\lambda = 635$ nm using the AAS.

2.1.2. Column run

Fixed-bed column runs were carried out using a glass column (11 mm in diameter), constant-flow, stainless steel pump and an ISCO fraction collector. An exhausted IRA 900 loaded with carminic acid was regenerated using 2% NaOH + 3% NaCl.

2.2. Reagents and materials

Deionized water and analytical grade reagents were used to prepare the feed solution. The anion exchanger used was an Amberlite™ IRA 900 Industrial Grade Chelating Resin. Table 1 depicts its characteristics.

Table 1
Physical and chemical characteristics of IRA 900 resin

Functional groups	Quaternary ammonium
Moisture holding capacity	48–54%
Mean size	0.500–0.700 mm
Uniformity coefficient	≤1.6
Maximum operating temperature	75°C (Cl form)

2.3. Synthesis of adsorbent

Twenty grams of IRA 900 was treated with 0.5 mg/L carminic acid (Fischer Scientific, 90% C.I. 75470, Natural Red 4) at neutral pH and agitated for 1 h at room temperature using a handmade mechanical shaker. The modified resin was washed with deionized water and dried at room temperature. Fig. 1 represents a schematic representation for the modification process.

2.4. Adsorption studies

Adsorption studies were carried out by mixing 0.1 g IRA 900 resin loaded with carminic acid with 100 mL of a 20 mg/L Cr(VI) solution. The mixture was shaken for 3 h to reach equilibrium.

3. Results and discussion

3.1. Effect of pH

The adsorption of Cr(VI) oxyanions was investigated under different experimental conditions. One such condition was changing the pH level from 4 to 8. One hundred milliliters of the solution with an initial concentration of 20 mg/L was passed through a column of carminic acid modified beads at varying pH levels, as depicted in Fig. 2. It should be noted that the removal efficiency decreased with increasing pH level and shows a maximum removal value at a pH level of 4.3. This is because the hydrogen atoms in the hydroxyl groups of carminic acid are replaceable by metal or oxygen atoms and form stable complexes with chromium. At higher pH values, the negatively charged carminic acid surface sites did not favor the adsorption of chromate oxyanion due to the electrostatic repulsion.

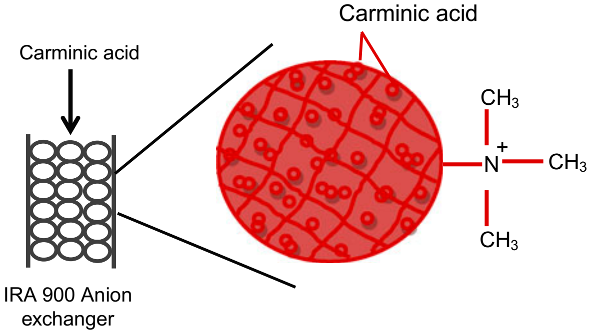

Fig. 1. Sketch of carminic acid loading process.

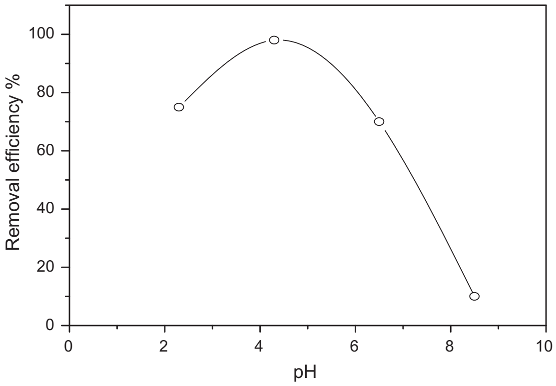

Fig. 2. pH effect on the removal of Cr(VI). Conditions: 0.1 g carminic resin, 200 mL of 10 mg/L Cr(VI).

3.2. Effect of competitive oxyanions (sulfate, selenate, arsenate, and molybdate)

Wastewater usually contains an obvious number of oxyanions coexisting with chromate species that invariably implies competition for available adsorption sites. Therefore, it is important to investigate the competitive influence of certain anions and oxyanions.

The interfering effects of MoO_4^{2-}, SeO_4^{2-}, and AsO_4^{2-} on the adsorption of 5 ppm CrO_4^{2-} and $Cr_2O_7^{2-}$ were studied using 0.1 g of resin. The presence of such competing oxyanions showed significant adsorption at lower pH value (4.3), as depicted in Fig. 3, due to the formation of hydrogenated oxyanions, which could form complexes with carminic acid hydroxyl groups [26]. Furthermore, when the pH value was raised to 4.3, there was no competition observed between CrO_4^{2-}, $Cr_2O_7^{2-}$, and the above-mentioned oxyanions. For this reason, all column runs were carried out at a pH value of 4.3.

Furthermore, the investigation of the effect of sulfate at higher concentrations range (120–10,000 mg/L) indicates a strong influence on the removal of chromate oxyanions. The data depicted in Fig. 4 show that when the concentration of sulfate is 120 mg/L, the removal efficiency reaches the maximum. However, upon increasing the concentration of sulfate, the removal efficiency decreases to 20% when the concentration reaches 10,000 mg/L.

3.3. Adsorption mechanism

The IRA 900 surface modified with carminic acid is generally covered with a large number of hydroxyl groups that play an important role in the adsorption process [25]. The proposed mechanism was based on the fact that at lower pH values, the surface hydroxyl

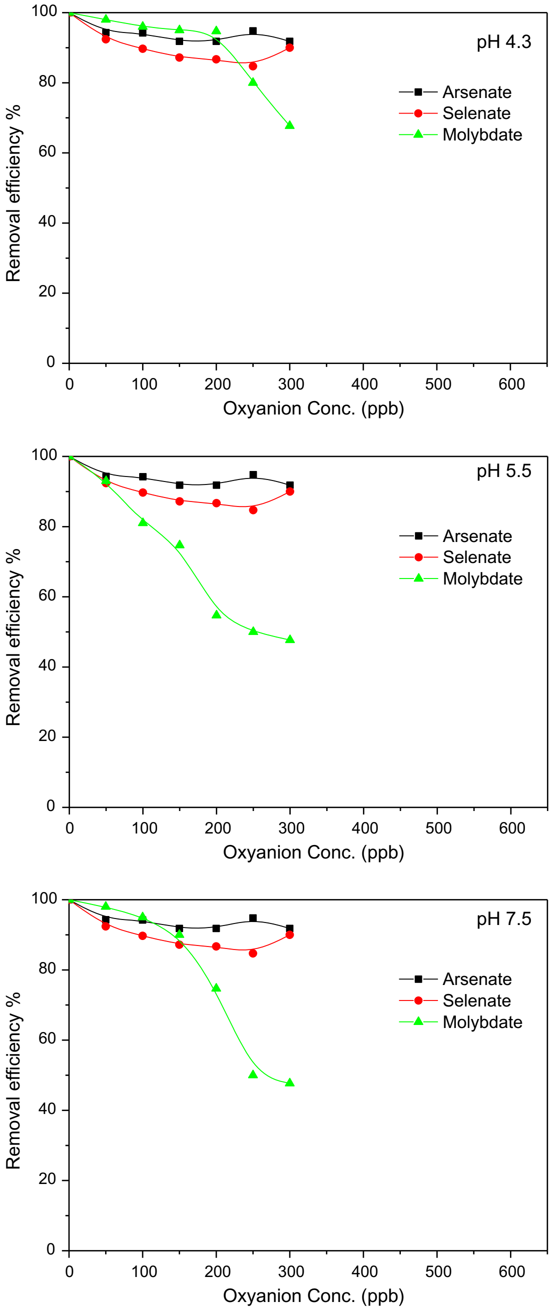

Fig. 3. Oxyanions effect on the removal of Cr(VI) at different pH values. Conditions: 0.1 g carminic resin, 200 mL of 10 mg/L Cr(VI).

groups were found to be positively charged, the chromate species found as 60% $HCrO_4^-$ and 40% $Cr_2O_7^{2-}$ (Fig. 5), and the only possible way is the electrostatic interaction between positive and negative charges. When the pH value is increased to 4.3, uptake of chromate increases since there is no competition with the other oxyanions at this pH level.

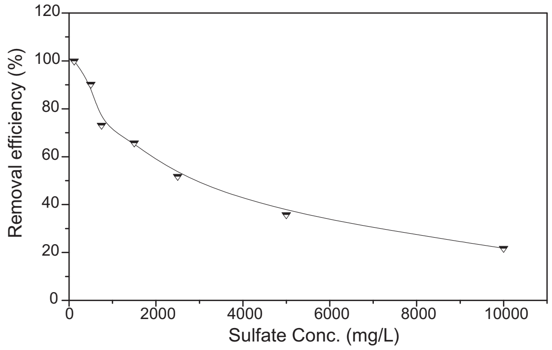

Fig. 4. Effect of sulfate anions on the removal of Cr(VI) at different pH values. Conditions: 0.1 g carminic resin, 200 mL of 10 mg/L Cr(VI).

However, when the pH value is increased to 8, the uptake of chromate ions decreases since at higher pH values, the adsorption surface sites are negatively charged, which increases the electrostatic repulsion between the chromate and the adsorbent. The adsorption mechanism of chromate can be explained as shown in Fig. 6.

3.4. Adsorption isotherm

Adsorption isotherms are basic requirements for establishing the adsorption systems and providing information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutants under the system conditions. The Langmuir model [28] is the most frequently used isotherm model in the literature. This model describes the nonlinear equilibrium between an adsorbed pollutant and a pollutant in the solution at a constant temperature. This model is simple, gives a good description of experimental behavior in a large range of operating conditions, and

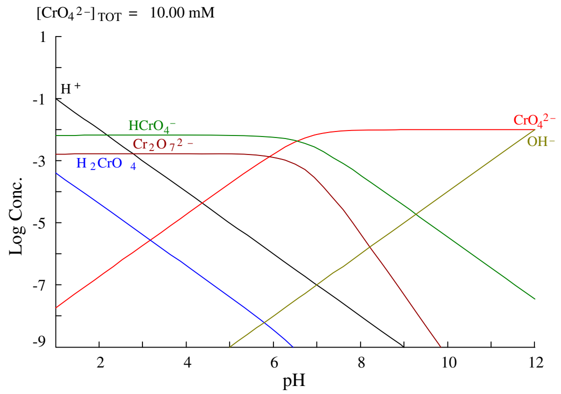

Fig. 5. MEDUSA curve obtained for chromate species at different pH.

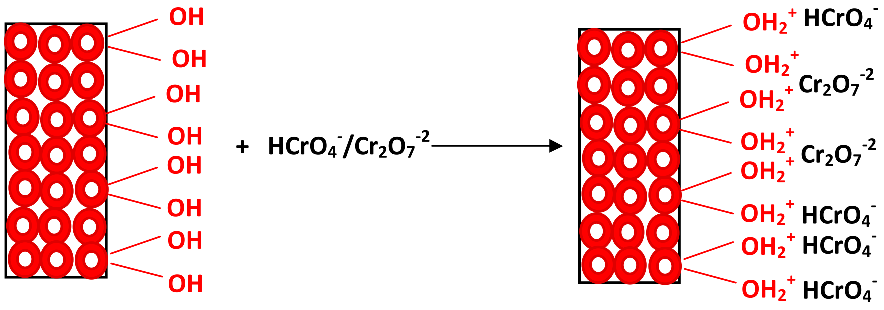

Fig. 6. Proposed mechanism for the chromate adsorption.

is characterized by a limited number of adjustable parameters. The linearized form of the Langmuir equation can be represented as:

$$C_e/q_e = (C_e/q_{max}) + (1/bq_{max})$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mg/g; C_e is the equilibrium concentration in mg/L; q_{max} is the maximum absorption at monolayer coverage in mg/g; and b is the equilibrium constant related to the energy of adsorption. The Langmuir model assumes uniformity in the heat of adsorption [28–30]. The amount of molybdate adsorbed at equilibrium per unit mass of resin, q_e, was calculated by: $q_e = V(C_o - C)/m$, where V is the volume of molybdate solution in L; C_o and C_e are the initial and equilibrium concentrations in mg/L, respectively; and m is the mass of adsorbent in g. The plot of q_e vs. C_e is shown in Fig. 7. The linear plot of C_e/q_e vs. C_e shows that the adsorption obeys the Langmuir isotherm model (Fig. 8). The Langmuir isotherm shows that the amount of chromate adsorbed increases as its concentration increases up to saturation point.

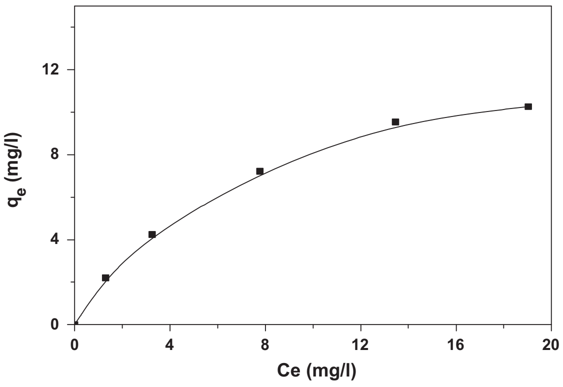

Fig. 7. Carminic loaded IRA 900 resin.

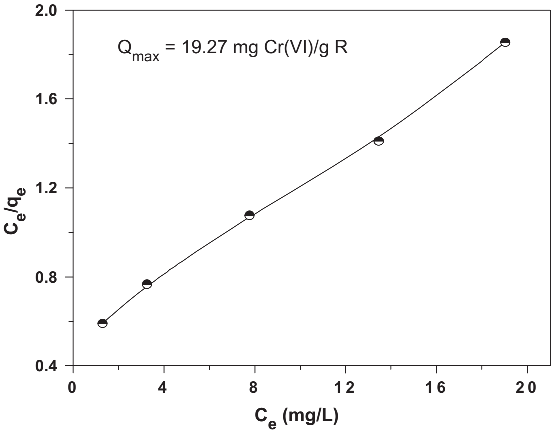

Fig. 8. Linearization of the adsorption isotherm (Langmuir) of Cr(VI).

3.5. Fixed-bed column run

Fig. 9 shows the effluent history during a fixed-bed column run using the IRA900 and a carminic-acid loaded IRA900 strong base anion exchanger. The data

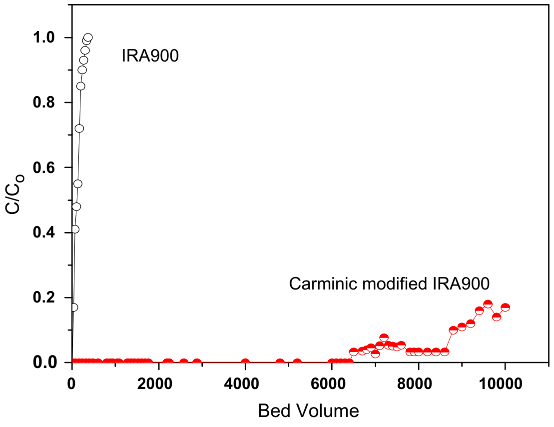

Fig. 9. Column run effluent histories for the effects of modification with carminic acid on the breakthrough of 5 mg/L $Cr_2O_7^{2-}$.

reveal that chromates broke through almost immediately after the start of the column run with the IRA 900, while the carminic acid-loaded IRA 900 broke through after about 9,000 bed volumes.

3.5.1. Effect of pH

On the other hand, the column run data for the effect of pH indicate that chromates start to breakthrough after 9,000 bed volumes at a pH level of 4.3 (Fig. 10). However, upon increasing the pH level, the number of treated bed volumes decreases gradually to reach early breakthrough at pH 8.5.

3.5.2. Effect of interfering ions

Column run data obtained for the competing effect of oxyanions indicate that at pH 4.3, all contender oxyanions, such as arsenate, selenate, and molybdate, start breakthrough almost immediately after the beginning of the column run, as illustrated in Fig. 11.

3.6. Fixed-bed column run for real leachate wastewater

The investigation of the removal efficiency of carminic modified anion exchanger using column run with a real ash leachate wastewater with a composition depicted in Table 2 indicates the same behavior as that obtained with the synthetic wastewater under the same experimental conditions.

The results prove that the adsorption of chromate leads to a change in the color of the carminic acid modified anion exchanger from red to brown as a result of the composition overlay of chromate with carminic acid molecules. This color change can be used as a visible sign for the complete exhaustion of the bed as depicted in Fig. 12.

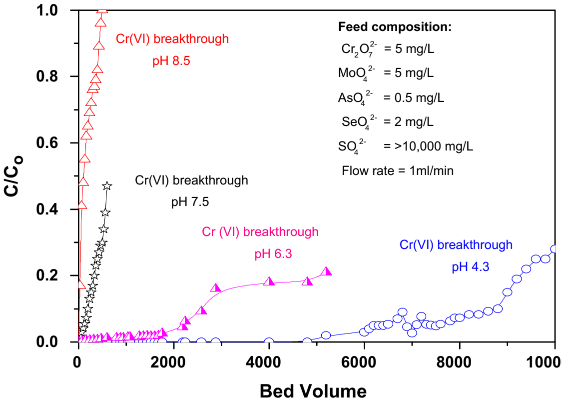

Fig. 10. Column run effluent histories for the effects of pH on breakthrough of 5 mg/L $Cr_2O_7^{2-}$.

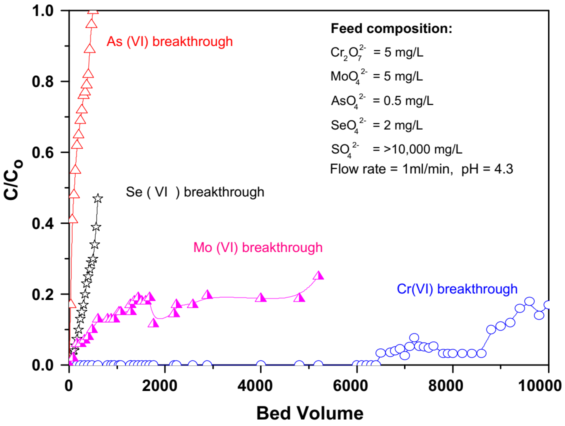

Fig. 11. Column run effluent histories for the effects of MoO_4^{2-}, SeO_4^{2-} and AsO_4^{2-} on breakthrough of 5 mg/L $Cr_2O_7^{2-}$.

3.7. Regeneration, rinsing, and reuse

The exhausted bed of carminic acid-loaded IRA 900 was regenerated using 0.5% NaOH. Concentrations profiles of molybdate during the process of desorption are provided in Fig. 13. Note that in less than 30 bed volumes, almost the entire amount of chromate was desorbed completely from the bed. It is important to mention that during the regeneration process, some of the loaded carminic acid leached out with NaOH. By increasing the pH to alkaline, carminic acid becomes ionized, giving rise to leaching out from the resin matrix.

Following regeneration, the bed was rinsed with 0.01 M HCl to bring down the pH level from alkaline to a near-neutral condition. For resin reuse, the regenerated and rinsed material was subjected to four more exhaustion/regeneration cycles to obtain a full idea

Table 2
Leachate wastewater during the fixed bed column run

No.	Parameter	Synthetic sample	Real sample
1	pH	9.90	9.90
2	SO_4^{2-} (mg/L)	10,000	12,000
3	AsO_4^{2-} (μg/L)	200	180
4	MoO_4^{2-}(mg/L)	4.43	4.0
5	Chromate (mg/L)	5.30	5.30
6	SeO_4^{2-} (mg/L)	1.60	1.50

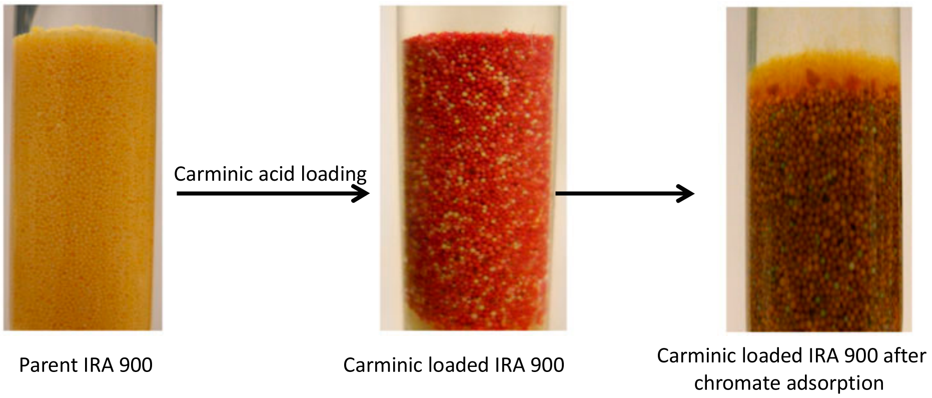

Fig. 12. Color change of IRA 900 during carminic acid loading process and after chromate adsorption.

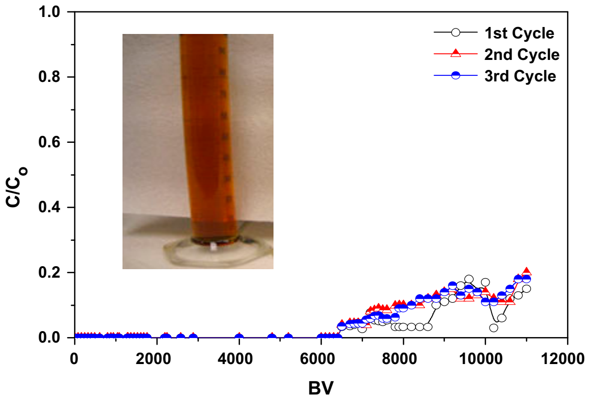

Fig. 13. Column run effluent histories for the effects of regeneration on breakthrough of 5 mg/L $Cr_2O_7^{2-}$.

regarding the resin capacity after the process of regeneration; note that the chromate removal capacity slightly decreased among the different cycles due to the leaching of some loaded carminic acid.

4. Conclusions

The process of adsorption and preconcentration of Cr(VI) was investigated to determine and quantify the adsorption behavior and capacity of a carminic loaded IRA 900. After loading the carminic acid, the IRA 900 resin possessed a large number of hydroxyl groups that were dispersed in the gel phase of the beads. This gave rise to the selective removal of Cr(VI) species even in the presence of higher concentrations of other competitive anionic species. Following adsorption, carminic acid-loaded IRA 900 can be efficiently regenerated with 0.5% NaOH in less than 30 bed volumes. Subsequent rinsing with a 0.01 M HCl solution for less than 15 bed volumes ensured that the column was ready for another adsorption cycle. After regeneration, the removal efficiency of Cr(VI) for the removal capacity of the second, third, and fourth cycles remains the same.

References

[1] Z. Kowalski, Treatment of chromic tannery wastes, J. Hazard. Mater. 37 (1994) 137–141.
[2] M. Cieslak-Golonka, Toxic and mutagenic effects of chromium(VI), Polyhedron 15 (1995) 3667–3689.
[3] F.N. Acar, E. Malkoc, The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L., Bioresour. Technol. 94 (2004) 13–15.
[4] J.W. Patterson, Waste Water Treatment, Science, New York, NY, 1977.
[5] G. Tiravanti, D. Petrluzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1977) 197–207.
[6] S. Dahbi, M. Azzi, M. de la Guardia, Removal of hexavalent chromium from wastewaters by bone charcoal, Fresenius J. Anal. Chem. 363 (1999) 404–407.
[7] Y. Orhan, H. Buyukgangor, The removal of heavy metals by using agricultural wastes, Water Sci. Technol. 28 (1993) 247–255.
[8] A. Merly Xavier, A. Logeswari, S. Mano, Removal of chromium from real tannery effluent by using bioadsorbents, Int. J. Eng. Sci. 7 (2013) 35–40.
[9] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Biosour. Technol. 47 (1994) 257–264.
[10] T.S. Singh, K.K. Pant, Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, Sep. Purif. Technol. 36 (2004) 139–147.
[11] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium (VI) from solution by coconut husk and palm pressed fibres, Environ. Technol. 14 (1993) 277–282.
[12] APHA, Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA, Washington, DC, 1992.

[13] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.

[14] C.P. Huang, M.H. Wu, The removal of chromium(VI) from dilute aqueous solution by activated carbon, Water Res. 11 (1977) 673–679.

[15] C. Namasivayam, R.T. Yamuna, Microbial and plant derived biomass for removal of heavy metals from wastewater, Chemosphere 30 (1995) 561–578.

[16] R. Saliba, H. Gauthier, The use of eucalyptus barks for the adsorption of heavy metal ions and dyes, Adsorpt. Sci. Technol. 20(2) (2002) 119–129.

[17] A. Agrawal, V. Kumar, B.D. Pandey, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils, Miner. Process. Extr. Metall. Rev. 27(2) (2006) 99–130.

[18] M. Horsfall Jr., F. Ogban, E.E. Akporhonor, Impact of cell wall structure on the behavior of bacterial cells as sorbents of cadmium and Lead, Chem. Biodivers. 3(2) (2006) 161–565.

[19] J. McLean, T.J. Beveridge, Chromate reduction by Pseudomonas isolated from a site contaminated with chromated copper arsenate, Appl. Environ. Microbiol. 67(3) (2001) 1076–1084.

[20] S.S. Ahluwalia, D. Goyal, Microbial and plant de-rived biomass for removal of heavy metals from wastewater, Bio. Technol. 98(12) (2007) 2243–2257.

[21] G. Naja, B. Volesky, Behavior of mass transfer zone in a biosorption column, Environ. Sci. Technol. 40(12) (2006) 3996–4003.

[22] A.I. Zouboulis, M.X. Loukidou, K.A. Matis, Bio-sorption of toxic metals from aqueous solutions by bacteria strain isolated from metal polluted soils, Process Biochem. 39 (8) (2004) 909–916.

[23] E. Kulczycki, F.G. Ferris, D. Fortin, Impact of cell wall structure on the behavior of bacterial cells as sorbent of cadmium and lead, Geomicrobiol. J. 19(6) (2002) 553–556.

[24] B. Godlewska-Żyłkiewicz, Microorganisms in inorganic chemical analysis, Anal. Bioanal. Chem. 384 (2006) 114–123.

[25] M. Nishimura, J.M. Thomas, IR study of the interaction of hydroxyl groups of silica gel with Cr species of Phillips' type catalysts, Catal. Lett. 21(1–2) (1993) 149–155.

[26] A. Ganguli, A.K. Tripathi, Bioremediation of toxic chromate from electroplating effluent by chrome reducing *Pseudomonas aeruginosa* A2Chr in two biore-actors, Appl. Microbiol. Biotechnol. 58(3) (2002) 416–420.

[27] D.R. Lovely, E.J.P. Phillips, Reduction of chromate by *Desulfovibrio vulgaris* and its C3 cytochrome, Appl. Environ. Microbiol. 60(2) (1994) 726–728.

[28] C. Modrogan, D.G. Apostol, O.D. Butucea, Study of Hexavalent chromium from wastewater by ion exchange, Environ. Eng. Manage. J. 12(5) (2013) 929–935.

[29] C. Balan, I. Volf, D. Bilba, Chromium (VI) removal from aqueous solution by purolite base anion exchange resin with gel structure, Chem. Ind. Chem. Eng. Q. 19(4) (2013) 615–628.

[30] V.V. Konovalova, G.M. Dmytrenko, R.R. Nigmatullin, M.T. Bryk, P.I. Gvozdyak, Chromium(VI) reduction in a membrane bioreactor with immobilized Pseudomonas cells, Enzyme Microb. Technol. 33(7) (2003) 899–907.

[31] Y.G. Liu, W.H. Xu, G.M. Zeng, C.F. Tang, C.F. Li, Experimental study on reduction by *Pseudomonas aeruginosa*, J. Environ. Sci. 16(5) (2004) 797–801.

[32] D.F. Ackerley, C.F. Gonzalez, M. Keyhan, R. Blake, A. Matin, Mechanism of chromate reduction by the *Escherichia coli* protein, NfsA, and the role of different chromate reductases in minimizing oxidative stress during chromate reduction, Environ. Microbiol. 6(8) (2004) 851–860.

[33] C.R. Myer, B.P. Carstens, W.E. Antholine, J.M. Myers, Chromium (VI) reductase activity associated with the cytoplasmic membrane of anaerobically grown *Shewanella putrefaciens* MR-1, J. App. Microbiol. 88(1) (2000) 98–106.

[34] S. Viamajala, B.M. Peyton, J.N. Petersen, Modeling chromate reduction in *Shewanella oneidensis* MR-1: Development of a novel dual-enzyme kinetic model, Biotechnol. Bioeng. 83(7) (2003) 790–797.

[35] M. Sharanavard, A. Ahmadpourand, M. Reza Doosti, Biosorption of hexavalent chromium ions from aqueous solutions using almond green hull as a low-cost biosorbent, Eur. J. Sci. Res. 58 (2011) 392–400.

[36] F. Shafqat, H.N. Bhatti, M.A. Hanif, A. Zubair, kinetic and equilibrium studies of Cr(III) and Cr(Vi) sorption from aqueous solution using Rosa gruss an teplitz (red rose) waste biomass, J. Chil. Chem. Soc. 53 (2008) 1667–1672.

[37] S.S.Shaukat, Progress in Biomass and Bioenergy Production, first ed., InTech, Karachi, 2009, p. 444.

[38] K.K. Singh, S.H. Hasan, M. Talat, V.K. Singh, S.K. Gangwar, Removal of Cr(VI) from aqueous solutions using wheat bran, Chem. Eng. J. 151 (2011) 113–121.