Sorption of chromium (VI) from electroplating rinse water by strong base anion exchanger: equilibrium and kinetic studies

Prasanna S Koujalagi, Harish N Revankar, Raviraj M Kulkarni and Vijayendra R Gurjar

Department of Chemistry, KLS, Gogte Institute of Technology, Belagavi 590 008, affiliated to Visvesvaraya Technological University, Belagavi, Karnataka, India.

Email: pskoujalagi@git.edu

Abstract. Static-batch experiments are conducted to remove Chromium (VI) from rinse waters of electroplating bath on strong base anion exchanger Tulsion A-62 and results are depicted with respect to Chromium (VI) ions concentration, contact time and solution pH. The equilibrium state is established after 300 minutes of phase contact. As the adsorption process is a pH dependent, indicated the maximal removal of Chromium (VI) in the pH 6.0-7.0. The anion exchange resin is characterized by SEM with EDX and FTIR analysis. The equilibrium data for adsorption of Chromium (VI) was fitted with Langmuir and Freundlich models. The adsorption process followed reversible first order kinetics. Reports concluded that such anion exchangers could be used for the systematic removal of Chromium (VI) ions from water and wastewater.

Keywords. Adsorption, Anion exchanger, Chromium (VI), Electroplating rinse water.

1. Introduction
Chromium is an important heavy metal of environmental concern because of its extensive applications in industries like, leather tanning, textile dying, electroplating, metallurgical operations, paint and pigment manufacturing, mining processing, wood preservation, iron and steel production etc. This leads to the discharge of huge quantities of chromium into the aquatic environment due to unexpected releases or incompetent precautionary practices [1-3]. Chromium is found in aquatic media in various chemical forms with oxidation states ranging from −4 to +6, but only the +3 and +6 states are stable. Under oxidizing conditions Cr6+ is more stable and Cr3+ is more stable under reducing conditions. Each of these oxidation states are characterized by different toxicity, chemical and biological properties [4]. The extent of chromium contamination in the hydrosphere is increasing every day. Chromium (VI) is primarily present as chromate (CrO4^{2−}) and dichromate (Cr₂O₇^{2−}) forms posing powerful toxicity in all living beings and is a well known carcinogen. The toxicity of Chromium (VI) is 1000 times more than trivalent chromium [5]. The US-EPA has fixed the highest chromium level in drinking water as 0.1ppm [6-7]. Thus, Chromium removal is a highly essential pollution abatement technique prior to discharge industrial effluents into the water bodies. Several methods are proposed in the literature to decontaminate the Chromium (VI) polluted waters. Few of them are chemical precipitation, adsorption, ion exchange, electro kinetic remediation, membrane processes, bioremediation, solvent extraction etc. Most of these methods have limited scope due high capital.
investments and operational costs [8-9]. The effective and facile method for removal of Chromium (VI) from effluents is the ion exchange and the adsorption. The intention of the current research was to investigate the efficiency of Tulsion A-62 to remove Chromium (VI) from rinse water of chrome plating bath by varying pH of the solution, time of phase contact, Chromium (VI) concentration and quantity of Tulsion A-62. Adsorption obeyed Freundlich and Langmuir isotherms.

2. Methodology
Rinse solutions containing Chromium (VI) were collected from a chrome plating industry. Ion exchanger Tulsion A-62 in chloride form was received from Thermax Limited, Pune, India. The resin was strong base anionic macroporous crosslinked with polystyrene having functional group quaternary ammonium-I. The bead diameter of Tulsion A-62 was 0.3-1.2 mm accounts for 41% moisture with ion exchange capability of 0.72 m.eq./250 g. The resin was pre-processed prior to the experiments using NaOH and HCl solutions and cleaned with de-ionized water and dried in air. Static-batch experiments were carried out by stirring 30 ml of rinse water containing Chromium (VI) with a definite quantity of resin for a period of 6 hours at 303 K in a temperature controlled shaking unit. Afterwards the solution was subjected for the analysis of Chromium (VI) spectrophotometrically with standard diphenyl carbazide (DPC) method at 540 nm [10]. Chromium (VI) recovery factors were calculated [11] using the equation (1).

\[
\% R = \frac{C_a}{C_o} \times 100
\]

where \( C_a \) and \( C_o \) are the Chromium (VI) concentrations on Tulsion A-62 and in the initial solution (in m.eq.) respectively.

Coefficient distribution constant is given by the equation (2).

\[
K_d = \frac{q_e}{C_e}
\]

where \( q_e \) and \( C_e \) are the metal ions (in m.eq.) sorbed on Tulsion A-62 and present in the solution at equilibrium.

3. Results and Discussion

3.1. Effect of pH
The impact of pH in the removal of Chromium (VI) ions by Tulsion A-62 resin was considered at various pH values between 4.0 - 9.0. Figure 1 showed the highest removal rate was between the pH 6.0-7.0 for 0.03758M electroplating rinse water containing Chromium (VI). It was observed that above pH 7.0 there was a decrease in removal efficiency of Chromium (VI) due to the fact that the formations of chromium precipitate. Below pH 7.0 the adsorption was less because of the struggle between surfeit of chromate and hydrogen ions for the bonding plats [12-14].
3.2. Effect of interactivity time
Static-bed assessments were performed to understand the removal kinetics of Chromium (VI) with 0.025 g of anion exchanger in fixed volume and fixed concentration of rinse water from chrome plating bath. At different time span the Chromium (VI) concentration in each of the sample was estimated spectrophotometrically. It is seen from figure 2 that the rate of adsorption of Chromium (VI) increases with the time. Almost 99% of Chromium (VI) was removed in 30 minutes of contact [15]. Removal percentage of Chromium (VI) increased rapidly up to 300 minutes and thereafter reached the equilibrium. In the beginning the Chromium (VI) was removed fast due to excessive number of plats on the resin surface and after attaining equilibration due to saturation of the resin plats the interactivity time had shown no much impact on removal of Chromium (VI).

3.3. Effect of resin quantity
Experiments were conducted to study the impact of resin quantity by shaking the rinse solutions of 0.03758 M from chrome plating bath with varying amounts of resin from 0.01-0.06 g for 6 hours at pH 7.0. It was very clear from figure 3 that for the highest Chromium (VI) removal, 0.025 g of resin was required and beyond that the removal efficiency was no longer affected [16-17]. Increase in the quantity of adsorbent,
the removal efficiency was increased and density of adsorption was decreased. The attributed fact that few of the resin matrix sites might have remained unadsorbed during the process of adsorption. This experiment indicated that Chromium (VI) removal was increased as with the resin quantity due to maximum active sites with larger surface area [18].

![Figure 3. Effect of resin quantity on removal of Chromium (VI)](image)

3.4. Effect of Chromium (VI) concentration

The concentration of rinse water from chrome plating bath was varied between 0.0094 to 0.06263 m.eq. From figure 4, the distribution coefficient was highest in the beginning for Chromium (VI) removal and then decreased as the metal ion concentration increased. This may be the fact that initially more adsorption due to maximum active plats available on the resin and later because of saturation of the resin matrix with Chromium (VI) no more increase in adsorption.

![Figure 4. Effect of concentration of Chromium (VI)](image)
3.5. Characterization of anion exchanger
Scanning Electron Microscopic (SEM) pictures of Tulsion A-62 were shown in Figure 5.a-b. The microscopic look at the surface of the resin adsorbed with Chromium (VI) was not as smooth as like before. More defects on the surface of the resin were observed. It was inferred that it could be the sorption of anions containing Chromium (VI) on the surface of Tulsion A-62. The chemical analysis with energy dispersive X-ray (EDX) spectra was performed and was illustrated in figure 6 revealed that Tulsion A-62 had particularly of carbon and chlorine that could be from the matrix material of polymer and exchangeable ion of anion exchange resin. Meantime, elemental chromium (5.04 % wt) was noticed in the elemental composition of Tulsion A-62 after the adsorption process. This confirmed the Chromium (VI) adsorption onto Tulsion A-62. Figure 7. a-b illustrated the fourier transform infra-red (FTIR) spectra of Tulsion A-62. The FTIR spectrum of the exchanger (Figure 7a) revealed a wide peak at about 3428 cm⁻¹, that could be due to O-H stretching vibration of hydroxyl group [19]. In the meantime, peaks at 3015, 2924 and 2856 cm⁻¹ corresponds to C-H stretching of aromatic ring of polystyrene divinyl benzene matrix of anion exchanger [20]. Further, a significant peak at 1458 cm⁻¹ corresponds to C-H bending of quaternary ammonium functional group of anion exchanger [21]. As shown in Figure 7b, the pattern of peak of Tulsion A-62 after adsorption is similar to that of anion exchanger however, an additional peak observed at 940 cm⁻¹ attributed to Cr-O stretching vibration, which truly indicated the presence of chromium onto anion exchanger [1].

![Figure 5. SEM micrographs of Tulsion A-62 (a) before (b) after adsorption of Chromium (VI)](image)
Figure 6. EDX spectra of Tulsion A-62 after adsorption of Chromium (VI)

Figure 7. FTIR spectra of Tulsion A-62 (a) before (b) after adsorption of Chromium (VI)

3.6. Adsorption isotherms
To optimize the interaction of adsorbent with adsorbate the equilibrium statistics was fitted to Langmuir and Freundlich equilibrium models. The Langmuir isotherm model is represented as,

\[
\frac{C_e}{q_e} = \left( \frac{1}{K_Lq_m} \right) + \frac{C_e}{q_m}
\]  

where \(C_e\) and \(q_e\) are the initial and equilibrium metal ion concentrations, \(q_m\) and \(K_L\) are constants denote the capacity and energy of adsorption respectively. Figure 8 represented a linear curve that proved the adsorption on Tulsion A-62 following the Langmuir isotherm. This isotherm suggested that the adsorbent
surface has a monolayered homogeneous adsorption with equivalent energy of activation. Table 1 depicts the obtained results. The Freundlich adsorption isotherm model represents a heterogeneous surface energy system and is represented by the linear equation as (4).

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

(4)

where \(q_e\) denotes capacity of adsorption at equilibrium and \(C_e\) is metal ion concentration at equilibrium. The constants, \(K_F\) and \(n\) are acquired by the plot of \(\ln q_e\) versus \(\ln C_e\). As \(K_F\) increases the capacity of adsorption of Tulsion A-62 also increases. The results showed that the equilibrium records were well obeyed the Freundlich model and the values of Freundlich model are presented in Table 1. On comparing the correlation coefficient (\(R^2\)) values, it is seen that Freundlich model has better performance than Langmuir model for representing the equilibrium data. This could be because of some of the adsorbed metal ions might have diffused into the channel of the resin [4], a similar phenomenon of multi-molecular layer adsorption.

Separation factor \(R_L\), a non-dimensional parameter of Langmuir isotherm, \((R_L = 1/(1 + bC_0))\), showed that the Chromium (VI) adsorption on Tulsion A-62 was favorable because of \((0 < R_L = 0.68 < 1)\) [22].

![Figure 8. Langmuir isotherm for Chromium (VI) adsorption on Tulsion A-62](image)

### Table 1. Parameters of adsorption isotherm models

| Anion exchanger | Parameters of Freundlich isotherm | Parameters of Langmuir isotherm |
|-----------------|----------------------------------|---------------------------------|
|                 | \(K_F\)   | \(n\)  | \(R^2\) | \(K_L\) | \(q_{m}^a\) | \(R^2\) |
| Tulsion A-62    | 7682.98  | 1.11   | 0.96    | 15.1    | 81.48         | 0.94   |

* \(q_{m}\) mmol/g resin
3.7. Adsorption Kinetics

Reversible first-order kinetics describes the rate of sorption of Chromium (VI) on Tulsion A-62. It also suggests the necessary residence time of sorption of metal ions on Tulsion A-62. From figure 9, the forward \( k_f \), backward \( k_b \) and the reaction rate coefficient \( k \) were evaluated [23-24] for Chromium (VI) adsorption from solution of chrome plating bath having the concentration 0.03758M. The data \( k_f \) \((2.705 \times 10^{-3}) \gg k_b \(4 \times 10^{-6}\) indicated the dominance of adsorption.

![Figure 9. Adsorption kinetics of Chromium (VI) on Tulsion A-62](image)

4. Conclusions

According to the literature ion exchange resins are the capable polymeric substances employed for the purification of polluted water with chosen thrash. So the resin efficiency was presented here. The maximum elimination of Chromium (VI) by Tulsion A-62 is found to be in the pH between 6.0 - 7.0. The kinetics of adsorption depends on the resin dosage and chromium concentration. Equilibrium data followed the Freundlich and Langmuir isotherms. Interpretation of Chromium (VI) adsorption is well indicated by the non-dimensional separation factor \( (R_L) \). Results represented that Tulsion A-62 is a competent material for the elimination of Chromium (VI) from solutions of chrome plating units.

References

[1] Rajiv Gandhi M Viswanathan N Meenakshi S 2010 Adsorption mechanism of hexavalent chromium removal using Amberlite IRA 743 resin Ion Exch Let 3 25-35
[2] Koujalagi P S, Divekar S V, Kulkarni R M and Cuerda-Correa E M 2016 Sorption of hexavalent chromium from water and water-organic solvents onto an ion exchanger Tulsion A-23(Gel) Desal Wat Treat, 57(50) 23965-23974
[3] Firouzabadi H, Shariati A and Karimi B 1993 Chromium (VI) Based Oxidants IV, Zinc Chlorochromate Nonahydrate \( \text{Zn(ClCrO}_3\text{)}_{9} \cdot 9\text{H}_2\text{O}\) as An Efficient and Mild Oxidizing Agent, Part 2 Iran J Chem Chem Eng, 12(1) 32-38
[4] Xiaofan Li, Shaoyuan Shi Hongbin Cao Yuping Li and Dongyao Xu 2018 Comparative Study of Chromium(VI) Removal from Simulated Industrial Wastewater with Ion Exchange Resins Rus J Phy Che A, 92(6) 1229–1236
[5] Koujalagi P S, Divekar S V, Kulkarni R M and Nagarale R K 2013 Kinetics, thermodynamic and adsorption studies on removal of chromium(VI) using Tulsion A-27(MP) resin Desal Wat Treat, 51(16-18) 3273-3283
[7] Kunin R Tavares A Forman R and Wilber G 1984 *New developments in the use of ion exchangers and adsorbents as precoat filters in Ion Exchange Technology*, ed D Naden and M Streit, Ellis Horwood Chichester, pp 563-578

[8] Malkoe E, Nuhoglu Y and Dundar M 2006 Adsorption of chromium (VI) on pomace-an olive oil industry waste: Batch and column studies *J Hazard Mater*, **B138** 142-151

[9] Aksu Z Gonen F and Demircan R 2002 Biosorption of chromium (VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon *Process Biochem* **38** 175-186

[10] Sharma S K Petrushevski B and Amy G 2008 Chromium removal from water: a review *J Water Supply:Research and Technology-AQUA*, **57**(8) 541-553

[11] Lakatos J, Brown S D and Snape C E 2002 Coals as sorbents for the removal and reduction of Cr(VI) from aqueous waste streams *Fuels*, **81** 691-698

[12] Koujalagi P S, Revanakar H N and Kulkarni R M 2020 Studies on Hexavalent Chromium Removal from Electroplating Rinse Solution onto an Anion Exchanger *AIChE J* **56**(1) 040003(1-8)

[13] Narjes H B Monireh G, Maryam K, Simin J D, Nasibeh R and Zaman K M 2018 Green Removal of Toxic Pb(II)from Water by a Novel and Recyclable Ag/γ-Fe2O3@r-GONanocomposite *Iran J Chem Eng* **37**(1) 29-37

[14] Ayuso E A, Sanchez A Gand Querol X 2003 Purification of metal electroplating waste waters using zeolites *Water res*, **37** 4855-4862

[15] Koujalagi P S, Divekar S V and Kulkarni R M 2018 Adsorption studies of hexavalent chromium on weak base macroporous anion exchanger Tulsion A 2X(MP) in water and organic solvent mixed media *Asian J Chem*, **30**(5) 1083-1087

[16] Hanif M A Nadeem R, Bhatti H N, Ahmad N R and Ansari T M 2007 Ni(II) biosorption by Cassia fistula (Golden Shower) biomass *J Haz Mater*, **139**(2) 345-355

[17] Rengaraj S Yeon K H, Kang S Y Lee J U, Kim K W and Moon S H 2002 Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin *J Hazard Mater*, **B92** 185-198

[18] Rengaraj S and Moon S H 2002 Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins *Water res*, **36**(7) 1783-1793

[19] Ali Abdullah J, Al Lafi A, Alnana T, Al Masri W, Amin Yand Alkfri M 2018 Adsorption Mechanism of Lead on Wood/Nano-Manganese Oxide Composite *Iran J Chem Eng*, **37**(4) 131-144

[20] Kauspediene D, Kazlauskienė E, Cesuniene R, Gelfiūnienė A, Raguaskas R and Selskiene A 2013 Removal of the phthalocyanine dye from acidic solutions using resin with the polystyrene divinylbenzene matrix *Chemija*, **24** 171-181

[21] Ghosh S Dhole K J Tripathy M K, Kumar R and Sharma R S 2015 FTIR spectroscopy in the characterization of the mixture of nuclear grade cation and anion exchange resins *J Radioanal Nucl Chem*, **304** 917-923

[22] Alishahi S M, Naushad M Ahamad T Alothman Z A and Aldalbahi A 2014 Synthesis, characterization of curcumin based ecofriendly antimicrobial bio-adsorbent for the removal of phenol from aqueous medium *Chem Eng J*, **254** 181-189

[23] Haddad D, Mellah A, Nibou Dand Khemaissa S 2018 Promising enhancement in the removal of uranium ions by surface-modified activated carbons: kinetic and equilibrium studies *J Environ Eng*, **144**(5) 04018027

[24] Gode F and Pellivan E A 2003 A comparative study of two chelating ion-exchange resins for the removal of chromium (III) from aqueous solution *J Hazard Mater*, **B100** 231-243

[25] Cheng Ting, Chen Chen, Tang Rong, Han Cheng-Hui and Tian Yuan 2018 Competitive Adsorption of Cu, Ni, Pb and Cd from Aqueous Solution onto Fly Ash-Based Linde F(K) Zeolite *Iran J Chem Eng*, **37**(1) 61-72

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