Chromium(VI) ions were removed from industrial wastewater. In this regard, a rig was fabricated carrying alkaline anion resin. Various experiments were carried out by varying pH, temperature and volumetric flow rate of solution by employing a rig to study the kinetics of the ion exchange process. The rate constant \(k\) and maximum solid phase concentration of exchanged solute \(q_0\) were calculated using the Thomson equation to scale up the purification process of industrial runoff of chromium(VI) from the tanning, photography and ceramic industry. Experimental optimization revealed that developed setup will remove chromium(VI) to a level of 5 mg/dm\(^3\) from 300 mg/dm\(^3\) in 40 000 dm\(^3\) of wastewater. To achieve the best results for the flow rate of 10 000 dm\(^3\)/day, 12.03 kg of anionic resin were recommended by fixing the pH of the setup at 7.4 while maintaining the treatment temperature at 20 °C.

1. INTRODUCTION

Chromium salts are extensively use in various industries such as tanneries, ceramics, glass, photography, leather and electrochemical industries. Owing to inappropriate wastewater treatment facilities, waste streams from these industries may contain an objectionable quantity of heavy metals like cadmium, mercury, lead, cobalt, zinc and most importantly chromium. As a matter of fact, chromium is moderately present in the
Earth’s crust. It takes 4th place in 29 biologically significant elements and 17th in non-gaseous elements. Chromium ions in water originate from both natural and man-made pollution [1]. Regarding the former one, geological erosion is the major source of incorporation. It is one of the most notorious heavy metals as it has a tendency to accumulate through the food chain [2]. Its two most common compounds are those of trivalent Cr(III) and hexavalent Cr(VI). Cr(III) is neither corrosive nor irritating. Obstinately, trivalent chromium in small doses is required as a dietary component for human, plant, and animal metabolism. The deficiency of chromium Cr(III) in humans leads to certain types of diabetes, cardiovascular diseases, and nervous system disorders [3]. However, Cr(VI) is oncogenic and produces 1000 times more toxicity than trivalent chromium. Cr(VI) ions are mobile and hence they readily get into underground waters and make them toxic [4–6].

The International Agency for Research on Cancer (IARC) has placed Cr(VI) in Group 1 (carcinogenic to humans) as even its low concentrations can cause allergic effects to living organisms. On the other hand, its high concentration causes irritation on skin which may lead to ulcer and other contact dermatitis [7]. Moreover, standards for its exposure in industrial plant were determined and published by the health act (OSHA), 1970, American Conference of Governmental Hygienists (ACGH) and The American National Standards Institute (ANSI). According to the World Health Organization standards for drinking water, the maximum contaminant level (MCL) of Cr(VI) is 0.05 mg/dm$^3$ [8]. Hence, the presence of high concentration of chromium contaminants, especially Cr(VI), may cause detrimental effects to both human health and ecology [4, 9, 10]. Due to its capability of damaging DNA, its elimination from wastewater and especially drinking water is of prodigious significance [11, 12]. Treatment technologies such as coagulation, chemical precipitation, solvent extraction, electrolysis, ultrafiltration, membrane separation, adsorption and electrodialysis have been developed for removing Cr(VI) from industrial runoff [11, 13, 14]. However, capital and operational costs often limit efficiency and the effectiveness of these methods [15]. In contrast, ion exchange has proved to be the most promising and low cost method to eliminate Cr(VI) from drinking water [16, 17] as the improved sorption capacity of ion-exchange resins may have advantages over existing processes. The process has proven its worth by not only removing metals, ionized organic chemicals, organic amines but also by organic and inorganic anions from wastewater. Further, the process can utilize either naturally occurring resins or synthetic ion exchange resins. The former consists of complex aluminosilicates with sodium as a mobile ion like zeolites and later are manufactured by the copolymerization of styrene and divinylbenzene [18–20].

Tremendous work has been reported for the use of cation exchange resins in the removal of chromium from aqueous solutions. Rengaraj et al. [21] utilized synthetic cation exchange resins (IRN77 and SKN1) and studied the effect of various parameters on Cr(VI) removal. Further, they utilized them for the removal of Cr(VI) from a nuclear power plant coolant water. They found that the resins were capable removing 100 mg/dm$^3$ of chromium from aqueous solution in 98%. In addition, they tested the resin IRN77 for the
removal of Co(II), Cr(III) and Ni(II) and reported 95% removal under optimal conditions [22]. However, limited work has been reported on the utilization of anionic exchange resins for the removal of Cr(VI). Anionic resins can be used over the entire pH range as they are highly ionized carrying OH\textsuperscript{−}. The effectiveness of various anion exchange resins like Spectra/Gel for removing Cr(VI) ions from synthetic wastewater has been evaluated over wide range of initial concentrations and favorable results were obtained [23].

The objective of the present study was to evaluate the effectiveness of another synthetic strong base anion resin Purolite A-400 for capturing Cr(VI) ions from its simulated wastewater solution. Moreover, the study focused on the generations of breakthrough data for the parameters like flow rate, temperature, pH and initial solution concentration using an anionic exchanger. The constants of the Thomson equation, rate constant $k$ and maximum solid phase concentration of exchanged solute $q_0$ at the best conditions were calculated to be used in scaling up the process. These constants can be used to find the amount of anionic exchanger required for the commercial scale design. A number of investigations have been reviewed but no major findings have been reported for the scale up studies of ion exchangers for commercial scale purpose. This study can be taken to bridge this gap.

2. EXPERIMENTAL

Materials and methods. The stock solution of Cr(VI) varied from 0 to 600 mg/dm\textsuperscript{3}. It was prepared by dissolving of analytical reagent grade di-hydrated sodium dichromate salt (Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}·2H\textsubscript{2}O, Merck, Germany) in doubly distilled water. The ion exchange process was carried out utilizing Purolite A-400, anionic exchange resin, which was purchased from Lenntech. The physicochemical properties and specifications, as reported by the suppliers, are given in Table 1. Distilled water was prepared on lab scale to minimize the external disturbances in the stock solution.

Table 1. Physical and chemical properties of Purolite A-400

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total capacity, Cl\textsuperscript{−} form</td>
<td>1.3 eq/dm\textsuperscript{3}</td>
</tr>
<tr>
<td>Moisture retention, Cl\textsuperscript{−} form</td>
<td>48–54%</td>
</tr>
<tr>
<td>Particle size range</td>
<td>300–200 µm</td>
</tr>
<tr>
<td>Reversible swelling, Cl\textsuperscript{−} → OH\textsuperscript{−} (maximum)</td>
<td>20%</td>
</tr>
<tr>
<td>Temperature limit, Cl\textsuperscript{−} form</td>
<td>100 °C</td>
</tr>
<tr>
<td>Temperature limit, OH\textsuperscript{−} form</td>
<td>60 °C</td>
</tr>
<tr>
<td>Particle size range &lt;300 µm (maximum)</td>
<td>300–1200 µm</td>
</tr>
<tr>
<td></td>
<td>1 wt. %</td>
</tr>
<tr>
<td>Uniformity coefficient (maximum)</td>
<td>1.7</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1080 mg/dm\textsuperscript{3}</td>
</tr>
</tbody>
</table>
Characterization. The residual concentration of Cr(VI) was determined through Rayleigh WFX-210 atomic absorption spectrometry (AAS) by employing a Cr-hollow cathode lamp at 4 and 6 mA current and 357.9 nm wavelength using air acetylene flame, hence indicating the initial and final effluent concentration from the anionic exchanger/resin bed. Further, the gradual fading in color of the solution can be well seen in comparison with the chromium free solution, i.e., distilled water. Also, the exhausted resin after the ion exchange process has a dark red color in comparison with fresh resin which was almost white.

Experimental setup. A lab scale experimental rig was fabricated (Fig. 1). A heater, with a proper safety integrity system (SIS), was utilized to maintain the desired temperature of stock solution (SS). The stock solution with known initial concentration was collected in a mixing tank in order to homogenize it. A suitable arrangement for maintaining constant liquid flow rate was made by installing a small scale centrifugal pump. A rotameter (0–65 dm³/h) was installed for the flow rate measurement. An ion exchange column with the internal diameter of 1.27 cm, cross sectional area of 1.2661 cm² and bed length of 12.5 cm was installed. It has a system for resin loading and unloading. A series of trials were carried out to eliminate Cr(VI) ions from its synthetic solution through the ion exchange process. To perform scale up studies, the best operating parameters like initial concentration of Cr(VI), pH, temperature and flow rate were determined. In all experimental runs, the weight of the anionic exchange resin bed was kept constant at 6 g (moist basis).

Adsorption experiments. The batch method was used to study the removal of hexavalent chromium ions from its SS. A standard curve was drawn, using the dilution method, for the known initial concentration (mg/dm³) and final concentration (AAS value). The SS of known initial concentration was charged into the heater with the set point of desired temperature. The solution was then homogenized in a mixing tank and
was pumped to the ion exchange column. The flow rate was controlled by a flow control valve at the discharge line of pump and was monitored by a rotameter installed. Afterwards, the SS was passed through the bed containing anionic exchange resin. The samples were taken from the drain points before and after ion exchange bed for analysis. During the experiment, fresh resin was loaded into the ion exchange bed for each run. The used resin was collected and preserved in a separate container and its regeneration with different alkaline solutions under different parameters was left for new studies. The experimental steps followed during each experimental run are presented in Fig. 2.

During initial investigations, the treatment temperature was fixed at 15 °C, pH at 7.4, volumetric flow rate at 6.5 dm³/h and hydraulic bed load of 54.16 m/h. The experimental results revealed that the removal of Cr(VI) was maximum (71.7% in terms of concentration reduction) at 300 mg/dm³ of initial Cr(VI) concentration. Hence, as a conclusion, 300 mg/dm³ was selected to be used in the generation of breakthrough data. All other parameters were determined in the same manner. The breakthrough data was generated (Table 2) with known diameter, length of column and mass of resin bed at the best operating conditions (Cr(VI) initial concentration 300 mg/dm³, equivalent to AAS scale value of 113.33 mg/dm³, temperature 20 °C, volumetric flow rate 8.0 dm³/h and pH 7.4) and was finally used in the scale-up study for finding the amount of anionic resin bed on a typical industrial scale. The data was generated keeping all the parameters fixed while varying the total volume of the synthetic solution.

Fig. 2. Experimental steps followed
Table 2

Generation of breakthrough data and analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>Volume used [dm$^3$]</th>
<th>NaOH solution volume [cm$^3$]</th>
<th>$C_e$</th>
<th>$\varepsilon$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>20</td>
<td>8.98</td>
<td>92.07</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>30</td>
<td>0.52</td>
<td>99.54</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>40</td>
<td>7.22</td>
<td>93.62</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>50</td>
<td>8.01</td>
<td>92.93</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>60</td>
<td>16.42</td>
<td>85.50</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>70</td>
<td>13.11</td>
<td>88.42</td>
</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>80</td>
<td>14.40</td>
<td>87.29</td>
</tr>
<tr>
<td>8</td>
<td>4.5</td>
<td>90</td>
<td>19.34</td>
<td>82.93</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>100</td>
<td>29.48</td>
<td>73.98</td>
</tr>
<tr>
<td>10</td>
<td>5.5</td>
<td>110</td>
<td>14.51</td>
<td>87.19</td>
</tr>
</tbody>
</table>

pH of the solution was fixed at 7.4 by using 0.1 mol/dm$^3$ sodium hydroxide solution. The fixed initial atomic absorption scale concentration of 113.33 mg/dm$^3$ (obtained against 300 mg/dm$^3$) was used to calculate the percentage removal efficiency of Cr(VI):

$$\varepsilon = \frac{C_i - C_e}{C_i} \times 100\%$$

where, $\varepsilon$ is the percentage removal efficiency, $C_i$ influent Cr(VI) ion concentration (mg/dm$^3$ or meq/dm$^3$) at the start of experimental run, $C_e$ effluent Cr(VI) ions concentration (mg/dm$^3$ or meq/dm$^3$). The generated data was plotted to estimate the kinetic equation constants from slope-intercept of the kinetic equation proposed by Thomas to describe the removal of the contaminants in the ion exchange column:

$$\ln \left( \frac{C_i}{C_e} - 1 \right) = \frac{k q_0 M}{Q} - \frac{k C_i V}{Q}$$

where $k$ is the rate constant, dm$^3$/day meq, $q_0$ maximum solid phase concentration of exchanged solute, eq/kg of resin or meq/g, $m$ weight of the resin, kg, $V$ volume of solution passed through column, dm$^3$, and $Q$ flow rate, dm$^3$/d. $\ln(C_i/C_e - 1)$ vs. $V$ was plotted, (Fig. 4), and results were analyzed by using the curve fitting statistical technique. The analysis of these results was based on the coefficient of correlation $R$. The coefficient lies in the range of $-1 < R < 0$, i.e., $R \rightarrow -1$, 0–[ revealing a negative linear relationship. The constants of Thomas equation were calculated by using the line best representing the data and the comparison of theoretical results for the amount of resin (moist basis) with experimental results, for the flow rates (500 dm$^3$/day and 1000 dm$^3$/day). Further,
the percentage error among the theoretical and the experimental values for scale up studies was calculated.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF INITIAL ION CONCENTRATION

The initial concentration of Cr(VI) in the stock solution was varied in the range of 0–600 mg/dm³. Removal of Cr(VI) ions increases with an increase in the initial concentration of Cr(VI) up to 300 mg/dm³ at fixed temperature of 20 °C when volumetric flow rate, hydraulic bed load, and Cr(VI) initial concentration was kept at 6.5 dm³/h, 54.16 m/h and 300 mg/dm³, respectively (Fig. 3a). On further increase in concentration, the removal does not increase, being even a little lower. This can be explained on the availability of maximum number of adsorption sites [24]. As the concentration of Cr(VI) ions increases, the number of collisions between ions and adsorption sites also increases. Beyond 300 mg/dm³, the resin matrix becomes saturated with Cr(VI) ions, thus, resulting in the decrease of removal efficiency.

3.2. EFFECT OF pH

pH influences the surface properties and ionic forms of chromium in its solution [25]. In acidic aqueous solutions (pH < 7), chromium ions exist mainly in the form of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{HCrO}_4^-$ ions, while in the form $\text{CrO}_4^{2-}$ ions in basic solutions (pH > 7) [23, 26]. Therefore, the influence of pH was examined in the range of 6–7.5 during the present studies. It can be deduced that maximum Cr(VI) removal was obtained at pH 7.4, (Fig. 3b). The effect of pH was examined at fixed temperature, volumetric flow rate, hydraulic bed load, and Cr(VI) initial concentration, i.e., 20 °C, 6.5 dm³/h, 54.16 m/h and 300 mg/dm³, respectively. The percentage removal of Cr(VI) ions was low when pH < 7 (Fig. 3b). However it increases at pH > 7. Similar observations were reported by Koujalagi et al. [24] who investigated adsorption of Cr(VI) ions on Tulsion A-27 anionic resin. They found that the percentage removal of Cr(VI) ions decreased in acidic region. The decrease in $\varepsilon$ at pH < 6 is due to the formation of species like $\text{H}_2\text{CrO}_4$ and $\text{HCrO}_4^-$ and lower number of Cr(VI) ions will be available for exchange in the anionic resin. Further, the removal trend seems to be decreasing on further increase in pH from 7.4 (Fig. 3b). It is due to the fact that as pH increases (in the aqueous solution of Cr(VI) ions), there is an abundance of hydroxyl ions and Cr(III) hydroxide precipitates. The similar effect was observed by Barakat et al. [23] while removing Cr(VI) from synthetic wastewater using Spectra/Gel anionic exchange resin. They associated the decrease in percentage removal to the appearance of species like Cr(OH)₃ and anionic Cr(OH)₄⁻ at strong basic conditions [4, 23]. Moreover, the similar decreasing effect in percentage removal was
observed during chromium removal using Tulsion A-27 anionic resin [24] and rice husk carbon [27]. It was reported that the removal mechanism depends on the complex interactions between the metal ions and resin. It may be simultaneously dominated by adsorption and ion exchange mechanisms [9]. Subsequently, pH dependence of ion exchange proves that metal ions are adsorbed according to the ion-exchange mechanism.

![Graphs showing the effect of various parameters on Cr(VI) removal](image)

**Fig. 3.** Effect of a) initial Cr(VI) concentration, b) pH, c) temperature, and d) volumetric flow rate on the reduction of Cr(VI) removal efficiency when 2 dm³ of synthetic solution was treated; pH 7.4, t 20 °C, hydraulic load 54.16 m/h, flow rate (a–c) 6.5 dm³/h, initial concentration (b–d) 300 mg/dm³

### 3.3. EFFECT OF TEMPERATURE

The effect of temperature on removal of Cr(VI) ions in aqueous media was investigated in the temperature range of 15–50 °C). 2 dm³ of synthetic solution was treated at the flow rate of 6.5 dm³/h, hydraulic load of 54.16 m/h and 300 mg/dm³ initial concentration. The results indicate that the removal efficiency of Cr(VI) ions reaches the maximum at 20 °C (Fig. 3c). Upon increasing temperature, the removal efficiency decreased. This effect can be explained based on solubility increase connected with increasing mobility of Cr(VI) ions at elevated temperatures. Similar effect was observed by Pandey et al. [28] in their study of kinetics and equilibrium of chromium adsorption on zeolite resin.
3.4. EFFECT OF VOLUMETRIC FLOW RATE

A 2 dm³ of synthetic solution was used, the temperature fixed at 20 °C, hydraulic load of 54.16 m/h and initial concentration of Cr(VI) 300 mg/dm³. The volumetric flow rate was varied between 6.5 and 11 dm³/h. The removal efficiency of Cr(VI) ions was low at both high and low flow rates. The rate of 8 dm³/h proved to be the optimum, leading to 90.62% removal of Cr(VI) (Fig. 3d). This trend can be explained on the basis of availability of vacant sites for ion exchange. At high volumetric flow rates, the sites remained vacant causing the decrease in percentage removal of Cr(VI). In conclusion, if the flow rate is kept high, contact time reduces. The highest removal of Cr(VI) ions was obtained at initial concentration of 300 mg/dm³, pH 7.4, volumetric flow rate of 8 dm³/h and temperature of 20 °C.

3.5. BREAKTHROUGH DATA ANALYSIS

The best results in Cr(VI) ion removal can be obtained at the following operating conditions: initial concentration of Cr(VI) 300 mg/dm³ temperature 20 °C and 8 dm³/h the volumetric flow rate, when 1.5 dm³ of synthetic solution was treated.

As is seen in Fig. 4, the exponential trend line showed good estimate of breakthrough data during owing to the largest value of $R = 738 \ (R^2 = 0.5448)$. Hence, the values of rate constants $k$ and maximum solid phase concentration of solute ($q_0$) are
determined as 17.42 dm³/day meq and 7.69 meq/g, respectively, using the equation of exponential trend line, while the flow rate was kept constant at 192 dm³/day. Hence, if a plant produces a total 40 000 dm³ of wastewater in a specific test run, 11.855 kg of resin will be required to reduce the concentration of hexavalent chromium from 300 mg/dm³ to 5 mg/dm³. Further, the amount of resin was theoretically calculated as 11.862 and 11.874 kg for 500 dm³/day and 1000 dm³/day, respectively, using Eq. (2). Moreover, the experimental data for 500 dm³/day and 1000 dm³/day was generated, using five data points, and shown in Fig. 5.

The exponential trend line was used for approximation. Hence, on the basis of experimental values, the amount of resin and the values of rate constants and solid phase solute concentration were determined. Further, the experimental and theoretical values were plotted (Fig. 6). As is seen, the calculated amounts of resin are in good agreement with the experimental ones.

### Table 1

<table>
<thead>
<tr>
<th>Flow rate [dm³/day]</th>
<th>Rate constant (k) [dm³/(day·meq)]</th>
<th>Maximum solid phase concentration (q₀) [meq/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>192</td>
<td>8.0</td>
<td>18.586 on average</td>
</tr>
<tr>
<td>500</td>
<td>20.8</td>
<td>7.698</td>
</tr>
<tr>
<td>1000</td>
<td>42.0</td>
<td>7.772 on average</td>
</tr>
</tbody>
</table>

Fig. 5. Thomas kinetic equation plots for two wastewater flow rates.
Removal of chromium(VI) from wastewater

Fig. 6. Theoretical and experimental values of mass of resin required for the two flow rates and percentage error (for treating volume of 40 000 dm³)

It can be an evidence to validate the generated breakthrough data. Finally, the experimental values of $k$ and maximum solid phase concentration of exchanged solute $q_0$ for ion exchange process from breakthrough data under the two flow rates for distilled water is presented in Table 3.

4. CONCLUSION

A simulated chromium(VI) solution was passed through a resin bed within the concentration range of 0–600 mg/dm³. The best operating conditions among the potential parameters like pH, temperature and volumetric flow rate were determined and the lowest concentration of the contaminant in the final solution was determined at initial concentration 300 mg/dm³, temperature 20 °C, pH = 7.4, volume of treated solution 1.5 dm³, and volumetric flow rate 8.0 dm³/h while fixing the anion exchange resin mass at 6.0 g (when moist). The generation of breakthrough data was the major focus. The data was generated for the best operating conditions to use it in scale up studies for the commercial scale design of ion exchange column after finding the amount of resin. The average values of constants of Thomson equation $k$ and $q_0$, for ion exchange process at different flow rates were 18.586 dm³/(day·meq), and 7.722 meq./g of resin.

In the leading part, theoretically obtained values for the amount of resin in a full scale design were compared with the values found experimentally at the two flow rates 1000 and 500 dm³/day. The percentage error was calculated which showed very good matching for distilled water (<1%). Using the average values of the Thomson equation, it can be concluded that if the plant operates on full capacity of 10 000 dm³/day (40 000 dm³), keeping initial concentration ($C_i$) at 300 mg/dm³ and maximum effluent concentration of 5 mg/dm³, regeneration will be required once every 4 days. Hence, for the above
mentioned capacity and flow rate, i.e., (1000 dm$^3$/day), the total mass of the resin required was calculated to be 12.03 kg.

REFERENCES

Removal of chromium(VI) from wastewater


