ECLÉTICA QUÍMICA

Eclet. Quim. 49 | e-1402, 2024

Original Article

https://doi.org/10.26850/1678-4618.eq.v49.2024.e1402

Determination of parameters and kinetic evaluation for chromium (VI) removal using four resins

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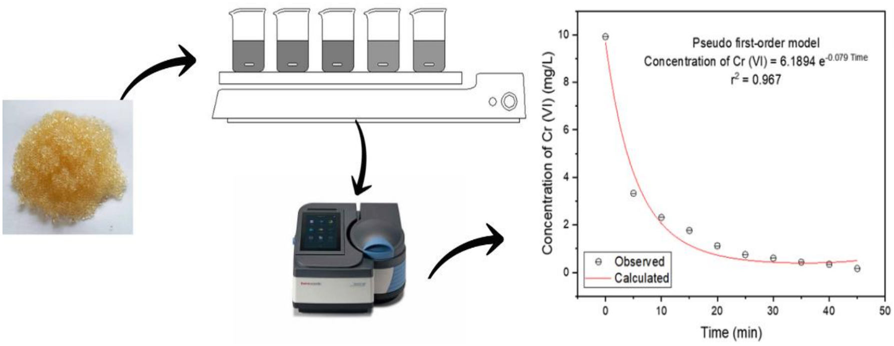
Abstract

This research aimed to identify optimal studied variables for chromium (VI) removal using four resins (IRA 96, IRA 400, DOWEX 1x8, and LEWATIT). A 1,5-diphenylcarbazide method was used for the quantification of chromium (VI). A factorial design with triple replication at the center point was used to evaluate pH, resin dose (g/100 mL), and initial chromium (VI) concentration. The optimal values for the four resins were a pH of 3, a resin concentration of 0.15 g/100 mL of solution, and an initial concentration of 10 mg/L of chromium. Then, an ANOVA study was done to compare the resins results using a p-value <0.05. The DOWEX resin presented the highest removal percentage (98.39%) for a reaction period of 45 minutes, with an exponential model that fits a pseudo-first-order kinetics with a coefficient of determination equal to 0.967.



Article History

Received November 11, 2022
Accepted April 24, 2024
Published June 07, 2024

Keywords

1. resins;
2. DOWEX;
3. chromium (VI);
4. pseudo first order;
5. kinetics.

Section Editor

Assis Vicente Benedetti

Highlights

- Dowex resin presented the highest percentage of removal.
- A factorial design with triple replication at the centre point was used.
- The exponential model adjusts to pseudo-first-order kinetics.

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1. Introduction

Industries such as leather tanning, dyeing and galvanizing release a large amount of untreated chromium-charged water, which constitutes a danger to living beings (Bhatti *et al.*, 2017). Industrial wastewater containing Cr(VI) is a complex threat to the environment (Liu *et al.*, 2015), (Tümer and Edebali, 2019). In these industrial effluents, chromium is present in trivalent and hexavalent forms. The toxicity of each depends on its state of oxidation: it can be carcinogenic, mutagenic and genotoxic (Bhatti *et al.*, 2017; Li *et al.*, 2018). Cr(VI) concentrations in wastewater can range from tenths to hundreds of milligrams per liter (Kahraman and Pehlivan, 2019). There are several methods to reduce chromium concentration in wastewater, such as chemical precipitation (Xie *et al.*, 2017), adsorption (Coşkun *et al.*, 2018), biosorption (Costa, 2017), reverse osmosis (Gaikwad and Balomajumder, 2017), electrocoagulation (Hu *et al.*, 2017), ion exchange (Korak *et al.*, 2017), electrodialysis (Sadyrbaeva, 2016), and photocatalysis (Wang *et al.*, 2016).

Ion exchange is an effective treatment for Cr(VI) removal (Gorman *et al.*, 2016). It has been shown that resins with styrene-divinylbenzene matrix and quaternary ammonium functional groups (Kusku *et al.*, 2014), N-methylglucamine tertiary amine polyamine, and sorption capacity can be used for the efficient removal of hexavalent chromium of wastewater due to their good thermal stability. To optimize the process, several authors use Freundlich and Langmuir isotherms to determine the relationship between the amount of chromium adsorbed by the resin and the concentration of chromium in the solution, together with adsorption kinetics to investigate the mechanism of chromium adsorption (Bajpai *et al.*, 2012; Polowczyk *et al.*, 2016).

This study aims to evaluate different types of ion exchange resins for the adsorption of Cr(VI) in industrial effluents and to determine the efficiency of each. The effect of using each resin, pH and chromium concentration have been studied, as well as the removal kinetics, through direct modelling of the obtained data.

2. Experimental

2.1. Analytical curve preparation

For the quantification of chromium (VI), the standard colorimetric method of 1,5-diphenylcarbazide was used (Pflaum and Howick, 1956) Cr-3500 APHA-AWWA-WEF, using a UV-VIS Genesys 150 spectrophotometer. Analysis grade potassium dichromate obtained from Sigma Aldrich was used as a standard (500 mg/L). The tested concentrations ranged from 0.2 to 1.2 mg/L of chromium (VI), using distilled water for the determinations. Measurements were taken at 540 nm wavelength.

Diphenylcarbazide reacts with Cr(VI) in acidic medium producing the colored complex Cr(III)-diphenylcarbazone **Eq. 1**:

$$2CrO_4^{2-} + 3H_4L + 8H^+ \rightarrow Cr(HL)_2^+ + Cr^{3+} + H_2L + 8H_2O \quad (1)$$

where, H_4L is 1,5-diphenylcarbazide and H_2L is diphenylcarbazone.

2.2. Experimental design

A factorial design of type 2^2 with triple replication in the central point was configured for each resin in the study. The factors studied were pH, resin concentration (g/100 mL) and initial chromium (VI) concentration. For pH adjustment, concentrated H_2SO_4 and 10% NaOH were used, measuring the entire operation with HANNA HI2211 pH/mV equipment, while all the weighing measurements were performed on a Mettler Toledo ME 204 analytical balance. The factor levels studied are presented in **Table 1**. The experiments were carried out in a pH range of 3 to 5 due to the precipitation of Cr(VI) ions at higher pH. The levels used for resin dosing were set in a range of 0.05 to 0.15 g to optimally evaluate the contact time (Patel *et al.*, 2022), while the Cr(VI) solution concentrations were set in a range where no deviation from Beer's Law is observed.

Table 1. Studied factor levels.

Factor	Low level	Central point	High level
pH	3.00	4.00	5.00
Dose (g/100 mL)	0.05	0.10	0.15
Concentration (mg/L)	10.00	30.00	50.00

2.3. Adsorption experiments

Amberlite IRA 96, Amberlite IRA 400, Dowex 1x8 and Lewatit MP-62, resins were purchased from Sigma Aldrich. For each resin, 7 experiments were configured (4 for the high and low levels, 3 for the central points) following what is indicated in **Table 1**. The experiments were performed in triplicate.

For the determination of the removal percentage, **Eq. 2** was used, where C_0 is the initial concentration and C_f is the final concentration.

$$\text{Remotion } (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

2.4. Optimization process

After executing the experimental runs for each resin and identifying the optimal test conditions, five replications were performed for each optimized experiment and an ANOVA was performed to evaluate the existence of significant differences between the resins used in the different experiments.

2.5. Kinetic study

A kinetic study was carried out with the resin that resulted in the highest rate of removal of chromium (VI) in solution. The sampling was carried out by taking 5 mL of solution every 5 minutes until completing 45 min reaction time (total volume 100 mL). The modelling process was carried out using the OriginPro 9.0 software fitting tool.

3. Results and discussion

3.1. Analytical curve

To quantify chromium (VI), a linear regression **Eq. 3** was obtained with a coefficient of determination equal to 0.9997.

$$\text{Absorbance} = 0.7729 * \text{Concentration} \quad (3)$$

3.2. Adsorption experiments

The results of the different combinations of the factorial design levels are shown in **Tables 2** and **3**. All the experiments were carried out under the same conditions. From **Table 3** it can be inferred that the highest percentage of removal was for the

DOWEX 1x8 resin. To enhance the interaction of resins with Cr(VI), a pH of 3 was chosen to facilitate the contact of H^+ ions with the surface, thus preventing them from becoming negatively charged and consequently reducing their adsorption capacity. On the other hand, low pH prevents the precipitation of Cr(VI), since at high pH, the interaction with OH^- ions favors the negative charge of the resin. Likewise, by increasing the dose of resin and decreasing the concentration of the Cr(VI) solution, an increase in the removal percentage is favored.

Figure 1 presents the Pareto plot for chromium removal. It can be seen that resin concentration, chromium concentration and pH have a significant effect ($p<0.05$) on the removal percentage. In the same way, the double interactions present a significant effect ($p<0.05$).

Table 2. Results obtained from the experimental design for IRA 96 and IRA 400 resins under study.

			IRA 96			IRA 400		
pH	**Cc resin (g)**	**Cc Cr(VI) (mg/L)**	**Absorbance**	**Cr final (mg/L)**	**Cr(VI)% Removal**	**Absorbance**	**Cr final (mg/L)**	**Cr(VI)% Removal**
3	0.05	10	0.2677	6.93	30.72	0.2656	6.87	31.27
		50	0.7275	37.65	24.70	0.6219	32.18	35.63
	0.15	10	0.1001	2.59	74.09	0.1099	2.84	71.57
		50	0.4175	21.61	56.79	0.2924	15.13	69.74
4	0.10	30	0.3256	16.85	43.83	0.2759	14.28	52.41
			0.3393	17.56	41.47	0.2723	14.09	53.02
			0.3395	17.57	41.42	0.2719	14.07	53.09
5	0.05	10	0.2859	7.40	26.00	0.2654	6.87	31.33
		50	0.8219	42.54	14.93	0.6691	34.63	30.74
	0.15	10	0.1439	3.73	62.75	0.1147	2.97	70.33
		50	0.6316	32.69	34.62	0.3215	16.64	66.72

Table 3. Results obtained from the experimental design for Dowex and Lewatit resins under study.

			IRA 96			IRA 400		
pH	**Cc resin (g)**	**Cc Cr(VI) (mg/L)**	**Absorbance**	**Cr final (mg/L)**	**Cr(VI)% Removal**	**Absorbance**	**Cr final (mg/L)**	**Cr(VI)% Removal**
3	0.05	10	0.1641	4.25	57.54	0.2607	6.75	32.55
		50	0.6527	33.78	32.44	0.6990	36.17	27.65
	0.15	10	0.0336	0.87	91.31	0.1008	2.61	73.93
		50	0.0774	4.00	91.99	0.4300	22.25	55.49
4	0.10	30	0.1304	6.75	77.51	0.4809	24.89	17.04
			0.1352	7.00	76.67	0.4375	22.64	24.52
			0.1251	6.47	78.42	0.4763	24.65	17.84
5	0.05	10	0.1670	4.32	56.80	0.3047	7.88	21.16
		50	0.4278	22.14	55.72	0.8811	45.60	8.80
	0.15	10	0.0355	0.92	90.82	0.1870	4.84	51.61
		50	0.0893	4.62	90.76	0.6581	34.06	31.88

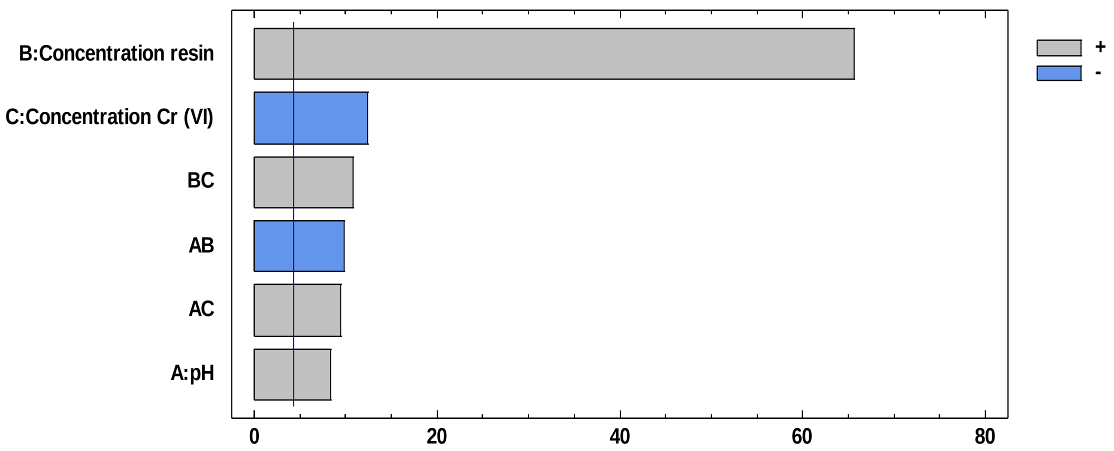

Figure 1. Pareto plot for chromium removal using DOWEX resin.

Figure 2 presents the graph of the main effects where it is observed that as the concentration of the chromium solution increases, the percentage of removal begins to decrease (negative slope). Likewise, as the pH and resin dosage increase, the percentage of removal increases (Patel *et al.*, 2022).

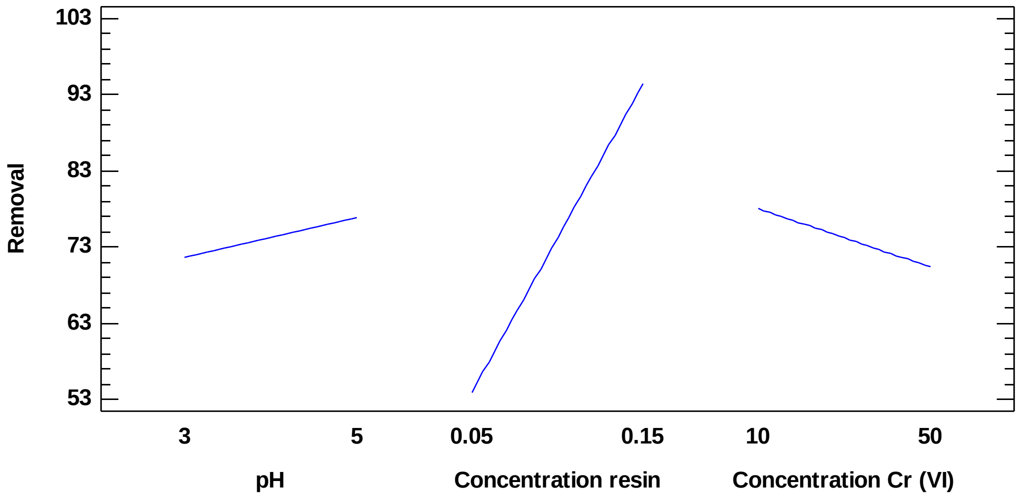

Figure 2. Main effects plot for chromium removal.

3.3. Adsorption studies

Table 4 shows the percentage of chromium removal for each resin in its optimized form. The analysis of variance reports a $p < 0.05$, which indicates a significant statistical difference between the resins under study.

Figure 3 illustrates the box-and-whisker plot for the experiment. The variation of the results for the conditions of each resin is minimal. However, DOWEX resin has the highest chromium (VI) removal percentage (98.40%) from the solution, which is why it could be considered the resin with the most effective chromium decontamination process in different effluent types.

Table 4. Percentage of removal for different resins.

Replicate	IRA 96	IRA 400	DOWEX	LEWATIT
1	84.96	87.28	98.20	76.56
2	84.97	86.83	98.36	75.96
3	84.58	87.17	98.24	75.95
4	84.77	86.75	98.49	76.21
5	84.90	86.72	98.40	75.90

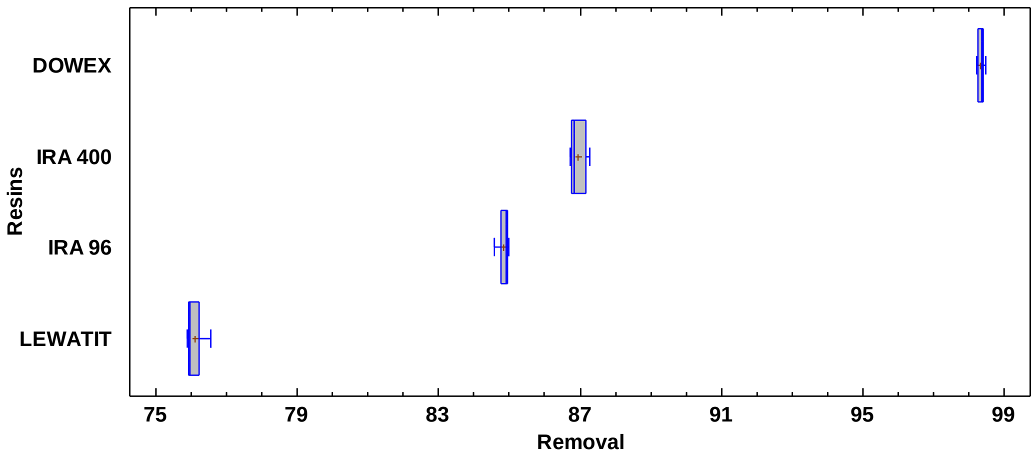

Figure 3. Box-and-whisker plot for chromium removal (%).

To perform the kinetic study, the optimal conditions for working with the DOWEX resin were taken, starting with an aqueous chromium solution of 10 mg/L, taking a sample of 5 mL every 5 min for a period of 45 min. The results are presented in **Table 5**.

Table 5. Removal kinetics data for the DOWEX resin.

Time (min)	Concentration Cr (mg/L)
0	9.92
5	3.33
10	2.31
15	1.76
20	1.12
25	0.75
30	0.60
35	0.43
40	0.34
45	0.16

3.4. Kinetic study

The mathematical model that determines the chromium (VI) adsorption kinetics for DOWEX resin is a pseudo-first-order model (Ok *et al.*, 2014) with an adjusted coefficient of determination of 0.967, a value that explains the variability that the model can estimate. **Equation 4** and **Fig. 4** present the model obtained:

$$\text{Concentration} = 6.1894e^{-0.079*\text{Time}} \quad (4)$$

where 6.1894 corresponds to the initial concentration (in mg/L) y 0.079 to the rate constant (in min^{-1}).

In the **Fig. 4** it is observed that around the first 5 min there is a rapid removal of chromium (VI), which is usually found under the forms of $HCrO_4^-$ and $Cr_2O_7^{2-}$, them it slows down after 10 min as pointed out by Xing *et al.* (2022) and Ok *et al.* (2014).

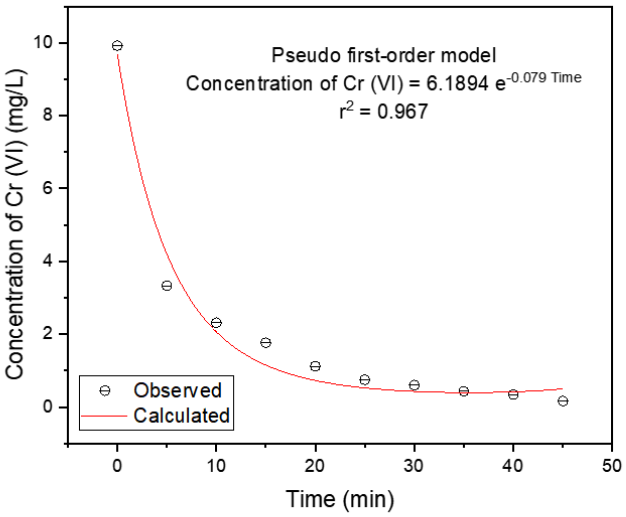

Figure 4. Adsorption kinetics for DOWEX resin.

Research has shown that pH, temperature, resin dose, contact time and initial chromium (VI) concentration are all significant factors in the chromium (VI) adsorption process, using Freundlich, Langmuir and Scatchard adsorption isotherms (Kahraman and Pehlivan, 2019). In this research study, the influence of pH, resin dose and initial chromium (VI) concentration were studied by direct modelling of the data, identifying an exponential model. The direct adaptation of data to mathematical models has been developing increasingly since it allows a clear appreciation of the adsorption behavior (Gaikwad and Balomajumder, 2017).

On the other hand, (Hashem *et al.*, 2018) have reported bioremediation processes for chromium (VI) removal using *Syzygium cumini* bark as an adsorbent, achieving removal rates of 99.9% in 15 min using 3 g of adsorbent. In this study, using DOWEX resin, a removal of 98.39% was obtained in 45 min of reaction time using only 0.15 g of resin with an initial chromium concentration of 10 mg/L.

4. Conclusions

An analytical technique using visible ultraviolet spectroscopy was used to quantify chromium, identifying DOWEX resin as the most appropriate to remove chromium in solution, achieving 98.39% effectiveness when working at a pH of 3 with a dose of 0.15 g/100 mL and an initial chromium (VI) concentration of 10 mg/L in solution. The equation found corresponds to an exponential model that fits a pseudo-first-order kinetics with a coefficient of determination of 0.967 registering a velocity constant equal to 0.079 min^{-1}.

Authors' contributions

Conceptualization: Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Data curation:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Formal Analysis:** Ramirez-Revilla, S. A.; Camacho-Valencia, D.; Ortiz-Romero, D.; **Funding acquisition:** Not applicable; **Investigation:** Ramirez-Revilla, S. A.; Camacho-Valencia, D.; Ortiz-Romero, D.; **Methodology:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Project administration:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Resources:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Software:** Not applicable; **Supervision:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Validation:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Visualization:** Ramirez-Revilla, S. A.; Ortiz-Romero, D.; **Writing – original draft:** Ramirez-Revilla, S. A.; Camacho-Valencia, D.; Ortiz-Romero, D.; **Writing – review & editing:** Ramirez-Revilla, S. A.; Camacho-Valencia, D.; Ortiz-Romero, D.;

Data availability statement

All data sets were generated or analyzed in the current study.

Funding

Not applicable.

Acknowledgments

Not applicable.

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