



ADSORPTION OF CHROMIUM IONS ON OIL SHALE WASTE

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ABSTRACT

The adsorption of chromium (III) ions onto retorted shale, a waste product of the pyrolysis of oil shale, was investigated as a function of initial pH, temperature, and initial metal ion concentration. Adsorption experiments were carried out in a batch system and the uptake of the metallic ion was studied by using an initial concentration range of 200-500 mg L⁻¹. The pseudo-first and pseudo-second order models were used to predict the rate constants of the adsorption system. Both Langmuir and Freundlich models were used to fit the equilibrium data; however, the former resulted in best fitting. Thermodynamic parameters such as enthalpy, free energy, and entropy changes were calculated. The values of such parameters showed that Cr(III) adsorption was favored at high temperatures.

KEYWORDS

chromium (III), heavy metals, retorted shale, adsorption isotherms, wastewaters

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1. INTRODUCTION

The presence of heavy metals in streams and lakes has been responsible for several health problems in human and other living beings. These metal ions are released to the ecosystem at elevated concentrations as a result of unregulated application and inappropriate waste-disposal practices. In particular, chromium has received considerable attention because it is a toxic metal and it does not undergo biodegradation. The main sources of water contamination with chromium ion are industrial wastewaters from leather tanning, electroplating, textile, metal processing, paint and pigments, dyeing, and steel fabrication.

Among various methods available to reduce heavy metal concentrations from wastewaters are chemical precipitation, ion-exchange, membrane filtration, and adsorption. In the last few decades, adsorption has received much consideration and has become an alternative to conventional precipitation. Adsorption is a process that involves the contact of an aqueous phase with a particulate phase, which has the ability to remove or store one or more solutes present in the solution. The use of adsorbents, e.g., activated carbon (ElShafey et al., 2002; Lyubchik et al., 2004) and ion exchange resins (Dabrowski et al., 2004) to remove trace metals from aqueous systems has been widely investigated. However, these can be considered expensive materials; thus, researchers have been encouraged to look for other adsorbent materials that are both efficient and less expensive. Several cheap and abundant materials have been studied for the adsorption of heavy metals, such as peat (Brown and Allen, 2000; Kertman et al., 1993), clays (Celis et al., 2000; Cooper et al., 2001), diatomite (Khraisheh et al., 2004), chitosan (Mckay et al., 1989), sawdust (Taty-costodes et al., 2003; Shukla et al., 2002), siderite (Erdem and Ozverdi, 2005), and spent grain (Low et al., 2000).

In the present investigation, retorted shale (RS), a waste product obtained in the pyrolysis (550 °C) of oil shale, was studied as a possible cost-efficient adsorbent to remove chromium ion from wastewater. Since RS holds several organic and inorganic functional groups, it has high potential for heavy metal adsorption. In addition, the technological development for the beneficial use of this material is needed, considering that oil shale is abundant in 31 countries (Al-Qodah, 2000) and

Brazil has the second largest reserve in the world and possesses the most advanced technology. The Industrialization Business Unit of *Xisto Brasileira* (UN-SIX) belongs to Petrobras (Brazil) and is located in the town of São Mateus do Sul, in the State of Paraná (PR). This unit falls under the largest Brazilian shale reserve, the *Irati* formation, where 7800 tons of shale are extracted daily, producing a solid waste called retorted shale (RS), which accounts for 80 to 90 % of the raw materials used in the production process. However, the use of this waste represents one of the biggest problems associated with the industrialization of shale throughout the world.

Therefore, this study aims to evaluate the possibility of using shale waste as an adsorbent for removing Cr(III) ions from effluents using an adsorption technique. The investigated aspects included initial ion concentration, contact time, and pH of the solution.

2. EXPERIMENTAL

2.1 Materials

The retorted shale used in this study was obtained from São Mateus do Sul, State of Paraná, Southern Brazil. It was ground as received, sieved down to 75 µm, and used without any further treatment. All Cr(III) synthetic solutions were prepared dissolving chromium nitrate in deionized water.

2.2 Methods

2.2.1 Equilibrium studies

In batch adsorption experiments, a fixed mass of RS (1 g) was weighed, transferred to 120-mL flasks, and brought into contact with 100 mL of a Cr(III) solution of desired concentration. The flasks were sealed and stirred for 7 h at 260 rpm in a thermostatic shaking bath and maintained at constant temperature (30, 40, and 50 °C). The samples were taken at specific time intervals. Each experiment was repeated three times and the results are given as averages. At the end of the experiments, the adsorbent was removed by filtration through a normal filter paper and the chromium concentration in the supernatant

solution was measured by atomic absorption spectroscopy (Varian, Espectr AA-110 model). The effect of pH on adsorption was studied for 5 h at 30°C and the pH was adjusted by adding either 1.0-M NaOH or 1.0-M HCl to the Cr(III) solution (200 mg L⁻¹).

The amount of adsorbed Cr(III) and the percent adsorption (%) were calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

$$\text{Percent adsorption (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where q_t is the amount of Cr(III) adsorbed (mg g⁻¹) at different times (t), V is the volume of the solution (L), W is the weight of the adsorbent (g), and C_0 and C_t are the chromium concentrations (mg L⁻¹) at the beginning of the experiment and at a later time " t ", respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of adsorbent material

Physical and chemical analyses of RS were carried out using conventional chemical methods and analytical techniques available. The specific surface area of RS was determined by the BET method from the adsorption-desorption isotherm of nitrogen at its liquid temperature (77 K) (NOVA 2000 BET system). Particle size was obtained in a SILAS model 1064 analyzer. The surface charge of the RS was measured at different pH's using the potentiometric titration method. Adsorption kinetics assays were performed in batch reactors on a shaking incubator (TECNAL). The characteristics of the retorted shale were as follows: surface area (BET): 65.083 m² g⁻¹, density: 1.139 g cm⁻³, and average particle size: 19.1 μm. The chemical composition of the RS is shown in Table 1. In addition to the major components, the RS also contains MnO, V₂O₅, SrO, CuO, ZnO, ZrO₂, NiO, and sulfur, which account for the remaining 15.85 % of the overall composition. It was observed that the chemical constituents of RS were comprised mainly by acids, bases, and amphoteric

Table 1. Chemical composition of the retorted shale.

Chemical analysis	
Constituents	Weight %
SiO ₂	55.6
Al ₂ O ₃	11.4
Fe ₂ O ₃	8.60
CaO	3.50
K ₂ O	2.85
Na ₂ O	1.60
TiO ₂	0.60

oxides, which assured the presence of active groups of mineral species and organic residues on the grain surface, suggesting good adsorption behavior.

3.2 Effect of initial pH

The pH is one the most important factors in adsorption processes, as it influences the chemistry of heavy metals solutions (i.e., hydrolysis, complexation, redox reactions, and precipitation) and strongly affects the speciation and sorption availability of heavy metals. Thus, the effect of pH on Cr(III) uptake was examined from solutions with pH ranging from 1 to 7. Figure 1 shows the effect of the solution pH on the adsorption of Cr(III) at 30 °C, for an initial concentration of 200 mg L⁻¹. It is observed that adsorption of chromium increases as the pH increases and decreases with decreasing pH, since the binding sites are more protonated at low pH and, hence, less available to retain chromium ions. The maximum uptake of this ion was obtained at pH ~ 5.5. Above this pH value,

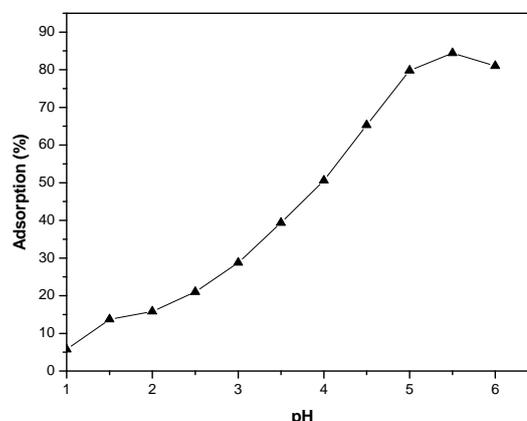


Figure 1. Effect of pH on Cr(III) adsorption by RS.

insoluble chromium hydroxide starts precipitating from the solution, making true adsorption studies impossible.

3.3 Effect of contact time and initial concentration

To establish an appropriate contact time between RS and Cr(III) ions, the adsorption capacities of the metallic ions were measured as a function of time. The experimental results for Cr(III) adsorption on RS for various concentrations of Cr(III) at 30 °C are shown in Figure 2. It is confirmed that the higher the concentration of the solution the better the adsorption is, following an expected trend. The equilibrium time required for maximum Cr(III) removal is 240 min. No further uptake was observed even after this contact time. Therefore, the isotherms were set for 7 h in all cases to allow sufficient time for equilibrium.

3.4 Kinetic studies

In order to investigate the mechanism of adsorption, the applicability of the pseudo-first-order and pseudo-second-order adsorption models via experimental data was tested. The first-order rate expression of Lagergren (Ho and McKay, 1999) is given as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e and q_t are the amounts of adsorbed Cr(III) (mg g^{-1}), at equilibrium and at time t , respectively;

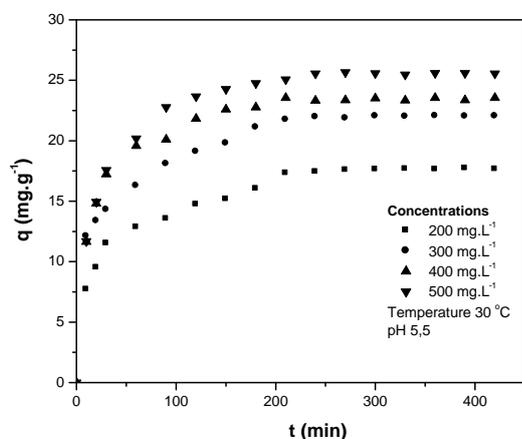


Figure 2. Effect of stirring time and initial concentration on Cr(III) adsorption by RS at 30 °C.

and k_1 (min^{-1}) is the rate constant of first-order adsorption capacity (Ho and McKay, 1999). After integration and application of the boundary condition $q_t = 0$ at $t = 0$. Equation (3) gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The slope and intercept of the plot of $\ln(q_e - q_t)$ versus t was used to determine the first-order rate constant k_1 .

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity (Ho and McKay, 1999) may be expressed in the form of:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second-order. Integrating equation (5), and taking into account that the initial adsorption rate (V_0) is $V_0 = k_2 q_e^2$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Thus, the slope and intercept of the plot of t/q_t versus time t was used to calculate the second-order rate constant k_2 and the parameter q_e .

Figure 3 shows the pseudo-second-order plot for Cr(III) adsorption at an initial concentration of 200 mg L^{-1} and different temperatures. Figure 4 shows the same plots at 30 °C and at different Cr(III) concentrations. The parameters calculated of both pseudo-first order and second-order rate

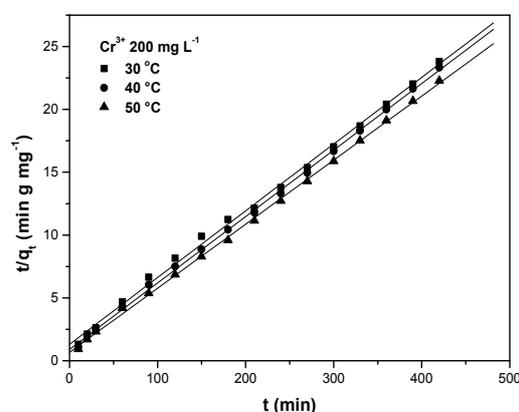


Figure 3. Pseudo-second-order plot of Cr(III) adsorption kinetics by RS at different temperatures and initial chromium concentration of 200 mg L^{-1} .

Table 2. Kinetic parameters of Cr(III) adsorption by RS at different temperatures.

C_0 (mg L ⁻¹)	Temp. (°C)	First-order		Second-order			
		k_1	R^2	k_2	q_e (mg g ⁻¹)	V_o (mg g ⁻¹ min ⁻¹)	R^2
200	30	0.0215	0.9808	0.0021	18.82	0.744	0.9976
400	30	0.0118	0.9384	0.0016	23.68	0.897	0.9964
200	40	0.0165	0.9820	0.0031	18.91	1.108	0.9991
400	40	0.1360	0.9298	0.0026	24.38	1.545	0.9972
200	50	0.0199	0.9822	0.0040	19.61	1.538	0.9992
400	50	0.0095	0.9675	0.0030	26.28	2.072	0.9979

equations for the Cr(III) concentrations of 200 and 400 mg L⁻¹ at 30, 40, and 50 °C were determined and are shown in Table 2. The correlation coefficients for the pseudo-second order are higher than 0.995 for all systems. This suggests that the sorption system is not a first-order process and that a pseudo-second-order model can be considered. This latter model is based on the assumption that the rate-limiting step may be chemisorption, involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Ho and McKay, 1999). The results of Table 2 indicate that k_2 , V_o , and q_e vary with the initial Cr(III) concentration. For the pseudo-second-order model, the rate constant decreases with increasing initial Cr(III) concentration, whereas the initial adsorption rate increases with increasing initial Cr(III) concentration. For the pseudo-second-order model, both rate constant and initial adsorption rate increase significantly with increasing

temperature from 30 to 50 °C. This result may be interpreted as an indication of some specific interaction between the solid adsorbent and chromium ions.

To evaluate the activation energy of this adsorption process, the dependence of the pseudo-second order rate constant on temperature was expressed in terms of the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (7)$$

Where k is the rate constant as a function of temperature T (K), A is the frequency factor, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and E_a (kJ mol⁻¹) is the activation energy for the adsorption process. The magnitude of activation energy can indicate the type of sorption. The activation energy for physical adsorption is usually not higher than 4.2 kJ mol⁻¹, since the forces involved are weak. Chemical adsorption is specific and involves forces much stronger than physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemical adsorption are encountered, namely, activated and non-activated, the latter being less frequent. Activated chemical adsorption means that the rate varies with temperature according to a finite activation energy (between 8.4 and 83.7 kJ mol⁻¹) in the Arrhenius equation. In non-activated chemical adsorption, chemisorptions occur very rapidly, suggesting that the activation energy approaches zero (Smith, 1981). The activation energy can be obtained from the slope of the plot of $\ln k$ versus $1/T$ (Figure not shown) and was found to be 26.22 kJ mol⁻¹. This value is an indication that the adsorption process involves chemical forces.

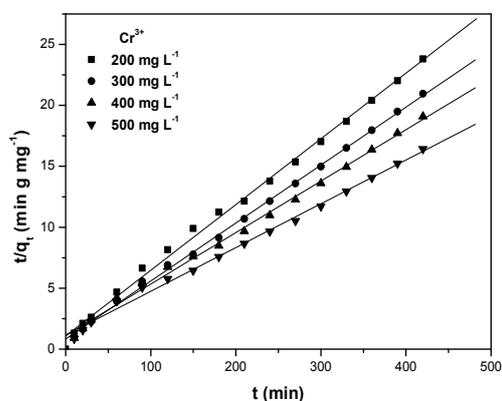


Figure 4. Pseudo-second-order plot of Cr(III) adsorption kinetics by RS at different temperatures and initial chromium concentration of 200 mg L⁻¹.

3.5 Adsorption isotherms

The equilibrium adsorption isotherm is important in order to describe the interactive behavior between solutes and adsorbent and in the design of the adsorption systems. The widely used Langmuir isotherm (Langmuir, 1916) has found successful applications in many real sorption processes. It can be expressed as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (8)$$

This, in linearized form, can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{b} \quad (9)$$

where C_e is the solution concentration at equilibrium (mg L^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), and q_m and b are Langmuir constants related to maximum adsorption capacity (mg g^{-1}) and adsorption energy (L mg^{-1}), respectively. A plot of C_e/q_e versus C_e over the entire concentration range produces a straight line, which is an indication of the applicability of the Langmuir isotherm for the system under consideration.

The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of a monolayer. This model assumes that different sites with several adsorption energies are involved in the adsorption process. The Freundlich isotherm can be expressed as:

$$q_e = K_F C_e^{1/n} \quad (10)$$

A linear form of the Freundlich expression can also be obtained as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Pollard et al., 1991). The intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$ at given experimental conditions provide the values of K_F and $1/n$, respectively.

The linearized Langmuir and Freundlich adsorption isotherms obtained at 30, 40 and 50 °C

are shown in Figures 5 and 6, respectively. The plots in Figure 5 demonstrate that the Langmuir equation provides an accurate description of the experimental data, which is further confirmed by the high values of the correlation coefficient (Table 3). In general, the Langmuir model fitted the results slightly better than the Freundlich model, since all R^2 values are higher than 0.98. This suggests that the adsorption of Cr(III) ions by RS is of monolayer-type and is in accordance with the observation that the adsorption from an aqueous solution usually forms a layer on the adsorbent surface (Mattson and Mark, 1971). It is also observed that the values of Langmuir constants, b and q_m , increased with increasing temperature, i.e., the adsorption capacity and intensity are enhanced at higher temperatures, suggesting a chemical interaction

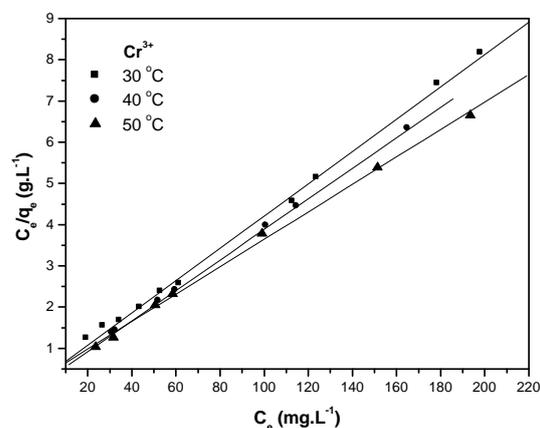


Figure 5. Linearized Langmuir isotherms obtained from Cr(III) adsorption by RS.

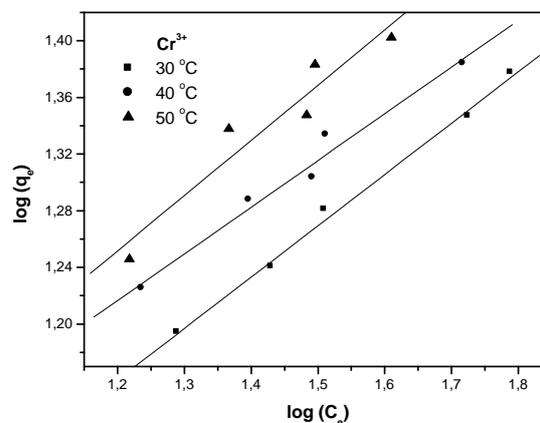


Figure 6. Linearized Freundlich isotherms obtained from Cr(III) adsorption by RS.

Table 3. Correlation coefficients and parameters for Langmuir and Freundlich isotherms of Cr(III) adsorption by RS.

T(°C)	Langmuir Constants			Freundlich constants		
	b (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2	K_F (mg g ⁻¹)	N	R^2
30	0.0900	25.23	0.9968	5.3348	2.73	0.9621
40	0.1070	27.68	0.9974	4.1900	2.06	0.9810
50	0.1410	30.09	0.9980	6.5196	2.71	0.8910

between adsorbent and adsorbate. As seen in Table 3, the monolayer maximum adsorption capacity (q_m) was 30.09 mg g⁻¹ at the optimum pH (5.5) and temperature (50 °C). The increase in the equilibrium adsorption capacity of Cr(III) with temperature indicates that higher temperatures favor Cr(III) removal by adsorption on RS.

Table 4. Equilibrium parameter, R_L , values.

C_o (mg g ⁻¹)	Temperature (°C)		
	30	40	50
200	0.052	0.045	0.034
300	0.036	0.030	0.023
400	0.027	0.023	0.017
500	0.022	0.018	0.014

The essential features of Langmuir's isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined by the following relationship (Hall et al., 1966):

$$R_L = \frac{1}{1 + bC_o} \quad (12)$$

where C_o is the initial metal ion Cr(III) concentration (mg L⁻¹) and b is Langmuir's constant. The value of R_L indicates whether the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L values for Cr(III) adsorption at different temperatures and concentrations are given in Table 4. These values indicate that the adsorption is more favorable at higher initial chromium concentrations. This indicates that the adsorption of Cr(III) onto RS is feasible at the concentrations studied (Erdem and Ozverdi, 2005; Lin and Juang, 2002).

Table 5. Adsorption maximum capacities of this work and the literature.

Adsorbent	q_m (mg g ⁻¹)	Reference
Bark	19.45	Randall et al., 1974
Zeolite	26.00	Leppert, 1990
Retorted Shale	30.09	This work
Activated carbon	43.46	Lyubchik et al., 2004
Peat	76.00	Kertman et al., 1993
Chitosan	92.00	McKay et al., 1989

Table 6. Thermodynamic parameters of Cr(III) adsorption by RS.

T (°C)	$\ln b$	ΔG^o (kJ mol ⁻¹)	ΔH^o (kJ mol ⁻¹)	ΔS^o (J mol ⁻¹ K ⁻¹)
30	8.451	- 21.30		
40	8.623	- 22.45	18.62	131.59
50	8.899	- 23.91		

A comparison of the maximum capacity, b , of RS with other adsorbents reported in the literature is given in Table 5. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups, and surface areas. The adsorption capacity of RS was relatively high when compared with bark and zeolite. However, the adsorption capacity is much lower than some sorbents of organic origin, such as activated carbon, peat, and chitosan. The capacity of

chitosan is almost 21 times higher than RS; however, since chitosan is nonporous and soluble in acidic solutions, it must be chemically modified in order to improve its sorption capacity.

3.6 Thermodynamic studies

Thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) for the adsorption process were determined using the following equations (Boonamnuyvitaya et al., 2004):

$$\Delta G^0 = -RT \ln b \quad (13)$$

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (14)$$

where R is the ideal gas constant, T is the solution temperature (K), and b is Langmuir's constant. The slope and intercept of van't Hoff plots of $\ln b$ versus $1/T$ were used to determine ΔH^0 and ΔS^0 . These results are listed in Table 6. The negative values of (ΔG^0) indicate that the adsorption of Cr(III) onto RS is spontaneous. The positive value of (ΔH^0) shows that the adsorption is an endothermic process. The positive value of (ΔS^0) indicates random increase at the solid-solution interface during the adsorption of Cr (III) onto RS.

4. CONCLUSIONS

Based on the physicochemical and batch adsorption experiments, it can be concluded that RS is effective in removing Cr(III) from aqueous solutions. The Langmuir equation confirms the equilibrium isotherm for the three temperatures and the entire concentration range studied. However, fitting the isotherm data with the Freundlich equation also yields a good correlation coefficient. The adsorption capacity increases with increasing temperature. The positive enthalpy value of the process shows that Cr(III) adsorption onto RS is endothermic, although spontaneous, and the kinetic studies suggest that adsorption involves activated or chemisorption processes.

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