Sorption Characteristics of Cr(III) onto Florisil: Kinetics, Thermodynamics and Equilibrium Studies

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Abstract

In this study, the efficiency of florisil was investigated for the removal of Cr(III) using batch type sorption under different experimental conditions namely pH, sorbent amount, contact time and temperature. The maximum sorption capacity of florisil for Cr(III) ions was determined as 67.5 mg g^{-1}, at pH 6.0, with a contact time of 60.0 minutes at 25°C. The equilibrium kinetics, isotherms, and thermodynamics of Cr(III) ion sorption onto florisil were also studied and it was evaluated that the sorption kinetics of Cr(III) on florisil followed pseudo-second-order model. The equilibrium data were in good agreement with the Langmuir isotherm model indicating monolayer coverage on the sorbent surface. In addition, thermodynamic studies revealed that the sorption of Cr(III) onto florisil was spontaneous and exothermic. The presented method was applied to the determination of Cr(III) in ultra–pure, tap, bottled drinking and waste water samples and high recoveries obtained confirmed the accuracy of the proposed study. The overall results have demonstrated that florisil is a promising and efficient sorbent and a good candidate for the removal of Cr(III) from aqueous solutions.

Keywords – Chromium, Sorption, Inductively Coupled Plasma Mass Spectrometry, Florisil.

1 Introduction

Environmental pollution caused by Chromium (Cr) has become a serious threat to human beings in recent years [1]. Chromium originates both from natural sources and human activities like wood preserving, electroplating, leather tanning, porcelain and ceramics manufacturing, photoengraving and alloy production etc [2]. It may contaminate environmental waters and enter human body through intake of water, penetrate biological membranes and cause serious health problems [3]. According to the United States Environmental Protection Agency, the maximum acceptable concentration for total chromium in drinking water is 100 μg L^{-1} and a stricter threshold limit (50 μg L^{-1}) has been set by the World Health Organization and China [4]. Chromium exists in several oxidation states, but the most predominant forms are Cr(III) and Cr(VI) in aquatic systems [5].

Cr(VI) is considered to be a priority pollutant and has a definitely adverse impact on living organisms. It is toxic to both plants and animals as well as may cause several diseases like liver, kidney, lung and gastrointestinal cancers [6]. Although Cr(III) is an essential to mammals for the maintenance of glucose, protein and lipid metabolism, it is also a potential hazard especially in aquatic environment [1]. Thus it becomes very necessary to remove chromium from waters before it releases into the environment.

Several methods have been developed for the removal, determination and preconcentration of chromium from waters including membrane separation [1], coagulation [7], ion exchange [8], adsorption [9], extraction [10] and precipitation [11]. Among these methods, adsorption can be regarded as one of the most promising methods for removal of toxic metals from the aqueous solutions due to its flexibility, simplicity, high efficiency and relatively low cost. Generally, an ideal adsorbent should offer a stable matrix with abundant binding sites which is suitable for adsorption of heavy metal ions [12]. Florisil® is an inorganic support that reveals high resistance to chemical, thermal and radiation degradation and it was recently used in several studies due to its crystalline and well-ordered periodic pore structure [13, 14]. In the present study, Florisil® was proposed for the batch removal of Cr(III) ions from the aqueous solutions and the optimum parameters such as pH, sorption time, sorbent amount and sorbent capacity were determined. Moreover sorption kinetics and equilibrium isotherms of the sorption of Cr(III) ions were also elucidated.

2 Experimental

2.1 Material and Methods

All reagents and chemicals were of analytical grade. Ultrapure water (18.2 MΩ) was used throughout the study. Glassware and plastic ware were cleaned by soaking in 10% (v/v) nitric acid and rinsed with ultrapure water prior to use. Standard (1000 mg L^{-1}) Cr(III) and Cr(VI) stock solutions were prepared from by dissolving appropriate amount of chromium(III) nitrate, Cr(NO$_3$)$_3$ and potassium dichromate, K$_2$Cr$_2$O$_7$ in 2 mol L^{-1} HNO$_3$, respectively. Lower concentration standards were prepared daily from their stock standard solutions. Florisil® (magnesium silicate, particle size 150–250 μm, pore size 6–8 nm and surface area 170–300 m^2/g) was purchased from Merck (Darmstadt, Germany). Chromium analysis (m/z=52, natural abundance of %83.79) was made by an inductively coupled plasma mass spectrometer (ICP-MS). The Agilent 7700 (Tokyo, Japan) type ICP-MS instrument was equipped with a high solid nebulizer, a Peltier-cooled spray chamber (2°C), and an octopole collision/reaction cell with hydrogen gas pressurization (purity of 99.999%). The ICP-MS operating conditions can be seen in Table 1. The pH adjustments were done by using Orion 4 Star pH meter with a pH/ATC plastic-body electrode. In order to provide efficient mixing, Nüve water bath shaker equipped with a controlled thermostat (Turkey) was used in batch sorption studies.

Table 1. Operating conditions for ICP-MS.

Instrument Parameter	Condition
RF power	1550 W
RF frequency	27.12 MHz
RF Matching	1.80 V
Carrier gas	1.0 L min^{-1}
Collision gas	4.5 L min^{-1}
Plasma gas flow	15 L min^{-1}
Nebulizer pump	0.1 rps
Sample intake	0.5 mL min^{-1}
Spray chamber temperature	2 °C
Isotope measured	^{52}Cr

2.2 Sorption Studies

An accurately weighed amount of florisil was added into 20.0 mL of solutions in a 50–mL falcon tubes containing the specified concentrations of chromium ions. The mixtures were shaken in a thermostatic water bath at 25.0°C for a fixed period and at the end of shaking period, the contents were filtered through filter paper. The filtrate was analyzed for final chromium concentration using ICP-MS. The effects of pH, sorbent amount, contact time and temperature on the sorption process were realized using the same methodology. The amounts of Cr(III) sorbed onto sorbent, q_e (mg g^{-1}), were calculated using Equation (1).

$$q_e = \frac{V(C_i - C_e)}{m} \qquad (1)$$

where C_i and C_e (mg L^{-1}) are initial and equilibrium concentrations of metal ions, m (g) is the weight of sorbent in the solution and V (L) is the volume of the solution.

2.3 Sorption Kinetics

Sorption kinetic studies are important since they describe the solute uptake rate which controls the residence time of sorbate at the solid–liquid interface and also provide valuable insights into the reaction pathways [15].

Pseudo–first–order (Equation 2) and pseudo–second–order (Equation 3) models were applied in order to investigate the sorption kinetics of Cr(III) onto florisil. Moreover, the rate-limiting step of the sorbate onto the florisil was determined using the intra-particle diffusion model (Equation 4). The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). Meanwhile, the capacity values calculated from the pseudo–first and second–order models were compared with that obtained from the experimental data. The kinetic models can be presented as follows,

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \frac{1}{q_1} \qquad (2)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_2^2}\right) + \frac{t}{q_2} \qquad (3)$$

$$q_t = k_p t^{1/2} + C \qquad (4)$$

where q_t is the amount of metal ion sorbed (mg g^{-1}) at time (t), q_1 is the maximum sorption capacity (mg g^{-1}) and k_1(min^{-1}) is the rate constant for pseudo–first–order sorption, q_2 is the maximum sorption capacity (mg g^{-1}) and k_2 (g mg^{-1} min^{-1}) is the rate constant for the second-order sorption, C (mg g^{-1}) is the intercept and k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). From plots of t/q_t versus t for the second–order reactions, the k_2 and q_2 values were calculated by using the values of intercept and slope. According to the equation (4), a plot of 1/q_t versus 1/t should be a straight line with a slope of k_1/q_1 and intercept 1/q_1, when the sorption process follows the first-order equation. The slope of the plot q_t vs $t^{1/2}$ yields k_p values and intercept gives C values [15].

2.4 Sorption Isotherm Models

The sorption equilibrium was investigated by using two well-known isotherm models (Langmuir and Freundlich) to provide the fundamental physicochemical data and

investigate the applicability of sorption process at a fixed temperature and pH. The equilibrium conditions of the sorption process were described by utilizing the linearized equations indicated below,

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (5)$$

$$\ln q_e = \ln K_F + n_F \ln C_e \qquad (6)$$

here q_m (mg g^{-1}) and b (L mg^{-1}) are constants in Langmuir's equation which are referred to the maximum sorption capacity and the binding energy, respectively [16]. Also q_e and C_e parameters represent the equilibrium sorption capacity and the equilibrium concentration, respectively. Moreover K_F is the Freundlich's constant (mg g^{-1}) and n_F is a dimensionless number in this model [17].

2.5 Thermodynamic Parameters
The effect of reaction temperature on the sorption of Cr(III) was studied at 25.0 and 40°C while keeping the other parameters constant (20.0 mL of 100.0 μg L^{-1} Cr(III) solution, 30.0 mg sorbent, pH of 6.0). The corresponding standard Gibbs free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o) were calculated utilizing the well-known equations 7–9 [18]. The Gibbs free energy of sorption was estimated from the following equation,

$$\Delta G^o = -RT \ln K_c \qquad (7)$$

Standard entropy change ($\Delta S°$) and standard enthalpy change ($\Delta H°$), of sorption process can be found from van't Hoff equation as shown below,

$$\ln K_c = -\Delta H^o_{ads} / RT + \Delta S^o / R \qquad (8)$$

where R is the gas constant, K_c is sorption equilibrium constant computed using the following equation,

$$K_c = C_s / C_e \qquad (9)$$

where C_s is the amount of adsorbed by sorbent, and C_e is the equilibrium concentration of ion in the solution. The plot of ln K_c versus $1/T$ should be linear. $\Delta H°$ and $\Delta S°$ were computed from the slope and intercept of van't Hoff plots of ln K_c versus $1/T$ [19].

3 Results and Discussion
3.1 Effect of pH
The solution pH is one of the most important factors in controlling the sorption of different species by a given sorbent. The effect of pH on sorption of 20.0 mL of 100.0

μg L^{-1} Cr(III) was studied for 50.0 mg of florisil at 25°C. The pH of the solutions was adjusted within 2.0 and 10.0 and the mixtures were shaken for 120 minutes. After filtration, sorption percentage was determined. As can be seen from Figure 1, Cr(VI) was not taken up by the sorbent at any pH values and the quantitative (>90%) sorption of Cr(III) occurred in the pH range of 2.0–8.0, whereas the sorption was rather low (<50%) at pH 10.0. According to chromium speciation diagrams, in the pH range of 3–8, the possible Cr species are Cr^{3+}, Cr(OH)$^{2+}$, Cr(OH)$_2^+$ etc. [20] The sorption phenomena may be explained by the electrostatic interactions between the negatively charged sorbent surface and the positively charged chromium species. On the other hand, at pH values higher than 8.0, Cr(III) could probably be suffering from hydrolysis, forming Cr(OH)$_4^-$ and Cr(OH)$_3$ species which may promote a decrease in the sorption capacity [21]. A sorption pH of 6.0 was selected in the subsequent experiments to be on the safe side.
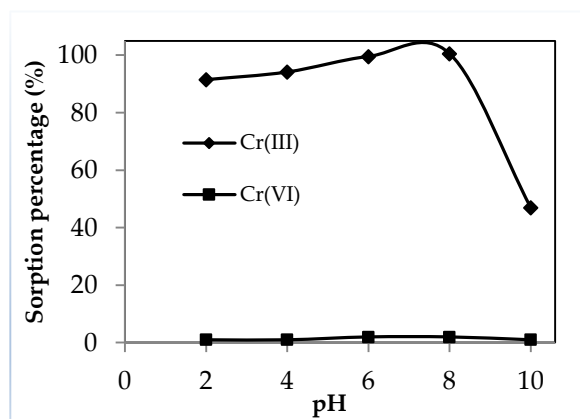

Figure 1. Effect of pH on the sorption of Cr(III) and Cr(VI) towards florisil sorbent (100 μg L^{-1} Cr(III) and Cr(VI), 20.0 mL sample volume, 120.0 min. contact time, 50.0 mg sorbent at 25.0°C sorption temperature).

3.2 Effect of Sorbent Amount
Sorbent amount is an important factor to be optimized in order to achieve high recoveries for the removal of the analytes. In order to determine the optimum sorbent amount, sorbent amounts varying from 5.0 – 100.0 mg were added into 20.0 mL of Cr(III) solutions and shaken for 120.0 minutes (pH of 6.0). As can be seen from Figure 2, the removal of Cr(III) was even high (~80%) with a very small sorbent amount (5.0 mg) and increased with higher sorbent amounts. For the quantitative sorption of Cr(III) ions, a sorbent amount of 30.0 mg (sorbent amount/solution volume ratio of 1.5 mg/mL) was used in the following studies as no further increase in sorption after a certain amount of sorbent was observed.
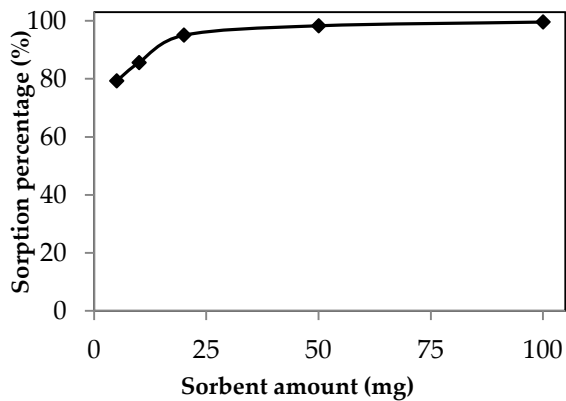
Figure 2. Effect of florisil sorbent amount on sorption (100 µg L^{-1} Cr(III) solutions, 20.0 mL sample volume, pH 6.0, 120 min. contact time, at 25°C sorption temperature).

3.3 Effect of Sample Volume
In order to explore the possibility of analytes from large volumes, the effect of sample volume on the retention of Cr(III) was also investigated. For this purpose, 20.0, 50.0, 100.0, 250.0, and 500.0 mL sample volumes at a constant absolute amounts of Cr(III) (2.0 µg) were prepared. All the other parameters were kept constant at their respective optima. As can be seen from Figure 3, almost quantitative recoveries (85-98%) were obtained even with a sample volume of 250.0 mL. This provides the use of the proposed methodology with relatively large sample volumes. On the other hand, almost 50 % percent sorption was obtained for Cr(III) for 500.0 mL of sample volume.
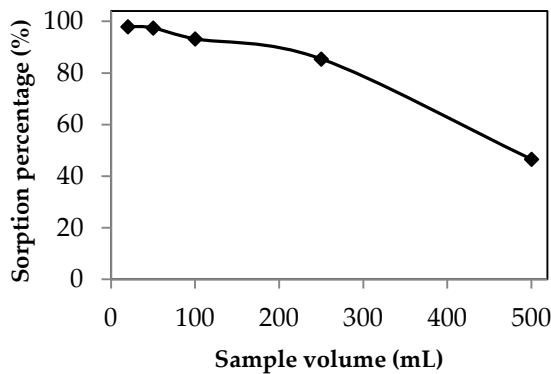

Figure 3. Effect of sample volume on sorption (2.0 µg Cr(III) solutions, 30.0 sorbent amount, pH 6.0, 120 min. contact time, at 25°C sorption temperature).

3.4 Sorption Kinetics
The kinetic study of sorption is important since it depicts the uptake rate of adsorbate, and controls the residual time of the whole sorption process. Figure 4a depicts the effect of contact time on the sorption of Cr(III) onto florisil. As can be seen from the figure, the sorption has increased with increasing contact time up to 60.0 minutes. After this equilibrium time, the sorption efficiency was almost constant probably due to the decrease in the diffusion rate since the sites of the sorbent are covered with Cr(III) ions. As a result, 60.0 minutes of a sorption time was used in the subsequent experiments. The kinetic examination of sorption process is also an important factor since the rate of sorption process influences the attainment of equilibrium in a reasonable amount of time. Therefore, the kinetics of Cr(III) sorption onto florisil was investigated to explore the sorption mechanism using the pseudo-first-order, the pseudo–second–order and intraparticle diffusion kinetic models. Plots of pseudo–first–order, pseudo–second–order and intraparticle diffusion kinetic models are shown Figures 4b, c and d, respectively. Table 2 shows the sorption kinetics parameters of Cr(III) sorption on florisil at 25°C. As seen from the results, the correlation coefficient values (R^2) of pseudo–second–order model were higher than that of pseudo–first–order model. Moreover, when the sorption data was processed to determine whether intraparticle diffusion fits the sorption process, it was investigated that the intraparticle diffusion may not the rate–controlling step. Based on these results, it was concluded that the sorption of Cr(III) onto florisil was best described by pseudo–second–order model.
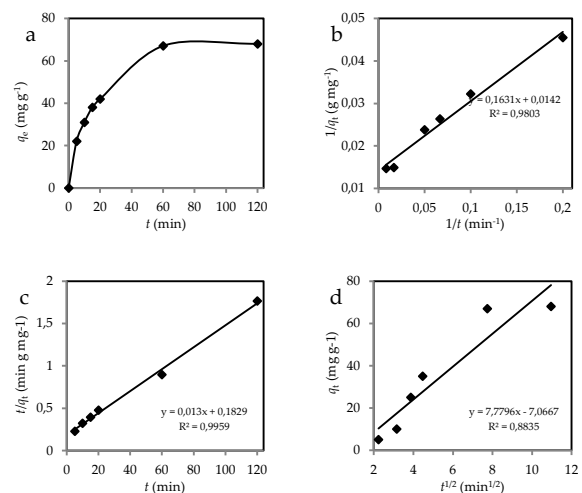

Figure 4. a) Effect of contact time on the sorption of Cr(III) towards sorbent, b) pseudo-first-order model's plot, c) pseudo-second-order model's plot and d) intraparticle diffusion model's plot.

Table 2. Kinetic parameters of various models fitted to experimental data.

q_{exp} (mg g^{-1})	First-order model			Second-order model			Intraparticle diffusion model		
	q_1 (mg g^{-1})	k_1 (min^{-1})	R^2	q_2 (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	C (mg g^{-1})	k_p (mg g^{-1} min$^{-1/2}$)	R^2
67.50	70.42	11.49	0.9803	76.92	0.0009	0.9959	-7.07	7.78	0.8835

3.5 Sorption Isotherm Models

Sorption isotherm models represent the relationship between the amounts of adsorbate sorbed per unit mass of sorbent and the concentration of sorbate in the equilibrium solution at a given temperature. The sorption isotherm models provide information on sorption mechanisms, surface properties and affinity of a sorbent towards metal ions [18,19]. In order to study the sorption isotherms, the experiments were carried out with 30.0 mg florisil sorbent and 20.0 mL Cr(III) solutions with various initial concentrations between 1.0 – 500 mg L^{-1} at pH 6.0 at a contact time of 60.0 minutes. The obtained results were depicted in Figure 5 and the detailed parameters of sorption isotherms are listed in Table 3. The results have indicated that the sorption of Cr(III) ions onto florisil sorbent well fitted with the Langmuir model since a higher correlation coefficient value was obtained (R^2=0.9965). In other words, the sorption process took place at the binding sites on the surface of the sorbent which is regarded as monolayer sorption. Moreover, the maximum Langmuir sorption capacity (q_m) for Cr(III) sorbed by florisil was calculated as 71.43 mg g^{-1} which was closed to the experimental data obtained *(q_{exp}=67.5 mg g^{-1}).*

Table 3. Isotherm model's constants for florisil sorbent.

q_{exp} (mg g^{-1})	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n_F	R^2
67.50	71.43	0.043	0.9965	0.416	0.513	0.8245

Additionally, the essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant separation factor, R_L, which is given by Equation (10) [22].

$$R_L = \frac{1}{1 + bC_i} \qquad (10)$$

where b is the Langmuir constant and C_i is the initial concentration of the metal ion in solution. The separation factor, R_L, represent the shape of the isotherm and the nature of the sorption process as given below. The R_L value gives the nature of the process: If $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable and $R_L = 0$ irreversible. The calculated R_L values versus initial Cr(III) concentration are represented in Figure 5d. As it can be seen from this figure, the values of R_L are in the range of 0–1 at all initial metal concentrations. These results indicate that sorption process is extremely favorable.

3.6 Sorption Thermodynamics

The effect of temperature on the sorption process is important since it affects the extent and rate of sorption and provides information about possible sorbate–sorbent interaction. The change in the percent sorption Cr(III) onto florisil was investigated for 25.0 and 40 0°C using 100.0 µg L^{-1} Cr(III), at a pH of 6.0, with 30.0 mg sorbent for 60.0 minutes of contact time. As a result, a decrease (~15%) in percent sorption value with the increase in the temperature was observed. The summary of the thermodynamic parameters are given in Table 4. The negative ΔG^o values increased with temperature, indicating the spontaneity of the sorption process onto florisil. The negative ΔH^o indicated the exothermic nature of the sorption process and negative values of ΔS^o (decrease in entropy) are a sign of the system becoming less random.
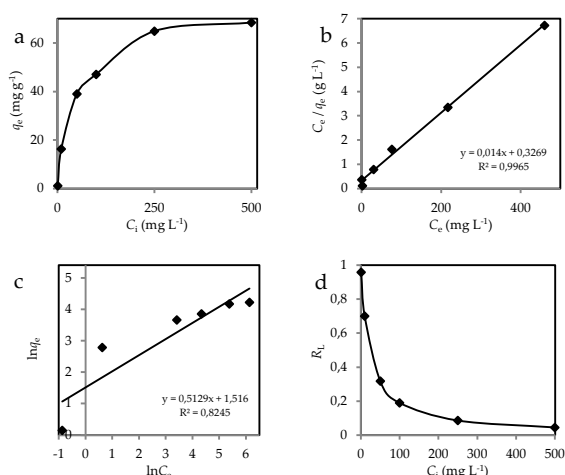

Figure 5. a) Variation of the amount of Cr(III) sorbed with the initial concentration of Cr(III) solution, b) Langmuir model's plot, c) Freundlich model's plot and d) Separation factors' (R_L) plot.

Table 4. Thermodynamic parameters for the sorption Cr(III) by florisil

T (K)	K_c	ΔG^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})
298	79.60	-10.85	-0,2067	-72,46
313	19.60	-7.74		

3.7 Desorption from the Sorbent

The possibility of quantitative desorption of Cr(III) from florisil was studied using several eluents namely HCl (0.01, 0.1, 1.0, 4.0 M), HNO$_3$ (0.01, 0.1, 1.0, 4.0 M), EDTA (0.01 M) and KIO$_3$ (in 2.0 M HCl). The experiments were performed using 20.0 mL of aqueous solution of 100.0 µg mL^{-1} Cr(III) at a pH of 6.0 using 30.0 mg florisil. After sorption for 60.0 minutes, the desorption of Cr(III) from the sorbent was performed using 20.0 mL of the eluent solutions. Among the eluents tried in the study, only KIO$_3$ (in 2.0 M HCl) was sufficient for quantitative elution of Cr(III) (>90%) from the sorbent while the desorption percentage of the others varied between 5 and 70%. Moreover, in order to determine enrichment factor, sorption studies were performed using variable sample volumes (20.0, 50.0, 100.0, 250.0, and 500.0 mL) using an absolute amounts of Cr(III) (2.0 µg) in the solutions. After desorption with 20.0 mL of KIO$_3$ (in 2.0 M HCl), the eluates were analyzed with ICP-MS. The results demonstrated the efficiency of the method since an enrichment factor of 25 was obtained using the proposed method.

3.8 Interference Studies

In order to investigate the interference effects of several ions (Cd(II), Fe(III), Ni(II), Cu(II) and Pb(II)) on Cr(III) sorption, the experiments were performed in such a way that various concentrations of these ions were prepared an spiked with Cr(III). For this purpose, 0.1, 1.0 and 10.0 mg L^{-1} concentrations of above mentioned ions were prepared in 20.0 mL of 0.1 mg L^{-1} Cr(III) and the sorption behavior of the sorbent towards Cr(III) in the presence of towards listed ions were investigated. Any effect causing at least 15% decrease in sorption was considered as interference. As can be seen from Table 5, for all three investigated concentrations of Cd(II), Fe(III), Ni(II), Cu(II) and Pb(II), no remarkable interference effect on Cr(III) sorption was observed.

Table 5. Summary of interference study.

Ion	Concentration (mg L^{-1})	Cr (III) Sorption percentage (%)
Cd	0.10	99
	1.00	99
	10.0	98
Fe	0.10	99
	1.00	98
	10.0	98
Ni	0.10	99
	1.00	97
	10.0	97
Cu	0.10	98
	1.00	98
	10.0	97
Pb	0.10	99
	1.00	98
	10.0	97

3.9 Real Sample Analysis

To evaluate the accuracy and applicability of the proposed method, sorption/desorption experiments were performed with ultra–pure, tap, bottled drinking and waste water samples. The water samples were filtered through MFS membrane filter (pore size 0.45 µm) and analyzed as soon as possible after sampling. The water samples were spiked with various amounts of Cr(III) (10 µg L^{-1}) and the analysis was carried out under the optimized conditions described above. Blank samples were also prepared in the same manner and analyzed by ICP–MS and all were below the detection limit. The percentage sorption values were obtained as 94.2 (±0.8), 88.1 (±1.2), 86.4 (±2.3) and 75.6 (±3.4) for ultrapure, bottled drinking, tap and waste water samples, respectively. The results have indicated that the proposed procedure is suitable for the determination of Cr(III) ions and has potential for application in water remediation studies.

3.10 Comparison with Other Sorbents

Table 6 summarizes the comparison of sorption of Cr(III) by florisil and other sorbents used in literature [23-31]. It can be seen that in most of the cases, Cr(III) uptake value by florisil is highly competitive and the sorbent has the less, comparable or better sorption capacity values than those reported previously. The high sorption values with good relative standard deviation values are some of the advantages of the proposed method. Consequently it can be concluded that florisil is a promising sorbent for the removal of Cr(III) ions in waters.

Table 6. Comparison of sorbent capacities for Cr(III) sorption.

Sorbent	q_m (mg g^{-1})	Reference
Modified peanut sawdust	7.7	[23]
Yellow passion-fruit shell	85.1	[24]
Animal bones	60.9	[25]
Diatomite treated with microemulsion	11.55	[26]
Agave lechugilla biomass	14.2	[27]
Eucalyptus bark	45.0	[28]

Turkish brown coal	13.52	[29]
Lewatit S 100	20.28	[30]
Activated carbon	39.56	[31]
Florisil	67.5	This work

4 Conclusions

This work has demonstrated that florisil can be used as an effective sorbent for the removal of Cr(III) ions from aqueous solutions. The effects of several factors such as pH, sorbent amount, contact time, and temperature on the sorption of Cr(III) ions were investigated. Equilibrium data best fitted to Langmuir isotherm model, indicating the monolayer coverage of the Cr(III) ions onto florisil. Pseudo-second-order kinetic model provided the best correlation with the experimental data. Thermodynamic parameters indicated that, under the studied temperature range, the sorption of Cr(III) by florisil was feasible and had a spontaneous and exothermic nature. The desorption form the sorbent was realized with KIO_3 (in 2.0 M HCl). The applicability of the proposed method tested with ultra pure, tap, bottled drinking and waste water samples and it was found that the proposed procedure is suitable for the determination of Cr(III) ions in real samples. Overall, this study suggests that florisil is a promising sorbent for the removal of Cr(III) ions from aqueous solutions.

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