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Sorption of Cr(III) and Cr(VI) to $K_2Mn_4O_9$ nanomaterial a Study of the effect of pH, time, temperature and interferences

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Abstract

A Rancieite type material ($K_2Mn_4O_9$) nanomaterial was synthesized and tested for the removal of chromium (III) and chromium (VI) from aqueous solutions. The synthesized nanomaterial was characterized using powder XRD and SEM. XRD showed weak diffraction peaks at only at the angles associated with $K_2Mn_4O_9$. The SEM corroborated that the nanoparticles were present; however, the nanoparticles were clustered into larger aggregates. Batch studies were performed to determine the optimum pH, capacity, time dependency, interferences, and the thermodynamics of the binding. The optimum pH for the binding of Cr(III) and Cr(VI) were determined to be pH 5 and pH 2, respectively. Isotherm studies were performed at temperatures of 4 , 25 , and 45 for Cr(III) and Cr(VI) and showed binding capacities of 21.7 mg/g, 36.5 mg/g, 41.8 mg/g for Cr(III). The Cr(VI) binding capacities were 4.22 mg/g, 4.08 mg/g, and 3.25 mg/g at the respective temperatures. The thermodynamic studies showed that the binding processes for the reactions were spontaneous and endothermic, with a ΔH was 17.54 kJ/mol for Cr(III) and 6.05 kJ/mol for Cr(VI). The ΔG of sorption for Cr(III) were determined to be -3.88 kJ/mol, -5.83 kJ/mol and -7.03 kJ/mol at the aforementioned temperatures. The ΔG values for the Cr(VI) sorption were determined to be -4.89 kJ/mol, -5.64 kJ/mol, and -6.05 kJ/mol. In addition, the ΔS values for Cr(III) and Cr(VI) were determined to be 77.92 J/mol and 39.49 J/mol, respectively. The thermodynamics indicate that the binding of Cr(III) and Cr(VI) is spontaneous and endothermic.

Keywords

Nanoparticles; Cr(III); Cr(VI); adsorption; thermodynamics

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1. Introduction

Chromium (Cr) is one of the most abundant elements in nature, primarily found in two oxidation states, chromium (VI) or chromium (III) [1]. The most common contact with chromium is through food and water, with it occurring naturally in many vegetables, fruits, meats [2]. Chromium (III) is a macronutrient essential for health and is known to regulate carbohydrates, lipids, and proteins [2]. A shortage of this nutrient can lead to heart conditions, disruption of metabolisms, or diabetes [3]. However, excess chromium(III) can cause adverse health effects such as skin rashes [3]. Chromium(VI) on the other hand is strongly toxic due to its high oxidation potential and ability to penetrate biological membranes [3]. It is structurally similar to sulfate, making it able to accumulate in cells [4]. The body can naturally reduce hexavalent chromium to the trivalent form however, excessive amounts of Cr (VI) cause DNA damage, which can cause cancer, birth defects, respiratory problems, and many other health problems [2].

Chromium is commonly used in production of nonferrous and ferrous metals, leather processing, production of catalysts, development of pigments, and other wide array of applications in industry [2]. Increased use of chromium in anthropogenic activities have resulted in an increase of contamination in the air, soil, and water. Overtime chromium in the air settles in the soil, and migrates into the groundwater. Chromium, has been regulated to an MCL of 100 µg/L in the drinking water as set by the Environmental Protection Agency, making it a priority pollutant [2]. The adverse effects of chromium can also be seen in plant wildlife with microbe mediated processes such as carbon mineralization, nitrogen transformation, and the mineralization of phosphorus and sulfur being disrupted [2].

A wide variety of hexavalent chromium removal techniques have been investigated such as: sorption, membrane filtration, ion-exchange [5, 6]. Along with this, the types of materials incorporated has continually expanded and have progressed to include an array of materials such as: graphene substrates, polymers, and biosorption materials, seaweed biomass and wheat bran substrates [7–9]. The most frequently used techniques in industrial hexavalent chromium removal include the oxidation/reduction and precipitation of the chromium (VI/III) in the form of chromium (III) hydroxide [10]. However, many heavy metal removal methods are plagued by the common disadvantage of being economically impractical and producing high levels of contaminated waste [11]. Along with these disadvantages, there is an ongoing agenda for industries to decrease their environmental impact via exploration for alternative remediation technologies.

Nanomaterials provide a new avenue of research for the removal of pollutants from water. Due to the surface area, surface density of functional groups nanoparticles provide a highly reactive material for adsorption studies. The interest in nano-scale based adsorbents, such as nanoparticles, has increased in recent years as science advances. Nanotechnology allowed techniques using a smaller scale to be employed [12]. One example is the work done by Sharma et al. whom investigated the adsorption of chromium(VI) to aluminum oxide nanoparticles in aqueous solution. The aluminum oxide nanoparticle showed the ability to remove chromium (VI) from aqueous solution and the synthesis of the material used low-cost precursors making it economically feasible. Luther et al. have used iron and manganese

substituted iron oxide nanoparticles to remediate chromium from water showing binding capacities ranging from 7–10 mg/g [13]. Whereas, Cantu et al. have used Mn_3O_4 nanoparticles to remove arsenic from aqueous solution showing binding capacities ranging from 2.5 mg/g to 54.4 mg/g [14]. Transition metal sulfides have also shown promise in the remediation of toxic elements from aqueous solution for example Fe_7S_8 has shown promise in removing As(III) and As(V) [12]. Garcia et al. have shown the removal of both Cr(III) and Cr(VI) from solution using ferrite and manganese substituted ferrite, which showed binding capacities up to 16 mg/g for Cr(III). Whereas the Cr(VI) binding capacity was observed to maximize at approximately 8.5 mg/g [15].

In the current study the adsorption of Cr(III) and Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial was studied. The effects of pH on binding of chromium (III) and chromium (VI) to the nanomaterial were studied as well as the capacity of the chromium (III) and chromium (VI) to the nanomaterial at different temperatures. The thermodynamics of the binding process were investigated to determine the ΔG , ΔH , and ΔS . The thermodynamic parameters indicated binding of the chromium ions was adsorption to the surface of the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial.

2. Methodology

2.1 Synthesis of $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial

The nanomaterial was prepared using a method similar to Leroux et al [16]. KMnO_4 was dissolved in water to make a 600 mL solution with a 1M concentration. A 100 mL aliquot of concentrated HCl was added to the KMnO_4 solution, and the solution was subsequently heated to 60°C for approximately 90 minutes. After heating sample was cooled to room temperature, filtered, and washed using 18 MΩ deionized water. Subsequent to washing the sample was oven dried at 60°C overnight.

2.2 XRD characterization

The samples were ground into a fine powder and homogenized using a mortar and pestle. The XRD data for the samples were collected using a Rigaku Miniflex power X-ray diffractometer. The sample data was collected using the following parameters: a copper source ($K\alpha = 1.54 \text{ \AA}$) with a nickel filter, from 10° to 60° in 2θ, a 0.05° step, and a 5s counting time. Once the XRD data was collected, it was analyzed using the Fullprof Suite of programs and the crystal structure of the $\text{K}_2\text{Mn}_4\text{O}_9$ [12, 17].

2.3 SEM

SEM images were collected using a Zeiss LS-10 electron microscope. The sample images were collected using operating voltages of 18 and 26 kV, a current of 1.54 A, and a 4 mm working distance.

2.4 pH Study

The effect of pH on the binding of both Cr(III) and Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterials were tested from pH 2 to pH 6. Solution containing either 300 ppb of either Cr(III) or Cr(VI) were pH adjusted using dilute solutions of nitric acid and sodium hydroxide. Aliquots

consisting of 4.0 mL of the pH adjusted Cr solutions were added to 5mL test tubes, which contained 10 mg of the $K_2Mn_4O_9$ nanomaterial. Control samples containing only the pH adjusted Cr(III) and Cr(VI) solutions were prepared and treated similarly to the Cr samples. For statistical purposes, the controls and samples reactions were replicated in triplicate. The Cr samples and control solutions were equilibrated on a rocker for an hour at room temperature. Subsequent to equilibration the samples and the controls were centrifuged for 10min at 3,600rpm and the supernatants were decanted and saved for analysis using GFAAS.

2.5 Time Dependency Studies

Studies were performed at different time intervals and temperatures to determine the amount of time required and stability of the binding of Cr(III) and Cr(VI) to the $K_2Mn_4O_9$ nanomaterial. The reactions were performed at the optimum binding pH as determined from the pH study. In addition, a concentration of 30 ppm of either Cr(III) or Cr(VI) solutions were used. The solutions were adjusted to their optimal pH in accordance to the pH studies, using dilute solution of either nitric acid or dilute sodium hydroxide. A 4.0 mL aliquot of the pH adjusted Cr(III) or Cr(VI) were extracted and added to test tubes contacting 10 mg of the $K_2Mn_4O_9$ nanomaterial, this procedure was replicated in triplicate for statistical purposes. In addition control sample containing only the pH adjusted Cr solutions were also performed in triplicate for statistical purposed. The samples and control were equilibrated at temperatures of 4°C, 25°C, and 45°C and equilibrated on rockers for the following time intervals: 5, 10, 15, 30, 60, 90, and 120 minutes. Subsequent to equilibration, both the samples and controls were centrifuged at 3,600rpm for 10 minutes. The supernatants were decanted and saved for analysis using ICP-OES.

2.6 Interference Studies

Studies were performed to determine the effects and potential binding interference of cations and anions commonly found in water on the binding of Cr(III) and Cr(VI). The potential interferences on the binding were selected based on the ionic charge of the chromium species. For example, Cr(III) interferences included: Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . Whereas the Cr(VI) potential binding interferences included: Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} . Solutions containing either 300 ppb of Cr (III) or Cr(VI) were prepared in the presence of the potential interfering ion. The concertation of the interfering ions were studied individually at concentrations of 0.3 ppm, 3 ppm, 30 ppm, 90 ppm, 300 ppm, and 1000 ppm. In addition, a combined interference solution was created which contained either all the cations with Cr(III) all the anions with Cr(VI). The combined interference solutions consisted of each cation or each anion at concentrations of 0.3 ppm, 3 ppm, 30 ppm, 90 ppm, 300 ppm, and 1000 ppm. The interfering ion solution containing the respective Cr ion were pH adjusted to the optimum binding pH for the Cr ion. The pH of the solution was adjusted using either dilute nitric acid or dilute sodium hydroxide. Aliquots consisting of 4.0 mL of the pH solution were added to test tubes containing 10 mg of $K_2Mn_4O_9$ nanomaterial. In addition, control samples consisting of the pH adjusted solution were added to clean test tubes and treated the same as the reaction samples. All control and reaction samples were replicated in triplicate for statistical purposes. The reaction and control samples were equilibrated on rocked for 1 hour. Subsequent to equilibration, the samples and controls were centrifuged at

3,600 RPM for 10 minutes. The supernatants were decanted and saved for analysis using GFAAS.

2.7 Binding Capacities Studies and Thermodynamic Studies

The thermodynamic parameters (ΔG , ΔH , and ΔS) of binding and the binding capacities of Cr(III) and Cr(VI) to the $K_2Mn_4O_9$ nanomaterials were determined using adsorption isotherms. The adsorption isotherms were performed at three temperatures. The studies were performed using concentrations of either Cr(III) or Cr(VI) from 3, 30, 100, 300, and 1000 ppm at the respective optimum binding pHs. Aliquots of 4.0 mL were added to test tubes containing 10.0 mg of the $K_2Mn_4O_9$ nanomaterial, this was performed in triplicate at each concentration. The samples were equilibrated on a rocker for 1.0 hr and centrifuged at 3,600 rpm for 10 minutes. Subsequent to centrifugation, the supernatants were decanted and saved for analysis using ICP-OES. The reaction procedure was performed at temperatures of 4°C, 25°C, and 45°C. In addition, at each temperature the samples were equilibrated to temperature, and then pH adjusted to the optimum binding pH for the chromium ions. Furthermore, control samples consisting of only the chromium ion in solution were prepared in triplicate for each concentration and treated the same as the samples. All samples from this study were analyzed using ICP-OES.

2.8 GFAAS Analysis

A Perkin Elmer AAnalyst 800 atomic absorption spectrometer was used to collect portions of the data as mentioned above. The operating parameters for the GFAAS are presented in Table 1. All GFAAS analyses were performed using a calibration curves with R^2 values of .99 or higher.

2.9 ICP-OES Analysis

A Perkin Elmer Optima 8300 ICP-OES was used for data collection as mentioned above. The operating conditions of the ICP-OES are presented in Table 2. All ICP-OES analysis were performed using a calibration curves with R^2 values of .99 or higher.

3. Results and Discussion

3.1 Nanomaterial Synthesis and Characterization

Figure 1 shows the powder diffraction, the Fullprof fitting, the difference between the fitting and the sample data, as well as the Bragg diffraction peaks for the synthesized $K_2Mn_4O_9$ nanomaterial. The fitting was performed using the LeBail fitting procedure and the crystallographic data from the literature [16–18]. As can be seen in Figure 1 there is very little difference between the fitting and the actual XRD data as indicated by the small residual in the difference pattern. In addition, Table 3 shows the parameters of the fitting, which had a reduced χ^2 of 0.325. The Bragg peaks shown in the diffraction pattern at 11.81, 23.77, 35.98, 36.71, 39.89, 44.20, 46.63, and 52.34° in 2θ correspond to the 001, 002, 003, 100, 011, 101, 012, 102, 004, 013, and 103 diffraction planes consistent with the P-3 crystal structure of Rancieite [16,18]. Figure 2 A and Figure 2 B show the SEM images of the synthesized nanomaterials. As can be seen in both figure 2A and 2B the synthesized material appears to be an agglomeration of much smaller particles. The clusters of particles

appear to be approximately 200 nm in diameter; however, these clusters consist particles that are approximately 10–15 nm in diameter.

3.2 pH studies

The binding of Cr(III) and Cr(VI) under changing pH conditions was determined and is presented in Figure 3. As can be seen in Figure 3 the binding of both Cr(III) and Cr(VI) are pH dependent. Depending on the condition of the solution affects the ions present in the solution, under for acidic conditions Cr(VI) forms anions such as hydrogen chromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) species which result in low binding due to opposing charges [19]. However, at the same time the nanomaterial develop a positive charge, which causes a columbic attraction of the Cr(VI) and the $\text{K}_2\text{Mn}_4\text{O}_9$, which has been indicated in the interactions of Cr(VI) with other nanomaterials [13]. Whereas metal oxide materials generally develop a net negative charge as pH is increased, which results in an observed increased binding of cations higher pH's. The $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial falls into the class of phyllosulfates with other minerals such as birnessite, todorokite, which are layered materials with point of zero charge (PZC) in the range of 1.18 to 4.0 [20]. The PZC of $\text{K}_2\text{Mn}_4\text{O}_9$ has not been measured but it compound fall into the large class of phyllosulfates and the behavior of binding of the Cr(VI) ions indicates a low PZC, the intersection of the binding of the Cr(VI) and Cr(III) occurs at a pH of 2.73, which is in the range of similar materials. The binding data indicates that below pH 2.73 a net positive charge develops on the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial above pH 2.73 a net negative charge develops on the nanomaterial. The binding of both the Cr(III) and Cr(VI) was observed to be pH dependent. The Cr(VI) was only observed to bind at pH 2 and 3. The maximum binding for the Cr(VI) was observed at pH 2 with approximately 25% of the chromium being removed from the solution. Whereas, the Cr(III) ions were observed to increase in binding as pH increased and were observed to maximize around pH 5 to pH 6 as is observed in Figure 3 the binding reached approximately 30 to 35%. A similar study resulted in the same trend of chromium (III) with a different structured manganese oxide [21]. In addition, these binding trends were also observed by Luther et al. when studying Cr(III) and Cr(VI) binding to ferrite and manganese substituted ferrite [13]. Furthermore, similar results have been observed in the binding of Cr(III) and Cr(VI) to activated carbons synthesized through the contact arc method [22].

3.3 Time Dependency Studies

Figure 4 shows the results of the time dependency study for the binding of Cr(III) and Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial at temperatures of 4°C, 25°C and 45°C. As can be seen in Figure 4 A the Cr(III) binding is not affected by temperature very dramatically. In addition, the majority of the binding occurs within the first five minutes of contact between the Cr(III) and the nanomaterial, there is a little decrease and increase in the binding with contact time. However, there is no observable trend of increasing or decreasing in the binding of Cr(III) to the $\text{K}_2\text{Mn}_4\text{O}_9$. Figure 4 B shows the binding of the Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial. As can be seen in Figure 4 B there is no observable dramatic increase in the binding of the Cr(VI) the majority of the binding occurs within the first five minutes of contact. This indicates that the reaction occurring for the sorption of the Cr(III)

and Cr(VI) are both similar in nature, and are very fast occurring within the first five minutes of contact.

3.3 Binding Capacity Study

The adsorption capacities for both chromium (III) and chromium (VI) to the $K_2Mn_4O_9$ at the three specified temperatures, 4°C, 25 °C, and 45 °C are presented in Table 4. The data in Table 4 shows that chromium (III) bound significantly higher binding to nanomaterial than chromium (VI) at all three temperatures. The binding capacity of chromium (III) increased as the reaction temperature increased indicating. Whereas the binding capacity of chromium (VI) decreases slightly with the increases in reaction temperature. The isotherms for the binding of both Cr(III) and Cr(VI) to the $K_2Mn_4O_9$ nanomaterials were found to follow the Langmuir isotherm. The correlation coefficients (R^2) for the fitting of the Langmuir isotherms were 0.99 or better. Furthermore, the Langmuir isotherm indicate that both Cr(III) and Cr(VI) bound to the nanomaterial with monolayer adsorption. Similar studies in the sorption of Cr(III) and Cr(VI) to different materials such as inactivated biomass, iron oxides nanoparticles, manganese oxide nanoparticles, activated carbons have shown results generally with higher sorption of Cr(III) than Cr(VI) [13,14,23–25]. For example, the binding of Cr(III) and Cr(VI) to Mn_3O_4 was shown to have capacities of 18.7 mg/g, 41.7 mg/g, 54.4 mg/g and 2.5 mg/g, 4.3 mg/g, 5.8 mg/g, at temperatures of 4°C, 25°C, 45°C, respectively [14]. Different substitutions of manganese into ferrite nanoparticles has shown Cr(III) and Cr(VI) binding in the ranges of 3 mg/g and 7–10 mg/g, respectively [13]. Synthetic magnetite (Fe_3O_4) particles have been shown to have adsorption capacities for Cr(VI) and Cr(III) of 1,208 mg/kg (1.2 mg/g) and 555 mg/kg (0.555 mg/g), respectively [24]. Activated alumina and activated carbon have shown higher binding for Cr(VI) of 7.44 mg/g and 12.87 mg/g, respectively[25]. Different sources of activated carbon resulted in varied binding capacities. Further studies using activated carbon prepared from Logan seed have shown Cr(VI) binding capacities ranging from 21 to 35 mg/g. [26]. More complex systems have been developed for the sorption of Cr(VI) using powdered activated carbon, chitosan, single/multi-walled nanotubes, which have shown binding capacities of 46 mg/g, 35 mg/g, 20.3 mg/g and 2.5 mg/g, respectively [27]. With respect to Cr(III) binding difference activated carbons derived from coconut have shown binding capacities 10–16 mg/g and fiber cloths have shown binding capacities in the range of 36 to 40 mg/g [28].

3.4 Thermodynamics

The thermodynamics of the binding process were determined using the standard thermodynamic relationships and the data obtained from the isotherm data. The results of the thermodynamic studies are presented in Table 5, showing the ΔG , ΔH , and ΔS for both Cr species. The Gibbs free energy of binding was determined using equation 1 shown below:

$$\Delta G = -RT \ln k_{ads} \quad (1)$$

Where ΔG is the change in the Gibbs free energy, T is the temperature in Kelvin, R is the gas constant 8.314 J/Mol K, and k_{ads} is the adsorption coefficient. The observed trend in the ΔG binding for both the Cr(III) and Cr(VI) showed a more negative value. The more negative

the ΔG value the more favorable and spontaneous the binding process becomes. The results from the ΔG study indicate that both Cr(III) and Cr(VI) bind to the $K_2Mn_4O_9$ through an endothermic process, at their respective optimum binding pHs. The thermodynamics for the binding of Cr(III) and Cr(VI) have been studied for inorganic materials including manganese oxides, iron oxides, as well as many other inorganic materials [12–14,24,26]. From the literature it has been indicated that ΔG values smaller than 40 kJ/mol (absolute value) are indicative of physisorption [12]. In addition, it has been shown in the literature that ΔG values in the range of –34 to –40 are indicative of ion exchange mechanisms [12]. In the present study all the ΔG values were much less than 18 kJ/mol, indicating that the binding process for both Cr(III) and Cr(VI) was through physisorption. The ΔG of binding for both the Cr(III) and Cr(VI) ions were very similar in magnitude for the sorption to $K_2Mn_4O_9$. In the present study the Cr(III) ΔG values were found to range from –3.88 kJ/mol to –7.03 kJ/mol over the temperature range, 4°C to 45°C. Whereas the Cr(VI) ΔG values were found to range from –4.89 kJ/mol to –6.05 kJ/mol, over the temperature range, 4°C to 45°C. Similar ΔG of binding values have been observed in the literature as in the present study. The binding of Cr(III) to iron oxide nanomaterials has been shown to have ΔG 's in the range of –17 to –11.4 kJ/mol, whereas Cr(VI) binding to iron oxides have ΔG values in the range of –7.5 to –7.0 [13,24]. Mn_3O_4 nanomaterials have been shown to have Cr(III) ΔG values in the range of –2.7 to –13.7 kJ/mol [14]. Similarly, the ΔG of binding for Cr(VI) to Mn_3O_4 nanomaterials occurs in the range of –0.9 to –3.9 kJ/mol [14]. Substituted aluminum hydroxide base materials the ΔG of binding have been shown to be in the same range from –6.26 to –8.96 kJ/mol [29,30]. Naturally occurring clays have shown ΔG values in the range of –3.9 to –0.441 kJ/mol for the sorption of Cr(III) and Cr(VI), respectively; however, chemically modified clays have shown very high ΔG of sorption in the range of –40 kJ/mol [31].

The enthalpy and entropy of the reaction was calculated using standard thermodynamic relationships of ΔG , ΔH , and ΔS outlined below:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Substituting equation 1 into equation 2 the following equation was developed relating $\ln K_{ads}$ to ΔH , and ΔS as shown in equation 3:

$$\ln K_{ads} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

By plotting the $\ln K_{ads}$ against $1/T$ the ΔH is determined from the slope of the line, and the ΔS is determined from the intercept of the line. The thermodynamics plot for the binding of both Cr(III) and Cr(VI) is shown Figure 5. Both lines have negative slopes and positive intercepts, from which the enthalpy and entropy were determined. The enthalpy values in the present study for Cr(III) and Cr(VI) binding to the $K_2Mn_4O_9$ were determined to be slightly endothermic with values of 17.54 and 6.05 kJ/mol, respectively. The results in the present study correspond to studies performed with Cr(III) and Cr(VI) adsorption to other materials.

Mn₃O₄ as an adsorbent for Cr(III) and Cr(VI) enthalpy values of 70.6 and 19.1 kJ/mol [24]. Further studies have investigating Cr(III) and Cr(VI) binding to iron an manganese based nanomaterials have shown ΔH values from 17 kJ/mol to approximately 2.1 kJ/mol [13]. Furthermore, the higher ΔH values observed for the binding of Cr(III) compared to the binding of Cr(VI) have been observed for the binding of Cr to different materials including manganese oxides, iron oxides, iron-manganese oxides, as well as titanium dioxides [13,24]. The magnitude of the values in the present study for the ΔH indicate that the adsorption reaction is occurring through an endothermic process. In addition, the magnitude of the ΔH in the present study also indicate that the process is through physisorption.

The ΔS values found in the present study for Cr(III) and Cr(VI) were found to be positive indicating the reaction was a thermodynamically favorable. The values of entropy for Cr(III) were 77.92 J/mol and for Cr(VI) were 39.49 J/mol, as can be seen in Table 5. A similar study used Cr(III) and Cr(VI) to test binding to manganese ferric oxide and ferric oxide under light and dark conditions being ranging from 69.26 and 22.95 J/mol, respectively [13]. Whereas the binding of Cr(III) and Cr(VI) pure Mn₃O₄ nanomaterials have shown ΔS values of 268 and 72.8 J/mol, respectively. Similarly, the binding of Cr(III) and Cr(VI) to iron oxide nanomaterials have shown ΔS for Cr. Whereas the binding of The positive values indicate the system is becoming more disordered after the reaction has occurred indicating. The increase in entropy of the system can be attributed to different possible causes; for example, the release of K⁺ from the nanomaterial during the binding process, the release of surface bound water on the material into solution would cause changes in the entropy of the system. Furthermore, a reductive or oxidative dissolution of the material would result in the release of Mn ions into solution increasing the entropy of the system, which have been observed in different sorption systems (33).

3.5 Interference Studies

Figure 6A and Figure 6B show the results of the interference study. The potential binding interferences investigated for Cr (VI) were anionic in nature and are commonly found in natural waters, which included: chloride, nitrate, sulfate, phosphate. In addition, a study was performed to investigate the combination of all anions on the binding of the Cr(VI) ions from solution. Whereas, the potential interferences on the Cr(III) binding were cationic in nature and included: sodium, potassium, calcium, magnesium, and a combination of all the aforementioned cations. In general the Cr(III) exhibited less interference in binding than the Cr(VI), under the optimum binding conditions.

The effects of the cation interferences on Cr(III) binding are shown in Figure 6A. The presence of both sodium and potassium had little to no effects over the concentration range from 0.3 ppm up to 1000 ppm. However, the presence of Ca²⁺ showed a synergistic effect increasing the binding of the Cr(III) with increasing Ca²⁺ concentration in solution. The presence of Mg²⁺ in the solution show an dramatic increase in the Cr(III) binding, with a Mg²⁺ concentration of 3.0 ppm. Above the 3.0 ppm concentration of Mg²⁺ the Cr(III) binding stabilized and became relatively constant thereafter. The combined interference solution showed a slight decrease in the binding of the Cr(III) ions from solution with increasing interference concentration. However, the binding was not completely eliminated

in any of the studied conditions. Even in the combined interference study, where the solution contained 0.3 ppm of Cr(III), 1000 ppm Na^+ , 1000 ppm K^+ , 1000 ppm Ca^{2+} , and 1000 ppm Mg^{2+} . The total solution concentration of interfering ions corresponds to 135.2 mM with a Cr(III) concentration of 0.006 mM or a molar ratio of 23426: 1 interference: Cr(III). The data indicates a preference of the material to bind the Cr(III) over the hard cations investigated. This preferential binding has been observed with the binding of different cations to metal oxide based nanomaterials. For example, the binding of Cr(III) to Fe_3O_4 synthesized under high and low pressures show excellent binding of Cr(III) up to interference concentrations of 100 ppm [24]. Although the authors studied anionic interferences the cations were present in solution due to salts used to make the interference solutions had no effect [24]. Similar trends in preferential binding of Cr(III) over hard cations have also been observed in the binding of Cr(III) to biological materials [32].

Figure 6B shows the effects of the potential anionic interferences on the binding of Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial. The monovalent interferences investigated in the present study Cl^- and NO_3^- showed no effect on the binding of Cr(VI) to the nanomaterial. The binding of the Cr(VI) remained constant throughout all the concentrations from 0.3 ppm up to 1000 ppm. Whereas the SO_4^{2-} had a small effect on the Cr(VI) binding but only at high concentrations above 30 ppm. At 1000 ppm SO_4^{2-} , the binding of the Cr(VI) was only decreased by approximately 12–15% of the binding observed in the present of 0.3 ppm SO_4^{2-} . This shows a preferential binding of the Cr(VI) over SO_4^{2-} , which is an interesting result as the SO_4^{2-} generally behaves similar to Cr(VI) in solution.

As can be seen in Figure 6 B the binding effects of Cl^- were constant at 50% indicating that the concentration of Chromium (VI) had no effect on the binding of Cl^- throughout the analysis. The binding effects of NO_3^- were similar to the effects of Cl^- , having around 50% binding and no change in the Cr(VI) binding throughout the concentrations. The binding effects of SO_4^{2-} was shown to be affected by the concentration of Chromium (VI). The binding of SO_4^{2-} slightly increased as the concentration of Chromium (VI) decreased, being the highest of about 45% at 0.3 ppm and lowest at 36% binding at 1000 ppm of metal concentration. The combination of all anions and the individual anion, PO_4^{3-} , had very similar binding effects to Chromium (VI). Both increasing as the concentration of Chromium (VI) decreased, being highest at the lowest concentration 0.3 ppm with an approximate binding of 46% to both groups and having no effect on the binding of the material beyond a concentration of 30 ppm for Chromium (VI). The PO_4^{3-} had the largest effect on the binding of the Cr(VI) from solution. At the 3 ppm PO_4^{3-} solution concentration the Cr(VI) binding was decreased by approximately 20–30% of the observed binding at the 0.3 ppm level. The observed decreased in binding is even larger at 30 ppm PO_4^{3-} concentration. The binding is eliminated at concentrations above 30 ppm PO_4^{3-} concentrations. In the presence of the combined interference study where the solution contained 0.3 ppm of Cr(VI), 1000 ppm Cl^- , 1000 ppm NO_3^- , 1000 ppm SO_4^{2-} , and 1000 ppm PO_4^{3-} the binding of the Cr(VI) behaved similar to the binding observed with the PO_4^{3-} ions alone. The Cr(VI) binding interferences observed with the phosphate may be from columbic interactions the higher charge on the phosphate may be more strongly attracted to the surface of the nanoparticle thus blocking the binding of the Cr(VI) to the surface. Through the sorption of the PO_4^{3-} anion to the surface of the nanomaterial a net

negative charge on the surface is developed and thus inhibits the binding of the CrO_4^{2-} anion. As shown in the literature many monovalent anions have little to no effect on the binding of Cr(VI) iron based nanomaterials [24]. It has also been shown in the literature that polyatomic anions can affect the binding of Cr(VI) to different materials [24,34]. The interference of PO_4^{3-} on the binding of oxyanions has been observed in the literature for different anions. For example PO_4^{3-} has been observed to decrease the binding of As(V) to iron oxides from solution, as well as the binding of As(V) to manganese oxides, as well as As(V) binding to substituted ferrites [15,35–37]. In addition, the binding of Cr(VI) to manganese oxides, manganese ferrites have also been shown to be greatly affected by the presence of high concentrations of PO_4^{3-} anions. The observed decrease in binding have been attributed to competitive surface binding, at such a high interference concentration compared to Cr(VI) concentration, active site for sorption would be completely filled with PO_4^{3-} anions.

4. Conclusions

The $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial was successfully synthesized using a method from the literature. The $\text{K}_2\text{Mn}_4\text{O}_9$ material formed clusters of smaller particles. The binding of both Cr(III) and Cr(VI) was dependent on pH. The Cr(III) binding was found to increase from pH 2 through pH 6 whereas the Cr(VI) was found to bind highest at pH 2 and decrease with increase pH. The binding of the Cr(III) was determined to be independent of time the binding occurs within the first 5 minutes of contact and remains relatively constant thereafter. However, the Cr(VI) showed a small increase in binding with increasing time; but the majority of the binding occurred within the first five minutes of contact. Both Cr(III) and Cr(VI) binding was determined to be endothermic and the sorption process was determined through thermodynamic studies to be physisorption. In addition, the thermodynamics of the binding indicate the binding was a spontaneous and a thermodynamically favorable process. The binding of the Cr(III) in the presence of Ca^{2+} show in increase in the binding with increasing Ca^{2+} concentrations. In the presence of Mg^{2+} there was an observable decrease in the binding of the Cr(III) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial. The Na^+ interference showed a decrease in binding at higher concentrations. However, the binding of the Cr(III) in the presence of K^+ showed an initial effect however this was pretty constant throughout the study. However, the binding of the Cr(III) was never completely eliminated with any of the studied interferences even in the combined interference study. The combined interference and the PO_4^{3-} interference had the largest effect on the binding of the Cr(VI) completely eliminating the binding. The SO_4^{2-} had a negative effect observed at 300 ppm SO_4^{2-} concentration and above. Whereas the monovalent interferences had little to no observable effect on the binding.

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Highlights

- $\text{K}_2\text{Mn}_4\text{O}_9$ was successfully synthesized using low temperature and acidic media
- Cr(III) bound to the $\text{K}_2\text{Mn}_4\text{O}_9$ through a physisorption process optimally at pH 5
- Cr(VI) bound to the $\text{K}_2\text{Mn}_4\text{O}_9$ through a physisorption process optimally at pH 2
- Phosphate had the largest detrimental effect on Cr(VI) binding
- Cr(III) had little to no observed interference in the presence of hard cations

Figure 1.
X-ray diffraction pattern and fitting of the synthesized $K_2Mn_4O_9$ nanomaterial.

Figure 2.

Figure 5: Thermodynamic plot for the binding of Cr(III) and Cr(VI) to the $K_2Mn_4O_9$ nanomaterial at the optimum binding pHs.

Figure 3.
pH profile of the binding of Cr(III) and Cr(VI) to the $K_2Mn_4O_9$ nanomaterial from pH 2 through pH 6.

Figure 4.

A. Time dependency of Cr(III) binding to the $K_2Mn_4O_9$ nanomaterial. **B.** Time dependency of Cr(VI) binding to the $K_2Mn_4O_9$ nanomaterial.

Figure 5.

Thermodynamic plot for the binding of Cr(III) and Cr(VI) to the $\text{K}_2\text{Mn}_4\text{O}_9$ nanomaterial at the optimum binding pHs.

Figure 6.

A. Effect of hard cations on the binding of Cr(III) to the $K_2Mn_4O_9$ nanomaterial. **B.** Effect of common anions on the binding of Cr(VI) to the $K_2Mn_4O_9$ nanomaterial.

Table 1

GFAAS operating parameters used for the analysis of Cr binding to the K₂Mn₄O₉ nanomaterial.

Parameter	Temperature (°C)	Ramp Time (s)	Hold Time (s)
Pre-Dry	110	1	30
Dry	130	15	30
Char	1200	10	20
Atomization	2000	0	5
Clean out	2400	1	2

Table 2

ICP-OES operating parameters used for the analysis of Cr binding to the $K_2Mn_4O_9$ nanomaterial.

Parameter	Setting
λ	267.716 nm
RF power	1500 w
Nebulizer	Gemcone (low Flow)
Plasma Flow	15 L/min
Auxiliary Flow	0.2L/min
Nebulizer Flow	0.55 mL/min
Sample flow	1.50 mL/min
Injector	2.0 mm Alumina
Spray Chamber	Cyclonic
Integration Time	20 s
Replicates	3

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Fitting parameters and published lattice parameters of the synthesized $\text{K}_2\text{Mn}_4\text{O}_9$ reduced X^2 of 0.325

Table 3

Sample	a (nm)	b (nm)	c(nm)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	Space group
$\text{K}_2\text{Mn}_4\text{O}_9$ Synthesized	2.852(8)	2.842(8)	7.530(2)	90	90	120	P3-
$\text{K}_2\text{Mn}_4\text{O}_9$ published [18,16]	2.845(1)	2.845(1)	7.485(1)	90	90	120	P3-

Table 4

Capacities determined from Langmuir Isotherms of Cr(III) and Cr(VI) binding to $K_2Mn_4O_9$ synthesized nanomaterial at, 4, 25, and 45°C.

Sample	Capacity (mg/g)	Error ($\pm$ mg/g)
Cr(III) 4°C	21.7	0.75
Cr(III) 25°C	36.5	1.54
Cr(III) 45°C	41.8	1.75
Cr(VI) 4°C	4.22	0.47
Cr(VI) 25°C	4.08	0.28
Cr(VI) 45°C	3.25	0.32

Table 5

Thermodynamic parameters determined for the Langmuir Isotherms of Cr(III) and Cr(VI) binding to $K_2Mn_4O_9$ synthesized nanomaterial, at 4, 25, and 45°C.

Sample	G (kJ/mol)	H (kJ/mol)	S (J/mol)
Cr(III) 4°C	-3.88	17.54	77.92
Cr(III) 25°C	-5.83		
Cr(III) 45°C	-7.03		
Cr(VI) 4°C	-4.89	6.05	39.49
Cr(VI) 25°C	-5.64		
Cr(VI) 45°C	-6.05		