10-15-2014

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Cantu, Y., Remes, A., Reyna, A., Martinez, D., Villarreal, J., Ramos, H., Trevino, S., Tamez, C., Martinez, A., Eubanks, T., & Parsons, J. G. (2014). Thermodynamics, Kinetics, and Activation energy Studies of the sorption of chromium(III) and chromium(VI) to a Mn₃O₄ nanomaterial. *Chemical engineering journal* (Lausanne, Switzerland : 1996), 254, 374–383. <https://doi.org/10.1016/j.cej.2014.05.110>

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Published in final edited form as:

Chem Eng J. 2014 October 15; 254: 374–383. doi:10.1016/j.cej.2014.05.110.

Thermodynamics, Kinetics, and Activation energy Studies of the sorption of chromium(III) and chromium(VI) to a Mn_3O_4 nanomaterial

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Abstract

In this study, a manganese oxide, Mn_3O_4 was used to remove chromium(III) and chromium(VI) from aqueous solutions. The Mn_3O_4 nanomaterial was synthesized through a precipitation method, and was characterized using XRD, which confirmed the material had a crystal structure similar to hausmannite. In addition, using Scherrer's equation it was determined that the nanomaterial had an average grain size of 19.5 ± 1.10 nm. A study of the effects of pH on the binding of chromium(III) and chromium(VI) showed that the optimum binding pH was 4 and 3 respectively. Batch isotherm studies were performed to determine the binding capacity of chromium(III), which was determined to be 18.7 mg/g, 41.7 mg/g, and 54.4 mg/g respectively for 4°C, 21°C, and 45°C. Chromium(VI) on the other hand had lower binding capacities of 2.5 mg/g, 4.3 mg/g, and 5.8 mg/g for 4°C, 21°C, 45°C, respectively. Thermodynamic studies performed indicated the sorption process was for the most part controlled by physisorption. The ΔG for the sorption of chromium(III) and Chromium(VI) ranged from -0.9 to -13 kJ/mol, indicating a spontaneous reaction was occurring. The enthalpy indicated an endothermic reaction was occurring during the binding and show ΔH values of 70.6 and 19.1 kJ/mol for chromium(III) and Chromium(VI), respectively. In addition, ΔS for the reaction had positive values of 267 and 73 J/mol for chromium(III) and chromium(VI) which indicate a spontaneous reaction. In addition, the sorption process was found to follow pseudo second order kinetic and the activation energy studies indicated the binding process occurred through chemisorption.

Keywords

chromium(III); chromium(VI); adsorption; thermodynamics; Mn_3O_4 nanomaterials

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1. Introduction

Increasing levels of heavy metal ions present in water and sewage systems pose increasing threats to both environmental and human health [1–23]. In 2008 it was reported by the U.S. EPA, that approximately 97,379 pounds of chromium was released annually into the environment through wastewater discharge [2, 4]. Chromium exists commonly in two oxidation states, as either chromium(VI) or chromium(III) [2,4–7]. It is well known that chromium(VI) is carcinogenic, whereas chromium(III) is an essential nutrient [3–12]. Both chromium(VI) and chromium(III) are present in the environment at highly dangerous levels as industrial effluent discharges from steel works, oxidative dying, leather tanning industries, electroplating, volcanic eruptions, and cooling waters from coal fired power plants [2–6,13,14]. As a result, chromium is high on the list of priorities of the U.S. EPA's list of toxic pollutants [2,3]. AS a result of the contamination of the natural environment and the effects on human health it has become imperative to find an effective method to remove chromium from wastewaters.

Currently, a variety of methods have been developed to remove chromium from wastewaters, which include precipitation, ion exchange, reverse osmosis, electro-chemical precipitation, and adsorption [2, 4–6, 18, 20–22]. In addition, geopolymers, activated clays, chemical precipitation, and co-precipitation with metal hydroxides have also been investigated for the removal of chromium(VI) and chromium(III) from aqueous solution [8, 26, 27]. Other types of removal methods include: extraction, and ultrafiltration. However, most of these methods have major drawbacks, such as high costs. Overall, adsorption has proven to be one of the most effective methods for the removal of toxic metals from wastewaters due to its cost-effectiveness [3, 5, 16, 20]. Many low-cost adsorbents have been studied such as, steel wool, sawdust, pine needles, shells, cactus leaves, magnesium pellets and iron oxide pellets among others. Structured metal oxides, such as manganese oxide have proved to be effective adsorbents in part due to their microporous structure, which allows for greater adsorption and high binding capacities [13, 16–19].

Interest has grown towards the used of nanomaterials as adsorbents for the removal and detoxification of toxic metals, due to the high surface area and reactive properties of nanomaterials. Nanomaterials have been shown to be an efficient and economical way to remove heavy metals from water [25]. Researchers have focused on nanomaterials due to their large surface area that allows nanomaterials to adsorb larger amounts of metal ions. Additionally, like other bulk materials some nanomaterials exhibit magnetic properties, which allow removal of both the nanomaterial and the contaminants from the water using magnetic separation [3, 4, 25].

Previous studies have shown that both chromium(III) and chromium(VI) are effectively removed from solution through adsorption on to different materials. The sorption of chromium(VI) on to some nanomaterials has been show to first be reduced to chromium(III) which is followed by adsorption on to a metal oxide surface [3,6,11,20]. Removal of chromium ions has also been performed through the use of multiwall carbon nanotubes, instead of a metal oxide [21]. Although the method of adsorption and reduction with multiwall carbon nanotubes was successful, the process could be further simplified by

finding a binding source that does not require the reduction of chromium(VI) to chromium(III). The removal of metal ions from aqueous solution can occur through three general processes which are as follows: dissolution of the material and co-precipitation of the metal ion and dissolved nanomaterial; ion-exchange with surface bound hydroxide and or protons; and through the process of physisorption of the ion to the surface of the nanomaterial.

In the present study the adsorption of chromium(III) and chromium(VI) on to Mn_3O_4 nanoparticles was investigated. The nanomaterial was synthesized using a slow titration of MnCl_2 with dilute sodium hydroxide. Subsequently the solution was aged through heating the solution to convert the precipitated $\text{Mn}(\text{OH})_2$ to Mn_3O_4 . The Mn_3O_4 nanomaterial was then characterized using XRD, which showed the nanoparticles had the crystal structure of hausmannite. The effects pH on the binding of chromium o the nanomaterials was investigated as well as the capacity of the nanomaterial for both chromium(III) and chromium(VI) at different temperatures. The thermodynamics of the binding process were investigated, which included determining the ΔG , ΔH , and ΔS . The thermodynamic parameters will provide insight to the binding mechanism of chromium ions to the surface of the nanomaterial. The kinetics of the sorption process were studied at temperatures of 4, 25, and 45°C. From the kinetics data the activation energy for the process was determined using Arrhenius plots providing insight into the binding process.

2. Methods

2.1 Synthesis of nanoadsorbents

A 1.0 L 30.0 mM solution of MnCl_2 was titrated with 90 mL of 1 M NaOH for over 2 hours. The solution was heated to 90°C for 10–20 minutes to induce formation of the Mn_3O_4 . Subsequent to heating the solution was cooled to room temperature and centrifuged at 3000 RPM for 10 minutes. The supernatants were discarded and the test tubes containing the remaining nanomaterial were washed twice using 18M Ω DI water. The washed nanomaterials were then oven dried at 65° C for 12 hours to remove any residual water in the nanomaterials.

2.2 Nanomaterial Characterization

The X-ray diffraction patterns were collected using a Rigaku Miniflex X-Ray powder diffractometer, using a Cu source (Cu K_α). The scans were acquired from 15–60.4 in 2θ with a counting time of 2 seconds and a step of 0. 02° in 20. The collected diffraction pattern was then fitted using the Le Bail fitting procedure, in the Fullprof software package for confirmation of the structure of the nanomaterial. In addition, the average grain size of the nanomaterial was determined using the Scherrer's equation. The size analysis was performed using the full width half maximum of a minimum of three independent diffraction peaks for the Mn_3O_4 nanomaterial. The SEM analysis was performed on a Zeiss EVO-LS10. The samples were fixed to an aluminum post using carbon tape, and sputter coated using an Au-Pd sputtering target. The Instrument was operated at a voltage of 23.34 kV and a working distance of 4.5 mm.

2.3 pH Profile

Chromium(III) and chromium(VI) were tested for adsorption onto Mn_3O_4 nanomaterial over a pH range of 2–6. 300 ppb solutions of both chromium(III) and chromium(VI) were prepared and diluted, the pH adjustment was achieved using either dilute sodium hydroxide and/or dilute nitric acid to the desired pH. A 4.0 mL of the aliquot of the pH adjusted solution was transferred to a 5.0 mL test tube containing 10 mg of the nanomaterial in triplicate. In addition control samples were prepared in a similar manner without the presence of the nanomaterial. The test tubes were then capped and equilibrated on a test tube rocker for one hour. Subsequent to equilibrium the samples and controls were centrifuged at 3000 RPM for 10 minutes and the supernatants was saved further analysis. Each sample was repeated in triplicate for QA/QC and statistical purposes. The samples and controls then analyzed using a Perkin Elmer AAnalyst 800 in Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) mode. The amount of chromium bound to the nanoadsorbent was then determined by the difference method. In addition all calibration curves were generated for the study had correlation coefficients (R^2) of 0.99 or better.

2.4 Capacity Studies

The optimum binding pH for both chromium(III) and chromium(VI) was determined to be pH 4 from the pH profile study. The capacities were determined using isotherm studies with solutions containing 0.3, 3, 30, 300, and 1000 ppm of either chromium(III) or chromium(VI). The pH adjusted chromium solutions were added to test tubes containing 10 mg of manganese oxide (Mn_3O_4). Each concentration was repeated in triplicate and the control samples prepared in a similar manner as the samples. The test tubes were capped and put on a test tube rocker for one hour to insure equilibration, following the equilibration the sample and control test tubes were centrifuged at 3000 RPM for 10 min. The supernatant were saved and analyzed using a Perkin Elmer Optima 8300 DV ICP-OES. In addition, all calibration curves were generated for the study had correlation coefficients (R^2) of 0.99 or better.

2.5 Thermodynamic studies

Several thermodynamic studies were conducted for chromium(III) and chromium(VI) at different temperatures. The solutions were prepared at various concentrations the same as the capacity studies ranging from 0.3 ppm to 1000 ppm for chromium(III) or chromium(VI). The pH of the solution was adjusted to the optimum binding pH of 4. 4.0 mL aliquots of the solutions were added to test tubes, containing 10 mg of Mn_3O_4 , and equilibrated for one hour on a test tube rocker at temperatures of 4°C, 21°C (room temperature), and 45°C. Subsequent to equilibration samples and controls were then centrifuged for at 3000 rpm for 10 min. The supernatants were saved for analysis using ICP-OES (Inductively Coupled Plasma-Optical Electron Spectroscopy). Calibration curves were generated with correlation coefficients (R^2) of 0.99 or better. The study was performed in triplicate for QA/QC and statistical purposes.

2.6 Kinetic Studies

Solutions consisting of 3.0 mM of either chromium(III) or chromium(VI) were prepared from chromium(III) nitrate or potassium dichromate. A 4 ml aliquot was pH adjusted pH 4.0 using either dilute sodium hydroxide or dilute nitric acid at temperatures of 4°C, 25°C, or 45°C. The pH adjusted chromium solution was then added to a polyethylene test tube containing 10 mg of the Mn3O4 nanomaterial. The reactions were then equilibrated for the following times 10, 15, 20, 30, 60, 90, 120, and 240 minutes. Once the solutions were finished equilibrating for the specified time the samples were centrifuged for 5 minutes at 3,000 rpm and the supernatants were decanted and saved for analysis using ICP-OES. In addition, control samples containing only chromium ions were also processed the same as the reaction samples. Furthermore, the samples and control samples were prepared and analyzed in triplicate for statistical purposes.

2.7 Activation Energy Studies

Once the kinetic data was collected and the rate constant was determined for the reaction at the three different temperatures an Arrhenius plot was developed. The Arrhenius plot was developed by plotting the $\ln k$ against $1/T$ (in Kelvin). The linearized form of the Arrhenius equation is given below in equation 1:

$$\ln k = \frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad 1$$

Where k is the rate constant for the reaction at a given temperature, E_a is the activation energy for the process, R is the gas constant (8.314), T is the temperature given in Kelvin, and A is the frequency factor for a given reaction.

2.8 ICP-OES Analysis

ICP-OES analysis was performed using a Perkin Elmer Optima 8300 DV ICP-OES. Calibrations were conducted by using three standards, with the addition of a blank solution. The calibration range was between 1.00 ppm to 100 ppm. Samples over the range of the standards were diluted to be within range. The operating conditions for the ICP-OES are shown below in Table 1. Furthermore, all standards, controls, and samples were read in triplicate for statistical purposes.

2.9 GFAAS analysis

GFAAS analysis was performed using a Perkin Elmer AAnalyst 800 in Graphite Furnace Atomic Absorption mode. The operational parameters of the GFAAS are shown below in Table 2. The wavelength for the analysis was 357.9 nm with a hollow cathode lamp with a slit of 0.7 nm and a lamp current of 8 mA. A sample injection of 20 μ L and no matrix modifier was used for the analysis of chromium. Furthermore, all standards, controls, and samples were read in triplicate for statistical purposes.

3.0 Results and Discussion

3.1 X-Ray Diffraction Analysis

Figure 1 shows the X-Ray diffraction patterns collected for the synthesized Mn_3O_4 nanomaterial after washing and drying. The Bragg peaks for the synthesized Mn_3O_4 nanomaterial are indicated on the bottom of the plot. It was determined from the diffraction analysis that the nanomaterial was Mn_3O_4 in a tetragonal lattice with space group $I4_1/\text{AMD}$. The refined lattice parameters determined from the Le Bail fitting were as follows $a = 5.77$ nm, $C = 9.45$, $\alpha = \beta = \gamma = 90.0^\circ$, which match the parameters determined for hausmannite from the literature [28]. The Bragg peaks identified as present in the nanomaterial correspond to 200 (18.0°), 112 (28.9°), 200 (31.0°), 103 (32.3°), 211 (36.0°), 202 (36.5°), 004 (38.1°), 220 (44.4°), 301 (48.2°), 204 (49.9°), 105 (50.9°), 321 (58.5°), 224 (59.9°) and the from left to right in the plot (the peak positions are given in $2\theta^\circ$ in brackets). The average grain size of the nanomaterial was determined using the Scherrer's equation and analysis, using three independent diffraction peaks which gave an average grain size of the materials was determined to be 19.5 ± 1.10 nm. The small errors on the calculated size of the nanomaterials indicate low anisotropy and that the nanomaterials spherical in shape. Figure 2 A and B show a SEM Image of the synthesized nanomaterial. The SEM image indicates that the synthesized nanomaterials are spherical in shape. Furthermore, the SEM images shows that the nanomaterials are clustered together forming larger structures again with spherical shapes and diameters ranging from 30 to approximately 60 nm. The spherical natures of the nanomaterials seen in the SEM image corroborate the shape inferred from the XRD data.

3.2 pH Studies

Figure 3A and 3B show the pH binding for chromium(III) and chromium(VI) binding to manganese oxide (Mn_3O_4) nanomaterial from pH 2 to pH 6, respectively. In Figure 3 A, the abnormally high binding of chromium(III) at low pH, pH 2 and pH 3, is due to a redox reaction, occurring between the Mn and the Chromium(III) ions. The redox reaction has been noted in the literature and has been shown to occur at pH 2 and pH 3 (29). The redox reaction between the Mn in the nanomaterial and the chromium(III) results in the oxidation of the chromium(III) to chromium(VI). However, at pH 4 and above the binding of the Chromium(III) to the nanomaterial has decreased and stabilized indicating that the oxidation of the chromium(III) has stopped and the removal of the chromium is due to adsorption. Due to the presence of the redox reaction between the Mn in the nanomaterial and chromium(III) ions and the observation of the stabilized binding observed at pH 4 and above, pH 4 was selected as the optimum binding pH. The binding of the chromium(VI) ion is shown in Figure 2 B, as can be seen the binding decreases with increasing pH from 90% binding at pH 2 to approximately 20 % binding at pH 4. The pH profiles are in agreement with the literature for chromium binding to other metal oxide nanomaterials [9,10, 13, 26, 30]. For example, nano- Fe_3O_4 magnetic polymers have shown a similar pH binding trend of decreasing binding pH increases, with pH 2 having a maximum adsorption of 99% [2]. Similar binding trends have been observed with chromium binding to Fe_3O_4 , MnFe_2O_4 , TiO_2 , Al_2O_3 , Fe_2O_3 , and among other metal oxide nanomaterials [4, 31–41]. The relationship in the binding is generally due to the surface charge of the nanomaterial, at low

pH the surface of a nanomaterial is protonated giving the nanomaterial a slightly positive charge whereas at high pH the nanomaterial becomes neutral and then negatively charged. At high pH values above the zero point charge of the nanomaterial the surface of the nanomaterial is negatively charged and thus repulses the chromium(VI) anions and the binding becomes greatly diminished [4, 13]. Conversely, at a low pH chromium(VI) can be efficiently adsorbed from solution [18]. In general chromium(III) follows an opposite trend in the binding when compared to chromium(VI). However, at low pH in the presence of Mn nanomaterials redox reactions occur, as previously mentioned which disrupts the generally observed binding trend for chromium(III).

3.3 Capacity Studies

The adsorption capacities of chromium(III) and chromium(VI) binding to Mn_3O_4 were performed at three different temperatures, which were as follows: 4°C, 26°C and 45°C. The data presented in Table 3 shows chromium(III) had a much higher binding capacity to the Mn_3O_4 nanomaterial than the chromium(VI), approximately 9 times the binding capacity. However, the binding capacity was shown to increase with increasing temperature with a maximum capacity occurring at a temperature of 45°C for both chromium(III) and chromium(VI). It was evident at the 4°C study where the binding capacity for both chromium(III) and chromium(VI) were the lowest. The data from the capacity study was determined using an isotherm study, which was found to follow the Langmuir isotherm model. As shown in Table 2 the correlation for the fittings of the data to the Langmuir isotherm are all 0.99 (R^2) or better. The data fitting to a Langmuir isotherm indicate a monolayer adsorption is occurring. The adsorption of a monolayer of the ions on the materials at pH 4 indicates that at this pH the redox reaction occurring at lower pH's has stopped.

The data in the current study are for the most part in the same concentrations ranges as those other studies, using different nanoadsorbents of similar structure, where capacities for chromium(III) and chromium(VI) were 7 to 10 mg/g for chromium(III) and around 3 mg/g for chromium(VI) [4]. Other studies also confirm the higher binding capacities of chromium(III) when compared to chromium(VI) [6,17]. Zeolites have been shown to have capacities as high as 26 mg/g whereas Fly ash has shown to have capacities of 2.3 mg/g for chromium(III). Chromium(VI) has been shown to have a capacity of 5 mg/g on TiO_2 , 7.44 mg/g on activated alumina, 12.9 mg/g on activated carbon, and up to 51.5 mg/g on hydrous zirconium oxide [38, 42,43]. Other examples of capacities of chromium binding to different materials are presented in Table 4 for comparative purposes. However, data obtained from capacity studies do have a large variation, which presents limitations for comparisons. These limitations generally present due to differences in the reaction conditions. In addition, parameters such as size, porosity, and stability of the nanomaterial as well as all preparation methods can contribute to the variability of binding capacity [4].

3.4 Thermodynamic Studies

The thermodynamic data obtained determined from the present study is presented in Table 4–Table 6 for the Gibbs free energy, the enthalpy, and the entropy of the binding system. The change in the Gibbs free energy (ΔG) was calculated for both the chromium(III) and

chromium(VI) ions based on the relationship between the distribution coefficient or equilibrium constant between the chromium ions and the nanomaterial. The relationship between shown in equation 2:

$$\Delta G = -RT \ln K_d \quad 2$$

G is the calculated change in the Gibbs free energy, R is the gas constant (8.314 J/Mol⁻¹K⁻¹), T is the absolute temperature in Kelvin, and K_d is the distribution coefficient. The calculated thermodynamic values for the adsorption of chromium(III) and chromium(VI) onto Mn₃O₄ are presented in Table 5. The general trend in the changes in Gibbs free energy for both the chromium(III) and chromium(VI) ions gets more negative as temperature increases indicating a more spontaneous reaction as temperature increases. The thermodynamic parameters for the sorption of both chromium(III) and chromium(VI) has been studied in the literature for many different inorganic materials including metal oxides [4, 34, 38, 44]. For example Luther et al nanoma the thermodynamics of chromium (III) and chromium(VI) to Fe₃O₄ and MnFe₂O₄ terials [4]. For the binding to chromium(VI) to these nanomaterials the G for the sorption process range between -7.5 to -7.02 and was dependent on the temperature. Whereas, the binding of chromium(III) to the same materials was found to be between -17.16 to -11.40 KJ/mol. Which are were found to be slightly higher than the values found in the present study, which were -2.7 kJ/mol (277 K), -10.7 kJ/mol (298K) and -13.7 kJ/mol (318K) for chromium(III) and -0.9 kJ/mol (277 K), -2.8 kJ/mol (298 K) and -3.9 kJ/mol (318 K) for chromium(VI). A similar trend was observed for the change in the G in the present study as was observed by Luther et al, which the change becomes more negative with increasing temperature indicating a spontaneous process that is endothermic. In similar types of materials such as synthetic hematite the G was shown to be 1.6kJ/mol at 300 K, whereas with mixed aluminum-magnesium metal hydroxides the G has been shown to range from -6.26 to -8.96 kJ/mol [8, 45]. In modified clays the -40 kJ/mol showed a very spontaneous reaction [46]. The sorption of chromium(III) to bentonite has been shown to have a G of -3.91 kJ/mol and a G for chromium(VI) of -0.441 kJ/mol [44]. It has been shown in the literature that a G value below 18 kJ/mol (absolute value) indicates the reaction is an adsorption process dominated by physisorption [47]. However with a G value approximately from -34 to -40 kJ/mol indicates ion exchange is the predominate mechanism for the sorption equilibrium [47]. This would indicate that the present study the binding of both chromium(III) and chromium(VI) to the nanomaterials is predominately though physisorption and not ion exchange. Furthermore, the increase in magnitude for the calculated values indicates that adsorption becomes more favorable as temperatures increase, indicating the adsorption is through an endothermic process.

The determined H and S values for the present study are shown in Table 6 for the binding of both chromium(III) and chromium(VI) ions to the Mn₃O₄ nanomaterial. The relationship between G, H, and S and the relationship between G and the Ln K_d show in equation 2 and equation 3, respectively.

$$\Delta G = \Delta H - T\Delta S \quad 3$$

The following relationship can be determined substituting $\ln K_d$ into equation 2 to develop equation 4.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad 4$$

By plotting the $\ln K_d$ against $1/T$ (in K) the ΔH of the reaction can be determined from the slope of the line and from the intercept of the plot ΔS can be determined. Figure 4 shows the plots of $\ln K_d$ determined at the three different temperatures 277 K, 298 K and 318 K for both chromium(III) and chromium(VI) binding to the Mn_3O_4 nanomaterial. Table 6 shows the determined ΔH values for the binding of the chromium(III) and chromium(VI) to the nanomaterial. The positive values determined for the binding of both chromium(III) and chromium(VI) to the nanomaterial indicates that the reaction is endothermic in nature. In addition, the binding of chromium(III) ion to manganese oxide nanomaterial has a much higher ΔH than the chromium(VI) as can be seen in Table 6 indicating the chromium(III) ion binding is more endothermic than the binding of chromium (VI) ions. Furthermore, the apparent ΔH value of the binding of chromium(VI) was below 40 kJ/mol indicating that the binding occurred through physisorption, as was suggested by the ΔG results which has been indicated in the literature [43]. However, the apparent ΔH for the binding of chromium(III) ions to the nanomaterials was determined to above 40 kJ/mol, approximately 70 kJ/mol, indicating that the reaction is not driven solely through physisorption. For the binding of chromium(III) it may physisorption complimented by an ion exchange or chemisorption to the surface of the Mn_3O_4 nanomaterial.

The calculated entropy ΔS values for this study are shown in Table 6 for the binding of chromium(III) and chromium(VI) ions to Mn_3O_4 nanomaterial. The ΔS for the binding of both chromium(III) and chromium(VI) are both positive values and thus the binding is a thermodynamically favorable reaction. The very high entropy for the chromium(III) binding reaction would indicate that some material is being released from the Mn_3O_4 material which supports a binding mechanism that would involve ion exchange in addition to physisorption. Alternatively, reductive dissolution of the Mn_3O_4 could be occurring in the reaction mixture which would lead to an increase in the entropy of the system. Reductive and oxidative dissolution of nanomaterials has been suggest in the literature for the binding of different ions to nanomaterials [4, 19]. The lower entropy observed for chromium(VI) could indicate a reduction mechanism through which chromium(VI) is reduced to chromium(III) as a result of donation of electrons from the surface of the nanomaterial [4]. In a similar study, chromium(III) and chromium(VI) was tested with $MnFe_2O_4$ and Fe_3O_4 nanomaterial under light and dark conditions, the ΔS values obtained for chromium(III) were 69.26 J/mol and 22.95 J/mol for $MnFe_2O_4$ and Fe_3O_4 .

3.5 Kinetic Studies

The Results of the Kinetics study were found to best follow the second-order or pseudo order adsorption kinetics model. The linear second order and pseudo second order equation for the adsorption of a metal ion to the surface of an adsorbent is shown below in equation 5 [48]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad 5$$

Where q_t is the adsorption at any given time during the reaction, t is the time for the adsorption given in minutes, q_e is the equilibrium adsorption of the metal ion to the surface, and K is the rate constant for the given reaction. As can be seen in Figure 5 both the chromium(III) and chromium(VI) adsorption follow the second order or pseudo second order reaction kinetics. The correlation coefficients for both the chromium(II) and chromium(VI) are 0.99 or better. The pseudo second order kinetic model nicely simulated the data obtained in the study. From the kinetics plots the rate constants were determined as shown in Table 6. As can be seen in Table 6 the rate constant (k) for the reaction increased with increasing temperature. The observed increase in rate constant with increasing temperature indicates that the reaction is endothermic reaction for the binding of both chromium(III) and chromium(VI) to the Mn_3O_4 nanomaterial. The endothermic reaction was also indicated in the thermodynamic studies as mentioned earlier. The observed pseudo second order reaction kinetics has been shown to fit the data for chromium binding to magnetite nanomaterials, diatomite-magnetite supported nanomaterials, and chromium(VI) binding to maghemite nanoparticles [49, 50]. Furthermore the pseudo-second order kinetic model has also been used to model the adsorption kinetics of methylene blue on to palm kernel fiber [50]. The as well as the binding of cadmium(II) ions onto zero valent iron, As(V) adsorption onto clinoptilolite with iron or aluminum oxide, with comparable rates observed in this study for chromium(VI) and chromium(III) [51, 52]. It has been suggested that there is a activation process occurring during the adsorption process. As can be seen in the data for the sorption of chromium(III) and chromium(VI) the rate constant for the sorption of chromium(III) are much higher than the rate constants associated with the chromium(VI) ions. The higher observed rate constants for the chromium(III) may be an effect of the charge of the chromium(III) in solution which should be positive. Whereas the $Cr(VI)$ ions in solution have a net negative charge which may cause repulsion between the chromium(VI) and the hydration sphere around the nanomaterial and thus slow the kinetics of adsorption. There are a number of important factors for adsorption of an ion to any material. However, there must be an attractive force between the material and the ions before the process starts. The Kinetics for the chromium(VI) may be slowed by breaking apart of the hydration sphere and the diffusion to the surface of the material as compared to the chromium(III).

3.6 Activation Energy Studies

From the kinetics data obtained at different temperatures the activation energy for the binding of both chromium(III) and chromium(VI) was determined as shown in Table 7, and the Arrhenius plot is shown in Figure 6. As can be seen in Table 7 the activation energy for the binding of both chromium(III) and chromium(VI) to the Mn_3O_4 nanomaterials are very similar with only a difference of approximately 8 kJ. The slight difference in the activation energy for the binding process may be indicating a slight different affinity of the metal ions to the Mn_3O_4 nanomaterial. However, the similarity in the activation energy for the binding of both ions does indicate that the ions are going through a similar process in binding. The

magnitude if the activation energy can be used to help elucidate the mechanism occurring for the binding, whether the binding is through physisorption or through chemisorption. Physisorption, a physical attraction generally has activation energies below 40 KJ/mol [52]. Whereas, chemisorption is a chemical process requires more energy and generally has activation energies above 40 kJ/mol [52]. The data from the activation energy studies indicates that the binding process for both the chromium(III) and chromium(VI) ions to the Mn_3O_4 nanomaterials occurs through chemisorption as both ions have activation energies above 40kJ/mol. The action energies are similar in magnitude to those observed for cadmium(III) binding to zero valent iron nanoparticles which was observed to be 54 kJ/mol [52].

4. Conclusions

A Manganese oxide nanomaterial, Mn_3O_4 , was synthesized, characterized using XRD, and tested for the removal of both chromium(III) and chromium(VI). The optimum binding pH for each material was determined using batch pH studied and was found to be pH 4 for chromium(III) and pH 3 for chromium(VI). The binding capacities of the nanomaterials were determined at temperatures of 4°C (277K), 25°C (298K), and at 45°C (318K), for chromium(III) these were 18.7 ± 2.1 mg/g, 41.7 ± 1.7 mg/g, and 54.4 ± 4.3 mg/g, respectively. The chromium(VI) binding capacities for the same temperature series were significantly lower 2.5 ± 0.3 , 4.3 ± 0.7 and 5.8 ± 0.3 mg/g, respectively. The thermodynamic parameters from the study indicate that the sorption of the chromium is spontaneous as determined from the negative ΔG values obtained from both the chromium(III) and chromium(VI). Also, the reaction of chromium(III) with the Mn_3O_4 nanomaterial occurs through a combination of physisorption and possibly ion-exchange, whereas the chromium(VI) sorption appears to be mainly physisorption. Furthermore, the ΔS showed an increase, which could be indicating that some ion-exchange is occurring during sorption, or the randomness at the surface and water interface is increasing during the sorption process. In addition, the sorption process was also found to follow pseudo second order kinetics, and from the activation energy studies the binding occurs through a chemisorption process.

Acknowledgments

Authors would like to thank the NIH UTPA RISE program (Grant Number 1R25GM100866-01), NSF, URM program (grant number DBI 9034013), HHMI (grant 52007568). The Authors acknowledge financial support from the Welch Foundation for supporting the Department of Chemistry (Grant number GB-0017), and UTPA for sponsoring this research project.

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Highlights

The binding of Cr(III) and Cr(VI) to Mn_3O_4 nanomaterials was investigated

Effects of pH, temperature, and time were investigated for the binding

Cr(III) capacity at 277, 294, and 318 K was 18.7, 41.7, and 54.4 mg/g

Cr(VI) capacity at 277, 294, and 318 K were 2.5, 43, and 5.8 mg/g

Thermodynamic parameters ΔG , ΔH , ΔS , and E_a were determined

Figure 1.

X-Ray Diffraction pattern for the synthesized Mn_3O_4 nanomaterials, showing the fitting, the difference pattern between the fitting and the raw data, and the Bragg peaks.

Figure 2.

A. SEM image taken at 123.55 K X of the synthesized Mn_3O_4 nanomaterials B. SEM image taken at 143.8 K X of the synthesized Mn_3O_4 nanomaterials. SEM images were taken after washing and drying at 60°C for 24 hours.

Figure 3.

A. Effect of pH on the binding of a 300 ppb solution chromium (III) from chromium (III) nitrate to Mn_3O_4 at 25°C. **B.** Effect of pH on the binding of a 300 ppb solution chromium (VI) from potassium dichromate to Mn_3O_4 at 25°C.

Figure 4.

A. Thermodynamic plot for the sorption of chromium(III) to the Mn_3O_4 nanomaterial after 1 hour of contact time. **B.** Thermodynamic plot for the sorption of chromium(VI) to the Mn_3O_4 nanomaterial after 1 hour of contact time.

Figure 5.

A. Kinetics plots for chromium(III) chromium(VI) (B) at temperature of 4°C, 25 °C, and 45°C for the reaction of 3 mM chromium ion with 10 mg of the Mn_3O_4 nanomaterial. **B.** Kinetics plots for chromium(VI) at temperature of 4°C, 25 °C, and 45°C for the reaction of 3 mM chromium ion with 10 mg of the Mn_3O_4 nanomaterial.

Figure 6.

Arrhenius plot for the chromium(III) and Chromium(VI) binding to the Mn_3O_4 nanomaterial, data obtained from the kinetics for the chromium(III) and chromium(VI) kinetics at different temperatures.

Table 1

ICP-OES operational parameters used for the analysis of chromium concentrations in solution after reaction with the different nanoadsorbents.

Parameter	Setting
λ	267.716 nm
RF power	1500 W
Nebulizer	Gemcone (low flow)
Plasma Flow	15 L/min
Auxiliary Flow	0.2 L/min
Nebulizer Flow	0.55 L/min
Sample Flow	1.50 mL/min
Injector	2.0 mm Alumina
Spray Chamber	Cyclonic
Integration Time	10–20 seconds

Table 2

GFAAS operational parameters used for the analysis of chromium concentrations in solution after reaction with the different nanoadsorbents.

	Pre-Dry	Dry	Char	Atomization	Clean
Temperature (°C)	110	130	1200	2300	2450
Ramp Time (s)	1	5	10	0	1
Hold Time (s)	20	30	20	5	2
Argon Flow (mL/min)	250	250	250	0	250

Table 3

Capacity for the adsorption of chromium (VI) and chromium (III) to Mn_3O_4 after 1 hour of contact time determined using the Langmuir Isotherm at various temperatures.

Temperature (°C)	Cr(VI) (mg/g)	Error ± (mg/g)	Langmuir Correlation Coefficient	Cr(III) (mg/g)	Error ± (mg/g)	Langmuir Correlation Coefficient
4	2.5	0.3	0.99	18.7	2.1	0.99
21	4.3	0.7	1.0	41.7	1.7	0.98
45	5.8	0.3	0.99	54.4	4.32	0.99

Table 4

Capacities for chromium to different metal oxide materials from the literature.

Material	Chromium Capacity (mg/g)	Chromium Species	Reference
AlOOH	2.158	Chromium(VI)	31
Fe ₃ O ₄ (nanoparticles)	21.7	Chromium(VI)	32
Fe ₃ O ₄ (nanoparticles)-diatomite	69.2	Chromium(VI)	32
Fe ₃ O ₄ (micro particles)	10.6	Chromium(VI)	32
Fe ₃ O ₄ ((micro particles)-diatomite	11.4	Chromium(VI)	32
γ-Fe ₂ O ₃ (nanoparticles)	15.6	Chromium(VI)	33
TiO ₂	14.56	Chromium(VI)	34
Wollastonite-Fly ash	0.271	Chromium(VI)	35
Bagasse fly ash	259.0	Chromium(III)	36
Bauxite	0.5	Chromium(VI)	37
Bauxite	0.4	Chromium(VI)	37
Hydrous titanium(IV) oxide	5.0	Chromium(VI)	38
Red Mud	21.1	Chromium(VI)	39
Zeolite	19.67	Chromium(III)	40
Zeolite	0.65	Chromium(VI)	41

Table 5

Calculated change in Gibbs free energy for the binding of Cr (III) and Cr (VI) to the Mn_3O_4 nanomaterial at various temperatures.

Chromium Species (Temp. K)	G (kJ/mol)	Error G ($\pm$ kJ/mol)
Cr (III) (277)	-2.9	0.1
Cr (III) (298)	-10.7	0.9
Cr (III) (318)	-13.7	1.2
Cr (VI) (277)	-0.9	0.1
Cr (VI) (298)	-2.8	0.02
Cr (VI) (318)	-3.9	0.14

Table 6

Thermodynamic parameters ΔH and ΔS calculated for the binding of chromium(III) and chromium(VI) binding to Mn_3O_4 nanomaterials.

Chromium Species	ΔH (kJ/mol)	ΔS (J/mol)
Cr (III)	70.6	267.7
Cr (VI)	19.1	72.8

Table 7

Rate constants determined for the reaction of chromium(III) and Chromium(VI) binding to Mn_3O_4 nanomaterials at temperatures of 4°C, 25°C, and 45°C.

Reaction	k (g mg ⁻¹ min ⁻¹)	R ²
Chromium(III) 4°C	3929	0.99
Chromium(III) 25°C	19834	0.99
Chromium(III) 45°C	89000	0.99
Chromium(VI) 4°C	0.36	1
Chromium(VI) 25°C	3.65	1
Chromium(VI) 45°C	12.35	0.99

Table 7

Determined activation energies for the binding of chromium(III) and chromium(VI) to the Mn_3O_4 nanomaterials.

Reaction	$E_a(\text{KJ})$	R^2
Chromium(III)	52.5	1
Chromium(VI)	60.7	0.99