Evaluation of Batch and Equilibrium Cr 6+ adsorption on Fe 3 O 4 nanoparticles via isothermal and kinetic studies

Rimmy Singh (✉ rimmisingh250@gmail.com)

DPG Institute of Technology and Management

Rachna Bhateria

Maharshi Dayanand University

Research Article

Keywords: Hexavalent chromium, removal efficiency, isotherms, adsorption capacity, recovery

Posted Date: August 8th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1248502/v2>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Since many centuries, we have progressively tracked our capacities in the field of water contamination. An intense increase in heavy metals have led to the problems needing priority concerns. This experimental work aims to investigate the adsorption of Cr^{6+} ions onto magnetite nanoparticles. The Fe_3O_4 nanoparticles were synthesized by one-step chemical reduction method and characterized by using High Resolution Transmission Electron Spectroscopy (HRTEM), Selected Area Electron Diffraction (SAED), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD) to evaluate the details about nanoparticles. HRTEM analysis determined the average size of 42.90 nm and spherical morphology of the nanoparticles. To study the effect of different process variables such as concentration of Cr^{6+} ions ($10\text{--}60\text{ mgL}^{-1}$), pH ($1\text{--}9$), temperature ($15\text{--}40^\circ\text{C}$), Fe_3O_4 NPs dose ($10\text{--}80\text{ mg}$) and contact time ($15\text{--}60$ minutes) and to optimized them, conventional batch experimental method was used. Various models were applied to the obtained data to mathematically conclude it. Maximum adsorption capacity (0.15 mg g^{-1}) was calculated by Langmuir model. Additionally, Freundlich, Temkin and D-R models were also interpreted to find the best fit. In this study, Temkin model was found the best fit with a correlation coefficient (R^2) of 0.99. However, Pseudo second order describes the adsorption kinetics and thermodynamic study concluded the spontaneity and exothermic nature of the process. The recovered nanoparticles were used 3 times to find the regeneration capacity. Hence, the results demonstrates that Fe_3O_4 nanoparticles can be the potential material for heavy metal removal from wastewater and additional modifications can enhance their efficiency for further applications.

1. Introduction

Increasing global problem of pollution has threatened the world with future consequences. There is leapfrogging growth in contamination of potable water with heavy metals, organic compounds, dyes, and other such kind of pollutants. Amongst these global issues, heavy metal pollution has dominated the system. Heavy metals including, but not limited to lead, Chromium, Cadmium, Mercury, Arsenic etc. have contributed majorly and are responsible for severe health ailments. Accumulation of heavy metals in water and environment is the most urgent problem of water contamination needed to be prioritized before it's too late to act. Wastewater discharge from industrial and mining sources is responsible for the heavy metal pollution. Among various heavy metals, major focussed heavy metal is hexavalent chromium (Cr^{6+}) in wastewater [1, 2]. The use of chromate and dichromate in textile, paint, electroplating, metallurgy, leather tanning etc. industries have contributed high levels of Cr^{6+} in discharged effluents [1, 3]. The hexavalent form of chromium is 500 times more lethal and carcinogenic than trivalent form [4]. According to "United States Environmental Protection Agency (USEPA)", the maximum permissible limit for Cr^{6+} discharge in surface water is 0.1 mgL^{-1} and in potable domestic water is 0.05 mgL^{-1} [5].

Highly toxic Chromium (Cr^{6+}) metal ion is regarded as the "carcinogenic, teratogenic and mutagenic" element to humans as well as animals [6]. Though there have been many technologies such as ion exchange, precipitation, chemical reduction etc. to remediate chromium and other heavy metals. But

adsorption was found to be efficient method for removal of chromium from water and wastewater. Now, nanotechnology has entered the system with high profile properties and advantages over conventional adsorbents. Nanotechnology is the art of manipulating matter down to nanoscale (1-100 nm). Iron oxides nanoparticles (NPs) especially magnetite nanoparticles (Fe_3O_4 NPs) have been widely used for the adsorption of heavy metals [7, 8, 9, 10, 11, 12, 13]. Padmavathy et al. [14] synthesized Fe_3O_4 NPs for extracting Cr^{6+} ions from synthetic solution. Isotherm modelling on equilibrium data revealed that Freundlich is the best fit for this work. In similar study, Fe_3O_4 nanoparticles were synthesized for the sorption of Cr^{6+} and Cr^{3+} ions from aqueous solution. The approximate size of Fe_3O_4 NPs was determined to be 22.4 ± 0.9 nm. Isothermal studies were carried out to find maximum capacity which were observed as 10.63 mg g^{-1} for Cr^{3+} ions and 3.46 mg g^{-1} for Cr^{6+} ions. Negative G and positive H values were determined by thermodynamic studies [15]. In comparison with activated carbon and clay, iron oxide nanoparticles have achieved favourable maximum adsorption capacity for removal and recovery of Cr^{6+} ions [16, 17]. It was observed that electrostatic attractions are considered weaker than chemical adsorption, hence, environmental conditions like pH, background ions and humic substances can affect adsorption. Therefore, consideration is needed while inspecting all these parameters during practical applications [18, 19, 20, 21].

In the present study, magnetite (Fe_3O_4) nanoparticles of spherical shape were fabricated by chemical reduction of ferric chloride. The synthesized nanoparticles were then characterized to know the structural and morphological characteristics of the NPs by employing Transmission Electron Microscopic techniques, X-Ray Diffraction and Energy Dispersive X-Ray spectroscopy. Batch experiments were conducted to determine the effect of pH, adsorbent dose, initial ion concentration, temperature, and contact time on the removal of chromium from aqueous solution. Isotherm and kinetic studies were conducted to investigate the process and mechanism of chromium adsorption on magnetite nanoparticles. Thermodynamic parameters were also derived to observe the spontaneity and feasibility of adsorption.

2. Experimental

2.1 Chemical reagents and Instruments

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (98%), Sodium borohydride (NaBH_4), and Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were used and were of analytical grade. Stock solutions (1000 mg L^{-1} , 100 mg L^{-1} and 50 mg L^{-1}) were processed from $\text{K}_2\text{Cr}_2\text{O}_7$ in double distilled water. By using pH meter (Mettler Toledo AG, FEP 20), the pH of the solution was measured and regulated accordingly by 0.1N HCl and 0.1N NaOH. "Inductively Coupled Plasma Mass Spectrometry (ICP-MS)" (Agilent's 7900 ICP-MS) was used to detect the final concentrations of Cr^{6+} ions.

2.2 Synthesis of Fe_3O_4 nanoparticles

Chemical reduction method was used to prepare Fe_3O_4 NPs. Black precipitates of Fe_3O_4 were observed on addition of NaBH_4 in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution. The synthesised NPs were washed with ethanol and calcined for 5 hours [22]. However, to confirm the composition and structure of nanoparticles, these were subjected to various characterization techniques.

2.3 Characterization techniques

The morphology of nanoparticles was characterized using High Resolution Transmission Microscopy (HRTEM- Tecnai G2 20) at 200KeV. The samples were ultrasonicated before exposing to the carbon coated copper grid. Elemental composition of magnetite nanoparticles was determined by Energy Dispersive Spectroscopy (EDS). Moreover, Selected Area Electron Diffraction (SAED) reveals the crystallinity of fabricated nanoparticles. X-Ray Diffraction (XRD) was used to study the crystal structure of the synthesized nanoparticles.

2.4 Batch Adsorption experiment

All batch experiments were performed to investigate the adsorption of Cr^{6+} on magnetite nanoparticles at 25°C with stirring speed of 200 rpm. For determining equilibrium pH, 20mg of adsorbent dose (magnetite nanoparticles) was added to 50 ml of 50 mg L^{-1} chromium stock solution at different pH ranging from 1–9 for 30 minutes. The pH was adjusted using HCl and NaOH. All experiments were conducted similarly by altering the parameter to be optimized and keeping all other parameters constant. ICP-MS (Agilent's 7900) was used to detect final concentration of Cr^{6+} ions in solution. The equilibrium adsorption capacity (q_e) of magnetite nanoparticles is "the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1})" and was calculated from the equation given below:

$$q_e = \frac{(C_0 - C_e)V}{w}$$

1

initial Cr^{6+} ion concentration is denoted by C_0

equilibrium ion concentration by C_e

V is the volume of the solution (L),

W is the dry weight of Fe_3O_4 NPs.

The Cr^{6+} ion adsorption % was calculated by using given Eq. (2):

$$\text{Crremoval\%} = \frac{(C_0 - C_e)}{C_0} \times 100$$

2

Where, C_0 and C_e are the Cr^{6+} ion concentrations (mg L^{-1}) at initial and equilibrium, respectively.

2.5 Equilibrium isotherms and kinetic analysis

About 70 years ago, Langmuir and Freundlich isotherms were firstly introduced and still they are the two mostly used adsorption isotherm equations. The success reason of their wider acceptability is their undoubted ability of fitting into an extensive range of data. In this study, Temkin and Dubinin-Radushkevich (D-R) isotherm was also applied to the obtained data. These isotherms were used as mathematical tools to evaluate adsorption equilibrium of Cr^{6+} on magnetite nanoparticles. The adsorption equilibrium data was obtained at 25°C with pH 2 with agitation at 200 rpm. Pseudo first order, second order and intraparticle diffusion kinetic models were also used to fit the data [23, 24, 25].

3 Results And Discussion

3.1. Synthesis and characterization of iron oxide nanoparticles.

The morphology of magnetite nanoparticles was determined by High Resolution Transmission Electron Microscopy (HRTEM). The obtained images of synthesized nanoparticles at different magnification scales are shown in Fig. 1(a-d). The fabricated nanoparticles were arranged in a beaded chain like structures with spherical morphology. The average size of the magnetite nanoparticles revealed by HRTEM was 42.90 nm. The polycrystalline nature of magnetite nanoparticles was confirmed by Selected Area Electron Diffraction Pattern (SAED) as shown in Fig. 1(e). The Energy Dispersive X-Ray (EDX) peaks showed the constituents of the fabricated nanoparticles before and after Cr^{6+} adsorption (Fig. 2a, b). The EDX composition includes the iron, oxygen, copper, and carbon peaks. The copper and carbon peaks were due to sample mounting on carbon coated copper grid. The X-Ray Diffraction (XRD) of the powdered magnetite nanoparticles give the structural information. The XRD pattern is shown in the Fig. 3. The Fe_3O_4 nanoparticles possess orthorhombic structure with lattice constant (a) value of $2.799 \text{ \AA}$. The XRD spectra showed multiple peaks at angle $2\theta = 34.08, 38.47, 58.35, 83.99, 85.46$ with hkl values of 023, 112, 006, 028, 173 (COD database, 96-900-2027) [26]. By using different peaks, crystallite size was determined by the following Scherer equation [27]:

$$D = \frac{k\lambda}{b\cos\theta}$$

3

Where D is the “crystallite size (nm)”, λ is the “wavelength (Cu K α = 0.154)”, b is the “full width at half maxima” (rad) for diffraction peak, k is the constant having value equal to 0.9 and θ is the “diffraction angle in degrees”.

3.2 Batch experimental studies

3.2.1. Variation in pH

The solution pH gives an idea about the effect of functional groups of adsorbents, the solubility of metal ions, adsorbate's degree of ionization and the counter ion concentration during the reaction [28]. Fe_3O_4 contains Fe^{2+} therefore, hydrolysis products such as FeOH^+ , $\text{Fe}(\text{OH})_2^0$, and $\text{Fe}(\text{OH})_3^-$ varies with fluctuations in pH [29, 30, 31]. Different chromium species such as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, HCr_2O_7^- , HCrO_4^- commonly exists in aqueous solution. The Cr^{6+} removal decreases with increase in pH (as shown in Fig. 4). The reason behind such behaviour may be the presence of more H^+ ions or HCrO_4^- as major species at lower pH as OH^- groups are neutralised by H^+ ions and thus facilitates adsorption. At high pH, due to the presence of CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, abundance of OH^- species hinders the diffusion of dichromate ions and decreases the percent removal with increasing pH [32]. Hence, maximum adsorption was observed at pH 2 and minimum at pH 9.

3.2.2. Variation in initial ion concentration

Variation of initial ion concentration on Cr^{6+} removal was studied by adsorption on magnetite nanoparticles. The initial Cr^{6+} ion concentration was studied in the range of 10–60 mg L^{-1} . The results obtained were plotted in Fig. 5 and the maximum (88.3%) removal percentage was observed at 10 mg L^{-1} . The removal percent decreases with increase in concentration (also reported earlier by [33, 32]). However, according to the surface chemistry related theories, with increasing ionic strength an electric double layer decreases resulting in reduced adsorption of heavy metals [34].

3.2.3. Variation in adsorbent dose

The removal efficiency increases with increase in adsorbent dose with maximum at 60 mg and then decreases on increasing dose as shown in Fig. 6. However, no remarkable increase was observed in adsorption efficiency on further addition of dose upto 90 mg. The reason behind can be the aggregation of clustering nanoparticles on increasing NPs dose and hence, the availability of adsorption sites got reduced. As the same amount of Cr^{6+} ions got adsorbed on the larger surface area resulted in reduction of adsorption capacity [35].

3.2.4. Variation in contact time

To study the effect of contact time on adsorption, a range of 15–60 minutes was selected, and graph was plotted (Fig. 7). On increasing agitation time, the Cr^{6+} removal also got increased. A maximum (75.3%) was observed at 50 minutes and removal percent decrease with increase in contact time. However, by increasing contact time, adsorption capacity got decreased.

3.2.5. Effect of temperature

Cr^{6+} adsorption was found to be decreased with increased temperature as represented by Fig. 8. The adsorption rate was increased suddenly from 15°C to 20°C and then declines with increasing temperature up to 40°C. maximum Cr^{6+} removal was achieved at 20°C and considered as optimum temperature. The

decreased removal with increased temperature was possibly due to the tendency of Cr^{6+} ions to remain in the aqueous phase [36].

3.3. Isothermal Studies

Adsorption isotherms are “represented as the relation between number of adsorbate molecules per unit mass of adsorbent and the residual adsorbate concentration in bulk solution at a constant temperature”. In this work, Langmuir, Freundlich, Temkin and D-R (Table 1) were evaluated by adsorption of Cr^{6+} on magnetite nanoparticles [37, 38, 39, 40, 41].

Langmuir isotherm describes the equilibrium between adsorbent and adsorbate where, adsorption process is limited to monolayer. It also describes the homogenous surface of adsorbent assuming that there are no sideways interactions between the nearby adsorbed molecules, where every molecule occupies a single adsorption site [42]. The Langmuir equation used is given below:

$$C_e/q_e = 1 / (K_L \times q_m) + C_e/q_m \quad (4)$$

Where, q_m is the Langmuir capacity and a plot between C_e/q_e vs C_e was used to calculate the value of constants as shown in Fig. 9a. The Langmuir constant (K_L) and maximum adsorption capacity (q_m) can be derived from the above Eq. 4 (Table 1). The value of q_m derived from Langmuir modelling is 0.154 mg g^{-1} . Separation factor (R_L) is another parameter which evaluates the feasibility of Langmuir isotherm and can be derived from the following equation:

$$R_L = 1 / (1 + K_L \times C_o) \quad (5)$$

The R_L indicates the nature of isotherm, when $R_L \gg 1$, then the adsorption is considered as unfavourable whereas when $R_L = 1$, there is a linear adsorption when $0 < R_L < 1$, there is favourable adsorption while $R_L = 0$, adsorption is irreversible

The R_L value for magnetite nanoparticles was found to be 0.767, which is less than one and showed potential interaction among Fe_3O_4 nanoparticles and Cr^{6+} ions.

The adsorption data was further evaluated to fit Freundlich isotherm equation. This model facilitates the heterogenous surface adsorption forming multilayers on the surface [43]. The Freundlich model equation is given below:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (6)$$

where, “ K_f and n are the Freundlich constants”. The graph plot between $\ln q_e$ vs $\ln C_e$ (Fig. 9b) gives the value of K_f (0.459) and n (18.28) (Table 1). The lower the value of $1/n$ (0.054) and higher value of n denotes efficient interactions among magnetite nanoparticles and chromium.

Temkin model was also evaluated for description of equilibrium mechanism by considering adsorbent-adsorbate interactions. The Temkin equation given below:

$$q_e = (R_T/B_T) \times \ln (A_T \times C_e) \quad (7)$$

gives the value of equilibrium binding constant (A_T) and Temkin constant (B_T). A curve was plotted q_e vs $\ln C_e$ (Fig. 9c) to get the linear equation and find the values of constant. The value of B_T is $24.33 \text{ kJ mol}^{-1}$ which is the heat of adsorption, further the value of B_T greater than 20 kJ mol^{-1} is the feature of physisorption.

D-R model is based upon multilayer adsorption model involving Van der Waal forces. It expresses adsorption mechanism with gaussian energy distribution onto heterogenous surfaces [44]. The equation to derive D-R parameters is given below:

$$\ln q_e = \ln q_m - K\epsilon^2 \quad (8)$$

$$\epsilon = RT \times \ln [1 + (1/C_e)] \quad (9)$$

$$E_m = \frac{1}{\sqrt{2K}}$$

10

The curve was plotted against $\ln q_e$ vs ϵ^2 (Fig. 10d). From D-R model, the value of q_m was 4.89 mg g^{-1} , this shows the maximum monolayer value of chromium adsorption per unit weight of adsorbent. The “value of mean free energy (E_m)” is 1.46 kJ mol^{-1} at 293 K. In D-R isotherm, adsorption can be one of these three conditions i.e. if $E_m < 8.0 \text{ kJ mol}^{-1}$, it is physisorption, $E_m = 8.0\text{--}16.0 \text{ kJ mol}^{-1}$ then it is ion exchange while if $E_m \approx 16\text{--}400 \text{ kJ mol}^{-1}$, it is chemisorption. Hence, it is assumed that “process and concentrations of adsorbate and adsorbent are involved in rate determining step and the adsorption is physisorption” according to this model.

Based on correlation value of the experimental data the best fit model were compared and R^2 order of the adsorption is Temkin $\approx$ Langmuir $\approx$ D-R $\approx$ Freundlich.

3.4. Adsorption kinetics

The adsorption data was analysed for kinetics study of chromium removal by Pseudo first order, second order kinetics and intraparticle diffusion (Table 2). The adsorption kinetic model estimates the rate and mechanism of adsorption reactions.

First order kinetic equation describes “the solute adsorption on the adsorbent surface”. The linear form of first order kinetics is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

A curve was plotted, $\log(q_e - q_t)$ against t to find the values of k_1 and q_e (Fig. 10a). A linearized form of pseudo second order equation is:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e) t \quad (12)$$

The value of rate constant k_2 (0.985) was derived by plotting a curve between t/q_t vs t (Fig. 10b) and are summarized in Table 3. The correlation coefficient (R^2) of Lagergren's first order and second order was found to be 0.68 and 0.98, respectively. Hence, pseudo second order kinetic model was the best fit to the experimental data.

Intraparticle diffusion model describes the adsorbate intraparticle uptake and pore diffusion during adsorption process. The linear equation for intraparticle model is:

$$q_t = k_i \sqrt{t} + x_i \quad (13)$$

A curve for intraparticle diffusion model (Fig. 10c) gives the value of X_i (0.076) at 293 K for 10 mg L^{-1} Cr^{6+} solution. The boundary layer effect is directly proportional to the value of X_i i.e. higher the X_i value, higher will be the boundary layer effect.

The adsorption of Cr^{6+} on magnetite nanoparticles is a three-step process which involves the transportation of Cr^{6+} ions to the surface of Fe_3O_4 nanoparticles from bulk solution. Secondly, Cr^{6+} diffusion to the interior of the Fe_3O_4 pores. And ultimately adsorption of Cr^{6+} onto active sites of Fe_3O_4 nanoparticles surface [45].

3.4.4. Thermodynamics of adsorption

To assess the adsorption feasibility and spontaneity, thermodynamic parameters have wide role to play as they give basic information to design adsorption process. Feasibility and spontaneity are governed by parameters such as entropy (ΔS°), heat of enthalpy (ΔH°) and Gibbs free energy (ΔG°). various equations were used to calculate the thermodynamic parameters of this adsorption process which were given as follows [46, 47, 48]:

Distribution coefficient can be calculated by the equation,

$$\ln K_d = \Delta S/R - \Delta H/RT \quad (14)$$

$$\text{where } K_d = q_e/C_e \quad (15)$$

$$\text{Equilibrium chromium concentration is given by, } \ln C_e = -\ln K_0 + \Delta H/RT \quad (16)$$

$$\Delta G = \Delta H - T\Delta S \text{ (17)}$$

By plotting a curve between $\ln K_d$ vs $1/T$ and $\ln C_e$ vs $1/T$ (Fig. 11a and 11b respectively) values of thermodynamic parameters were calculated (Table 3) from slope and intercept of obtained equation.

The adsorption of chromium on magnetite nanoparticles was observed to favour lower temperature. With increase in temperature, the adsorption rate decreases due to weak adsorbate-adsorbent interactions. The negative value of ΔG° is evident to feasibility and spontaneity of the adsorption process at a given temperature. The physisorption mechanism of adsorption was confirmed by the negative value of ΔH° which lie in the range of -20 to 40 kJ mol⁻¹ [49]. However, the positive ΔS° value suggests spontaneous adsorption.

3.5 Desorption studies

Recovery of adsorbent for reuse keep the process cost low. The adsorbent efficiency of adsorption and desorption was studied by conducting three adsorption and desorption cycles. In case of Cr⁶⁺, all the three cycles were observed to achieve 82%, 78% and 75% adsorption whereas desorption rate achieved was 80.2%, 75.8% and 68% as shown in Fig. 12. For desorption of chromium 0.005 M of NaOH was used to separate chromium from nanoparticles.

Conclusion

The present experimental study investigates the chromium adsorption efficiency onto Fe₃O₄ NPs. The sodium borohydride chemical reduction route was used to produce Fe₃O₄ NPs. The nanoparticles have maximum adsorption capacity of 0.15mg/g at pH 2. The adsorption equilibrium, thermodynamics and kinetics of chromium adsorption was analysed. The Langmuir, Freundlich, Temkin and D-R isotherm equations were applied to find the best model. According to kinetic studies, Pseudo second order model was in good agreement with the obtained data and best fit. The change in Gibbs free energy was found to be negative which indicates the feasibility and spontaneity of the adsorption.

Declarations

Ethical Approval

This statement is not applicable

Author's Contribution

The second Author has reviewed the manuscript.

Conflict of Interest

No conflict of interest to declare.

Funding Declaration

Funding is not applicable for this work

Availability of data and materials

This statement is not applicable

References

1. Aydın, Y.A.; Aksoy, N.D. Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. *Chem. Eng. J.* **2009**, *151*(1-3), 188-94.
2. Hena, S. Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer. *J. Hazard. Mater.* **2010**, *181*(1-3), 474-9.
3. Tanhaei, B.; Ayati, A.; Sillanpää, M. Magnetic xanthate modified chitosan as an emerging adsorbent for cationic azo dyes removal: Kinetic, thermodynamic and isothermal studies. *Int. J. Biol. Macromol.* **2019**, *121*, 1126-1134.
4. Dubey, S.P.; Gopal, K. Adsorption of chromium (VI) on low cost adsorbents derived from agricultural waste material: a comparative study. *J. Hazard. Mater.* **2007**, *145*(3), 465-70.
5. Sivakami, M.S.; Gomathi, T.; Venkatesan, J.; Jeong, H.S.; Kim, S.K.; Sudha, P.N. Preparation and characterization of nano chitosan for treatment wastewaters. *Int. J. Biol. Macromol.* **2013**, *57*, 204-12.
6. Beheshti, H.; Irani, M.; Hosseini, L.; Rahimi, A.; Aliabadi, M. Removal of Cr (VI) from aqueous solutions using chitosan/MWCNT/Fe₃O₄ composite nanofibers-batch and column studies. *Chem. Eng. J.* **2016**, *284*, 557-64.
7. Minh Tri, P.; Khim, K.S.; Hidajat, K.; Uddin, M.S. Surface functionalized nano-magnetic particles for wastewater treatment: adsorption and desorption of mercury. *J. Nanosci. Nanotechnol.* **2009**, *9*(2), 905-8.
8. Huang, Y.F.; Li, Y.; Jiang, Y.; Yan, X.P. Magnetic immobilization of amine-functionalized magnetite microspheres in a knotted reactor for on-line solid-phase extraction coupled with ICP-MS for speciation analysis of trace chromium. *J. Anal. At. Spectrom.* **2010**, *25*(9), 1467-74.
9. Mandel, K.; Hutter, F.; Gellermann, C.; Sextl, G. Modified superparamagnetic nanocomposite microparticles for highly selective HgII or CuII separation and recovery from aqueous solutions. *ACS Appl. Mater. Interfaces.* **2012**, *4*(10), 5633-42.
10. Liu, Y.; Wang, Y.; Zhou, S.; Lou, S.; Yuan, L.; Gao, T.; Wu, X.; Shi, X.; Wang, K. Synthesis of high saturation magnetization superparamagnetic Fe₃O₄ hollow microspheres for swift chromium removal. *ACS Appl. Mater. Interfaces.* **2012**, *4*(9), 4913-20.
11. Hakami, O.; Zhang, Y.; Banks, C.J. Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of Hg from water. *Water research.* **2012**, *46*(12), 3913-22.

12. Gupta, V.K.; Nayak, A. Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles. *Chem. Eng. J.* **2012**, *180*, 81-90.
13. Dui, J.; Zhu, G.; Zhou, S. Facile and economical synthesis of large hollow ferrites and their applications in adsorption for As (V) and Cr (VI). *ACS Appl. Mater. Interfaces.* **2013**, *5*(20), 10081-9.
14. Padmavathy, K.S.; Madhu, G.; Haseena, P.V. A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr (VI)) from wastewater by magnetite nanoparticles. *Procedia Technology.* **2016**, *24*, 585-94.
15. Luther, S.; Brogfeld, N.; Kim, J.; Parsons, J.G. Study of the thermodynamics of chromium (III) and chromium (VI) binding to iron (II/III) oxide or magnetite or ferrite and manganese (II) iron (III) oxide or jacobsite or manganese ferrite nanoparticles. *J. Colloid Interface Sci.* **2013**, *400*, 97-103.
16. Hu, J.; Chen, G.; Lo, I.M. Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. *Water research.* **2005**, *39*(18), 4528-36.
17. Hu, J.; Lo, I.M.; Chen, G. Performance and mechanism of chromate (VI) adsorption by δ -FeOOH-coated maghemite (γ -Fe₂O₃) nanoparticles. *Sep. Purif. Technol.* **2007a**, *58*(1), 76-82.
18. Hu, J.; Lo, I.M.; Chen, G. Removal of Cr (VI) by magnetite. *Water Sci. Technol.* **2004**, *50*(12), 139-46.
19. Hu, J.; Lo, I.M.; Chen, G. Comparative study of various magnetic nanoparticles for Cr (VI) removal. *Sep. Purif. Technol.* **2007b**, *56*(3), 249-56.
20. Yang, W.; Kan, A.T.; Chen, W.; Tomson, M.B. pH-dependent effect of zinc on arsenic adsorption to magnetite nanoparticles. *Water Res.* **2010**, *44*(19), 5693-701.
21. Yantasee, W.; Warner, C.L.; Sangvanich, T.; Addleman, R.S.; Carter, T.G.; Wiacek, R.J.; Fryxell, G.E.; Timchalk, C.; Warner, M.G. Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environ. Sci. Technol.* **2007**, *41*(14), 5114-9.
22. Yuvakkumar, R.; Elango, V.; Rajendran, V.; Kannan, N. Preparation and characterization of zero valent iron nanoparticles. *Digest journal of nanomaterials and biostructures.* **2011**, *6*(4), 1771-6.
23. Sivaraj, R.; Namasivayam, C.; Kadirvelu, K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste Manage.* **2001**, *21*(1), 105-10.
24. Sağ, Y.; Aktay, Y. Kinetic studies on sorption of Cr (VI) and Cu (II) ions by chitin, chitosan and *Rhizopus arrhizus*. *Biochem. Eng. J.* **2002**, *12*(2), 143-53.
25. Dima, J.B.; Zaritzky, N. Performance of Chitosan Micro/Nanoparticles to Remove Hexavalent Chromium from Residual Water. In *Advanced Nanomaterials for Water Engineering, Treatment, and Hydraulics* **2017**, 262-288.
26. Fei, Y.; Frost, D.J.; Mao, H.K.; Prewitt, C.T.; Haeusermann, D. In situ structure determination of the high-pressure phase of Fe₃O₄. *American Mineralogist.* **1999**, *84*(1-2), 203-6.
27. Yuan, P.; Fan, M.; Yang, D.; He, H.; Liu, D.; Yuan, A.; Zhu, J.; Chen, T. Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr (VI)] from aqueous solutions. *J. Hazard. Mater.* **2009**, *166*(2-3), 821-9.

28. Kumari, M.; Pittman Jr, C.U.; Mohan, D. Heavy metals [chromium (VI) and lead (II)] removal from water using mesoporous magnetite (Fe₃O₄) nanospheres. *J. Colloid Interface Sci.* **2015**, *442*, 120-32.
29. Cornell, R.M.; Schwertmann, U. The iron oxides: structure, properties, reactions, occurrences and uses. *John Wiley & Sons*, **2003**.
30. Chowdhury, S.R.; Yanful, E.K.; Pratt, A.R. Chemical states in XPS and Raman analysis during removal of Cr (VI) from contaminated water by mixed maghemite–magnetite nanoparticles. *J. Hazard. Mater.* **2012**, *235*, 246-56.
31. Rajput, S.; Pittman Jr, C.U.; Mohan, D. Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water. *J. Colloid Interface Sci.* **2016**, *468*, 334-46.
32. Sharma, Y.C.; Srivastava V. Comparative studies of removal of Cr (VI) and Ni (II) from aqueous solutions by magnetic nanoparticles. *J. Chem. Eng. Data.* **2011**, *56*(4):819-25.
33. Sharma, Y.C.; Srivastava, V.; Weng, C.H.; Upadhyay, S.N. Removal of Cr (VI) from wastewater by adsorption on iron nanoparticles. *Can. J. Chem. Eng.* **2009**, *87*(6), 921-9.
34. Onyancha, D.; Mavura, W.; Ngila, J.C.; Ongoma, P; Chacha, J. Studies of chromium removal from tannery wastewaters by algae biosorbents, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*. *J. Hazard. Mater.* **2008**, *158*(2-3), 605-14.
35. Ren, G.; Wang, X.; Huang, P; Zhong, B.; Zhang, Z.; Yang, L.; Yang, X. Chromium (VI) adsorption from wastewater using porous magnetite nanoparticles prepared from titanium residue by a novel solid-phase reduction method. *Sci. Total Environ.* **2017**, *607*, 900-10.
36. Sari, A.; Tuzen, M. Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies. *J. Hazard. Mater.* **2008**, *160*(2-3):349-55.
37. Foo, K.Y.; Hameed, B.H. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **2010**, *156*(1), 2-10.
38. Wang, A.; Zhou, K.; Liu, X.; Liu, F.; Chen, Q. Development of Mg–Al–La tri-metal mixed oxide entrapped in alginate for removal of fluoride from wastewater. *RSC adv.* **2017**, *7*(50), 31221-9.
39. Ma, A.; Ke, F.; Jiang, J.; Yuan, Q.; Luo, Z.; Liu, J.; Kumar, A. Two lanthanide-based metal–organic frameworks for highly efficient adsorption and removal of fluoride ions from water. *Cryst. Eng. Comm.* **2017**, *19*(16), 2172-7.
40. Tassist, A.; Lounici, H.; Abdi, N.; Mameri, N. Equilibrium, kinetic and thermodynamic studies on aluminum biosorption by a mycelial biomass (*Streptomyces rimosus*). *J. Hazard. Mater.* **2010**, *183*(1-3), 35-43.
41. Hussain, Z.; Daosheng, L.; Xi, L.; Jianxiong, K. Defluoridation by a Mg–Al–La triple-metal hydrous oxide: synthesis, sorption, characterization and emphasis on the neutral pH of treated water. *RSC Adv.* **2015**, *5*(55), 43906-16.
42. Liu, L.; Luo, X.B.; Ding, L.; Luo, S.L. Application of nanotechnology in the removal of heavy metal from water. In *Nanomaterials for the Removal of Pollutants and Resource Reutilization*. **2019**, 83-147.

43. Vasiliu, S.; Bunia, I.; Racovita, S.; Neagu, V. Adsorption of cefotaxime sodium salt on polymer coated ion exchange resin microparticles: kinetics, equilibrium and thermodynamic studies. *Carbohydr. Polym.* **2011**, *85*(2), 376-87.
44. Celebi, O.; Üzümlü, Ç.; Shahwan, T.; Erten, H. N. A radiotracer study of the adsorption behavior of aqueous Ba²⁺ ions on nanoparticles of zero-valent iron. *J. Hazard. Mater.* **2007**, *148*(3), 761-767.
45. Tehrani-Bagha, A.R.; Nikkar, H.; Mahmoodi, N.M.; Markazi, M.; Menger, F.M. The sorption of cationic dyes onto kaolin: Kinetic, isotherm and thermodynamic studies. *Desalination.* **2011**, *266*(1-3), 274-80.
46. Li, H.; Huang, G.; An, C.; Hu, J.; Yang, S. Removal of tannin from aqueous solution by adsorption onto treated coal fly ash: kinetic, equilibrium, and thermodynamic studies. *Ind. Eng. Chem. Res.* **2013**, *52*(45), 15923-31.
47. Mohapatra, M.; Hariprasad, D.; Mohapatra, L.; Anand, S.; Mishra, B.K. Mg-doped nano ferrihydrite—A new adsorbent for fluoride removal from aqueous solutions. *Appl. Surf. Sci.* **2012**, *258*(10), 4228-36.
48. Xue, F.; Xu, Y.; Lu, S.; Ju, S.; Xing, W. Adsorption of cefocelis hydrochloride on macroporous resin: kinetics, equilibrium, and thermodynamic studies. *J. Chem. Eng. Data.* **2016**, *61*(6), 2179-85.
49. Guerra, D.J.; Da Silva, R.A. Kinetic and thermodynamic studies of Brazilian illite–kaolinite in natural and intercalated forms as adsorbents to removal of Zn²⁺ from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers.* **2014**, *45*(1), 268-74.

Tables

Table 1: Adsorption parameters for Cr ⁶⁺ removal					
T (K)	<i>Langmuir</i>				
298	1/q _m	R ²	K _L (mg L ⁻¹)	q _m (mg g ⁻¹)	R _L
	6.481	0.92	0.261	0.154	0.767
	<i>Freundlich</i>				
298	1/n	R ²	n	lnK _f	K _f
	0.054	0.11	18.28	0.778	0.459
	<i>Temkin</i>				
298	B _T	R ²	lnA _T	A _T	
	24.433	0.99	2.442	0.0869	
	<i>Dubinin and Radushkevich (D-R)</i>				
298	q _m (mg g ⁻¹)	R ²	K (mol ² J ⁻²) ×10 ⁻⁷	E _m (KJ mol ⁻¹)	
	4.89	0.34	2.33	1.463	

Table 2: kinetic parameters for Cr (VI) adsorption

Pseudo first order			
60mg/L			
T(K)	k ₁	R ²	q _e
298	0.065	0.68	0.98
Pseudo second order			
298	k ₂	R ²	q _e
	0.985	0.98	0.139
Intraparticle diffusion			
298	k _i	R ²	X _i
	0.0063	0.79	0.076

Table 3: Various thermodynamic parameters for Cr⁶⁺ adsorption process

Van't Hoff plot	
ΔG (kJ/mol)	-13.23
ΔH (kJ/mol)	-2.297
ΔS (kJ/mol)	0.045
R^2	0.37

Figures

Figure 1

(a-d) TEM images of synthesized Fe_3O_4 nanoparticles (e) SAED pattern of the corresponding nanoparticles.

Figure 2

EDX spectra of Fe_3O_4 nanoparticles (a) before and (b) after Cr^{6+} adsorption

Figure 3

XRD pattern of Fe_3O_4 nanoparticles at different angles i.e. $\theta=10-90^\circ$

Figure 4

Variation of Cr^{6+} adsorption with pH [adsorbent dose: 20 mg, initial Cr^{6+} concentration: 50 mg L^{-1} , contact time: 30 minutes, temperature: 25°C]

Figure 5

Variation of Cr^{6+} adsorption with initial ion concentration [pH: 2, adsorbent dose: 20 mg, contact time: 30 minutes, temperature: 25°C]

Figure 6

Variation of removal percent with adsorbent dose [pH: 2, initial Cr^{6+} concentration: 10 mg L^{-1} , contact time: 30 minutes, temperature: 25°C]

Figure 7

Variation of Cr^{6+} adsorption with contact time [pH: 2, adsorbent dose: 60 mg, initial Cr^{6+} concentration: 10 mg L^{-1} , temperature: 25°C]

Figure 8

Variation of Cr^{6+} adsorption with temperature [pH: 2, adsorbent dose: 60 mg, initial Cr^{6+} concentration: 10 $mg\ L^{-1}$, contact time: 50 minutes]

Figure 9

(a) Langmuir isotherm (b) Freundlich isotherm (c) Temkin isotherm

(d) D-R isotherm

Figure 10

(a) Pseudo first order (b) Pseudo second order (c) Intraparticle diffusion

Figure 11

Van't hoff plots for K_d (a) and C_e (b) for Cr^{6+} adsorption

Figure 12

Consecutive adsorption-desorption cycles