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An Experimental Study on Removal of Heavy Metal Ions from Synthesized Metal Salt Solution by Adsorption Using Magnesium Ferrite Nanoparticles

Sana Ahmed[1], Sarika Anand[2], Shriya Tiwari[3], Shweta Garg[4], and Rajani M R[5]

[1,2,3,4,5]Dayanand Sagar College of Engineering, Bengaluru, India

ABSTRACT—

The advent of Nanotechnology has opened doors to various applications. Its application in water treatment is being explored extensively. Previous works show that Nanoparticles, particle size ranging between 1-100 Nanometers, are highly effective in the adsorption of heavy metal ions from wastewater. The following project employs the use of Magnesium Ferrite ($MgFe_2O_4$) Nanoparticles for the removal of Cr^{6+} ions from synthesized solutions. The $MgFe_2O_4$ Nanoparticles were characterized using Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Characterization confirms the presence of $MgFe_2O_4$ with small quantities of impurities. Chromium stock solution was prepared using Potassium Dichromate ($K_2Cr_2O_7$) salt. Standard solution for calibration of Atomic Absorption Spectrophotometer (AAS) was prepared using MERCK standards of 1000 ppm. Experiments were conducted for chromium at different concentrations ranging 50-150 ppm by varying the pH between 2-6 and adsorbent load 0.2-0.67g/l. Samples were collected at regular intervals by separating the Nanoparticles from the solution using Neodymium magnets. Collected samples were analyzed in the AAS (Model: AA500) and percentage removal was calculated. Minitab 17 software was used to design and generate optimum conditions using Central Composite Design (CCD). Experiments were carried out for the optimum conditions generated. Percentage removal of chromium was 82.90%. Langmuir and Freundlich isotherms were developed. Chromium followed the Langmuir isotherm. Kinetics of adsorption was developed and it was found that chromium followed Pseudo First order kinetics.

***Index Terms*— Chromium, Adsorption, Nanoparticles, Magnesium Ferrite, Cr (VI).**

I. 1. INTRODUCTION

With rapid industrialization, water pollution by chemicals has become a serious problem. The upward demand for clean and fresh water has given rise to the search for new processes and methods to get unpolluted water which is used for various purposes. Water resources are sources of water that are potentially useful. Uses of water include agricultural, industrial, household, recreational and environmental activities. The majority of human uses require fresh water. 97% of the water on the Earth is salt water and only three percent is freshwater; slightly over two thirds of this is frozen in glaciers and polar ice caps.

The residual unfrozen freshwater is found mostly as groundwater, with only a small fraction present above ground or in the air. Fresh water is a renewable resource, yet the world's supply of groundwater is steadily declining, although it is still unclear how much natural renewal balances this usage, and whether ecosystems. Water is one of the main concerns of the world today. Disposal of wastewater from an industrial plant is a difficult and costly problem. Most petroleum refineries, chemical and petrochemical plants have onsite facilities to treat their wastewaters so that the pollutant concentrations in the treated wastewater comply with the local and/or national regulations regarding disposal of wastewaters into community treatment plants or into rivers, lakes or oceans.

The governments of numerous countries have striven to find solutions to reduce this problem. Many pollutants threaten water supplies, but the most widespread, especially in developing countries, is the discharge of raw sewage into natural waters; Sewage, sludge, garbage, and even toxic pollutants are all dumped into the water. The pollution caused by toxic heavy metal ions is considered to be riskier because heavy metals are non-biodegradable. They become extremely toxic when not metabolized by the human body, accumulating in the body tissues and interrupting normal body functions and thus causing a number of diseases. The contributions of this study are as follows:

- Prepared Magnesium ferrite Nanoparticle using Oxalyl Dihydrazide (ODH) that was used as a fuel.
- Batch process study was performed to find the optimum conditions to remove heavy metal ions from wastewater.
- Studied the effect of parameters like adsorbent load, pH & initial concentration on the removal of heavy metal ions.
- Determined the kinetics and the adsorption isotherms involved.

The following section elaborates upon the related work performed. Next, the theoretical background and the theory after which the experimental setup is outlined. Subsequently, the experimental data is investigated. And finally, section 6 concludes the experimental study.

II. 2. RELATED WORK

This work focuses on maximum adsorption using ferrite nanoparticles related to which experimental work was carried out based on the following literature survey. Parameters to be considered and varied were recognized and various insights were gathered.

1) 2.1 Magnesium Ferrite

Magnesium ferrite Nanoparticle are Nano-phase spinel ferrites, stable and nontoxic in nature. Their insolubility in waste and their high surface area makes them potential adsorbents for removal of contaminants from polluted water. Spinel ferrites are the compounds having a general formula AB_2O_4, in which the A-site is tetrahedrally coordinated and occupied by divalent cations and B-site is octahedrally coordinated and occupied by trivalent iron Fe^{3+} [20] [21].

In recent years, ferrite Nanoparticles have received applications in the diverse fields such as mineral separation, magnetic storage devices, catalysis, magnetic refrigeration system, drug delivery system, cancer therapy and magnetic cell separation. Magnesium Ferrite is an important spinel ferrite which finds application in the fields of heterogeneous catalysis, adsorption, sensors, and magnetic technologies. [20].

Since this study involves chromium adsorption, relevant articles that performed chromium adsorption were collated and their observations are discussed in the subsequent section.

2) 2.2 Chromium Adsorption

Chromium occurs in several oxidation states ranging from -2 to +6. However only trivalent chromium Cr^{3+} and hexavalent Chromium Cr^{6+} are predominant. Cr6+is highly mobile, soluble, and bioavailable. Major species include chromate and dichromate. Cr^{3+} is the dominant form of Chromium at low pH (<4). Cr^{6+} is highly toxic, teratogenic, and mutagenic.

Adsorption studies were performed by rotating 0.1g Maghemite Nanoparticles with 20ml or 40m metal salt solution in a glass vial at room temperature. The pH of the suspension for Cr^{6+} and Ni^{2+} was adjusted to 2.5 and 8.5 respectively. Volumes of 3ml of samples were taken at specific time intervals. Cr^{6+} and Ni^{2+}, adsorption equilibrium studies were conducted by varying the initial concentration of 40ml of metal salt solution from 5 to 200mg/L of adsorbent at pH 2.5 and 8.5 respectively. In their study, they reported that, the percentage uptake of Cr^{6+} decreased gradually with increase in pH, maximum removal of Cr^{6+} occurred at pH 2.5 with 100mg/L initial concentration and 0.1g adsorbent load. [14]

Adsorption of Cr^{6+} from aqueous solution was also done with Nano Beta-FeOOH. Using Beta-FeOOH Nanoparticle and studying the effect of time, adsorption experiments were conducted at the initial Cr^{6+} concentration of 20mg/L. Stopper conical flasks were taken from the rotary shaker at 10min, 30min, 60min, 90min,120 min, 180min, 240min and 360min Rate of removal was high. At first 10 min 67% of Cr^{6+} was removed. Equilibrium was obtained after an hour. In their study of Adsorption of Cr^{6+} from aqueous solution with Nano-Beta-FeOOH: Using Beta-FeOOH Nanoparticle Cr^{6+}removal efficiency was high at pH<7, sharply decreased at 8 and was non-occurring at pH 9. [26]

The use of Iron oxide magnetic Nano-adsorbents for Cr^{6+} removal from aqueous solution was also previously studied [1]. They reported that the optimum pH for adsorption of Cr^{6+}on Iron Oxide Nanoparticle was found to be within 2-3. Furthermore, nanostructured graphite Oxide, Silica Nanoparticle for removal of Chromium were used [17]. They observed that the percentage Removal decreases with increase in initial metal ion concentration. At low heavy metal ion concentration, percentage removal was found to be high and gradually decreased with an increase in heavy metal ion concentration. At 30ppm of Cr^{6+}, percentage of removal was 63% and at 200 ppm of Cr^{6+}, percentage of removal was 25.9%.

Following a discussion of the techniques and chemicals used, the next section provides a brief explanation of the underlying chemical theory.

III. 3. EXPERIMENTAL SETUP

Experiments were performed to achieve efficient removal of heavy metal ions from wastewater using adsorption techniques. The process was carried out with the use of synthesized Magnesium Ferrite Nanoparticle as adsorbent by Combustion technique and Oxalyl Dihydrazide as the fuel. The procedure adopted is described in the following sections.

1) 3.1 Preparation of Fuel

Oxalyl Dihydrazide (ODH) was used as the fuel in the combustion process for removal of Hexavalent Chromium ions from their synthesized solutions respectively. The reaction for the synthesis of ODH is given below.

$$\mathbf{C_6H_{10}O_4 + N_2H_4.\ x\ H_2O \rightarrow C_2H_6N_4O_2}$$

The physical properties of ODH such as its molecular formula, weight, melting point and density are detailed in Table 1.

Table 1: Properties of ODH

Property	**Remarks**
Molecular Formula	$C_2 H_6 N_4 O_2$
Molecular Weight	118.09 g/mol
Melting Point	240 °C
Density	1.458 g/cm^3 at 23° C)

2) 3.2 Preparation of Oxalyl Dihydrazide ($C_2H_6N_4O_2$)

The steps involved in the preparation of ODH are given below.

(i) 100 ml of Diethyl Oxalate is taken in a burette and added dropwise to a beaker containing 100 ml of Hydrazine Hydrate and 232ml of double distilled water. These liquids cause an exothermic reaction.

(ii) The reaction is carried out for 2 hours by continuous stirring using a glass rod.

(iii) The mixture is then left to settle for 24 hours after which it is filtered using a Muslin cloth.

(iv) Post filtration the wet ODH is kept for drying in a hot air oven at 120°C for 2 hours.

(v) 75g of dried ODH powder was obtained.

The fuel is obtained as a result of the experimental steps explained. The following section gives the reaction and steps involved in the chemical synthesis of the absorbent that is required to carry out the adsorption.

3) 3.3 Preparation of Absorbent

Magnesium Ferrite Nanoparticle was synthesized to be used as the adsorbent. The Fuel i.e., Oxalyl Dihydrazide (ODH) was used to prepare Magnesium ferrite Nanoparticles by combustion method. The reaction that was followed in the preparation of Magnesium ferrite is as follows:

$$\mathbf{Mg(NO_2)_3 + 2\ Fe(NO_3)_3 + 4\ C_2H_6N_4O_2}$$

$$\downarrow$$

$$\mathbf{MgFe_2O_4 + 12\ N_2\uparrow + 12\ H_2O + 8\ CO_2\uparrow}$$

1.48 grams of $Mg(NO_2)_3$, **4.8** grams of $Fe(NO_3)_3$, and **4.7** grams of $C_2 H_6 N_4 O_2$ gives **1.5** grams of Magnesium Ferrite Nanoparticle.

(i) The reactants Magnesium Nitrate 1.8g, Ferric Nitrate 4.8g and ODH 4.7g were taken in a 150ml Silica Crucible, dissolved in minimum quantity of double distilled water and was Magnetically Stirred for 5 min to obtain Uniform Composition.

(ii) After attaining Uniform Composition, the mixture was kept in a Muffle Furnace which was operating at 600° C. The Combustion Process took place within 3 to 4 minutes. After which the product was calcined for 10 minutes.

(iii) 1.5g of Magnesium ferrite was obtained as a result of the following experiment.

4) 3.4 Design of Experiment

The experiments were designed using MINITAB.17 software where the parameters Initial concentration, pH and adsorbent load were varied. The details are elaborated in the next few sections and the same can be seen in a concise manner in Table 2.

Table 2: Design of Experiments

Sl No	**Heavymetal**	**Ph Range**	**Initial Concentration (Ppm)**	**Adsorbent Load (G/L)**
1	Chromium (Cr^{6+})	2.0-6.0	50-150	0.33-1.0

5) 3.3.1 Central Composite Design (CCD)

The parameters, initial metal ion concentration, pH, temperature, and adsorbent dosage were chosen as independent variables. According to the software, a factorial experimental design of 24 is used with 7 replicates at the center point, thus 31 trials were conducted. To measure the precision property replicates of the center point was selected to verify any changes in the estimation procedure. There are 5 levels of independent variables which are -2, -1, 0, +1, +2.

This work is focused on the removal efficiency of heavy metal ions from wastewater. Also, the effect of independent variables like metal ion concentration (X1), (X2 – pH), (X3 – Initial concentration), (X4 – Adsorbent Load) and dependent output variable on removal efficiency is studied.

6) 3.3.2 CCD Analysis by Response Surface Methodology (RSM)

The results of the experimental design were studied and interpreted by statistical software, MINITAB16 (PA, USA) to estimate the response of the dependent variable, for regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations. The matrix tabulated chromium experiments can be seen in Table 3.

RunOrder	PtType	Blocks	pH	C_O	AL
1	-1	1	4.00000	100.000	0.050000
2	-1	1	4.00000	50.000	0.100000
3	1	1	5.18921	129.730	0.070270
4	0	1	4.00000	100.000	0.100000
5	-1	1	6.00000	100.000	0.100000
6	0	1	4.00000	100.000	0.100000
7	1	1	5.18921	70.270	0.070270
8	-1	1	4.00000	150.000	0.100000
9	0	1	4.00000	100.000	0.100000
10	1	1	2.81079	70.270	0.129730
11	1	1	2.81079	129.730	0.070270
12	0	1	4.00000	100.000	0.100000
13	1	1	2.81079	70.270	0.070270
14	-1	1	2.00000	100.000	0.100000
15	1	1	2.81079	129.730	0.129730
16	-1	1	4.00000	100.000	0.150000
17	1	1	5.18921	70.270	0.129730
18	0	1	4.00000	100.000	0.100000
19	1	1	5.18921	129.730	0.129730
20	0	1	4.00000	100.000	0.100000

Table 2: Matrix for Chromium Experiments

In Table 3, Co stands for Initial Concentration and AL for Adsorbent Load. Now, the experimental procedure will be briefed.

7) 3.4 Experimental Procedure

Adsorption experiments were carried out with the adsorbent that was synthesized. The samples obtained from these experiments were then analyzed using an Atomic Absorption Spectrophotometer and the results were studied.

8) 3.4.1 Preparation of Stock Chromium Salt Solution

To prepare the metal ion solution, 2.82g of Potassium Dichromate was weighed and taken in a standard Volumetric Flask. To this double distilled water was added till the mark. Dilute Hydrochloric Acid (0.1N) and Sodium Hydroxide (0.1N) solutions were used to maintain the pH of the solution.

9) 3.4.2 Chromium Experiments

(i) The initial concentration of Chromium Solution was taken.

(ii) Magnesium Nanoparticle (Adsorbent) was added.

(iii) The solutions were kept for shaking on a Rotary shaker at 180 rpm.

(iv) The samples were separated using Neodymium Magnets.

(v) The samples were collected for Chromium analysis

(vi) The samples were analysed in the AAS

IV. 4. EXPERIMENTAL RESULTS

Experiments carried out to find the maximum removal of metal ions from synthesized solution by adsorption using Magnesium ferrite nanoparticles as adsorbent. Characterization of the synthesized Magnesium ferrite nanoparticle was done using SEM, XRD and FTIR spectrophotometer. The result from characterization was studied to determine the morphology, composition and chemical formula of the synthesized nanoparticles. Experiments designed

using MINITAB 17 was performed to find the percentage removal and optimization was carried out. Experiments for the optimized parameters obtained from the software were carried out and percentage removal was calculated. Langmuir and Freundlich isotherms were developed. Kinetics of the reaction was studied using the equilibrium data at optimum conditions.

1) 4.1 Characterization of MgFe2O4 Nanoparticle

2) 4.1.1 Scanning Electron Microscope (SEM)

For unused $MgFe_2O_4$ NP, Scanning Electron Microscope (VEGA3 TESCAN) was used for determining the morphology and structure of the Magnesium ferrite nanoparticle. Fig. 4.1 and Fig. 4.2 shows the spinel structure of particles which differ in size with un-evenness on the surface in the form of projections or pores. At 64.4kX SEM magnification the particle size is found to be in the range of 42.75-72.3nm.

Voids and pores are created as a result of release of large amount of gases during the combustion process and the particles are agglomerated together. Similar results have been reported earlier [30][36], in which MgFe2O4 NPs were synthesized by combustion method using glycine as fuel. The morphology shows the presence of nanoparticles in the form of clusters, which indicates the basic nature of magnetic Nanoparticles [6] [20].

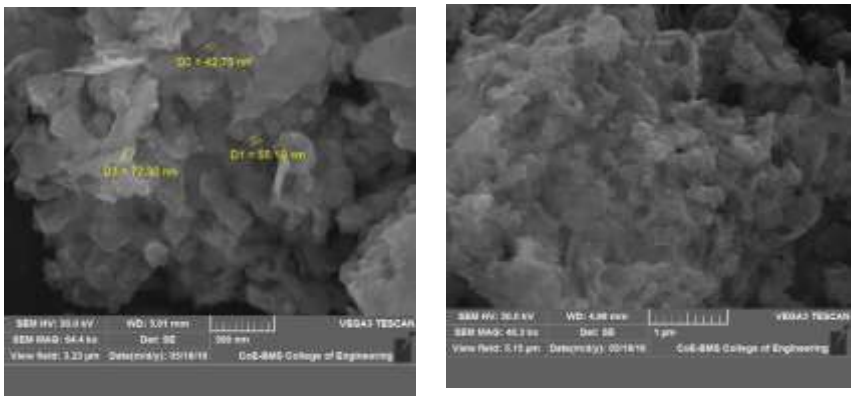

Fig 1: SEM image of Magnesium ferrite nanoparticles.

3) 4.1.2 X-ray Diffraction (XRD)

The crystal size of MgFe2O4 NPs was determined by X-ray diffraction analysis. The applied current and voltage was 30mA and 45kV respectively. Scanning was done from 0º to 80º at a scan rate of 1.2º per minute.

Several peaks were obtained which indicated the composition of the NP to be $MgFe_2O_4$ before adsorption. After adsorption, peaks were obtained for both $MgFe_2O_4$ and Chromium in the form $Cr_2Fe_2O_4$. This indicates the adsorption of Chromium metal ion. The average crystallite size is determined using Scherer's equation: **$D=0.9\lambda/b*\cos\theta$** [40].

θ= wavelength of the incident x-ray; b= width of the XRD peak at half height; 0.9= Shape factor.

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
30.1176	314.13	0.2722	2.96485	26.94
35.4479	1165.99	0.2035	2.53029	100.00
43.0847	321.19	0.1594	2.09783	27.55
53.4368	131.67	0.1522	1.71328	11.29
56.9966	301.94	0.2336	1.61443	25.90
62.5837	553.71	0.2194	1.48306	47.49

Table 4: Peak List

Average particle size before adsorption was 38.84nm and after adsorption of chromium was 29.83nm.

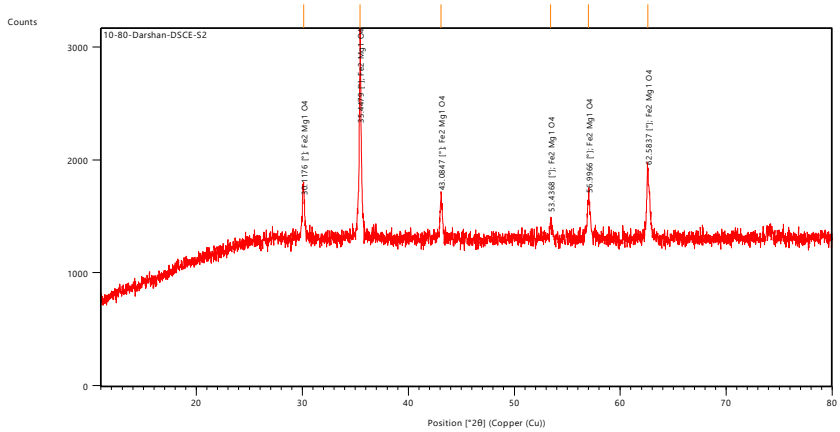

Fig 2: XRD pattern of Magnesium ferrite nanoparticles

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	98-002-4229	70	Magnesioferrite	0.000	0.602	$Fe_2 Mg_1 O_4$

Table 5: Pattern List

4) 4.1.3 Fourier Transform Infrared (FTIR) Spectrometer

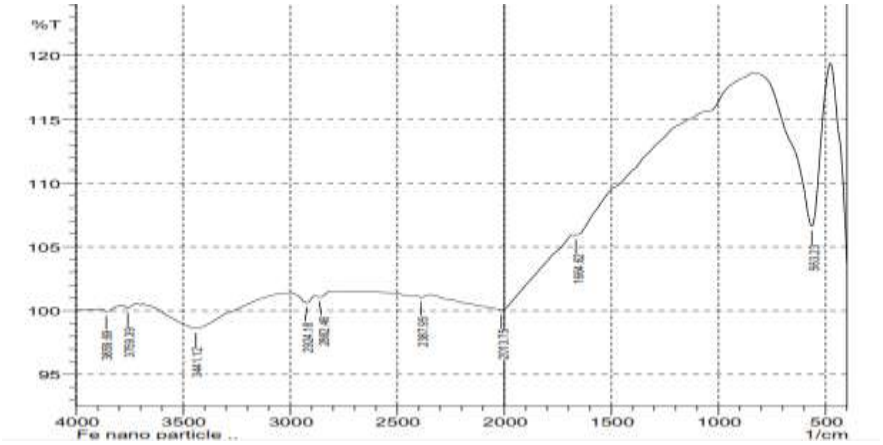

Fig 3: FT-IR spectra of Magnesium ferrite nanoparticles

Interpretation of FT-IR analysis: [6], [30]

- FT-IR spectra was in the range of 400-4000 cm^{-1}
- A high intensity peak at 563.23 cm-1 indicates the presence of Fe-O stretching bond at the tetrahedral site.
- Another high intensity peak in the range 400-500 cm-1 indicates the presence of Mg-O stretching bond at the tetrahedral site.
- Small intensity peaks in the range 1500-4000 cm-1 indicate the presence of impurities like H-O, C-O, C-H in small quantities.

No.	Peak	Intensity	Corr. Intensity	Base(H)	Base(L)	Area	Corr. Area
1	563.23	106.624	12.583	833.28	476.43	-20.318	6.66
2	1664.62	105.934	0.063	1668.48	833.28	-44.235	-2.772
3	2013.75	100.046	3.548	2343.59	1681.98	-5.024	5.066
4	2862.46	101.05	0.127	2411.1	2343.59	-0.332	0.016
5	2862.46	101.064	0.214	2885.6	2812.31	-0.388	0.036
6	2924.18	100.611	0.631	2999.41	2885.6	-0.49	0.136
7	3441.12	98.599	0.016	3607.01	3439.19	0.604	0.082
8	3759.39	100.188	0.31	3788.32	3718.88	-0.108	0.044
9	3859.69	99.943	0.015	3882.76	3857.76	-0.003	0.001

Table 6: Peaks and Intensities

5) 4.1.4 Characterization after Adsorption

The adsorbent after chromium adsorption was characterized by SEM and XRD.

6) 4.1.5Scanning Electron Microscope (SEM)

The Fig 24 shows SEM image of the Nano-structure of the adsorbent after conducting the adsorption experiments.

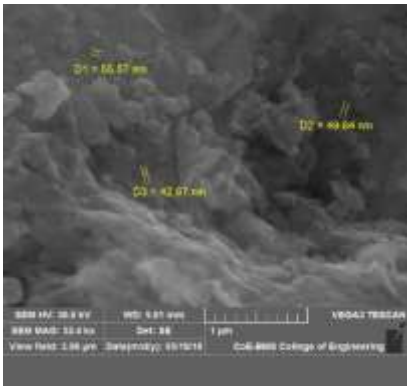

Fig 4: SEM image of Magnesium ferrite NP after Chromium adsorption

7) 4.1.6 X-ray Diffraction (XRD):

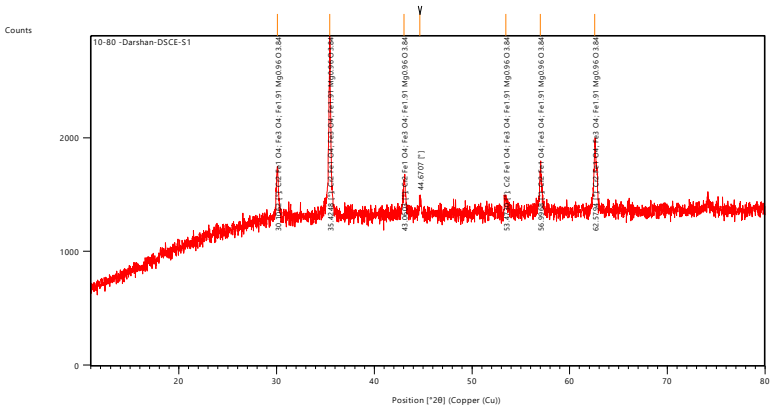

Fig 5: XRD pattern of Magnesium ferrite NP after Adsorption of Chromium

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]
30.1062	295.62	0.3446	2.96595	30.36
35.4248	973.77	0.2560	2.53188	100.00
43.0603	228.64	0.2299	2.09896	23.48
44.6707	113.02	0.1169	2.02696	11.61
53.4730	97.18	0.1734	1.71220	9.98
56.9968	323.31	0.1853	1.61443	33.20
62.5794	520.20	0.2279	1.48315	53.42

Table 7: Peak List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	98-004-4526	82	Chromite	0.000	0.969	$Cr_2 Fe_1 O_4$
*	98-016-5105	57	Magnetite	0.000	0.649	Fe_3O_4
*	98-016-2645	80	Magnesioferrite	0.000	0.798	$Fe_{1.91} Mg_{0.96} O_{3.84}$

Table 8: Pattern List

8) 4.2 Experimentation results:

MINITAB 17 Software was used to generate experiments. The parameters considered were pH, Adsorbent load and Initial metal ion concentration.

9) 4.2.1 CCD analysis and optimization by RSM for Chromium

The effect of adsorption parameters like, initial metal ion concentration, pH and adsorbent load was studied by statistically designed experiments using CCD. According to the software, a response surface design of 2^3 is used with 1 replicate at the center point which resulted in 20 trials.

The limits for adsorption parameters were predefined through literature survey. Initial metal ion concentration of 50-150 ppm, pH of 2-6 and adsorbent load of 0.05-0.15 g/150ml was set for experimentation. Table 9 shows the levels of variables which were used in the experiment for the removal of Chromium.

Independent variables	**Range and Level**				
	-2	**-1**	**0**	**+1**	**+2**
Initial Chromium ion concentration (ppm)	**50**	**70.27**	**100**	**129.73**	**150**
pH	**2**	**2.81**	**4**	**5.189**	**6**
Adsorbent Load	**0.05**	**0.0703**	**0.1**	**0.1297**	**0.15**

Table 9: Levels of Variables for Chromium

10) 4.2.2 Response Surface Design

The following second-degree polynomial equation explains the state of the system:

Y= 287 - 53.2 pH - 1.93 Co - 746 AL + 5.49 pH*pH + 0.00582 Co*Co - 792 AL*AL - 0.091 pH*Co + 62 pH*AL + 9.15 Co*AL; where Y is the percentage removal.

Percentage removal was calculated using: **% Removal = (Co - C)/Co** [13] [15] [30].

Where, Co → Initial Concentration (ppm); C → Concentration at time t (ppm)

RunOrder	PtType	Blocks	pH	Co	AL	%removal
1	-1	1	4.00000	100.000	0.050000	2.53
2	-1	1	4.00000	50.000	0.100000	53.50
3	1	1	5.18921	129.730	0.070270	14.04
4	0	1	4.00000	100.000	0.100000	24.84
5	-1	1	6.00000	100.000	0.100000	17.70
6	0	1	4.00000	100.000	0.100000	24.84
7	1	1	5.18921	70.270	0.070270	18.19
8	-1	1	4.00000	150.000	0.100000	11.02
9	0	1	4.00000	100.000	0.100000	24.84
10	1	1	2.81079	70.270	0.129730	41.85
11	1	1	2.81079	129.730	0.070270	34.12
12	0	1	4.00000	100.000	0.100000	24.84
13	1	1	2.81079	70.270	0.070270	69.30
14	-1	1	2.81079	100.000	0.100000	61.60
15	1	1	2.81079	129.730	0.129730	82.90
16	-1	1	4.00000	100.000	0.150000	28.93
17	1	1	5.18921	70.270	0.129730	43.35
18	0	1	4.00000	100.000	0.100000	24.84
19	1	1	5.18921	129.730	0.129730	27.65
20	0	1	4.00000	100.000	0.100000	24.84

Table 10: Experiments for Chromium; Co- Initial Concentration; AL- Adsorbent Load.

11) 4.2.3Optimization of response:

The second-degree polynomial equation is solved and the optimum values for the variables are obtained using response optimizer in Minitab 17. Table 11 gives the optimum parameters obtained from the Minitab software for Chromium.

Adsorbent	**Initial Metal ion Concentration (ppm)**	**pH**	**Adsorbent Load (g/150ml)**	**Y Percentage Removal**	**D Desirability Index**
$MgFe_2O_4$ NP	**50**	**2**	**0.1118**	**82.92**	**1**

Table 11: Optimized parameters for Chromium

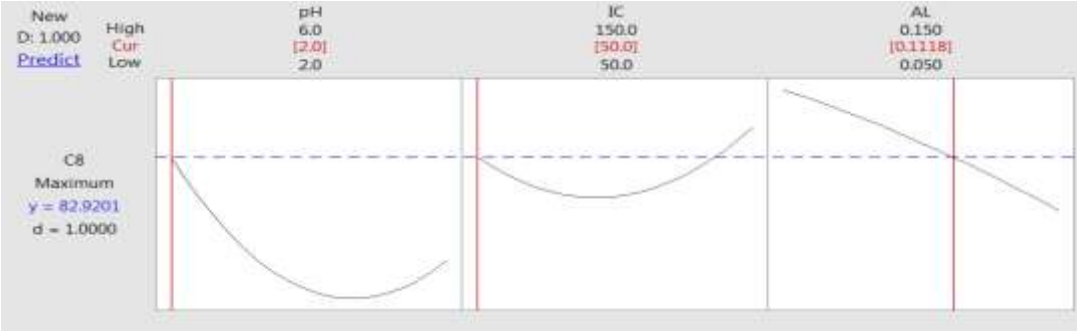

Fig 6: Optimized parameters for Chromium

Experimental result for optimized conditions is shown in Table 12 below. pH was maintained at 2, the initial concentration at 50ppm and the adsorbent load was 0.1118g/150ml of the solution. Due to adsorption, there was a gradual decrease in the Chromium ion concentration and equilibrium was attained at 120 minutes.

Time (min)	Concentration of chromium in solution (ppm)	Percentage Removal
0	50	0
15	26.22	47.8
30	17.75	64.66
45	17.49	65.18
60	15.71	68.73
75	13.68	72.77
90	9.95	80.19
105	9.17	81.74
120	8.93	82.22
135	10.22	79.65

Table 12: Optimization results for chromium

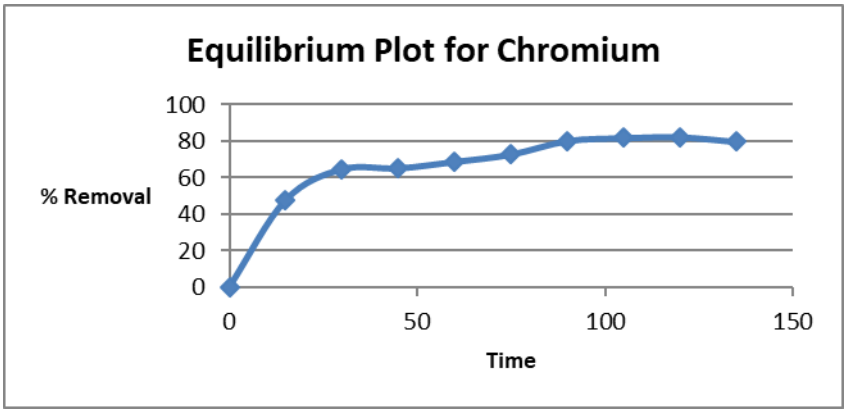

Figure 7: Equilibrium plot for Chromium

12) 4.3 Adsorption Isotherms

13) 4.3.1 Langmuir Isotherm:

This model is applicable to monolayer adsorption whose adsorbent surface consists of equal number of identical sites [13] [31]. The Langmuir isotherm (Langmuir, 1918) is shown by $\mathbf{C_e/q_e = 1/(bq_m) + C_e/q_m}$ [38]

q_e - Amount of adsorbed metal (mg/g); C_e - Unadsorbed metal Concentration (mg/l); q_m - Maximum amount of metal per unit weight of absorbent; b - Constant related to the affinity of the sites.

14) 4.4 Freundlich Isotherm

This model is applicable for adsorption on heterogeneous surfaces. Freundlich isotherm (Freundlich, 1906) is shown by $\mathbf{q_e = K_f.C_e^n}$.

q_e - Amount of Adsorbed metal per unit weight of adsorbent (mg/g); C_e - Unadsorbed metal concentration in solution at equilibrium (mg/l); K_f & n - Freundlich constants.

Initial Concentration of Chromium (ppm)	**Equilibrium Concentration of Chromium (ppm) Ce**	**1/Ce**	**1/qe**	**lnCe**	**lnqe**
50	**23.25**	**0.043**	**0.04**	**-3.1465**	**-3.218**
100	**75.16**	**0.013**	**0.027**	**-4.3428**	**-3.612**
150	**138.98**	**0.0072**	**0.025**	**-4.9336**	**-3.688**

Table 13: Equilibrium adsorption of Chromium by $MgFe_2O_4$ NPs

$q_e = (C_i-C_f)*V/m$; $q_e = (50-23.25)*0.15/0.1 = 39.93$ mg/g

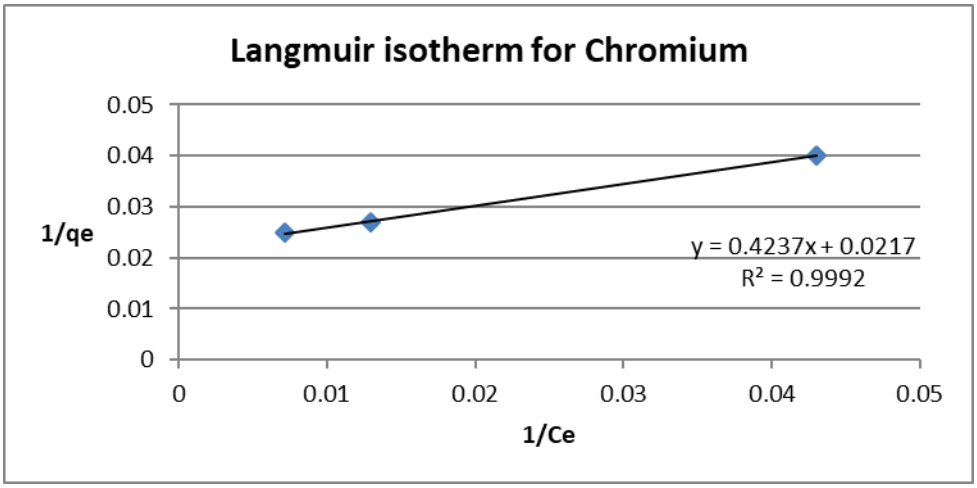

Fig 8: Langmuir Isotherm for chromium

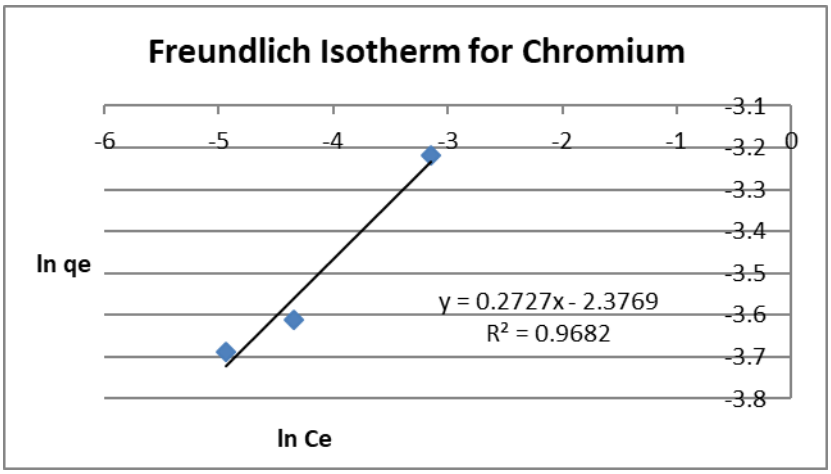

Fig 9: Freundlich Isotherm for chromium

Metal ion	**Langmuir isotherm**	**Freundlich isotherm**
	R^2	**R^2**
Chromium	**0.999**	**0.968**

Table 14: Isotherm values for Chromium

The above data for Chromium fits well with Langmuir isotherm. This is inferred by comparing the R^2 value for both Langmuir and Freundlich isotherms (0.999 for chromium). Thus, Chromium follows Langmuir isotherm which suggests homogeneous, monolayer adsorption on $MgFe_2O_4$ nanoparticles [31]. The adsorption may be chemical and physical in nature which is indicated by Langmuir isotherm [27] [31].

15) 4.5 Adsorption Kinetics

The kinetics of Chromium on $MgFe_2O_4$ nanoparticles was studied. The data obtained was studied using the following models:

- Pseudo first order kinetics
- Pseudo second order kinetics

16) 4.5.1 Pseudo first order model

It is also known as Lagregren kinetic equation [38]. This model is used to study the systems kinetics behavior.

The following equation is used for this model: $\mathbf{\ln (q_e-q_t) = \ln q_e - k_1 t.}$

q_e - Amount of Chromium Adsorbed at equilibrium (mg/g); q_t - Amount of Chromium adsorbed at time t (mg/g); k_1 - Pseudo first order rate constant (min-1); t - Time (mins)

17) 4.5.2Pseudo second order model

The following equation [38] is used for this model: $\mathbf{t/q_t = 1/kq_e^2 + t/q_e}$.

q_t - Amount of Chromium adsorbed at time t (mg/g); q_e - Amount of Chromium adsorbed at equilibrium (mg/g); k_2 - Pseudo second order equilibrium rate constant (gmol-1min-1); t - Time (min)

18) 4.5.3 Optimum values for Chromium

Adsorbent	**Initial Metal ion Concentration (ppm)**	**pH**	**Adsorbent Load (g/150ml)**
$MgFe_2O_4$ NP	**50**	**2**	**0.1118**

Table 15: Optimum values for chromium

19) 4.5.4 Adsorption kinetics at optimum conditions for Chromium

Time (mins)	q_t(mg/g)	$\ln(q_e-q_t)$	t/q_t
0	0	-	-
15	31.7	3.14	0.473
30	43	2.46	0.6976
45	43.347	2.43	1.038
60	45.2	2.2	1.312
75	48.427	1.85	1.548
90	53.4	0.31	1.685
105	54.44	-	1.928
120	54.76	-	2.191
135	53.04	-	-

Table 16: Adsorption Kinetics at optimum conditions for chromium

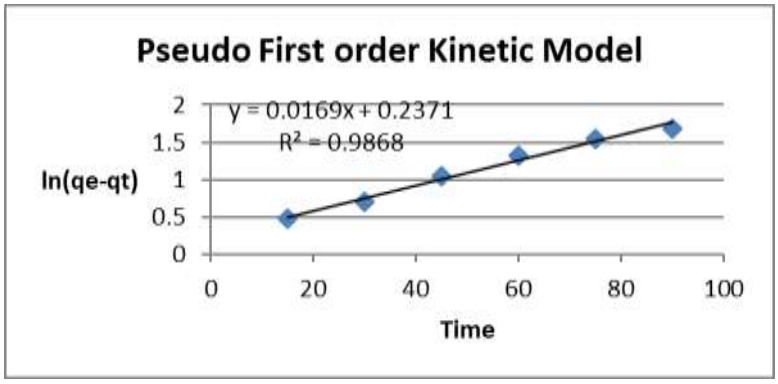

Fig 10: Pseudo first order kinetic model for chromium

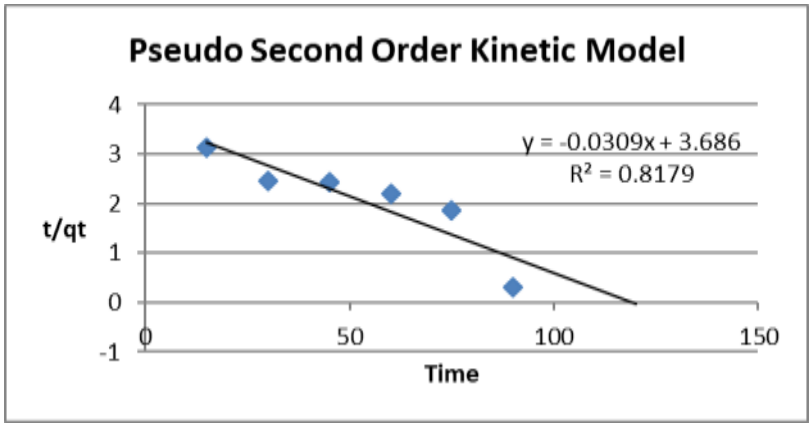

Fig 11: Pseudo second order kinetic model for chromium

20) 4.5.5 Kinetics for Chromium Summary table

Metal ion	**Pseudo First order**		**Pseudo Second order**	
	k_1	**R^2**	**k_2**	**R^2**
Chromium	**0.016**	**0.986**	**9.05×10^{-5}**	**0.817**

Table 17: Kinetic model summary

The regression study used to examine the Langergren model and pseudo first order model applicability is R^2. The values obtained from R^2 shows the models linearity. If the R^2 value is unity, then the model is better fit [17][38]. For Chromium, the values fit well with Pseudo First order Kinetics. The next section will elaborate on the conclusion of this work.

V. 5. Conclusion And Future Work

Flame combustion technique was used to prepare the Magnesium ferrite NPs and batch adsorption studies were carried out for hexavalent chromium. The Magnesium ferrite NPs obtained was characterized using SEM, XRD and FT-IR spectrophotometer. Analysis of the characterization results showed the presence of Magnesium ferrite in spinel form with a crystalline size of 38.84nm and the average particle size was found to be 42.75-72.3nm. Effect of parameters like initial metal ion concentration, pH and adsorbent load on the percentage removal of chromium ions in solution was studied by designing the experiments using Minitab 17 software. For chromium, the initial concentration was varied between 50-150ppm, pH 2-6 and the adsorbent load between 0.05-0.15g/150ml. Optimum conditions for hexavalent chromium were determined using RSM on Minitab 17 software where, for chromium, pH was found to be 2, initial metal ion concentration was 50ppm and the adsorbent load was 0.1118g/150ml. Maximum percentage removal achieved at optimum conditions for hexavalent chromium was 82.22. This shows that Magnesium ferrite NPs is a good adsorbent for the removal of chromium ions from the solution. Langmuir and Freundlich isotherms were developed and it was found that chromium was best fit for Langmuir isotherm. Confirmation to Langmuir isotherm indicates that the adsorption is homogeneous and monolayer in nature and it may be chemical and physical adsorption. Kinetic models were developed by using regression studies for chromium. The values obtained from R^2 shows the model's linearity. It was found that chromium followed Pseudo first order kinetics.

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