

# Magnetic Nanoparticles (MNPs) for Chromium Removal from Industrial Wastewater

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**Abstract:** Rapid industrialization is causing an emissive increase in discharge of heavy metals by their effluent streams. Water pollution by heavy metals occurs globally and has gained much attention due to their toxic and carcinogenic effects. This study addresses removal of chromium Cr (VI) using highly efficient, low cost and environment friendly Magnetic Nano-Particles (MNPs). MNPs were prepared by co-precipitation procedure in the presence of air using ferric and ferrous chloride salts. X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis was performed to characterize MNPs. Adsorbent Dose, pH, contact time with the pollutant and initial concentration was varied to determine maximum removal efficiency at optimized conditions. 96% of the Cr (VI) was removed using 0.3 g/L of MNPs at pH of 4 and equilibrium was achieved within short span of 10 minutes. Maximum adsorption capacity of 124 mg/g was obtained using Langmuir adsorption isotherm. Regeneration studies showed that MNPs retained their Cr(VI) removal capacity. Excellent adsorption capacity along with synthesis of MNPs from locally available material, easy separation, environment friendly composition makes MNPs a feasible solution to remove heavy metals like Cr (VI) from industrial wastewater.

**Keywords:** Magnetic nanoparticles, Adsorption, Isotherm, Chromium

## I. INTRODUCTION

Domestic, agricultural, and largely industrial waste containing high concentrations of heavy metals like chromium, lead, mercury and arsenic are regularly being dumped into open water bodies like rivers, lakes and oceans. This not only cause harm to the marine life but also the environment and human health. These metals when ingested or inhaled in small concentrations can cause a lot of harm to the human body [1-3]. Heavy metals accumulation is rapidly increasing in the environment and present obvious threat due to their persistence and have a potential for serious health consequences. These toxic substances could reach human beings through various absorption pathways of ingestion, dermal contact, in the drinking water system, inhalation, and oral intake. The intake of these chemicals then causes diseases and some maybe even fatal [4, 5].

It was reported that around 170,000 tons of chromium is dumped globally into the environment from industrial and manufacturing processes [6]. Hexavalent chromium (Cr VI) and trivalent chromium (Cr III) are the most stable forms of chromium. Cr VI is 500 times more toxic than trivalent form and responsible for causing harmful human health effects like respiratory, skin and hematological problems [7, 8].

Chromium is widely used in many industrial processes like tanneries, steel alloys, electroplating, textiles, pigments and other chemical industries which leads to high pollution of the metal. In different areas of Pakistan, chromium containing wastewater is directly dumped into surface water bodies without any treatment. From various regions in Pakistan the ground water samples show Cr variation ranging from <0.001 to 9.8 mg/L from residential areas of Kasur, Punjab province, whereas surface water contamination showed concentrations of 0.16–0.29 mg/L in Bara River, Nowshera, KPK province. These studies indicate how industrial waste water impacts on water quality. The Cr concentrations found in Pakistan increase the National Environment Quality standards which is 1 mg/L [9].

Table. 1 is showing the concentration of chromium in drinking water sources in various areas of Pakistan. According to World Health Organization (WHO) and National Drinking Water Quality Standards of Pakistan (NSDWQ), the limit for Chromium in drinking water allowed is 0.05 mg/L (50 PPB). National Environmental Quality Standards (NEQS) mentions the limit of 1mg/L. The presence of chromium in drinking water in various areas of Pakistan ranges up to 500 times greater than WHO and NDWQS limits. Moreover, the industrial effluent is also up to 350 times greater than NEQS limits for discharge.

Table 1 Contamination of Chromium in various areas of Pakistan

Sr. No.	Range	Mean	WHO and NDWQS For drinking water	NEQS Effluent Discharge standard	Times Higher	Location	Source	Ref.
01	0.025-9.8 mg/L	2.12	0.05 mg/L	1 mg/L	40	Kasur	Groundwater	[10]
02	0.005-410.60 mg/L	51.70 mg/L 228 mg/L		50-228 times	50-228	Peshawar	Industrial Effluent	[11] [12]
03	0.235-2.59mg/L				50	Peshawar	Drinking Water	[13]
04	4.57-6.36 mg/L				127	Sahiwal	Drinking Water	[14]
05		350 mg/L			350	Sheikhupura	industrial effluent	[12]
06		0.033 mg/L			Less but continuous consumption leads to7accumulation in body	Karachi	Ground Water	[15]
07	16.87-28.12 mg/L				560 times	Trimmu Barrage, Jhang	surface water	[16]
08	0.6-13.2 mg/Kg		2.3 mg/Kg (Permissible Limit, WHO)			Lahore Vegetable irrigated with municipal wastewater		[17]
09	11-50 mg/Kg		2.3 mg/Kg (Permissible Limit, WHO)			Faisalabad Vegetables and Crops		[18]

Various processes and methods have been used for their removal which include chemical precipitation[19], coagulation[20], complexation, activated carbon adsorption[21, 22], ion exchange[23], solvent extraction[24], foam flotation[25], electro-deposition, cementation [26], and membrane operations [27]. These processes have numerous disadvantages which include production of sludge, high energy demand and cost, technical difficulties and inefficient removal. Adsorption is a low-cost alternative to these methods with an efficient removal due to high surface area-to-volume ratio. With advancement in the field of nanotechnology, various types of MNPs have been developed for sewage coagulation, organic dyes removal, heavy metals removal and soil remediation etc. the removal of contaminants from wastewater. We opted for iron oxide MNP adsorbents for the removal as they have large surface area, high adsorption efficiency, greater number of sites available for adsorption, high magnetic properties, are a cost effective, low energy demand, easy and fast separation via permanent magnet/ magnetic field and less sludge production [28-30]. Furthermore, the nanoparticles can be regenerated by removing the contaminant adsorbed by magnetic separation.

In this study, MNPs were synthesized using chemical co-precipitation method. Chromium VI was used as a model adsorbent for its effective removal via adsorption with MNPs. These MNPs offer inexpensive and attractive solution for removal of heavy metals due to its high adsorption efficiency and easy removal techniques. The objective of this study includes: i) synthesis of MNPs, ii) optimization of parameters (Adsorbent Dose, pH, Contact Time and initial concentration) for maximum Cr VI removal, iii) regeneration of MNPs for reuse and iv) application of adsorption isotherm models for determining the adsorption behavior.

## II. METHODOLOGY

### a. Materials

Iron(III) Chloride Hexahydrate, Iron(II) Sulfate Heptahydrate, Ammonium hydroxide (25%), Sodium hydroxide, Ethanol, Humic acid, Potassium dichromate, Sulphuric acid, Phosphoric acid, Sodium hydroxide, Diphenylcarbazide, and Acetone were bought from Sigma and DaeJung. All chemicals were of analytical grade and were used without further purification. All the solutions were prepared using distilled water.

### b. Preparation of MNPs

Chemical co-precipitation was used for the synthesis of MNPs. 6.1g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 4.2g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were stirred using a magnetic stirrer in 100ml of distilled water at 500-600 rpm until a clear solution formed. The solution was then heated up to 90°C under continuous stirring and 20ml of ammonium hydroxide was added (at the rate of 1mL/min). The solution was heated for 30 mins at 90°C. The precipitates formed were allowed to cool and settle down. MNPs were separated using permanent magnet and were washed several times with distilled water and finally with ethanol to neutralize the pH. After washing, precipitates were heated at 105°C for the drying the precipitates. For characterization of the prepared nanoparticles Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) tests were conducted. XRD was performed to confirm the structure of the formed MNPs from the diffraction peaks obtained. SEM was done to determine the surface morphology and size of the MNPs.

### c. Adsorption Studies:

The efficacy of MNPs as Cr(VI) adsorbents was evaluated by batch adsorption tests. Optimized dose of MNPs were added into 50mL of solution containing desired amount of Cr(VI). pH was adjusted by using 0.1 M Hydrochloric Acid (HCl) and 0.1 M Sodium hydroxide (NaOH), followed by shaking in an orbital shaker for 30 minutes at 300 rpm. After shaking, MNPs with adsorbed Cr(VI) were separated with the help of a permanent hand-held magnet. The solution was again filtered by using whatman filter paper to remove the remaining MNPs. After filtration absorbance of each sample was measured to determine the concentration of remaining Cr(VI) present in the solution using the DPC (Standard Methods, 3500-Cr) method. After filtration absorbance of each sample was measured at 540nm to determine the concentration of residual Cr(VI) present in the solution using 1,5-Diphenylcarbazide (DPC). Equation 1 was used to calculate the percentage removal.

$$\% \text{ removal} = \frac{C_i - C_e}{C_i} \times 100 \dots \text{Equation 1}$$

Where  $C_i$  is Initial Cr concentration (mg/L) and  $C_e$  is Residual Cr concentration (mg/L).

The adsorption capacity of the MNPs were determined using equation 2:

$$q_e = \left( \frac{C_i - C_e}{m} \right) V \dots \text{Equation 2}$$

Where  $q_e$  is adoption capacity (mg/g),  $m$  is mass of adsorbent (g) and  $V$  is volume of solution (L).

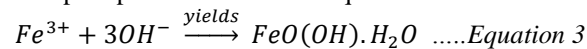
Adsorbent dose was varied from 0-400 mg/L, contact time from 0-80 minutes, effect of pH was observed from 2-9 and adsorption isotherm (initial concentration of Cr VI from 0-230 mg/L). Cr VI loaded MNPs were desorbed using 0.1 M HCl followed by neutralization with NaOH. Nanoparticles were stirred for 3 hours at room temperature. The adsorption – desorption was done for four cycles.

## III. RESULT AND DISCUSSION

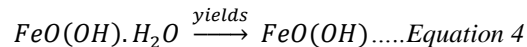
### a. Synthesis of MNPs:

Chemical reactions responsible for synthesis of MNPs are stated in equations (3-7)

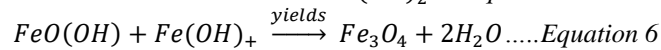
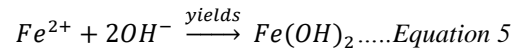
Ferric salts are hydrolyzed to form yellow precipitates as shown in equation 3



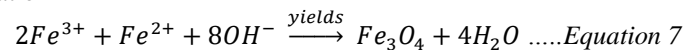
$Fe(OH)_3$  then gets converted into goethite due to dehydration equation 4



Ferrous salts also hydrolyses and reacts with goethite as shown (equation 5 and 6)



The overall reaction is shown in equation 14



Ferrous and ferric salts were hydrolyzed and dehydrated all together to form brown to black magnetite precipitates [28, 31-33].

### b. Characterization of MNPs:

XRD analysis was conducted by using Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) which revealed the crystalline structure of MNPs. The results are shown in graph 1 which can be indexed as primitive cubic system for by comparison with data from cubic  $Fe_3O_4$  (JCPDS no. 894319). The diffraction peaks at  $2\theta = 35.45^\circ$ ,  $63^\circ$  correspond to (3 1 1) and (4 4 0) respectively. Absence of impurity peaks indicates that the product is pure. Scherrer's equation (Equation 8) was used to confirm the size of the formed particles [34, 35].

$$\tau = \frac{K\lambda}{\beta \cos\theta} \dots \text{Equation 8}$$

Where  $\tau$  is mean size of crystal lattice,  $K$  is shape factor,  $\lambda$  is x-ray wavelength,  $\beta$  is Full Width at Half Maximum (FWHM) and  $\theta$  is the Bragg's angle.

According to Scherrer's equation, the average size of MNPs came out to be 32-45 nm.

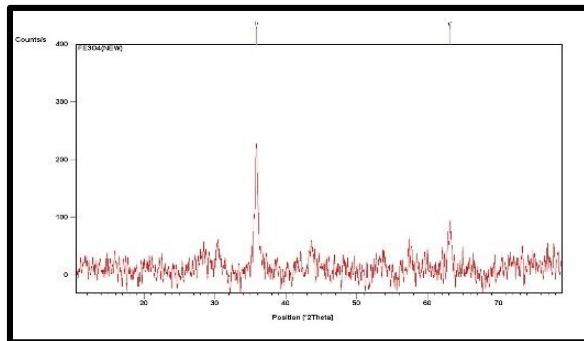


Fig. 1. XRD analysis of MNPs

SEM analysis showed relatively spherical shape of both MNPs. However, agglomeration here shows the strong magnetic nature of MNPs. Following pictures show the size of MNPs 28-40 nm.

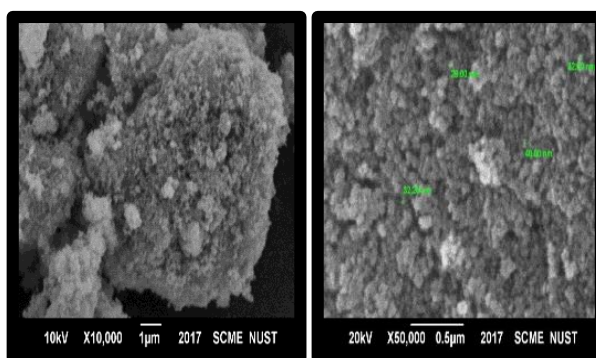


Fig. 2. Showing SEM analysis results under high power lens

*c. Effect of Dose, time, pH and Initial Concentration:*

For optimization of dose, experiments were conducted on Cr VI concentrations of 5, 10 and 20 ppm. Initially adsorbent dose was varied from 0-400 mg/L. Experiments were performed at room temperature (25°C) and shaking was done for 30 minutes. Figure 3 shows the final concentration of Cr VI after removal with MNPs. At dose of 300 mg/L, 99%, 97% and 94% Cr VI removal was observed at 5, 10 and 20 mg/L of initial chromium concentration. However, it was observed that increasing the dose of adsorbent did not increase the removal percentage significantly. So, 300 mg/L was taken for later experiments because at this dose, remaining concentration of Chromium (VI) was well below NEQS limits. All the above mentioned experiments were performed at Cr VI 10 mg/L of concentration. The validity of the result is confirmed by comparison of result with other studies. This attributed to the fact that higher adsorbent dosage has higher number of active sites [35-37]. However, by increasing the adsorbent dosage aggregation of MNPs take place which reduces the adsorption efficiency of Cr(VI) [38].

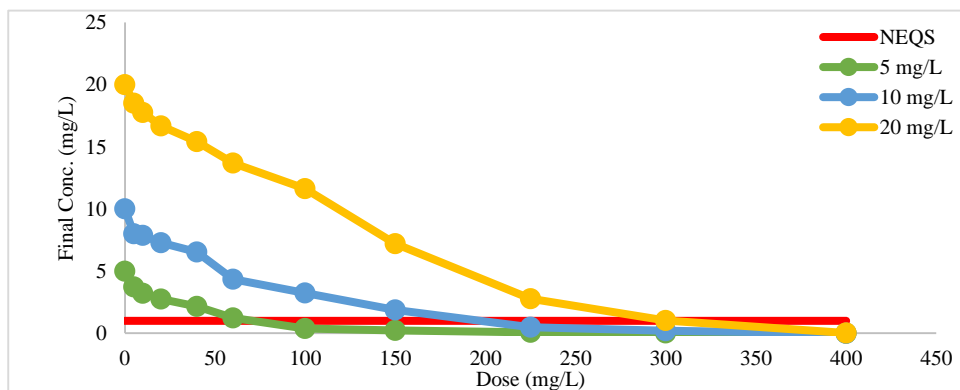


Figure 3 Effect of MNP dose on Cr VI removal

Effect of time was investigated from 0-80 minutes at room temperature (25°C). During initial time, the rate of removal of chromium was at much faster pace. Within 10 minutes at 300 rpm, more than 94% of Cr(VI) was removed. After 10 minutes, there was no

excessive removal and the removal efficiency remained almost the same afterwards. Figure 4 reveals as the contact time increases, chromium is rapidly removed from aqueous solutions and adsorbed on the MNPs. The rapid reaction between pollutant and adsorbent shows that the surface chemistry of MNPs was very much reactive with the Cr(VI) [39, 40].

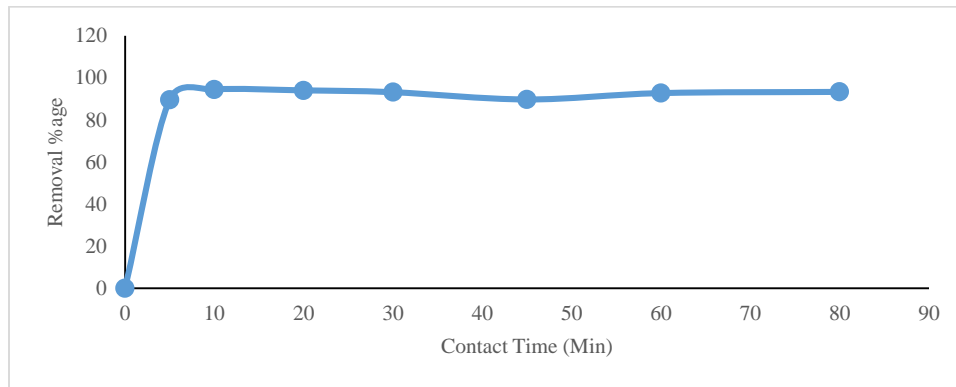
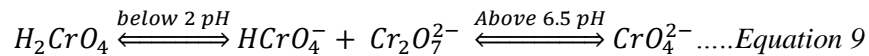


Fig. 4 Effect of Contact Time on Cr VI removal

The effect of solution’s pH on the adsorption of chromium on MNPs is shown in the figure 5. Figure reveals that pH plays an important role in Cr(VI) removal from aqueous solutions. At lower pH highest removal was observed, while with increasing pH removal decreased expressively. Highest removal was observed between 2-4 pH values. Effect of pH on chromium removal in the solution depends on the surface chemistry. Chromium exists in various forms in water which are highly dependent on pH of the water. Change in pH changes the forms of chromate ions as shown in equation 9:



Below 2 pH chromium is present in the form of chromic acid. As the pH increase than 2, chromic acid dissociates into mono ( $HCrO_4^-$ ) and dichromate ( $Cr_2O_7^{2-}$ ) anions. Above pH 6.5, chromate ions ( $CrO_4^{2-}$ ) dominates. It is visible from the equation that dichromate ( $Cr_2O_7^{2-}$ ) and chromate ( $CrO_4^{2-}$ ) ions have the same charge density but the concentration of chromium is more in dichromate ( $Cr_2O_7^{2-}$ ) ions [37, 41, 42]. Hence greater removal is observed in acidic pH range. Moreover free binding energy of mono ( $HCrO_4^-$ ) and dichromate ( $Cr_2O_7^{2-}$ ) anions is low which aids in their adsorption on MNPs [6, 43]. With the increase in pH the repulsion between negatively charged Cr(VI) species and  $OH^-$  increases which results in decreased Cr(VI) adsorption [44].

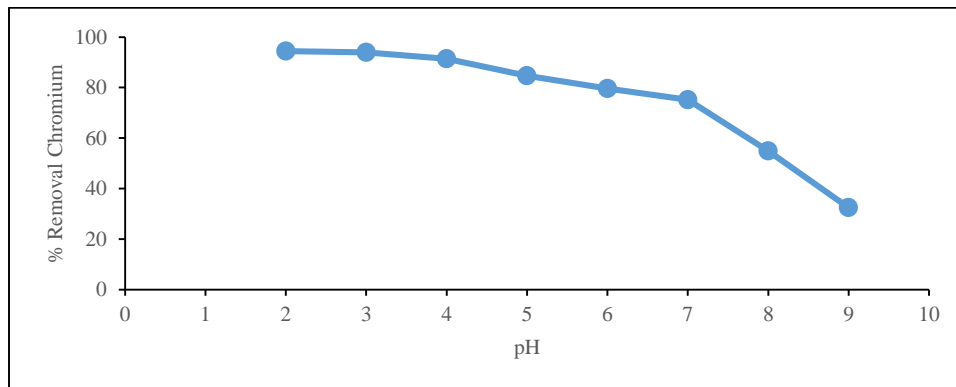


Figure 5 Effect of PH on adsorption of Cr (VI) by MNPs

To investigate the effect of initial concentration on adsorption capacity of MNPs, Cr (VI) concentration was varied from 0 to 230 mg/L. The experiments were performed on optimized conditions of dose (300 mg/L), contact time (10 minutes) and pH (2). Removal efficiency decreased from 99% to 13% with increasing initial concentration. Cr(VI) removal did not increase significantly after 125 ppm. This is due to the fact that MNPs have reached to its maximum adsorption capacity value [39]. All of the active sites have been occupied by Cr(VI) no further removal can be performed by MNPs. Decrease in removal efficiency with increasing pollutant’s concentration is confirmed by many researchers in the field. Figure 6 shows the maximum adsorption capacities came out to be 124 mg/g.

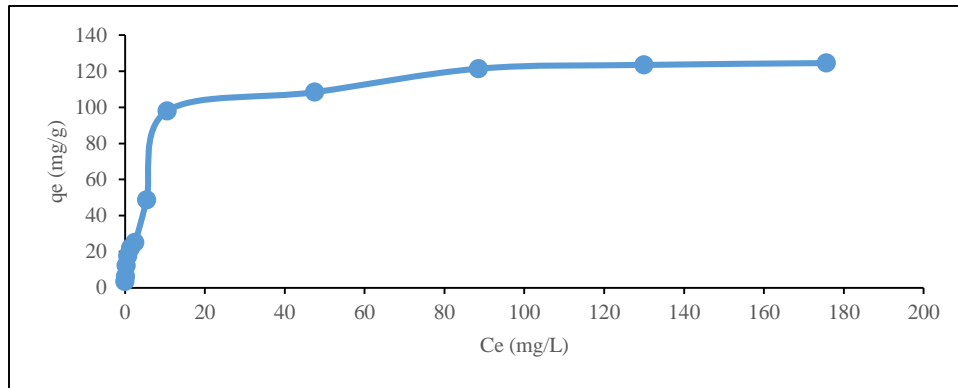


Figure 6 Effect of Cr (VI) concentration on adsorption by MNPs

d. Isotherm Study

Isotherm models predict the amount of solute that an adsorbent can adsorb onto their surface. Langmuir and Freundlich Isotherm models were used as they are well established and popular [6, 28, 45-47]. Langmuir Isotherm anticipates the relationship between change in adsorption and equilibrium concentration. The Langmuir Isotherm assumes:

- The monolayer adsorption on the homogenous surface.
- There is no interaction between adsorbate molecules.

The linear form of Langmuir adsorption isotherm is mentioned in equation 10:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{bQ_o} \dots \text{Equation 10}$$

Where  $C_e$  is the equilibrium concentration of solution (mg/L),  $Q_o$  is the maximum adsorption capacity of monolayer of adsorbent (mg/g),  $b$  is the Langmuir constant (L/mg) which is related to the affinity of binding sites [46-48]

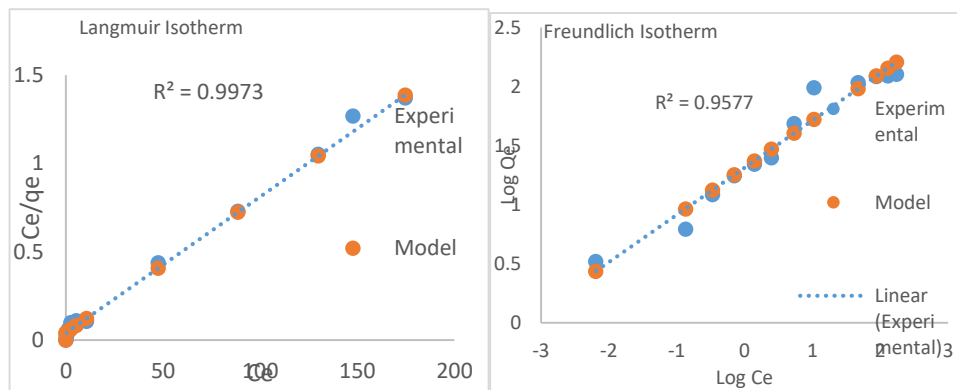


Fig. 7 Langmuir and Freundlich Adsorption Isotherms

The Langmuir parameters and the correlation coefficient of the adsorption data to this equation 10 are given in table 1. The Langmuir model effectively described the adsorption data with  $R^2 > 0.99$ . Thus, it shows the monolayer adsorption of heavy metals on the surface of MNPs. High values of  $b$  were reflected by the steep initial slope of the sorption isotherm, which indicates high affinity of MNPs for Cr VI. The fundamental characteristics of Langmuir equation can be interpreted in terms of a dimensionless constant separation factor shows favorable adsorption if its value is between 0 and 1. The  $R_L$  value assumes the nature and the feasibility of adsorption process.

Table.2: Langmuir and Freundlich Adsorption Isotherm Parameter

Langmuir Isotherm parameters		Freundlich Isotherm Parameters	
Qe (mg/g)	127.38	n	2.50
b (L/mg)	0.182	K <sub>f</sub>	20.49
R <sup>2</sup>	0.9973	R <sup>2</sup>	0.9973
R <sub>L</sub>	0 – 1		

Freundlich Isotherm predicts the relationship between the concentration of solute adsorbed on the surface of an adsorbent and the concentration of solute which is in contact with the adsorbent. In this Isotherm, adsorption is assumed on heterogenous surface. The linear form of Freundlich isotherm is given below (Equation 11):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \text{Equation 11}$$

Where  $K_f$  is the amount of solute adsorbed on the adsorbent surface (mg/g),  $n$  is the deviation from linearity of the adsorption [47].

It can be seen from figure 7 and Table 2 that  $K_f$  and  $n$  are corresponding to their maximum values. This implied that the binding capacity reached the highest value, and the affinity between MNPs and Cr was also higher at this condition. However,  $R^2$  values for Langmuir > Freundlich. So Langmuir fits better to data. Hence this indicated that adsorption is monolayer in nature.

Reuse and regeneration of adsorbents is of high importance due to the cost involved in the manufacturing. Hence it is necessary for the adsorbent to maintain its properties after multiple cycles of use. MNPs retained their removal percentages against Cr VI within 4 cycles.

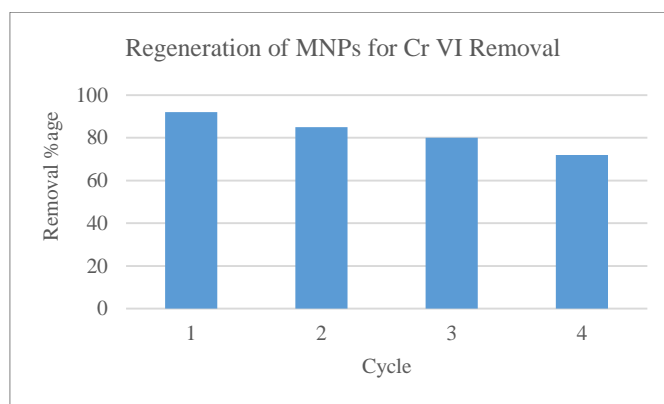


Fig.8

#### IV. CONCLUSION

In this paper Cr VI removal was investigated using magnetic nanoparticles. Maximum removal was observed using 300mg/L of MNPs dose, within 10 minutes of contact time at 300 rpm. Effect of pH was also examined and it was revealed that acidic pH aids in more Cr VI removal due to availability of dichromate ions. Moreover, effect of initial concentration was inspected and adsorption isotherms: Langmuir and Freundlich were applied on the data. Langmuir model was found to be the best fit. It is concluded that MNPs have high adsorption capacity for Cr VI and their regeneration up to four cycles indicated that MNPs can be used as an alternative adsorbent for industrial wastewater.

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