Magnetic Nanoparticles for Cr(VI) removal from Industrial Wastewater

BY

ASAD EJAZ KHAN   **NUST201304910BSCEE10213F**

AAKASHA MALIK   **NUST201306026BSCEE10213F**

KINZA RASOOL   **NUST201306204BSCEE10213F**

A thesis submitted in partial fulfillment of the requirements for the degree of

Bachelors of Engineering

In

Environmental Engineering

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

It is certified that the contents and forms of the thesis entitled

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Submitted by

ASAD EJAZ KHAN

AAKASHA MALIK

KINZA RASOOL

Have been found satisfactory for requirements of the degree of Bachelors of Engineering in Environmental Engineering

Supervisor: _____

Engr. Nida Maqbool

Assistant Professor

IESE, SCEE, NUST

DEDICATED

TO

OUR LOVING PARENTS AND FAMILIES

For their constant Support, Love and Encouragement

By virtue of whose prayers, we have been able to attain this position and whose hands are always raised for prayers, for our well-being

ACKNOWLEDGEMENT

We have no words at my command to express our profound sense of gratitude and innumerable thanks to **ALMIGHTY ALLAH**, the compassionate and merciful, the only creator and Lord of this universe, the entire source of knowledge and wisdom, who bestowed on us His blessings and gave us courage to complete the present studies and dissertation.

We owe all the possible tributes to the **Holy Prophet Muhammad (S.A. W.W)**, who is forever a model of guidance and knowledge for whole mankind and whose bounteous blessings enabled us to perceive the higher ideas of life, whose moral and spiritual teaching and love enlightened our heart, mind and flourish our thoughts to achieve success in the world.

We present our sincere gratitude to our respectable and worthy supervisor Engr. Nida, Institute of Environmental Sciences and Engineering, for her keen potential interest, skillful guidance, constructive criticism, and ever encouraging attitude throughout the course of research work.

We also wish to pay our heartiest gratitude to Engr. Arsalan Khalid and Engr. Aamir khan Institute of Environmental Sciences and Engineering, who provided the much-needed moral encouragement and moral support during our study and research.

Many thanks also go to Mr. Basharat Institute of Environmental Sciences and Engineering, for their unfailing moral support and guidance.

We are also very thankful to the Mr. Junaid Institute of Environmental Sciences and Engineering, for their guidance and support as senior Masters Student. We are very grateful to the staff of the Waste Water Lab and Chemistry lab, for the technical assistance.

Last but not least, Good friends are blessings of ALLAH ALMIGHTY, we shall ever pride on having very co-operative and sincere friends, seniors and class fellows.

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INTRODUCTION

1.1 Heavy Metals Pollution

Heavy metals are naturally found in the earth and due anthropogenic activities they are causing harm to the environment and human health. The concentration of these heavy metals is drastically increasing and cause harm not only in large quantities but minute concentrations can also lead to severe illnesses. These heavy metals also tend to bind to other compounds and form complexes which are much more difficult to be removed. Heavy metals pollution has drastically increased over the recent years especially in the aquatic environment and is one of the most serious problems in the world.

Domestic, agricultural, and largely industrial waste containing high concentrations of heavy metals like chromium, lead, mercury and arsenic are regularly being dumped into the rivers, lakes and oceans which not only cause harm to the marine life but also the environment and human health. These metals even when ingested or inhaled in small concentrations can cause a lot of harm to the human body. 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.

In different areas of Pakistan, we are facing severe public health problems due to accumulation of heavy metals in the water. The main contributors of water pollution are the byproducts which are present in the effluents of industries such as textile, tanneries, metal, dyes, fertilizers, pesticides, cement, petrochemical, energy, construction, steel alloys and others.

1.2 Chromium Toxicity and its Treatment Methods

Chromium is an abundant metal in the earth's crust and naturally occurs in coal, oil, soil, tobacco smoke, cement, topsoil and rocks, asbestos lining erosion and contaminated landfill sites. (ASTDR 2000). 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. It was reported that around 170,000 tons of chromium is dumped globally into the environment from industrial and manufacturing processes (Nirmala Ilankoon at al., 2014). It exists in several oxidation states with hexavalent and trivalent being the most stable forms. Hexavalent is 500 times more toxic than trivalent form and more difficult to remove from water (Becquer et al., 2003). Cr (VI) is known as a carcinogen which is responsible for causing harmful human health effects like respiratory, skin and hematological problems (Saha et al., 2011). It also has a toxic effect on plants by varying the germination process and also effecting the development and growth of roots, stems and leaves (Shanker et al., 2005). All chromium compounds are colored and the most important compounds are chromates and di-chromates of sodium and potassium (Wang et al., 2011).

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.

1.3 Heavy Metals Removal Strategies

Various processes and methods have been used for their removal which include chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations (Gunatilake S.K, 2015). These processes have numerous disadvantages which include production of sludge, high energy demand and cost and inefficient removal (M.A. Barakat et al.,2010). Adsorption is a low-cost alternative to these methods with an efficient removal due to high surface area-to-volume ratio. We opted for iron oxide magnetic nanoparticles adsorbents for the removal as they are a cost effective, low energy demand, easy separation, environmental friendly and efficient method (Kiomars Zargoosh et al., 2013). Furthermore, the nanoparticles can be regenerated by removing the contaminant adsorbed by magnetic separation.

1.4 Objectives

The objectives of our research are:

1. To synthesize two types of Magnetic Nanoparticles
   a. Bare Magnetic nanoparticles
   b. Humic Acid Coated magnetic nanoparticles

We synthesized both bare magnetic nanoparticles and humic acid coated nanoparticles with the same method. The method used was co-precipitation where two iron salts were used along with the addition of alkali. For the synthesis of humic acid coated nanoparticles there was an additional of step pf adding humic acid along with the alkali

2. Optimization of Parameters (Dose, Contact Time, pH, Initial Conc.)

   Dosage optimization: Range from 5 – 500 mg/30 mL

   Initial concentration optimization: Initial concentration was varied from 1-300 ppm

   Contact time at different temperatures optimization: Time was varied from 5 mins to 4 hours and temperature; room temperature, 25 °C, & 35 °C

   pH optimization: pH was varied from 2 to 9

3. To compare Magnetite NPs and HA – MNPs in the rate of metal adsorption

Applying isotherms and kinetic studies to the results. Freundlich and Langmuir isotherms to be applied.

Chromium can be adsorbed more effectively and efficiently by adsorption with magnetic nanoparticles. Our objective is to compare bare magnetic nanoparticles with humic acid coated magnetic nanoparticles.

Literature Review

2.1 Background

Wastewater pollution is a great environmental concern and is rapidly increasing due to rise in industrialization, urbanization and human population. Wastewater can originate from a combination of domestic, industrial, commercial or agricultural activities but our main focus is on industrial wastewater pollution as it the most toxic and hazardous waste which causes harm to humans, animals, aquatic life and the environment. The water availability is deficit in many countries including Pakistan due to improper discharge of untreated effluent, dumping of toxic and nuclear waste and air emissions which dissolve and pollute the water. Heavy metals pollution is very common now due to their importance of manufacturing many products in industries such as chemical, paint, plumbing, electroplating and tanneries. These heavy metals have adverse effects on both humans and plants and gets accumulated in the cells causing serious dysfunctions to the organs and metabolic processes, thus, effective removal of heavy metal ions from industrial wastes is of great significance (Kiomars Zargoosh et al., 2013).

Chromium is a major leather production pollutant and is entering our food chain and causing illnesses such as sinus cancers, abdominal pain and ulcers (Jaishankar, *et al.* ,2014). It is considered as one of the worst pollutants that which is hazardous to human and aquatic life (Shimin Zhou et al., 2014).

Many methods can be used for the removal of the heavy metals from industrial waste water but due to their numerous drawbacks, alternative methods are being researched on for a more environmental friendly and economic removal. Nanotechnology has great possible benefits to a variety of fields and can help improve the environment by much easier and effective solutions (M. Farahmandjou et al., 2015) Adsorption is considered as one of the most effective, efficient and economical method for the removal of contaminants from wastewater. Magnetic nanoparticles are now gaining a lot of attention due to their unique properties of high surface area-to-volume ratio, surface modifiability, exceptional magnetic properties, great biocompatibility, ease of separation using external magnetic field, reusability and relatively low cost (Nirmala Ilankoon, 2014).

For better and more refined magnetic nanoparticles coating is used as bare magnetic nanoparticles are prone to oxidation and tend to agglomerate which reduces their removal efficiency. To overcome these shortages, nanoparticles are coated resulting in a higher adsorption capacity (Shitong Yang et al., 2012).

2.2 Chromium Occurrence

Chromium is the 21st most abundant element in the Earth's crust and is used in many industrial activities (Saidur Rahman Chowdhury et al.,2010). Naturally occurring chromium exists due to the weathering of dissolved minerals and rocks which contain chromites and other chromium containing compounds present in the soil (Nriagu and Nieboer, 1988). Chromium exists in several oxidation states with trivalent and hexavalent being the most stable forms. Cr (VI) is more toxic than the trivalent form due to its high solubility and mobility. (Sandhya Mishra et al., 2015). On the other hand, Cr(III) is recognized as an essential trace metal in human nutrition. It is one of the major inorganic environmental pollutants, added in the environment through various natural and anthropogenic activities and harmful to not only the humans but also the environment. United States Environmental Protection Agency (USEPA) has strictly established an action level of 100 ppb for total chromium in drinking water. Exposure to high chromium concentrations in human beings can cause health problems such as respiratory illnesses, cancers such as sinus, skin rashes, and chronic liver disease (Shimin Zhou et al., 2014).

2.3 Sources of Chromium

2.3.1 Natural Sources
Chromium is an abundant metal in the earth and naturally occurs in coal, oil, soil, tobacco smoke, cement, topsoil and rocks, asbestos lining erosion and contaminated landfill sites. Chromium is primarily found in form of chromium (III) in nature. Leaching from topsoil and rocks is the most vital natural source of chromium entering into the water bodies. Furthermore, solid wastes from chromate-processing industries, due to improper disposal in landfill sites, can be sources of contamination for groundwater, where the chromium may accumulate for several years. (ATSDR, 2000).

2.3.2 Anthropogenic Sources

Chromium is widely used in textile industries, tanneries, wood preservation, chrome plating, dyes and pigments, steel alloys and glass industries. It is estimated that today more than 80% - 85% of leathers in the world are tanned by chrome tanning (*Nirmala Ilankoon et al., 2014).* Tanneries are considered to be a major source of pollution and their discharge in particular, is a potential environmental concern (Ros and Ganter et al., 1998). Chromium discharged from tannery effluents into the waters exceeds the worldwide standard limit of 0.5–15 mg/L. The National environmental quality standard of chromium is 1 mg/L and they seem to be increase these safe limits drastically due to increase in chromium pollution.

Around 600 leather tanneries are distributed all over the 4 provinces of Pakistan with majority being in the Punjab region (Saadia R. Tariq et al., 2005). Pakistan is considered as the major provider of leather finished products to the world market. Pakistan has the world's largest leather shoe manufacturing base (the eighth largest) (Hina Saeed et al., 2016). Sialkot itself has 250 tanning units producing more than 65,000 kg of leather per day (Uzaira Rafique et al., 2010).

The graph below shows concentrations of toxic metal discharge in Pakistan with chromium having the highest concentration in industrial effluent. Among which the main cities Lahore, Quetta, Peshawar and Multan show to be exceeding not only the National Environmental Quality standards but also the WHO limits. Tanneries, paint industries, textiles and metal plating are the major sources that contribute to this toxic metal.
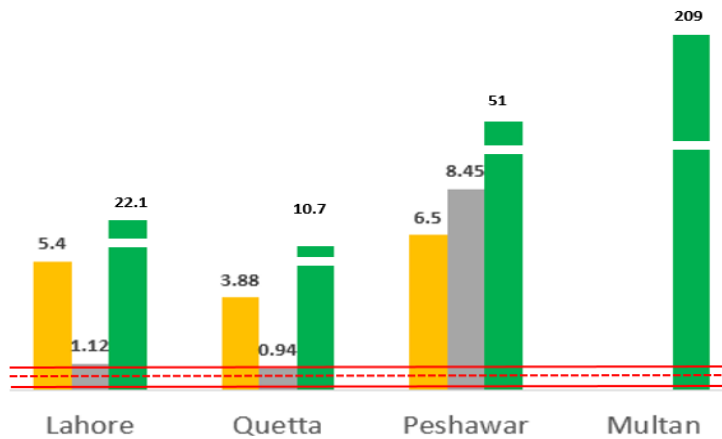
Graph.1 Heavy metals concentrations in various cities (Green for Cr)

Khattak , 2014
Hamid, *et al.* , 2016
Alam, *et al.* , 2008
Tariq, *et al. , 2010*

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2.4 Chromium Toxicity

2.4.1 Impacts of Chromium on Plants

Chromium toxicity mainly is caused by Cr(VI) rather than Cr(III) as it is mobile, high solubility and is readily adsorbed by the body. Since plants do not have a particular transport system for Cr, it is taken up with the help metal ions of sulfate or iron.

The adverse effects that this toxic heavy metal on plants include variation in the germination process, alters stem and leaf growth. Furthermore, it also inhibits processes such as photosynthesis, hydrolysis and respiration. The Cr ion directly disrupts the enzyme or other metabolites preventing the metabolic reactions to take place (Shanker AK et al., 2005).

2.4.2 Impacts on Human Health

Chromium as a pure metal has no toxic effect on the human body but it its hexavalent state it causes many adverse effects as hexavalent chromium is 500 times more toxic. The impacts include allergies on the skin, mucous membrane ulcerations, perforation of nasal septum, allergic asthmatic reactions, bronchial carcinomas, gastro-enteritis, hepatocellular deficiency and kidney oligo anuric deficiency (Francois Baruthio et al., 1991)

Respiratory illness:

When chromium is inhaled it causes an irritating effect in the respiratory tracts. Depending on the concentration of the heavy metal inhaled into the body it causes effects which include asthma, bronchitis, chronic rhinitis, congestion and hyperthermia.

Skin effects:

Chromium through dermal exposure cause allergies on the skin and it has known to produce dermatitis and irritation (Bruynzeel, Hennipman *et al.* 1988). Furthermore, it causes dryness, swelling, scaling, erythema and fissuring (MacKie 1981).

Carcinogenic effect:

Exposure to chromium compounds in many industries have been resulting in respiratory and sinus cancers. In addition to these there also has been studies show that it is known to cause lung

cancer [ATSDR 2000]. Chromium compounds are not only carcinogenic in humans but also show a potential threat of cancer in animals.

2.5 Removal Strategies

There are a number of process that have been used for the removal of heavy metals which include:

- **Ion exchange method:** This method is used method on a large scale for water treatment. This process attracts soluble ions from liquid phase to solid phase. This method is very cost effective and also work for low concentrations of heavy metals (Dizge et al., 2009). Cations and anions are separated by using an ion exchanger.

- **Membrane filtration:** Membrane filtration is being used widely for removing heavy metals from effluents. It also removes suspended particles, organic and inorganic pollutants. Membranes of various sizes are available depending upon desired results. Ultrafiltration membranes have removal efficiency of up to 90% (Rether et al., 2003).

- **Electrolysis:** This process uses electricity to separate metals from wastewater. Electricity is passed through the aqueous solution containing a cathode plate and an insoluble anode. Heavy metals are precipitated. Various methods include electro-flotation and electro-oxidation (Shim et al., 2014).

- **Adsorption:** This process is also widely used for heavy metals removal. This is the simplest method involving low-cost and non-toxic adsorbents. Some of them are activated carbon, alumina and magnetic nanoparticles. Many other adsorbents are being synthesized and functionalized with suitable functional groups (Anbia et al., 2014)

The reason we chose magnetic nanoparticles is because it outweighs all the cons of the methods mentioned. It's a more cost effective, environmental friendly and efficient method. The reason of its efficiency is because it has a high surface to volume ratio resulting in more number of active site, increasing adsorption. Iron oxide is widely used for the removal of heavy toxic metals as known to give removals of up to 90 -99 %. (M.A. Barakat et al.,2010)

Materials and Methodology

3.1 Materials

All reagents used for the synthesis of bare MNPs and HA coated MNPs were of analytical reagent grade and were utilized without further purging.

- Iron(III) Chloride Hexahydrate $FeCl_3.6H_2O$,
- Iron(II) Sulfate Heptahydrate $Fe_sO_4.7H_2O$,
- Ammonium hydroxide (25%),
- Sodium hydroxide,
- Ethanol,
- Humic acid,
- Potassium dichromate $K_2Cr_2O_7$,
- Sulphuric acid H_2SO_4,
- Phosphoric acid H_3PO_4,
- Sodium hydroxide NaOH,
- Diphenylcarbazide,
- Acetone and
- Distilled water was used for all the processes.

3.2 Methodology

3.2.1 Preparation of Stock and Standard Chromium Solution
100 mg/L of Cr(VI) stock solution was prepared by the adding 283 mg of oven dried potassium dichromate in 1000 mL of distilled water. For performing experiments, stock solution of Cr(VI) was serially diluted into different standard solutions (Fig 1).

3.2.2 Spectrophotometric Detection of Chromium

In order to estimate the quantity of Chromium (VI) we have used a UV/Vis spectrophotometer which measured the absorbance at the wavelength of maximum absorbance which in this case was 540 nm. The model used was Hach DR 2400. The spectrophotometric detection was carried out by using DPC method (Standard Methods, 3500-Cr), which will be described in the following section.

3.2.2.1 Working principle of Spectrophotometer

Spectrophotometry is used during the quantitative analysis of organic and inorganic compounds. The molecules are exposed to UV-light, which they absorb. Due to this, electrons become excited, and then move to higher energy orbitals. The spectrophotometer measures the light which is transmitted, known as transmittance. The absorbance is a result of measuring the difference between the light transmitted before and after the sample's exposure to UV light (Thomas and Burgess, 2007).

3.2.2.2 DPC (Standard Methods, 3500-Cr) Method

1,5-Diphenylcarbazide (DPC) (Standard Methods, 3500-Cr) method was used for the determination of chromium in the solution. The DPC solution was prepared by adding 250 mg of 1,5-Diphenylcarbazide in 50 mL of acetone. This method measures only Cr(VI). Cr(VI) combines with 1,5-Diphenylcarbazide in strong acidic solution to give pink-violet complex. To determine total Cr(VI), sample is digested with sulphuric acid mixture.

Figure 1 Serial dilutions

3.2.3 Chromium Calibration Curve

For Cr(VI) curve the stock solution was serially diluted from 0.1 – 1.2 mg/L. pH was maintained at 2.0±0.5 by using 0.2 M sulphuric acid. Lastly, 2.0 ml of DPC was added into each of the serially diluted solutions and the solutions were allowed to stand for 10 mins for color development. The absorbance was measured using UV-Vis spectrophotometer at 540 nm. A graph was plotted between the absorbance and concentrations which followed Beer-Lambert law i.e graph was linear.

Figure 2 Spectrophotometer Hach DR 2400

3.2.4 Synthesis of Bare and Humic Acid Coated MNPs

Chemical co-precipitation was used for the synthesis of bare and HA coated MNPs. This method creates a "blended" precipitate including at least two insoluble species that were simultaneously removed from the solution. Inorganic salts were dissolved in water to form a homogeneous solution. pH was adjusted by adding a suitable base. After precipitation, the precipitates were separated from the solution. Extra salts were removed by washing the precipitates several times. After washing the precipitates were oven dried followed by calcination for phase development. Detailed procedure for the synthesis has been described as follows:

- **Stirring:** 6.1g of FeCl$_3$.6H$_2$O and 4.2g of Fe$_5$O$_4$.7H$_2$O were stirred using a magnetic stirrer in 100ml of distilled water at 500-600 rpm. This process was carried out till the formation of a clear solution.

- **Heating:** The solution was then stirred at 500-600 rpm and heated up to 90°C for 30 minutes.

- **Alkali addition:** After heating the solution up to 90°C, 20ml of ammonium hydroxide was added at the rate of 1mL/min in the solution for the precipitate formation. Just after the addition of ammonia solution, the solution turned from reddish brown to black. During the whole process, continuous stirring was ensured. After alkali addition, the solution was again heated to 90°C along with stirring for 30 mins.

- **Settling:** The solution was then cooled and precipitates were allowed to settle at room temperature. The black precipitates formed were settled at the bottom of the flask forming sediment, separating from a clear solution. After that the clear solution was decanted off carefully.

- **Washing:** The black precipitates were washed with distilled water for 3 - 4 times to neutral the pH by removing extra salts. Lastly there are washed with ethanol 1 – 2 times. This process usually takes 1-2 days because proper settling of precipitates takes time. Otherwise, precipitates will be wasted with the decanted water.

- **Evaporation:** After washing, precipitates were heated at 105°C for the evaporation of water present. After evaporation, the dry precipitates were calcinated in muffle furnace for phase development at 500°C for 4 h.

- **Crushing:** After calcination, the precipitates were crushed by using pestle and mortar to a fine black powder. Crushing is very important in producing nano sized MNPs.

- **For HA coated MNPs**: The only difference was the addition of humic acid solution along with ammonium hydroxide. Humic acid solution was prepared by adding 0.5g of humic acid sodium salt in 50ml of distilled water (Liu et al., 2008). Rest of the method remained same.

Fig. 3 (a) Clear solution of two salts

Fig. 3 (b) Heating and stirring

Fig. 3 (c) Alkali addition
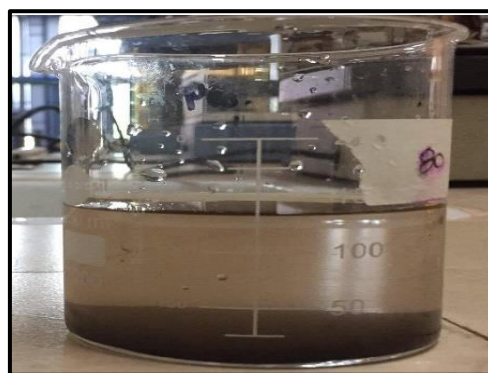
Fig. 3 (d) Washing and Settling

Fig. 3 (e) Crushing

Fig. 3 (f) MNPs

Figure 3 Synthesis of MNPs

3.3 Chromium Adsorption Studies

The bearing of the nanoparticles as Cr(VI) adsorbents was evaluated by batch adsorption tests. Optimized dose of bare Fe_3O_4 and HA-Fe_3O_4 was added into 50mL of solution containing desired amount of Cr(VI). pH was adjusted to 4-5 by using phosphoric acid and sodium hydroxide, followed by shaking in an orbital shaker for 10 mins and 30 mins at 200 rpms for bare Fe_3O_4 and HA-Fe_3O_4, respectively. After shaking, MNPs with adsorbed Cr(VI) were separated from the mixture with the help of a permanent hand-held magnet. After MNPs separation, the solution was again filtered by using Whatman filter paper to remove the remaining MNPs from the solution. 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 described above. Following formula was used to calculate the percentage removal.

$$\% \, removal = (Co - Ct)/Co \, \times 100$$

Where

Co = Initial Cr concentration

Ct = Residual Cr concentration

3.3.1 Working Range of Parameters
Working range of various parameters is described as follows:

i.   **Dose:** For optimization of dose, experiments were conducted on Cr(VI) concentrations of 5, 10 and 20 ppm. Initially dose was varied from 0-10 mg/L for both bare and HA coated MNPs.

ii. **pH:** pH was varied from 2 – 9 for both bare and HA coated MNPs.

iii. **Initial concentration:** Effect of initial concentration on Cr(VI) adsorption was investigated from 0-120 ppm for both bare and HA coated MNPs.

iv. **Separate the time and temp**

v. **Range of time and temperature:** Effect of time was investigated from 0-160 mins at room temperature, 25°C and 35°C. Same time and temperature were set for both bare and HA coated MNPs.

3.3.2 Isotherm Models

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.

3.3.2.1 Langmuir Isotherm

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.

Its equation is:

$$Ce/qe = 1/Qm \; b \; Ce + 1/Qm$$

Where C_e is the equilibrium concentration of solution (mg/L), Q_m is the adsorption capacity of monolayer, b is the Langmuir constant (L/mg) which is related to the affinity of binding sites (Dang et al., 2017)

3.3.2.2 Freundlich Isotherm

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. Its equation is given below:

$$Q_e = k_f \; Ce \; _{1/n}$$

Where K_f is the amount of solute adsorbed on the adsorbent surface, n is the deviation from linearity of the adsorption (K.S et al., 2015).

3.3.3 Isokinetic Studies

Kinetic studies provide valuable information about the mechanism of adsorption. In the batch processes, it investigates the controlling mechanism of the adsorption process as either mass transfer or chemical reaction to obtain the optimum operating conditions. ((Dang et al., 2017)

3.3.3.1 Pseudo 1st Order

Pseudo 1st order equation is given below

$$q = q_e(1-exp^{-k_1 t})$$

where q is the amount adsorbed at time t, q_e is the amount adsorbed at equilibrium and k_1 is first-order reaction rate constant (min^{-1}) (Dang et al., 2017)

3.3.3.2 Pseudo 2nd Order

Pseudo 2nd order equation is given below

$$q = k_2 q_e^2 t/(1+K_2 q_e t)$$

where q is the amount adsorbed at time t, q_e is the amount adsorbed at equilibrium and k_2 is the second-order reaction rate constant ($gmg^{-1} min^{-1}$) (K.S et al., 2015).

3.3.4 Characterization of Synthesized MNPs

For characterization of synthesized MNPs, following techniques were used:

- **X-ray Powder Diffraction (XRD) Analysis:** XRD analysis was done in order to determine the phase and crystalline structure of MNPs. The XRD patterns of MNPs were recorded using CuKα (1.5406 Å) radiation at room temperature. Sample were taken in the range of 10º to 90º in the 2θ scale. Step time was 0.4 sec (Lopez et al., 2009). X-rays are generated and made fall onto the sample. Sample is rotated at different angles. Rays having enough energy penetrate into the sample and diffraction spectrum is formed.

Figure 4 X-ray Diffraction

- **Scanning Electron Microscopy(SEM) Analysis:** SEM analysis was done to determine the size and surface morphology of MNPs. A high energy of electrons is focused on the solid sample. The interaction of rays with the sample gives the information about surface morphology, chemical composition and arrangement of materials, sample is made up of.

Figure 5 Scanning Electron Microscope

- **Fourier Transform Infrared Spectroscopy (FTIR) Analysis:** FTIR analysis was done to identify different functional groups due to coating on MNPs. Basic principle of FTIR is the

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absorbance of light by molecules in the infrared region. The absorbance corresponds to various bonds on the sample.

Figure 6 FTIR

Results and Discussion

4.1 Characterization of Synthesized Bare and HA Coated MNPs

4.1.1 X-ray Powder Diffraction (XRD) Analysis

The crystalline structure of both bare and HA coated magnetic nanoparticles was characterized by X-ray diffraction using Cu Kα (λ = 1.54 Aᵒ) radiation and the size of crystallite was calculated by using Scherrer's formula. The results are shown in graph 2 which can be indexed as primitive cubic system for by comparison with data from cubic Fe_3O_4 (JCPDS no. 894319) (Song et al., 2013). The diffraction peaks at 2θ= 35.45ᵒ, 63ᵒ correspond to (3 1 1) and (4 4 0) respectively. Absence of impurity peaks indicates that the product is pure. According to Scherrer's equation, the average size of MNPs came out to be 32-45 nm.
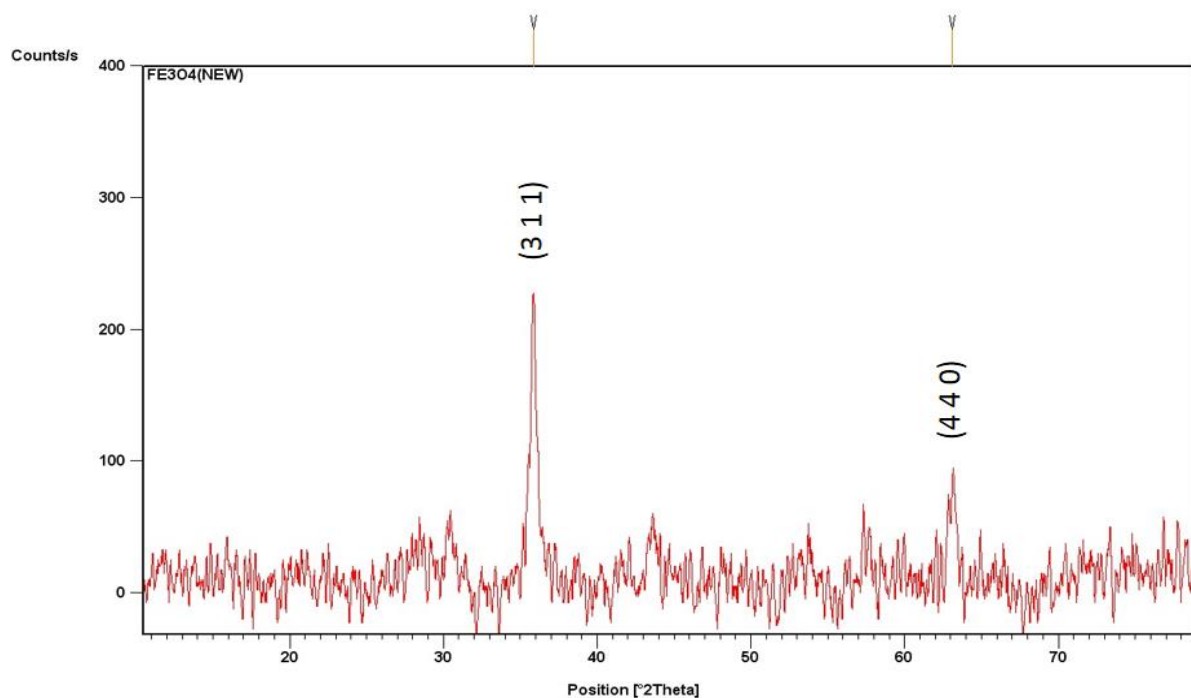
Graph 2 XRD analysis of MNPs

4.1.2 Scanning Electron Microscopy(SEM) Analysis

Surface morphology and size were confirmed by SEM. The results of analysis are shown in the figure 7(a) show the spherical structure of MNPs. However, the magnified figure 7(b) indicates the agglomeration of MNPs because of their strong magnetic nature. Moreover, size of MNPs

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from SEM analysis came out to be 28-40 nm which coordinates with our results from Scherrer's equation.
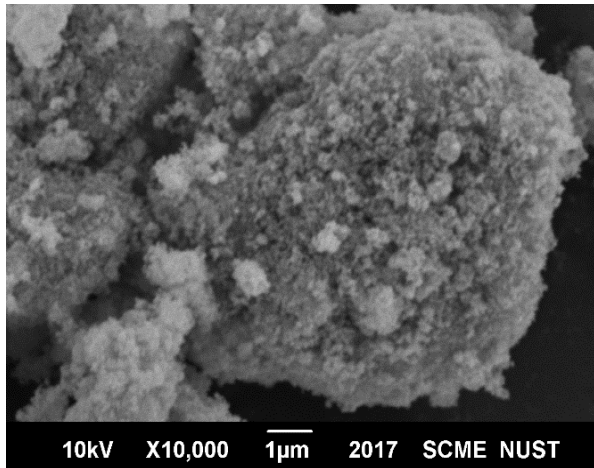
Figure 7(a) Showing SEM analysis results
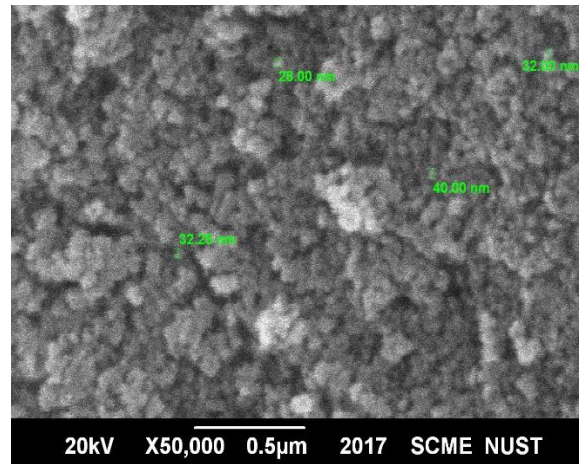
Figure 7(b) Showing SEM analysis results under high power lens

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis of the sample shows the successful coating of HA on the Fe_3O surface. The FTIR spectra shows both bare and coated HA coated MNPs centered at 563 cm^{-1} which indicates the stretching vibration of Fe-O bond. FTIR spectrum shows the successful coating of HA on the surface of MNPs at 1410 cm^{-1}, which indicates that the carboxylates anion interaction with FeO as the C=O stretches (Koesnarpadi et al., 2015).
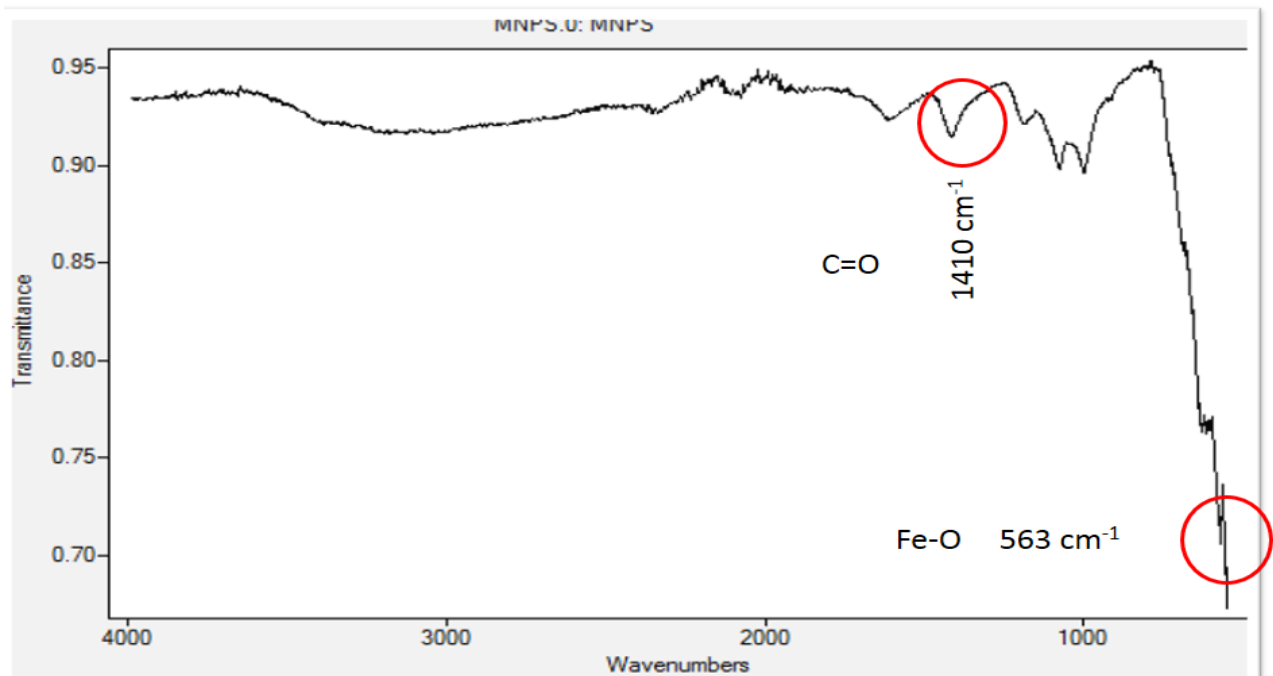
Graph 3 FTIR analysis results

4.2 Optimization of different Parameters

Results of optimization of parameters including dose of MNPs, contact time, pH, temperature and initial concentration are as follows:

4.2.1 Effect of Dose

For optimization of dose, experiments were conducted on Cr concentrations of 5, 10 and 20 ppm. Initially dose was varied from 0-10 mg/L for both bare and HA coated MNPs. Experiments on both type of MNPs were performed at room temperature and shaking was done for 30 mins. Graph 4(a) and 4(b) show the final concentration after removal by using bare and HA coated MNPs, respectively. Results of removal for both MNPs were almost similar. At MNPs dose of 300 mg/50 mL, 95% and 93% removal of Cr was observed at 10 ppm initial chromium concentration for bare and HA coated MNPs, respectively. However, maximum removal was observed at 500 mg/50 mL but 300 mg/50 mL was taken for later experiments because at this dose, remaining concentration of Chromium (VI) was well below NEQs limits. Moreover, similar work done by others show the same removal at 6g/L (K.S et al., 2015). Graphs show that the removal after 300 mg/50 mL did

not increase significantly. This attributed to the fact that lower adsorbent dosage has higher number of active sites. By increasing the adsorbent dosage aggregation of MNPs take place which reduces the adsorption efficiency of Cr(VI) (K.S et al., 2015).
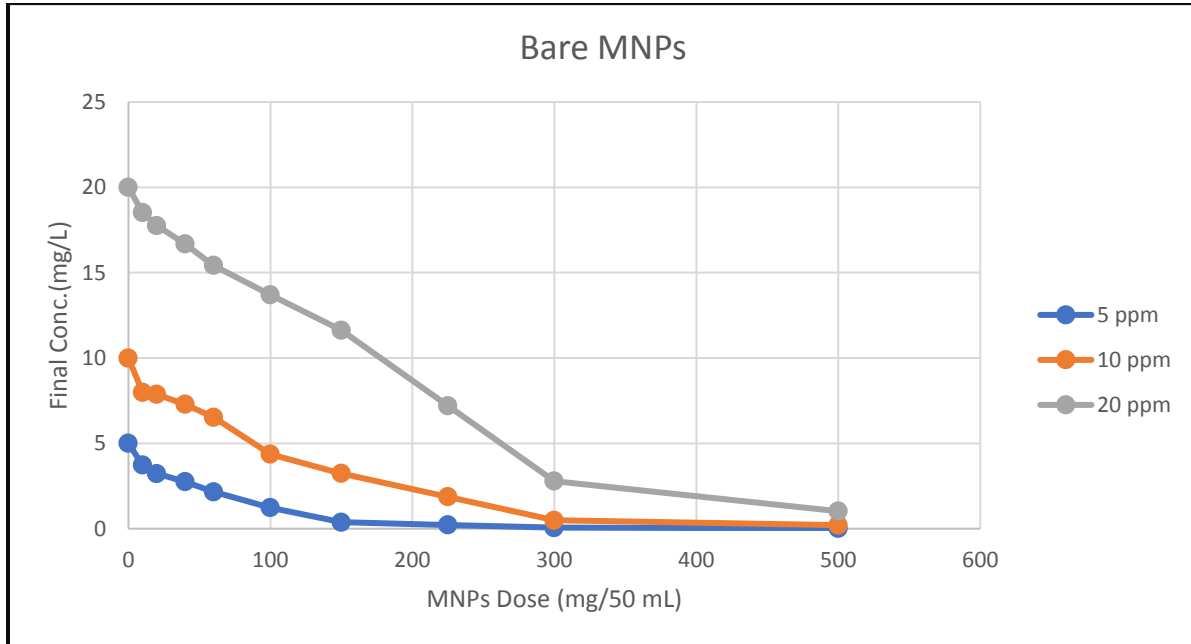
Graph 4 (a) Removal by using Bare MNPs
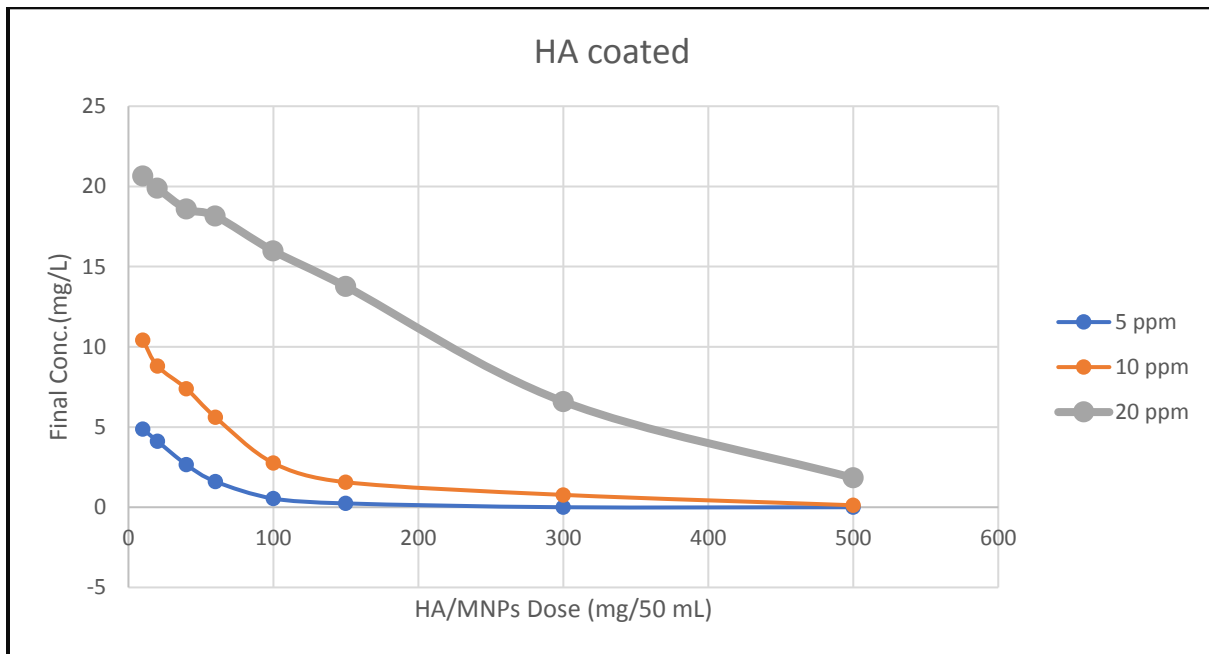
Graph 4 (b) Removal by using HA coated MNPs

4.2.2 Effect of pH

The effect of solution pH on the adsorption of chromium by using bare and HA coated MNPs is shown in the graph 5. Graph shows the increase in removal of chromium from pH 2-4 and then removal decreases after pH 4. Effect of pH on chromium removal in the solution depends on the surface chemistry. Metal oxides usually have their surfaces covered with hydroxyl groups. The surface charge is zero at zero point of charge pH_{pzc}, which is 6.5 for magnetite (K.S et al., 2015). The surface of MNPs is positively charged below pH_{pzc} which favors anion adsorption by electrostatic attraction. Above the pH_{pzc}, the surface is negatively charged which favors cation adsorption. Cr(VI) exists as chromates (CrO_4^{2-}). With the increase in pH($pH>pH_{pzc}$), the repulsion between negatively charged Cr(VI) species and OH^- increases which results in decreased Cr(VI) adsorption.
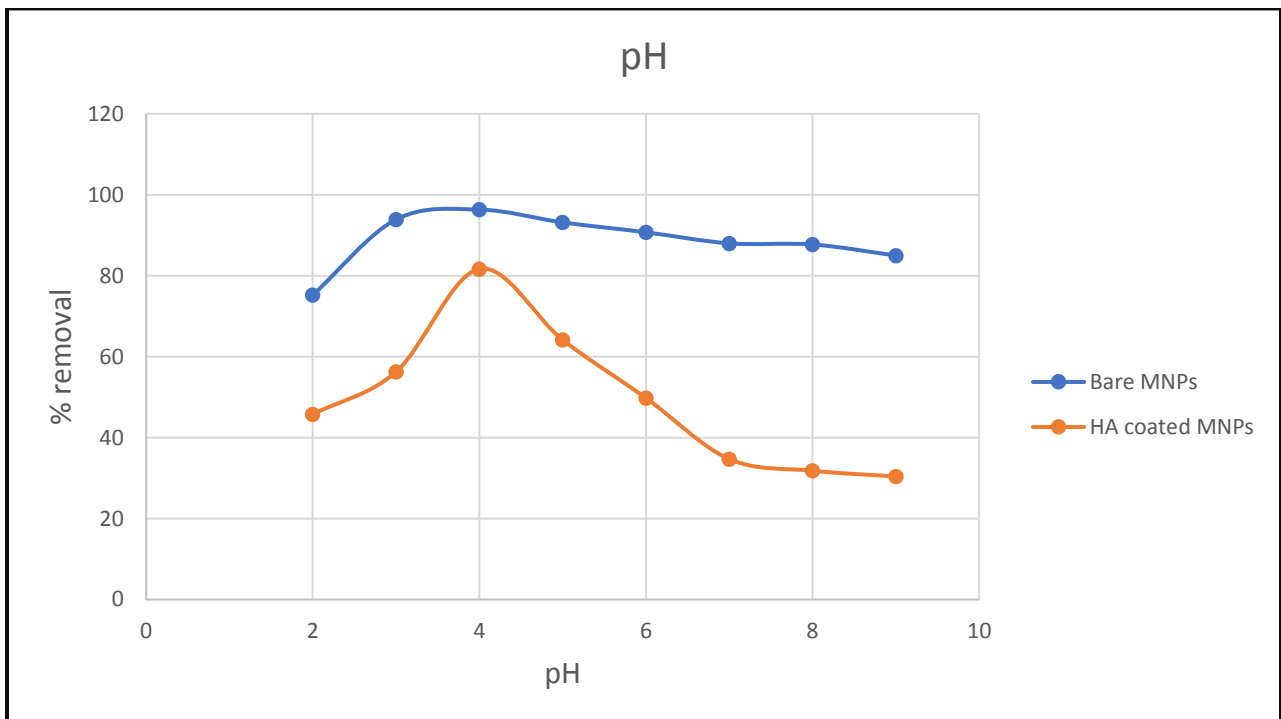
Graph 5 Effect of pH by using MNPs

4.2.3 Effect of Initial Concentration

Effect of initial concentration on Cr(VI) was investigated from 0-120 ppm for both bare and HA coated MNPs. All other parameters were kept constant. Cr(VI) removal did not increase significantly after 40 ppm. This can be explained from the fact that the maximum adsorption has reached at its maximum value. All of the active sites have been occupied by Cr(VI) and adsorption will not increase further. Graph shows the Adsorption capacities came out to be 5.12 and 4.9 mg/g for bare and HA coated MNPs, respectively as shown in the graph 6.
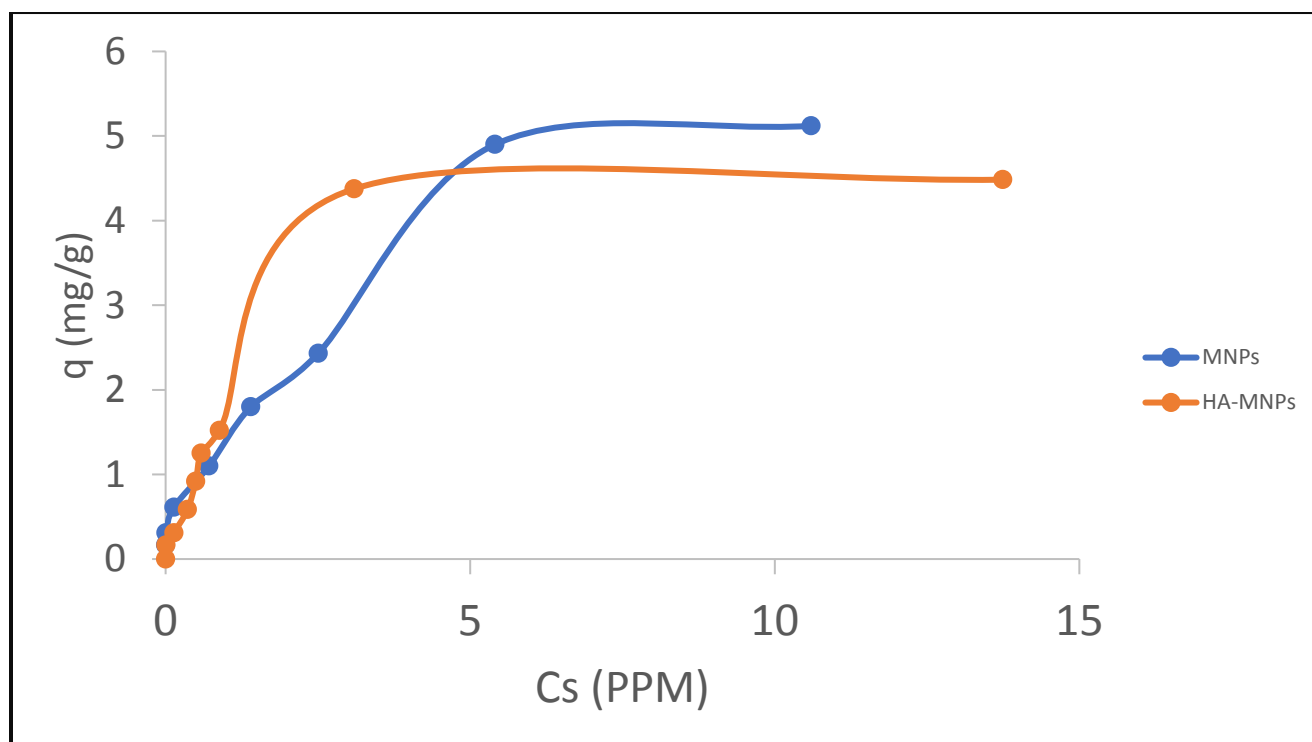
Graph 6 Adsorption capacities of synthesized MNPs

4.2.4 Effect of Time and Temperature

Effect of time was investigated from 0-160 mins at room temperature, 25°C and 35°C. On the experiment day, there was not a significant difference between room temperature and 25°C, so the results were almost same. Graph 7(a) shows the results of removal by using bare MNPs. Removal efficiency of Cr(VI) went up to 88% and 93% at 25°C and 35°C, respectively. Graph 7(b) shows the results of removal by using HA coated MNPs. Removal efficiency of Cr(VI) went up to

92% and 95% at 25°C and 35°C, respectively. Graphs also show that the maximum removal was achieved at 10 and 30 mins for bare and HA coated MNPs, respectively.
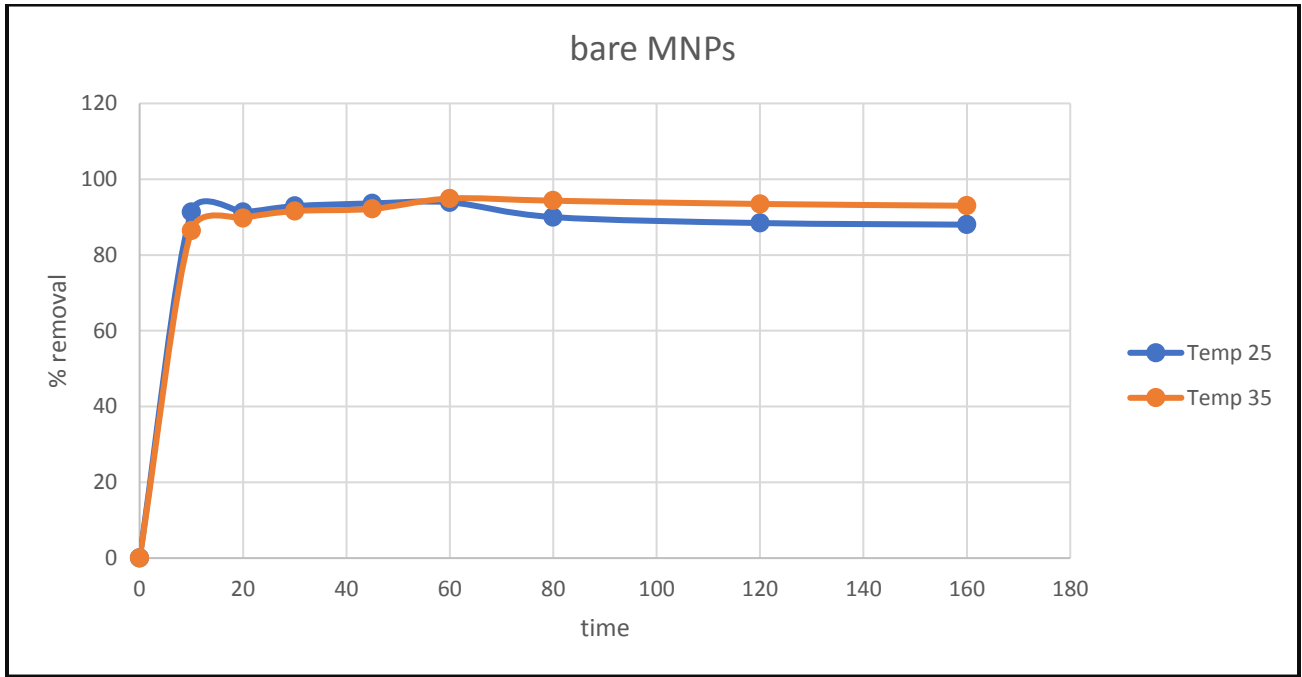
Graph 7(a) Effect of contact time by using bare MNPs
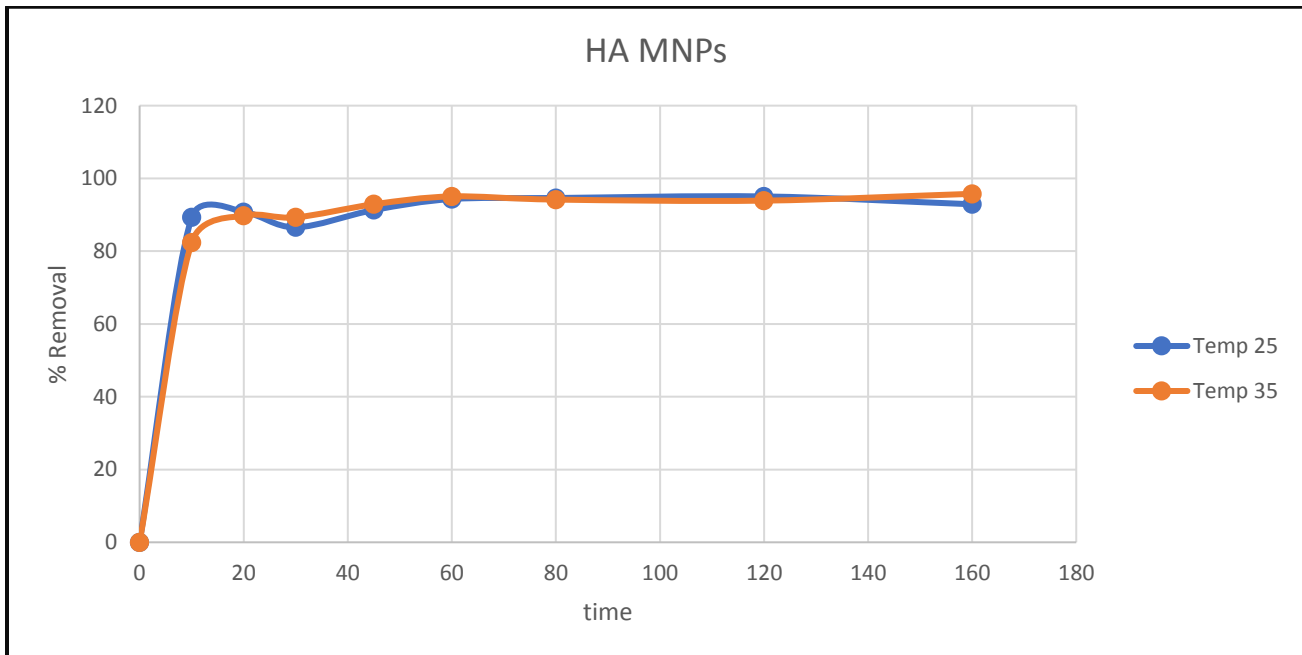
Graph 7(b) Effect of contact time by using HA coated MNPs

4.3 Isotherm Models

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 most commonly used.

4.3.1 Lamgmuir Isotherm

Langmuir Isotherm anticipates the relationship between change in adsorption and equilibrium concentration. The Langmuir Isotherm assumes the monolayer adsorption on the homogenous surface meaning no interaction between adsorbed molecules and majority of the sites have been captured by the adsorbate.

The adsorption capacities came out to be 5.84 and 4.38 mg/g for bare and HA coated MNPs, respectively. These values are in accordance with work done by others (Wenjun et al., 2013). The values of constants obtained from trendlines are summarized in the table 4.1.

Table 4.1: Langmuir isotherm constants values

Langmuir Isotherm parameters	Bare MNPs	HA coated MNPs
Qe (mg/g)	6.101000183	4.376803705
b (L/mg)	2.305477288	1.7284594
R^2	0.9935	0.9982

R_L values indicate the favorability of adsorption isotherm. Our R_L values came out between 0-1 indicating favorable adsorption (Padmesh et al., 2007). It can also be seen from the graphs given below, Langmuir Isotherm effectively describes the adsorption data with $R^2 > 0.99$ for both bare and HA coated MNPs.
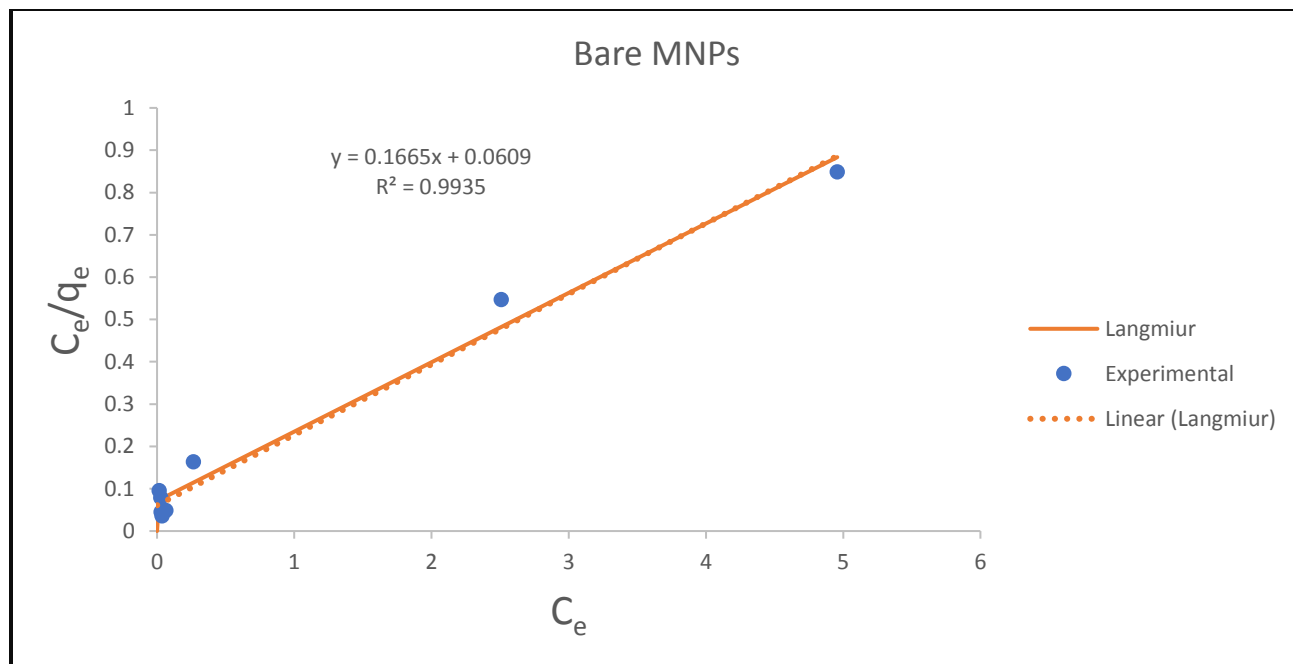
Graph 8(a) Langmuir Isotherm (bare MNPs)
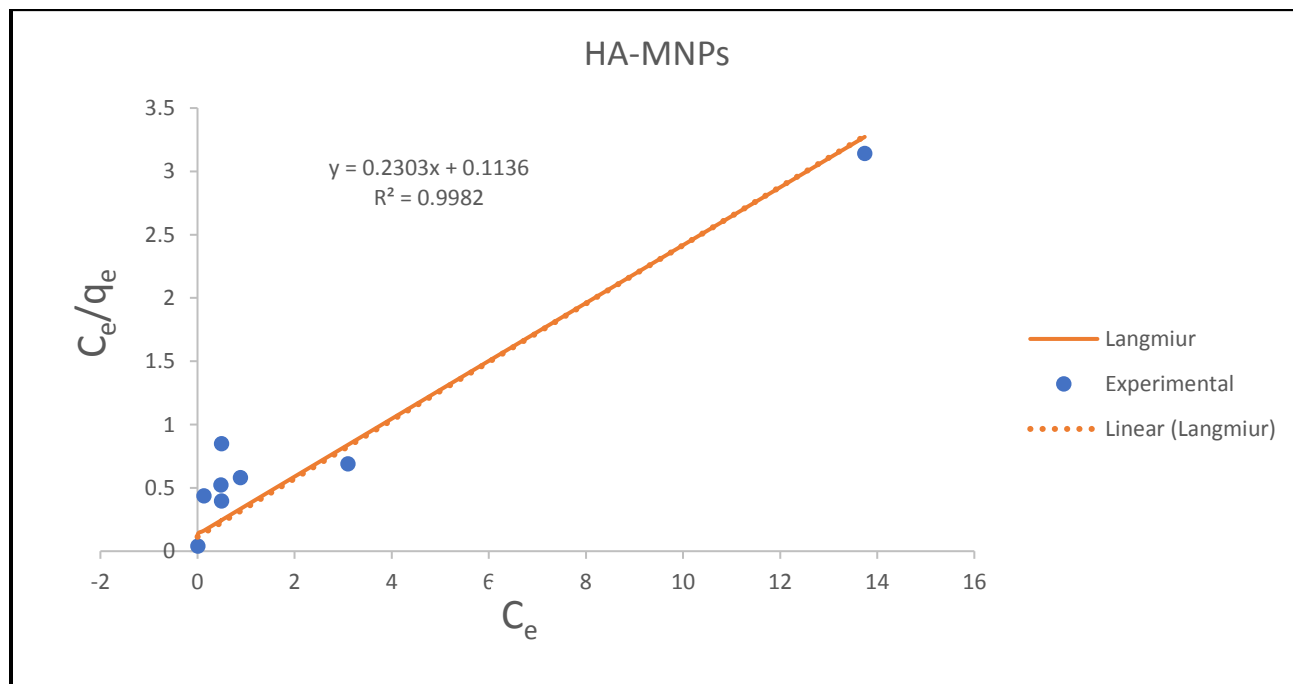
Graph 8(b) Langmuir Isotherm (HA coated MNPs)

4.3.2 Freundlich Isotherm

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.

Table 4.2: Freundlich isotherm constants values

Freundlich Isotherm parameters	Bare MNPs	HA coated MNPs
N	1.960017249	1.935070781
K_f	3.069905756	1.56404313
R^2	1	1

K_f values for bare MNPs are higher as compared to HA coated MNPs. It can be seen from the graphs given below that Freundlich Isotherm more effectively describes the adsorption data with R^2 values equal to unity for both bare and HA coated MNPs.
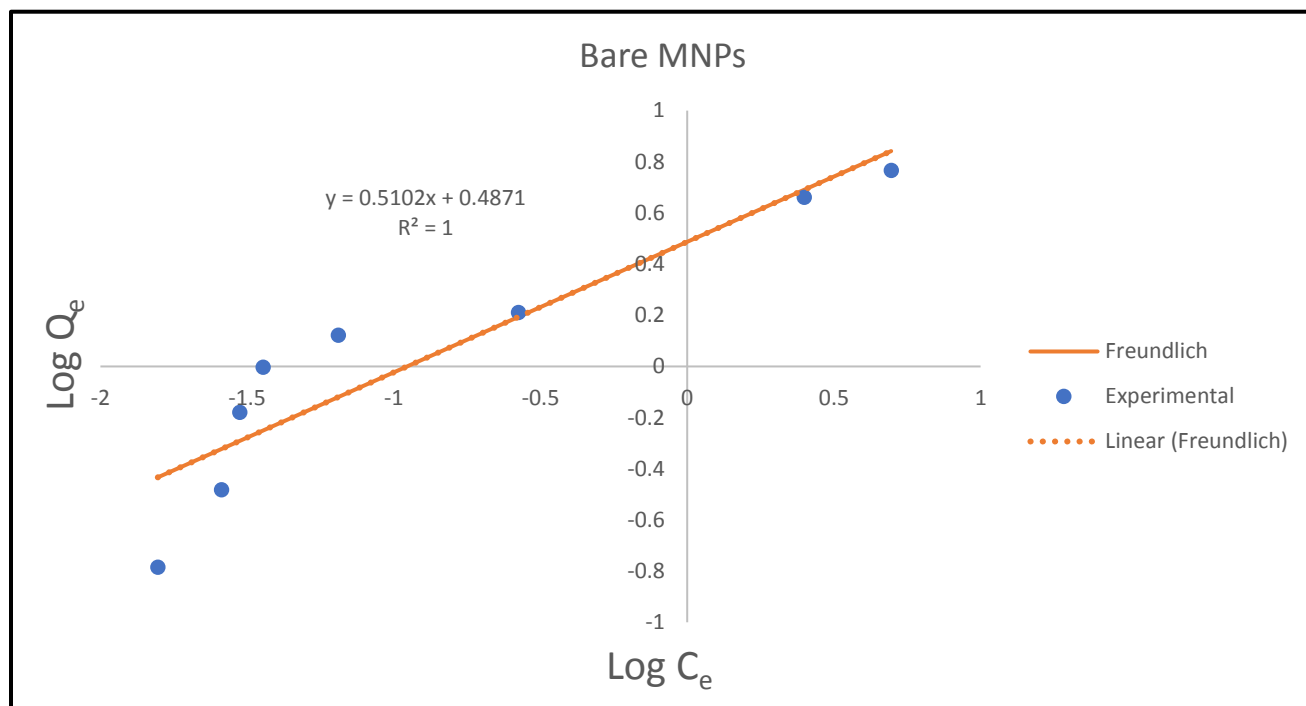
Graph 9(a) Freundlich Isotherm (Bare MNPs)
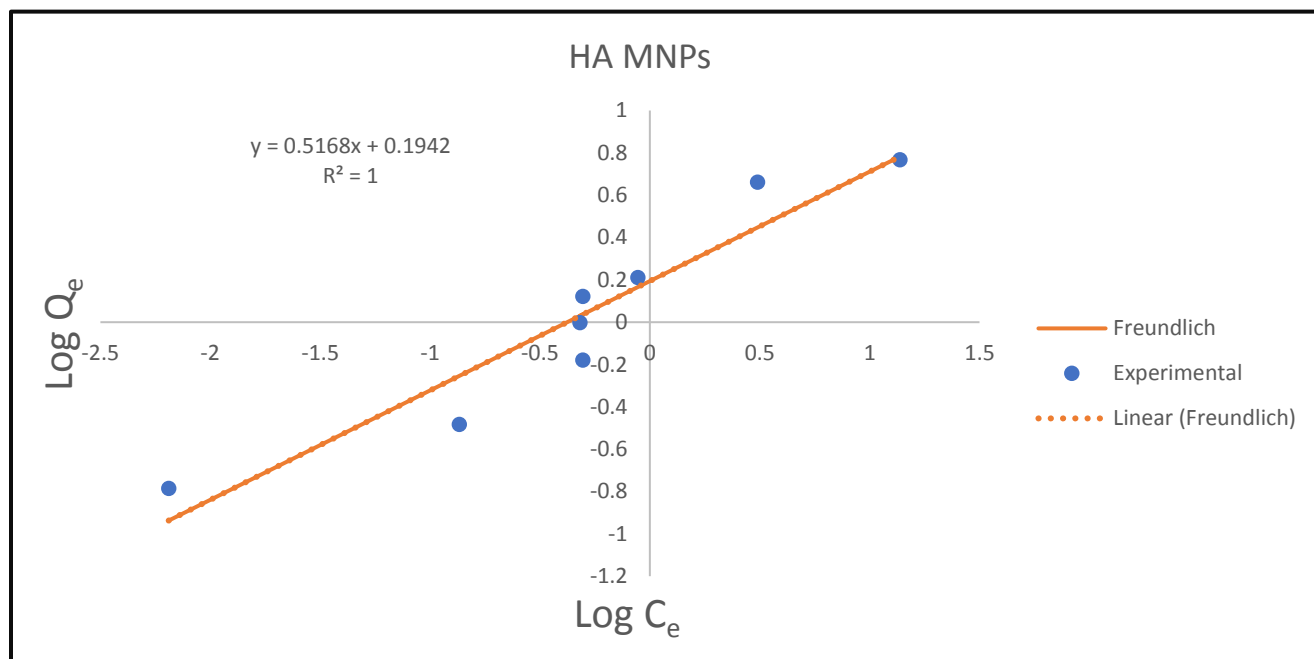
Graph 9(b) Freundlich Isotherm (HA coated MNPs)

Conclusion from the isotherms:

It can be seen that initial steep slope of Langmuir isotherms indicates the high values of b which show high affinity of Cr(VI) for synthesized MNPs. It can also be seen 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 (Padmesh et al., 2007).

However, it can be seen from above results that the Freundlich isotherm fits more to the adsorption data which is in accordance to other studies. Therefore, following conclusions were made from adsorption isotherms:

- Freundlich isotherm effectively describes the adsorption data as compared to Langmuir isotherm.
- Freundlich isotherm indicates adsorption on a heterogenous surface.

4.4 Kinetic Studies

Results obtained in the batch experiments were then used to investigate the kinetics of Cr(VI) adsorption on synthesized MNPs.

4.4.1 Pseudo 1st Order

The pseudo 1st order kinetic model for Cr(VI) adsorption on MNPs have been depicted in graphs 10(a) and 10(b). These graphs are showing the adsorption data at 25°C and 35°C for bare and HA coated MNPs, respectively.

Graph 10(a) Pseudo 1st Order (Bare MNPs)
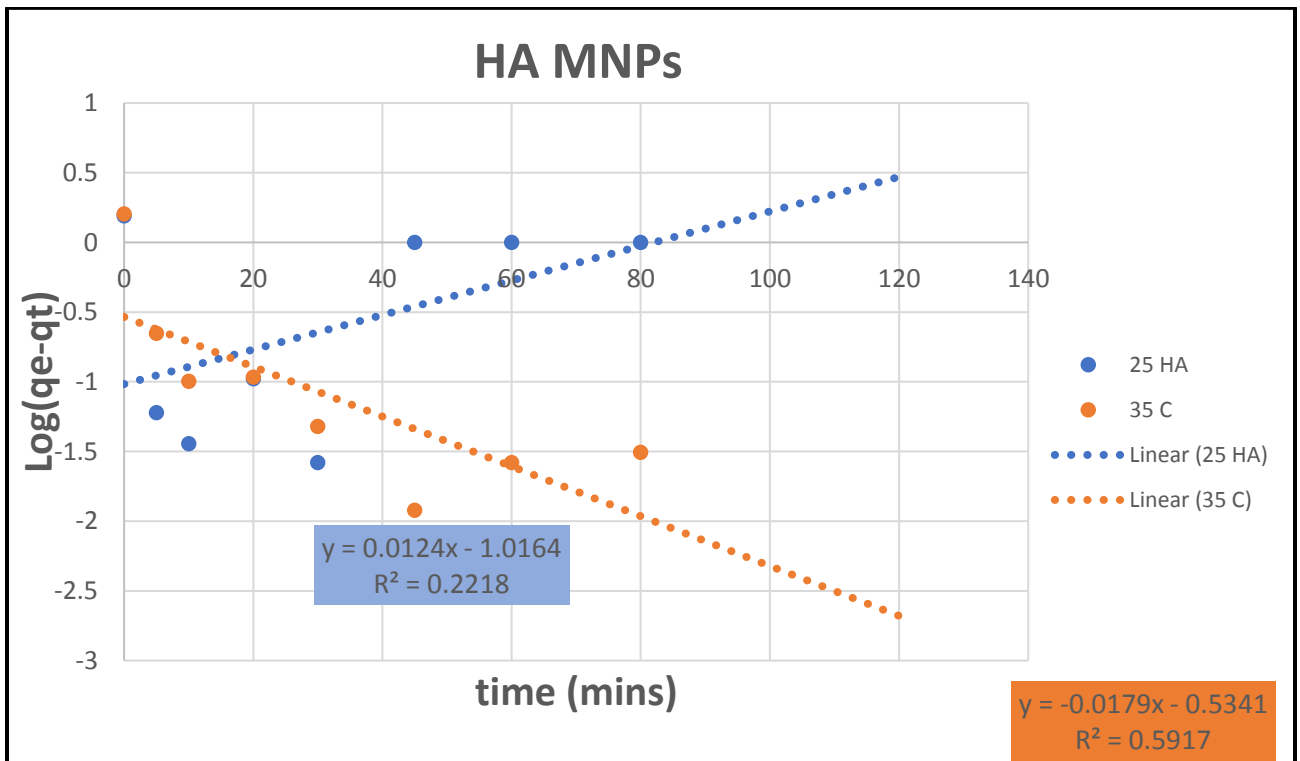
Graph 10(b) Pseudo 1st Order (HA coated MNPs)

All the parameters and constants obtained from trendline analysis are summarized in table 3. This table shows the higher k_1 values for bare MNPs at 25°C and 35°C as compared to HA coated MNPs. Moreover, results show that Q_e the higher values of HA coated MNPs.

Table 4.3: Pseudo 1st order constants values

Pseudo 1st order parameters	Bare MNPs		HA coated MNPs	
	25°C	35°C	25°C	35°C
K_1 (min^{-1})	0.0513569	0.0492842	-0.0285572	0.0412237
Q_e (mg/g)	0.18188631	2.51883662	10.38484455	3.420581953
R^2	0.6872	0.899	0.2218	0.5917

4.4.2 Pseudo 2nd Order

The pseudo 2nd order kinetic model for Cr(VI) adsorption on MNPs have been depicted in graphs 11(a) and 11(b). These graphs are showing the adsorption data at 25°C and 35°C for bare and HA coated MNPs, respectively.
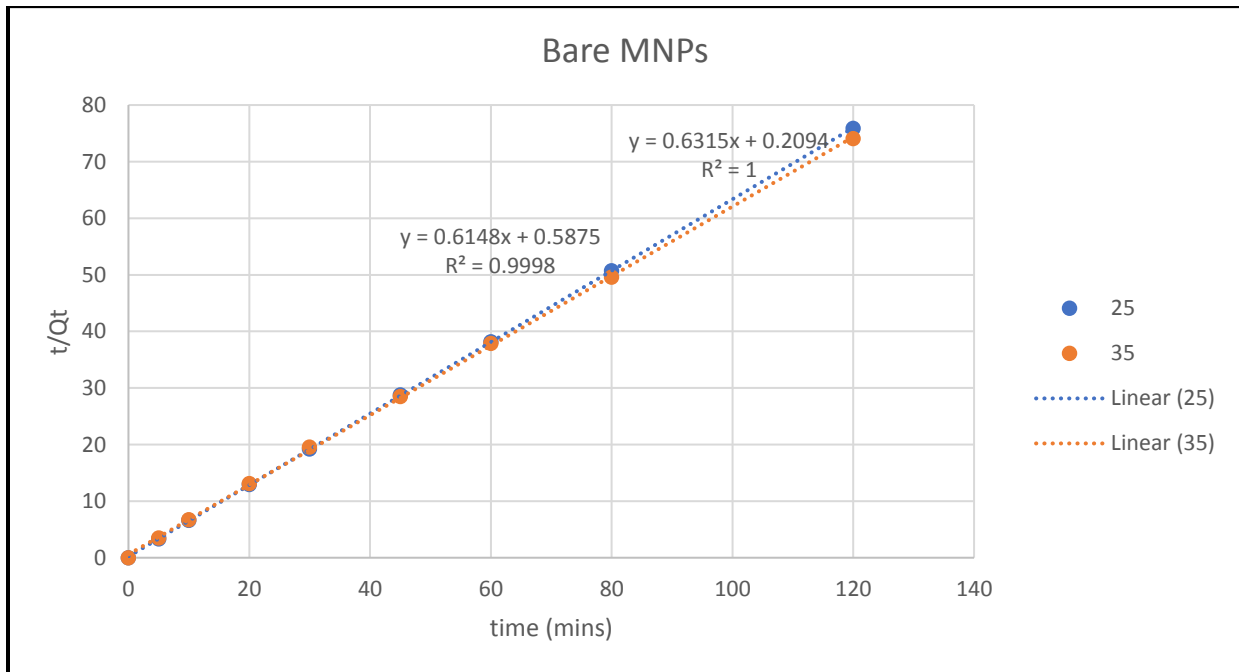
Graph 11(a) Pseudo 2nd Order (Bare MNPs)
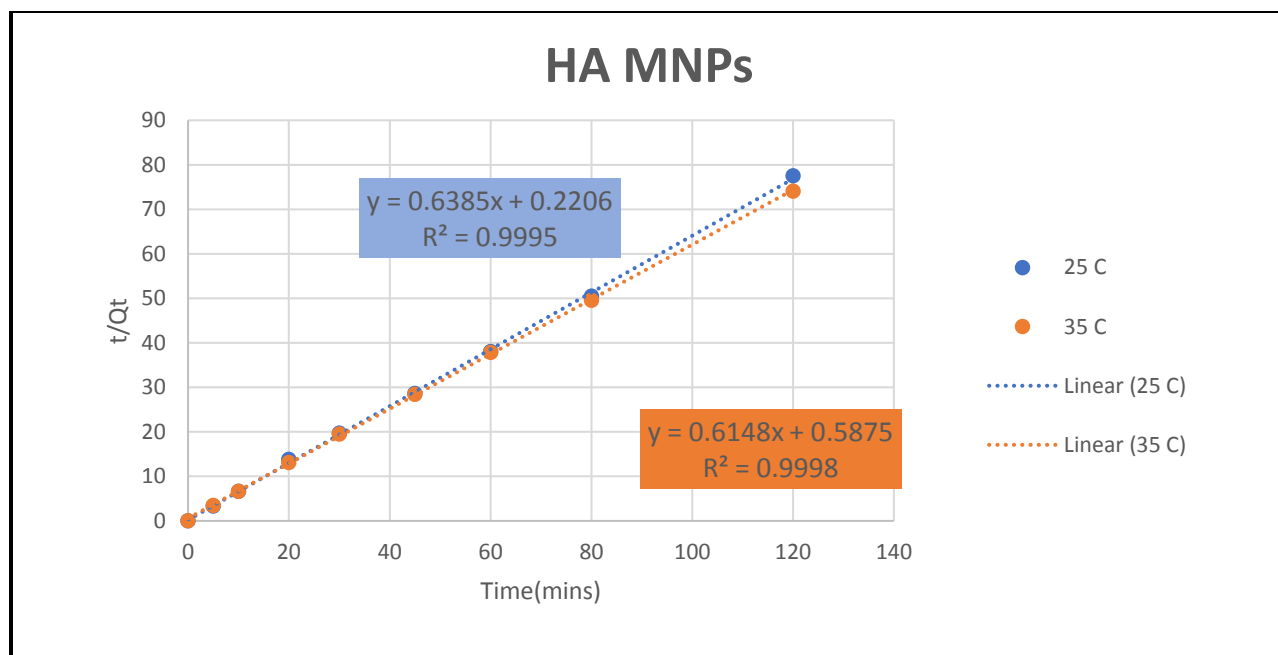
Graph 11(b) Pseudo 2nd Order (HA coated MNPs)

All the parameters and constants obtained from the trendline analysis are summarized in the table. These values show higher values of K_2 for bare MNPs at 25°C and 35°C as compared to HA coated MNPs. However, Q_e values are almost same for both bare and HA coated MNPs.

Table 4.4: Pseudo 2nd order constants values

Pseudo 2nd order parameters	Bare MNPs		HA coated MNPs	
	25°C	35°C	25°C	35°C
K_2 (mg^{-1} g min^{-1})	1.9044520	0.64304022	1.84806097	0.64336858
Q_e (mg/g)	1.58353128	1.62654522	1.566170713	1.62654522
R^2	0.9998	1	0.9995	0.9998

Conclusion:

Comparison of R^2 values of pseudo 1st and 2nd order reactions indicates that pseudo 2nd order fits better to the adsorption data. So, on the basis of analysis following conclusions are made:

- Pseudo 2nd order reaction describes experimental data more effectively.
- Pseudo 2nd order indicates chemisorption.

Conclusions and Recommendations

5.1 Conclusions

Bare and HA coated MNPs were successfully synthesized. They have very high affinity for Cr(VI) which makes them suitable for Cr(VI) removal. Following are the conclusions from our research work:

- Higher removal by using both MNPs was observed in the acidic range.
- Moreover, XRD, SEM and FTIR analysis showed successful synthesis and coating of MNPs.
- Optimized dose for both bare and HA coated MNPs is 300 mg/50 mL.
- Adsorption capacity came out to be 5.12 and 4.9 mg/g for bare and HA coated MNPs, respectively.
- Langmuir isotherm and Pseudo 2nd order fit better to the experimental data.

So, according to our research bare magnetic nanoparticles are better as compared to HA coated magnetic nanoparticles because they require lesser time to remove the same amount of Cr(VI).

5.2 Recommendations

Following recommendations are made:

1. MNPs can also be used for the removal of other heavy metals.
2. They can be used during membrane fabrication.
3. They can also be used in groundwater remediation.

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Appendices

Appendix-A

Batch experiments by using bare MNPs

1.1 Dose

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	% Removal (5 ppm)	% Removal (10 ppm)	% Removal (20 ppm)
5 ppm	50	0	0	0	0
5 ppm	50	10	25.43103448	20.04310345	7.417385057
5 ppm	50	20	35.48850575	21.3362069	11.18893678
5 ppm	50	40	44.97126437	27.08333333	16.57686782
5 ppm	50	60	56.75287356	34.69827586	22.86278736
5 ppm	50	100	75.43103448	56.39367816	31.48347701
5 ppm	50	150	92.38505747	67.60057471	50
5 ppm	50	300	98.70689655	95.04310345	86.08117816
5 ppm	50	500	99.56896552	97.91666667	94.88146552

1.2 pH

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	Time(mins)	pH	% Removal
10 ppm	50	300	10	0	0
10 ppm	50	300	10	2	75.21551724
10 ppm	50	300	10	3	93.89367816
10 ppm	50	300	10	4	96.3362069
10 ppm	50	300	10	5	93.17528736
10 ppm	50	300	10	6	90.73275862
10 ppm	50	300	10	7	88
10 ppm	50	300	10	8	87.71551724
10 ppm	50	300	10	9	85

1.3 Initial concentration

Initial Conc.(ppm)	Volume(mL)	Dose(mg)/50 mL	% Removal
0	50	300	0
1	50	300	99.35344828
2	50	300	93.2112069
4	50	300	91.55890805
6	50	300	88.14655172
8	50	300	82.48922414
10	50	300	74.92816092
20	50	300	72.95258621
40	50	300	64.67911877
80	50	300	40.64295977
120	50	300	26.18534483
160	50	300	18.77693966
200	50	300	12.60775862
250	50	300	9.511494253
300	50	300	4.477969349

1.4 Time and Temperature

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	Time(mins)	% Removal(25°C)	% Removal (35°C)
10 ppm	50	300	0	0	0
10 ppm	50	300	5	91.30747126	86.42241379
10 ppm	50	300	10	91.30747126	89.72701149
10 ppm	50	300	20	92.88793103	91.59482759
10 ppm	50	300	30	93.60632184	92.16954023
10 ppm	50	300	45	93.89367816	94.89942529
10 ppm	50	300	60	86.70977011	94.32471264
10 ppm	50	300	80	88.43390805	93.46264368
10 ppm	50	300	120	0	88.57758621

1.5 Langmuir Isotherm

Initial Conc	Cs	Qs	Experimental ce/qe	Model ce/qe	SE	SSE	Chi Sq
Ppm	mg/L	mg/g	g/L	g/L			
0	0			0	0	0	0
1	0.01569	0.1640517	0.095639362	0.073666522	0.000482806	0.000482806	0.00504819
2	0.025895	0.329017467	0.078704636	0.075339264	1.13257E-05	1.13257E-05	0.000143902
4	0.029876	0.661687333	0.045151235	0.075991747	0.000951137	0.000951137	0.021065586
6	0.035842	0.9940264	0.03605699	0.076969554	0.001673838	0.001673838	0.046422009
8	0.064655	1.322557471	0.048886475	0.081692316	0.001076223	0.001076223	0.022014744
10	0.265805	1.6223659	0.163837638	0.114662226	0.002418221	0.002418221	0.014759863
30	2.507184	4.582136015	0.547164881	0.48204122	0.004241091	0.004241091	0.00775103
40	4.956897	5.840517241	0.848708487	0.883567621	0.001215159	0.001215159	0.001431775

1.6 Freundlich Isotherm

Initial Conc	Log Ce	Ce	Log qe	Qe	log qe	SE	SSE	Chi Sq
Ppm		mg/L		mg/g				
0		0				0	0	0
1	-1.804382592	0.0156898	-0.78501926	0.1640517	-0.433	0.123586732	0.1235867	-0.1574
2	-1.58678073	0.0258952	-0.48278105	0.329017467	-0.322	0.025706096	0.0257061	-0.0532
4	-1.524677549	0.029876	-0.17934718	0.661687333	-0.291	0.012413891	0.0124139	-0.0692
6	-1.445612611	0.0358416	-0.00260208	0.9940264	-0.25	0.061416656	0.0614167	-23.603
8	-1.189396726	0.06465517	0.12141455	1.322557471	-0.12	0.058138485	0.0581385	0.47884
10	-0.575437511	0.2658046	0.21014881	1.6223659	0.1935	0.00027595	0.000276	0.00131
30	0.399186192	2.50718391	0.66106798	4.582136015	0.6908	0.000883379	0.0008834	0.00134
40	0.695209855	4.95689655	0.76645131	5.840517241	0.8418	0.005680564	0.0056806	0.00741

1.7 Pseudo 1st order

Time	Ct	Qt	Qe-Qt	log (Qe-Qt)	Ct	Qt	Qe-Qt	log (Qe-Qt)
			25°C				35°C	
min	mg/L	mg/g	mg/g		mg/L	mg/g	mg/g	
0	10	0	1.581657088	0.199112332	10	0	1.620233333	0.209577563
5	0.88362069	1.519396552	0.062260536	-1.205787142	1.3504	1.4416	0.178633333	-0.748037498
10	0.869252874	1.521791188	0.0598659	-1.222820481	1.0217	1.496383333	0.12385	-0.907103989
20	0.711206897	1.548132184	0.033524904	-1.474632454	0.8423	1.526283333	0.09395	-1.027103216
30	0.639367816	1.560105364	0.021551724	-1.666517981	0.7865	1.535583333	0.08465	-1.072373038
45	0.610632184	1.564894636	0.016762452	-1.77566245	0.5123	1.581283333	0.03895	-1.409492538
60	0.567528736	1.572078544	0.009578544	-2.018700499	0.4895	1.585083333	0.03515	-1.454074671
80	0.538793103	1.576867816	0.004789272	-2.319730494	0.3215	1.613083333	0.00715	-2.145693958
120	0.510057471	1.581657088	0		0.2786	1.620233333	0	

1.8 Pseudo 2nd order

Time	Ct	Qt	t/Qt	Ct	Qt	t/Qt
min	mg/L	mg/g		mg/L	mg/g	
		25°C			35°C	
0	10	0	0	10	0	0
5	0.88362069	1.51939655	3.290780142	1.3504	1.4416	3.468368479
10	0.86925287	1.52179118	6.57120377	1.0217	1.49638333	6.68277959
20	0.71120689	1.54813218	12.9187935	0.8423	1.52628333	13.1037269
30	0.63936781	1.56010536	19.2294704	0.7865	1.53558333	19.5365496
45	0.61063218	1.56489463	28.7559296	0.5123	1.58128333	28.4578981
60	0.56752873	1.57207854	38.1660319	0.4895	1.58508333	37.8528994
80	0.53879310	1.57686781	50.7334851	0.3215	1.61308333	49.5944619

120	0.51005747	1.58165708	75.8697956	0.2786	1.62023333	74.0634065

Batch experiments by using HA coated MNPs

2.1 Dose

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	% Removal (5ppm)	% Removal (10ppm)	% Removal (20ppm)
5 ppm	50	0	0	0	0
5 ppm	50	10	2.729885057	0	0
5 ppm	50	20	17.67241379	11.99712644	0.538793103
5 ppm	50	40	46.98275862	26.07758621	7.076149425
5 ppm	50	60	67.95977011	43.89367816	9.231321839
5 ppm	50	100	89.22413793	72.48563218	20.15086207
5 ppm	50	150	95.25862069	84.41091954	31.21408046
5 ppm	50	300	99.999	92.31321839	67.06178161
5 ppm	50	500	99.999	98.77873563	90.86961207

2.2 pH

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	Time(mins)	pH	% Removal
10 ppm	50	300	30	0	0
10 ppm	50	300	30	2	45.76149425
10 ppm	50	300	30	3	56.25
10 ppm	50	300	30	4	81.68103448
10 ppm	50	300	30	5	64.15229885
10 ppm	50	300	30	6	49.78448276
10 ppm	50	300	30	7	34.69827586
10 ppm	50	300	30	8	31.82471264
10 ppm	50	300	30	9	30.38793103

2.3 Initial concentration

Initial Conc.(ppm)	Volume(mL)	Dose(mg)/50 mL	% Removal
0	50	300	0
1	50	300	97.62931034
2	50	300	98.74281609
4	50	300	87.60775862
6	50	300	91.97796935
8	50	300	93.80387931
10	50	300	91.1637931
20	50	300	84.51867816
40	50	300	54.19061303
80	50	300	46.0308908
120	50	300	26.30507663
160	50	300	16.35237069
200	50	300	16.3433908
250	50	300	16.40804598
300	50	300	15.97222222

2.4 Time and Temperature

Initial Conc.	Volume(mL)	Dose(mg)/50 mL	Time(mins)	% removal (25°C)	% removal (35°C)
10 ppm	50	300	0	0	0
10 ppm	50	300	10	89.29597701	82.39942529
10 ppm	50	300	20	90.73275862	89.72701149
10 ppm	50	300	30	86.56609195	89.29597701
10 ppm	50	300	45	91.30747126	92.88793103
10 ppm	50	300	60	94.32471264	95.04310345
10 ppm	50	300	80	94.61206897	94.18103448
10 ppm	50	300	120	95.04310345	93.89367816
10 ppm	50	300	160	92.88793103	95.76149425

2.5 Langmuir Isotherm

			Experimental	Model			
Initial Conc	Cs	Qs	ce/qe	ce/qe	SE	SSE	Chi Sq
ppm	mg/L	mg/g	g/L	g/L			
0	0			0	0	0	0
1	0.006466	0.165589	0.039048488	0.133662812	0.00895187	0.00895187	0.22925012
2	0.135776	0.310704	0.436994696	0.163207203	0.074959591	0.074959591	0.171534327

4	0.4956897	0.584051724	0.848708487	0.245439279	0.363933737	0.363933737	0.428808881
6	0.4813218	0.919779693	0.523301224	0.242156561	0.079042322	0.079042322	0.151045551
8	0.4956897	1.250718391	0.396323952	0.245439279	0.022766184	0.022766184	0.057443372
10	0.8836207	1.519396552	0.581560284	0.334072689	0.06125011	0.06125011	0.10532031
30	3.0962644	4.483955939	0.690520694	0.839611394	0.022228037	0.022228037	0.032190254
40	13.742816	4.376197318	3.140355677	3.272106073	0.017358167	0.017358167	0.005527453

2.6 Freundlich Isotherm

`				Experimental	Model			
Initial Conc	Log Ce	Ce	Log qe	Qe	log qe	SE	SSE	Chi Sq
ppm		mg/L		mg/g				
0		0				0	0	0
1	-2.1893643	0.006466	-0.7850193	0.1640517	-0.937	0.023148114	0.0231481	-0.0295
2	-0.86717699	0.135776	-0.4827811	0.329017467	-0.254	0.052391859	0.0523919	-0.1085
4	-0.304790145	0.49568966	-0.1793472	0.661687333	0.0367	0.046693755	0.0466938	-0.2604
6	-0.317564433	0.48132184	-0.0026021	0.9940264	0.0301	0.001071962	0.001072	-0.412
8	-0.304790145	0.49568966	0.12141455	1.322557471	0.0367	0.007169746	0.0071697	0.05905
10	-0.053734124	0.88362069	0.21014881	1.6223659	0.1665	0.00190695	0.001907	0.00907
30	0.490838035	3.09626437	0.66106798	4.582136015	0.4479	0.045439515	0.0454395	0.06874
40	1.138075735	13.7428161	0.76645131	5.840517241	0.7824	0.000253725	0.0002537	0.00033

2.7 Pseudo 1st order

	25°C				35°C			
Time	Ct	Qt	Qe-Qt	log (Qe-Qt)	Ct	Qt	Qe-Qt	log (Qe-Qt)
min	mg/L	mg/g	mg/g		mg/L	mg/g	mg/g	
0	10	0	1.548132184	0.189808039	10	0	1.548132184	0.189808039
5	1.070402299	1.488266284	0.0598659	-1.22282048	1.760057471	1.373323755	0.174808429	-0.75743763
10	0.926724138	1.512212644	0.03591954	-1.44466923	1.027298851	1.495450192	0.052681992	-1.27833781
20	1.343390805	1.442768199	0.105363985	-0.97730781	1.070402299	1.488266284	0.0598659	-1.22282048
30	0.869252874	1.521791188	0.026340996	-1.57936781	0.711206897	1.548132184	0	#NUM!
45	0.567528736	1.572078544	-0.02394636	#NUM!	0.495689655	1.584051724	-0.03591954	#NUM!
60	0.538793103	1.576867816	-0.02873563	#NUM!	0.581896552	1.569683908	-0.02155172	#NUM!
80	0.495689655	1.584051724	-0.03591954	#NUM!	0.610632184	1.564894636	-0.01676245	#NUM!
120	0.711206897	1.548132184	0		0.423850575	1.596024904	-0.04789272	

2.8 Pseudo 2nd order

	25°C			35°C		
Time	Ct	Qt	t/Qt	Ct	Qt	t/Qt
min	mg/L	mg/g		mg/L	mg/g	
0	10	0	0	Qt	0	0
5	1.070402299	1.488266284	3.359613837	1.760057471	1.4416	2.330475747
10	0.926724138	1.512212644	6.612826603	1.027298851	1.496383333	4.419206266
20	1.343390805	1.442768199	13.86224066	1.070402299	1.526283333	9.082350807
30	0.869252874	1.521791188	19.71361133	0.711206897	1.535583333	12.83786487
45	0.567528736	1.572078544	28.62452399	0.495689655	1.581283333	18.10208417
60	0.538793103	1.576867816	38.0501139	0.581896552	1.585083333	24.00511891
80	0.495689655	1.584051724	50.50340136	0.610632184	1.613083333	31.30861272
120	0.711206897	1.548132184	77.51276102	0.423850575	1.620233333	47.84049274