Application of Granular Activated Carbon in Removal of Iron and Manganese from Salaulim Dam Reservoir

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Certificate

This is to certify that the project entitled ‘**Application of Granular Activated Carbon in Removal of Iron and Manganese from Salaulim Dam Reservoir**’ submitted by Swarand Gaonkar is a bonified work carried out in partial fulfilment of the degree of Master of Science, Goa University in the year 2019-2020. It is further certified that this project has not been the basis for any award of any other degree or diploma of any other university.

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Declaration

I hereby declare that the project work entitled

"Application of Granular Activated Carbon in Removal of Iron and Manganese from Salaulim Dam Reservoir"

Submitted to the Goa University, is a record of an original work done by me under the guidance of

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Chapter 1: Introduction

Description of Site:

The Salaulim Dam is located on the Salaulim River, a tributary of the Zuari River in Goa, India, is an integral component of the Salaulim Irrigation Project which envisages benefits of irrigation and drinking water supply.

The dam is a composite earth-cum-masonry dam of 42.7 meters (140 ft) height with a water spread area of 24 km^2. The river drains a catchment area of 227 km^2.

It was initially planned to provide irrigation to an ultimate potential of 14,326 hectares (35,400 acres) and water supply of 160 million liters per day (MLD) to South Goa; the water supply component for domestic and industrial use is now increased to 380 MLD.

The construction of the project was started in 1976 and the dam was completed in 2000, and the irrigation component is under final stages of completion having achieved an irrigation potential of 9,537 ha.

The reservoir submergence involved 20 villages which were partially or fully submerged. 3000 people were displaced and resettled. Mining areas were also submerged for which compensation was provided (Mausami, 2015)

Figure 1: Salaulim Dam Reserviours

Source:https://i.ytimg.com/vi/QdhjoztiZ3k/maxresdefault.jpg

High manganese level has been detected in the Salaulim reservoir in Goa, which supplies drinking water. The manganese content rises thrice a year in this water body, which has several ore heaps piled up on its banks. The content rises in May due to depleted water, July- August because of the rainfall and November-December when the canal is opened, the rise in the manganese content is controlled by using chemicals like lime which is recommended by National Environmental Engineering Research Institute (NEERI) (Jagtap, 2016).

Reported references: *https://timesofindia.indiatimes.com/city/goa/Manganese-level-forces-Selaulim-plant-to-stop-water-supply-for-a-day/articleshow/51505045.cms*

https://www.thehindu.com/news/national/other-states/high-manganese-content-found-in-goas-selaulim-reservoir/article5928221.ece

Need of Water:

The water in our bodies is essential for life. Without water, we can't survive. Since the water in our bodies is continually being used or lost, it needs to be continually replaced, and the best fluid to replace it with is water. Water is involved in every bodily function from digestion and circulation through to the control of body temperature and the excretion of waste products. The water in our bodies is continually being used or lost from the body. Some is used or absorbed by the functions it performs and some is lost through sweat, urine and faeces.

Organisms cannot survive without water for longer period of time. It is universal solvent which provides ionic balance and nutrients which supports all the forms of life (Smith, 2015).

Need of Water Analysis:

Water quality testing is important because it identifies contaminants and prevents water-borne diseases. Essentially, water quality testing makes sure that water is safe and meets local and international water standards. This type of testing can be completed using water sampling techniques and using technology to estimate the amount and level of chemicals. All water for human and animal use should be tested for safety. In addition to household water, recreational and agricultural water should also be tested (Dessalegn, 2019).

BOD, COD, TOC and O & G – sum parameters in Water Analysis:

There are about 40 million organic compounds known in the environment which cannot be defined individually with considerable analytical effort and in short time. Therefore, the so-called sum parameters are used. These parameters reflect effect and material characteristics of one or more substances. The most popular sum parameter in waste-water analysis are the BOD (biochemical oxygen demand), COD (chemical oxygen demand), O & C (Oil and Grease) and TOC (total organic carbon). The TOC reflects the organic pollution on the basis of a direct carbon determination. The other parameters are based on oxygen, which is required to reduce or to oxidize the samples substances (Arts, 2015).

1. BOD is the traditional, most widely used test to establish concentration of organic matter in wastewater samples (i.e., relative strength). BOD is based on the principle that if sufficient oxygen is available, aerobic biological decomposition (i.e., stabilization of organic waste) by microorganisms will continue until all waste is consumed. It is based on the accurate measure of DO (dissolved oxygen) at the beginning and end of a three-day period in which the sample is held in dark, incubated

conditions (i.e., 27°C). The change in DO concentration over three days represents the "oxygen demand" for respiration by the aerobic biological microorganisms in the sample (Arts, 2015).

2. COD is the most popular alternative test to BOD for establishing the concentration of organic matter in wastewater samples. The COD test only takes a few hours to complete, giving it a major advantage over the 5-day BOD test. Wastewater treatment system personnel can use COD as an almost real-time operational adjustment parameter. COD can test wastewater that is too toxic for the BOD test. The COD test should be considered an independent measure of the organic matter in a wastewater sample rather than a substitute for the BOD test. The COD test uses a chemical (potassium dichromate in a 50% sulfuric acid solution) that "oxidizes" both organic (predominate) and inorganic substances in a wastewater sample, which results in a higher COD concentration than BOD concentration for the same wastewater sample since only organic compounds are consumed during BOD testing. The most popular current testing method for COD involves using sealed and heated (i.e., closed reflux) low-range (3 - 150 ppm) or high-range (20 - 1500 ppm) pre-prepared vials that change color from orange to green based on the amount of oxidation and that are read using a laboratory colorimeter that measures the relative color change (Arts, 2015).

3. The TOC test is gaining popularity because it only takes 5 - 10 minutes to complete. Like COD, the TOC test can be used to rapidly estimate BOD concentration once a consistent TOC to BOD ratio is established on a particular wastewater stream. At the heart of the TOC test is a carbon analyzing instrument that measures the total organic carbon in a wastewater sample. Various heat and oxygen, ultraviolet radiation and chemical oxidant- based methods are available to measure TOC that are specific to the carbon analyzing instrument utilized. In the TOC test, organic carbon is converted to carbon dioxide (CO_2) and typically measured with an infrared analyzer (Arts, 2015).

4. O&G (Oil and Grease) consists of a group of related constituents that are of special concern in wastewater treatment due to their unique physical properties and highly concentrated energy content. The term O&G (oil and grease) has become the popular term replacing the term FOG (fat, oil and grease), although both terms refer to the same wastewater constituents. O&G constituents in wastewater can come from plants and

animals (e.g. butter, vegetable oils and fats) as well as petroleum sources (e.g., kerosene, lubricating oils). O&G are generally hydrophobic (i.e., “water-hating”) and thus have low solubility in wastewater, resulting in relatively low biodegradability by micro- organisms. O&G becomes more soluble (i.e., more easily dissolved) in wastewater at high temperatures and will form emulsions (i.e., oil-water mixtures) that will often separate back out of wastewater as temperatures become cooler; thus, O&G are notorious for causing sewer collection system problems (e.g., blockages, pump failures) (Arts, 2015).

Basis Water Quality Parameters:

Water quality testing is an important part of environmental monitoring. When water quality is poor, it affects not only aquatic life but the surrounding ecosystem as well. Parameters that affect the quality of water in the environment can be physical, chemical or biological factors. Physical properties of water quality include temperature and turbidity. Chemical characteristics involve parameters such as pH and dissolved oxygen. Biological indicators of water quality include algae and phytoplankton.

Parameter	Significance	Method for analysis	Range or lower limit of detection
Color	Contamination level	Platinum Cobalt Scale	-
Turbidity	Amount of suspended particles	Turbidometry	0.05 NTU
pH	Acidity or alkalinity	pH Metry	-
Specific Conductivity	Electrical conductivity	Conductometry	$5\ \mu\ seimens$
Total Solids (TS)	Amount of suspended and dissolved matter	Gravimetry	2.4 mg/L
Total Hardness	Amount of Ca^{2+} ions and Mg^{2+} ions	Titrimetry	1 mg/L
Total Alkalinity as $CaCO_3$	Dissolved minerals that help neutralize the water we drink	Titrimetry	5 mg/L

Chloride as Cl^-	Responsible for maintaining acid/base balance, transmitting nerve impulses and regulating fluid in and out of cells.	Titrimetry	1 mg/L
Sulphate as SO_4^{2-}	Excess level can lead to intestinal discomfort, diarrhea and consequently dehydration.	Gravimetry	0.5 mg/L
Nitrate as NO_3^-	Excess levels can cause methemoglobinemia, or "blue baby" disease.	Spectrophotometry	0.93 mg/L
Fluoride as F^-	Prevents dental diseases	Potentiometry	0.025 mg/L
Iron as Fe^{2+}	Essential for good health, helps transport oxygen in the blood	Spectrophotometry	0.008 mg/L
Manganese as Mn^{2+}	Small amount is essential for human health, too much manganese can be a risk to health	Spectrophotometry	0.020 mg/L
Dissolved Oxygen(DO)	Essential for the survival of fish and other aquatic organisms	Titrimetry	0.2 mg/L

1. Color may be expressed as “apparent” or “true” color. The apparent color includes color from dissolved materials plus that from suspended matter. By filtering or centrifuging

out the suspended materials, the true color can be determined. The procedure describes true color analysis. If apparent color is desired, it can be determined by measuring an unfiltered water sample (Parklawn, 2018).

2. Most customers judge the quality of drinking water by taste and odor. If the customer is satisfied with these qualities, it is assumed the water is safe to drink. Many harmful contaminants in water cannot be detected due to taste or smell and many of the contaminants found in drinking water that have a detectable taste or odor are not harmful. Sources of taste and odor problems can be found in surface water and groundwater.

   Source water protection involves the prevention of contaminants from entering the source. Surface water or groundwater may become contaminated by pollutants such as gasoline, industrial solvents or a wide variety of volatile organics. The removal of contaminants from surface water or groundwater is costly and may involve the use of aeration, powdered activated carbon, or both.

   If taste and odor must be controlled at the treatment plant, oxidation, aeration and adsorption can be effective in reducing taste and odor, and improved coagulation filtration (Denmark, 2015)

3. Turbidity is caused by suspended materials which absorb and scatter light. These colloidal and finely dispersed turbidity-causing materials do not settle under quiescent conditions and are difficult to remove by sedimentation. Turbidity is a key parameter in water supply engineering, because turbidity will both cause water to be aesthetically unpleasant and cause problems in water treatment processes, such as filtration and disinfection. Turbidity is also often used as indicative evidence of the possibility of bacteria being present.

   Turbidity measurements performed using proprietary nephelometric instruments are expressed as Nephelometric Turbidity Units (NTU). The nephelometric apparatus is designed to measure forward scattering of light at 90^o to the path of an incandescent light beam. Suspended particles present in a water sample reflect a portion of the incident light off the particle surface. The light reflected at 90^o is measured by a photoelectric detector and is compared against light reflected by a reference standard. No interference exists for the turbidity test (LaPerrire, 2016).

4. pH value is a good indicator of whether water is hard or soft. The pH of pure water is 7. In general, water with a pH lower than 7 is considered acidic, and with a pH greater than 7 is considered basic. The normal range for pH in surface water systems is 6.5 to 8.5, and the pH range for groundwater systems is between 6 to 8.5.

5. The alkalinity of the water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due primarily to the salts of week acids. Bicarbonates represent the major form of alkalinity. The measurement of alkalinity and pH is needed to determine the corrosiveness of the water.

   Consuming excessively acidic or alkaline water is harmful, warns the Environmental Protection Agency (EPA). Drinking water must have a pH value of 6.5-8.5 to fall within EPA standards, and they further note that even within the acceptable pH range, slightly high- or low-pH water can be unappealing for several reasons.

   High-pH water has a slippery feel, tastes a bit like baking soda, and may leave deposits on fixtures, according to the EPA website. Low-pH water, on the other hand, may have a bitter or metallic taste, and may contribute to fixture corrosion (Maher, 2015).

6. For regulatory and treatment purposes, total solids (TS) can first be classified as suspended or dissolved. Total solids, as defined by Standard Methods and EPA, is the material residue left in a vessel after evaporation of a sample and its subsequent drying in an oven at 103 to 105°C for one hour (T.P.Sivanandan, 2014).

7. Total suspended solids (TSS) is that portion of the Total Solids that are retained on a no-ash glass fiber filter disc of approximately 0.45 mm pore size. The wetted and weighed filter disc is placed in a filtering apparatus and a suction is applied. A measured volume of wastewater is passed through the filter. The filter containing the residue is then dried in an oven for one hour at 103 to 105°C. The sample is then cooled and weighed. The difference in weight of the dry filter before and after solids are passed through is the TSS milligrams (mg) of suspended solids per liter (L) of wastewater filtered.

   This inexpensive TSS test tells much about the wastewater character and can be run in less than two hours with fairly inexpensive equipment. The TSS test indicates whether it is likely that solids suspended in a wastewater can be removed by settling, floating or filtering. In order to remove all solids that were removed in the TSS Test, a filter similar to the TSS Filter paper (0.45 mm) must be used in full scale (T.P.Sivanandan, 2014).

8. The total dissolved solids (TDS) are the solids in the filtrate from the TSS test. The liquid which passes through the TSS filter is collected in a weighed dish and evaporated for an hour at 180°C ± 2°C. The dish is then re-weighed with the TDS equaling the difference between the dish weight before and after filling with filtrate and drying, in mg per liter of filtrate. Again, this inexpensive test can be run in less than two hours and will indicate the chemical or biological solids in a wastewater which cannot be removed through settling, floating or filtration (T.P.Sivanandan, 2014).
   These three solids tests can be related with Equation:
   $TDS = TS - TSS$

9. Hard waters are generally considered to be those waters that require considerable amounts of soap to produce foam and that also produce scale in water pipes, heaters, boilers and other units in which the temperature of water is increased. Hard water is appropriate for human consumption similar to that as soft waters, however it produces adverse actions with soap and thus their use for cleaning purposes is unsatisfactory and thus their removal from water is required. Hardness of waters varies from place to place. In general, surface waters are softer than ground waters. Waters are commonly classified based on degree of hardness:

Hardness (mg/L)	**Degree of hardness**
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard

   Hardness is caused by polyvalent metallic cations, though the divalent cations, such as calcium and magnesium cations are usually the predominant cause of hardness. In addition, hardness is also caused by Fe^{2+} and Mn^{2+} ions.
   $Ca^{2+}{}_{(aq)} + 2HCO_3^-{}_{(aq)} \longrightarrow CaCO_3{}_{(s)} + H_2O + CO_2$
   $Mg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Mg(OH)_2{}_{(s)}$

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as mg/L $CaCO_3$. It is determined by EDTA titrimetric method.

This method uses ethylenediaminetetraacetic acid (EDTA), chelating agents, which forms complex ions with $Ca^{2+}$and Mg^{2+} and other divalent ions causing hardness.

$M^{2+} + EDTA \longrightarrow [M.EDTA]_{complex}$

The successful use of EDTA for determining hardness depends on presence of an indicator which can show presence of excess EDTA in solution or when all the ions present in solution have been complexed. Eriochrome Black T (EBT) (blue color solution) serves as an excellent indicator to show when all hardness ions have been consumed. When small amount of EBT is added to hard water with pH >10, it combines with Ca^{2+} and Mg^{2+} ions to form weak complex ions (wine-red color solution).

$M^{2+} + Eriochrome\ Black\ T \longrightarrow [M.Eriochrome\ Black\ T]_{complex}$

During the titration with EDTA, all free hardness ions are complexed and subsequently, EDTA disrupts the wine-red complex as it can form a stable complex with the hardness ions. At this stage, solution color changes from red wine color to blue color, indicating the end of the titration (Sawyer, 2013).

10. Chloride in the form of chloride (Cl^-) ion is one of the major inorganic anions in water and wastewater. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Average estimate of excretion: 6 g of chlorides/person/day, additional chloride burden due to human consumption on wastewater: 15 mg/L. Along the seacoast chloride may be present in high concentration because of leakage of saltwater into the sewage system. It also may be increased by industrial process. In addition, a high chloride contents may harm metallic pipes and structures as well as growing plants.

    The measured chloride ions can be used to know salinity of different water sources. For brackish water (or sea water or industrial brine solution), it is an important parameter and indicates the extent of desalting of apparatus required. It also interferes with COD determination and thus it requires a correction to be made on the basis of amount present or else a complexing agent, such as $HgSO_4$ can be added. Further, chloride ions are used as tracer ions in column studies to model fate of different contaminants in soil and liquid media.

The amount of chloride ions is estimated by Mohr's method. The Mohr Method uses silver nitrate for titration (normality: 0.0141N). This corresponds to 1 mL of 0.0141 N equals to 1 mg chloride in solution. The silver nitrate solution is standardized against standard chloride solution, prepared from sodium chloride (NaCl). During the titration, chloride ion is precipitated as white silver chloride

$Ag^{+} + Cl^{-} \Leftrightarrow AgCl$ (Solubility product constant, $K_{sp} = 3\times10^{-10}$)

The indicator (potassium chromate) is added to visualize the endpoint, demonstrating presence of excess silver ions. In the presence of excess silver ions, solubility product of silver chromate exceeded, and it forms a reddish-brown precipitate. This stage is taken as evidence that all chloride ions have been consumed and only excess silver ions have reacted with chromate ions:

$2Ag^{+} + CrO_4^{2-} \Leftrightarrow Ag_2CrO_4$ ($K_{sp} = 5\times10^{-12}$)

This method works in range 0.15 to 10 mg/L chloride ions concentration (Hendrick, 2009).

11. Sulphate are found in appreciable quantity in all-natural waters, particularly high in arid and semi-arid regions where natural waters in general have high salt content. Sulphate salts are mostly soluble in water and impart hardness. Water with high concentrations has a bitter test. Sulphate may cause intestinal disorders. These ions can produce hydrogen sulfides as per following equation:

$SO_4^{2-} + organic\ matter \longrightarrow S^{2-} + H_2O + CO_2$ (in presence of anaerobic bacteria)

$S^{2-} + H^{+} \longrightarrow HS^{-}$

$HS^{-} + H^{+} \longrightarrow H_2S$

Sulphate can be determined by

- Gravimetric method of with ignition of residue
- Gravimetric method with drying of residue
- Turbidimetric method

Gravimetric method with ignition of residue:

Sulphate is precipitated in hydrochloric acid medium as barium sulphate by the addition of barium chloride. The precipitation is carried out near the boiling point temperature and after a period of digestion, the precipitate is filtered, washed with water until free of chloride, ignited weighed barium sulphate.

Gravimetric method with drying of residue

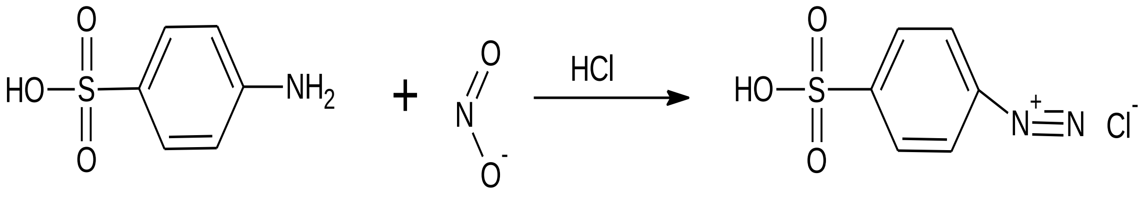
If organic matter is not present in the sample first method can be done without igniting and instead drying the residue and weighing.

Turbidimetric method

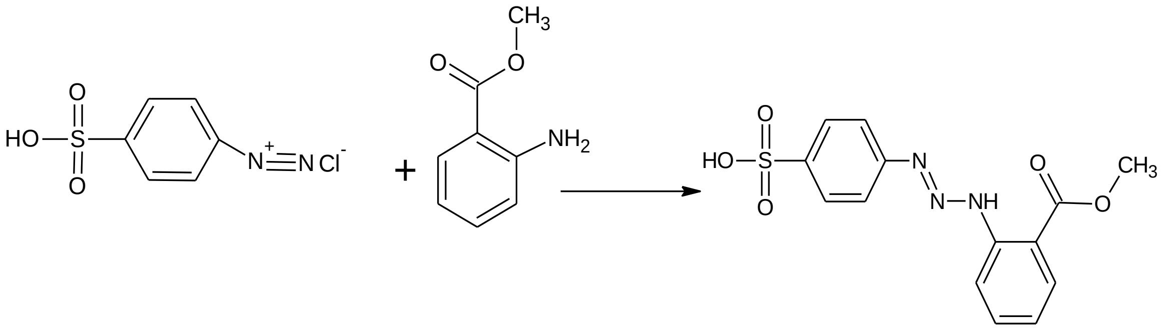
Turbidimetric method is method of measuring sulphate is based upon the fact that barium sulphate tends to precipitate in a colloidal form and that this tendency is enhanced in presence of sodium chloride – hydrochloric acid solution containing glycerol and other organic compounds. The absorbance of barium sulphate solution is measured by nephelometer or turbidimeter and the sulphate ion concentration determined by the comparison of the reading with a standard curve (Adu, 2014).

12. Nitrate is a well-known contaminant of ground and stream water. It is an important environmental and human health analyte, and thus its detection and quantification are considered to be essential. Spectrophotometric methods involve the use of common reactions, such as a reduction reaction followed by diazotization, nitration reactions, or others. Other methods involve the use of ion chromatography and specific ion electrodes. The well-known spectrophotometric methods for the determination of nitrate are based on the nitration of phenolic compounds, chromophoric acids, 2,4-xylenol, 2,6-xylenol, 3,4-xylenol, phenoldisulfonic acid, brucine and phenol 4-aminoazobenzene. Some sensitive spectrophotometric methods for determine nitrate utilize extractable ion associates of the nitrate ion with basic dyes, like crystal violet and nile blue.

    Determination of nitrate is based on the reduction of nitrate to nitrite in the presence of Zn/NaCl. The produced nitrite is diazotized with sulfanilic acid and then coupled with methylanthranilate to form an azo dye and was measured at 493 nm (Sunil, 2009).



sulfanilic acid



methylanthranilate Azo dye

13. Addition of fluoride to toothpaste and to drinking water has done much to reduce the occurrence of dental caries (cavities). Although addition of fluoride is certainly effective, too much fluoride can be harmful; therefore, it is important to have a convenient method for monitoring fluoride levels.

    A simple and widely used method uses a fluoride ion-selective electrode. This electrode in combination with a suitable reference electrode forms an electrochemical cell whose electrical potential is a function of fluoride ion concentration. To minimize the effects of varying ionic strength and interference from other ions, a buffer referred to as a total ionic strength adjusting buffer (TISAB) is added to all standards and the sample. The electrode is calibrated using a series of known concentrations of fluoride. The voltage of each solution is measured, and this voltage plotted as a function of concentration. The response of the sample is obtained in a similar manner and the concentration is then determined from the calibration curve (Carey, 2016).

Sources of Iron and Manganese in Water:

Natural sources of iron and manganese are more common in deeper wells where the water has been in contact with rock for a longer time. In coal mining regions of the state, these metals may also occur from both deep and surface mining activities.

Iron and manganese often occur together in groundwater, but manganese usually occurs in much lower concentrations than iron. Both iron and manganese are readily apparent in drinking water supplies. Both impart a strong metallic taste to the water and both cause staining.

Water coming from wells and springs with high iron and/or manganese may appear colorless initially but orange brown (iron) or black (manganese) stains or particles quickly appear as the water is exposed to oxygen.

Iron occurs in two oxidation states, the divalent or ferrous form (Fe^{2+}) and the trivalent or ferric form (Fe^{3+}). Iron in aqueous solution is subject to hydrolysis. The iron hydroxides formed, especially the ferric form, have very low solubility.

The divalent form (Mn^{2+}) predominates in most water at pH 4–7, but more highly oxidized forms may occur at higher pH values or result from microbial oxidation (Swistock, 2016).

Secondary Drinking Water Standards:

Iron and manganese are not health concerns in drinking water. Instead, they both have secondary or recommended drinking water standards because they cause aesthetic problems that make the water undesirable to use in the home and a bitter metallic taste that can make the water unpleasant to drink for both humans and farm animals.

Iron can also cause an orange or brown stain in sinks and in the laundry. Manganese often results in a dense black stain or solid. For these reasons, it is recommended that drinking water have no more than 0.3 mg/L (or 0.3 parts per million) of iron and less than 0.05 mg/L of manganese (Swistock, 2016)

Analysis of Manganese and Iron in water:

Estimation of Manganese as Mn^{2+}:

The PAN method is a highly sensitive and rapid procedure to measure low levels of manganese. The ascorbic acid reagent reduces all oxidized forms of manganese to Mn. The alkaline-cyanide reagent masks potential interferences. PAN Indicator then forms an orange-colored complex with Mn^{2+}. The measurement wavelength is 560 Nm (Inman, 2006).

Estmiation of Iron as Fe^{2+}:

FerroVer Iron Reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron (Fe^{2+}). The ferrous iron reacts with the 1-10 phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration. The measurement wavelength is 510 nm for spectrophotometers or 520 nm for colorimeters (Amgstrong, 2018).

Removing Iron and Manganese from Water:

Iron and manganese can be effectively removed from water using a number of treatment processes depending on both the form and concentration of the metals.

Method	Conditions for higher efficiencies
Ion Exchange	pH is greater than 6.7, the water hardness is between 3 and 20 grains per gallon (50- 350 mg/L) and the dissolved iron concentration is less than 5 mg/L, no oxidized forms
Polyphosphate Addition	Iron concentrations less than 2 mg/L. Generally ineffective in treating manganese.
Oxidizing Filter	Combined iron and manganese concentration should be in the range of 3 to 10 mg/L. pH should be at least 6.8 for iron removal and 7.5 for manganese removal.
Oxidation Followed by Filtration	Combined levels of iron and manganese should exceed 10 mg/L
Adsorption	Depends on various factors like adsorbent dose, contact time, pH. Also surface modification greatly enhance the adsorption efficiency

1. Water Softening (Ion Exchange):
   Conventional water softeners are sometimes effective for removing iron and small amounts of manganese. Water softeners are typically used to remove calcium and magnesium hardness in water by an exchange process. The calcium and magnesium are removed from the water and sodium is added in their place. Iron and manganese removal are accomplished in the same way by exchanging the iron and manganese for sodium. The iron and manganese are then removed from the softener resin bed through backwashing and regeneration.
   Removal efficiencies by softeners will vary depending on the iron concentration, water hardness and pH. Softeners are generally only recommended when the water pH is greater than 6.7, the water hardness is between 3 and 20 grains per gallon (50- 350 mg/L) and the dissolved iron concentration is less than 5 mg/L.

Oxidized forms of iron and manganese will foul the softener resin. Thus, it is critical that the raw water not come in contact with any oxidizing agents like air or chlorine before entering the softener. Using the softener resin bed as a mechanical filter for oxidized iron and manganese is generally not recommended. This could damage the resin bed and require much more frequent backwashing. If oxidized iron and/or manganese are present in the raw water, filtration should be used for removal (Swistock, 2016).

2. Polyphosphate Addition

   Water containing dissolved iron concentrations less than 2 mg/L may be treated using polyphosphate addition. Phosphate addition is generally ineffective in treating manganese. The phosphate is fed into the water using a chemical feed pump that often requires trial and error dose adjustments. In this case, the iron is surrounded or "sequestered" by the phosphate and is not actually removed from the water.

   There are some major drawbacks to this process. Although the sequestered iron will not cause objectionable stains, it will still give the water a metallic taste. In addition, if too much phosphate is added to the water, it will give the water a slippery feeling and it may also cause diarrhea. The polyphosphate may also be degraded in a water heater resulting in release of sequestered iron (Swistock, 2016).

3. Oxidizing Filters:

   Oxidizing filters both oxidize and filter iron and manganese in one unit. The filter is usually comprised of manganese treated greensand although other materials such as birm can also be used. In the case of a manganese greensand filter, the filter media is treated with potassium permanganate to form a coating that oxidizes the dissolved iron and manganese and then filters them out of the water. Because these units combine oxidation and filtration, they can be used to treat raw water with dissolved and/or oxidized iron and manganese.

   Manganese greensand filters require significant maintenance including frequent regeneration with a potassium permanganate solution as it is consumed during oxidation of the dissolved metals. In addition, these units require regular backwashing to remove the oxidized iron and manganese particles. The potassium permanganate solution used for regeneration is toxic and must be handled and stored carefully using specific safety measures.

When properly maintained manganese greensand filters are extremely efficient for moderate levels of both dissolved and oxidized iron and manganese. They are generally recommended when the combined iron and manganese concentration is in the range of 3 to 10 mg/L. Keep in mind that the frequency of maintenance (backwashing and regeneration) will increase as the metal's concentration increases.

Birm filters are similar to manganese greensand but they do not require regeneration because they utilize oxygen present in the raw water to oxidize the metals. As a result, the raw water must contain a certain amount of dissolved oxygen and the pH should be at least 6.8 for iron removal and 7.5 for manganese removal. Even under ideal conditions, manganese removal efficiency is highly variable with birm filters. Birm filters do require backwashing to remove accumulated oxidized metal particles (Swistock, 2016).

4. Oxidation Followed by Filtration:

When combined levels of iron and manganese exceed 10 mg/L, the most effective treatment involves oxidation followed by filtration. In this process, a chemical is added to convert any dissolved iron and manganese into the solid, oxidized forms that can then be easily filtered from the water. Chlorine is most commonly used as the oxidant although potassium permanganate and hydrogen peroxide can also be used. A small chemical feed pump is used to feed the chlorine (usually sodium hypochlorite) solution into the water upstream from a mixing tank or coil of plastic pipe. The mixing tank or pipe coil is necessary to provide contact time for the iron and manganese precipitates to form. It may be necessary to install an activated carbon filter to remove the objectionable taste and odor from the residual chlorine. Chlorine is not recommended as an oxidant for very high manganese levels because a very high pH is necessary to completely oxidize the manganese.

Significant system maintenance is required with these units. Solution tanks must be routinely refilled and mechanical filters need to be backwashed to remove accumulated iron and manganese particles. If a carbon filter is also installed, the carbon would need to be replaced occasionally as it becomes exhausted. The frequency of maintenance is primarily determined by the concentration of the metals in the raw water and the amount of water used (Swistock, 2016).

5. Other Treatment Methods:

   The methods described above are the most common processes for removing iron and manganese but others like aeration, ozonation, and catalytic carbon may also be effective. While these units may successfully treat iron and/or manganese, their cost should be carefully compared with more traditional treatment methods and, as always, you should obtain a written guarantee of their effectiveness.

   Aeration units may work by cascading, bubbling, or stripping the gas from the water. Aeration may be advantageous because it does not add chemicals to the water. Maintenance costs are low for aeration units, but the initial purchase costs are often higher than other treatment options. Aeration units also require a filter for removal of the oxidized iron and manganese which must be backwashed. The water should also be disinfected to keep bacteria from colonizing the aerator.

   Catalytic carbon adsorbs then oxidizes and filters dissolved iron in one unit. It is effective for concentrations of dissolved iron less then 1.0 mg/L. Maintenance requirements are less than oxidizing filters because no chemicals are added, but backwashing is still necessary. Catalytic carbon requires a minimum of 4.0 mg/L of dissolved oxygen in the source water. Some groundwater supplies may need pretreatment to increase the dissolved oxygen concentration.

   In recent years, ozonation has received more attention as a method for treating numerous water quality problems. Like chlorine, ozone is a strong oxidant, but it is a much more unstable gas that must be generated on-site using electricity. Once the ozone is produced, it is injected into the water where its oxides dissolved metals which must then be filtered. Ozone units are usually more expensive than other more conventional treatment options, but they may be useful where multiple water quality problems must be treated (i.e. bacteria and metals) (Swistock, 2016).

Common Method used in Treatment Plants for Removal of Iron and Manganese:

Removal of iron and manganese is based on their ease of oxidation and precipitation at higher pH. Coagulation is needed to facilitate better setting. Treatability studies are carried out with chlorine and $KMnO_4$ as oxidants. Alum and lime are added for coagulation and pH correction. Jar test experiments during treatability studies revealed that treatment with potassium permanganate at pH 7.7–8.0 was effective in the removal of iron, manganese and organics, which are responsible for causing colour and odour to water. The rate of chemical precipitation of iron and manganese is highly dependent on pH and also requires a highly aerobic environment. The oxidation step may be carried out by aeration or more usually by use of a strong oxidant such as chlorine or, where manganese removal is required, by $KMnO_4$ (Khadse, Patni, & Labhasetwar1", 2015)

Benefits of Adsorption as Removal technique:

Adsorption is economically feasible technique and technically easy to separate as the requirement of the control system is less. The benefits of adsorption process over other techniques are it has simple design, sludge free, easiest, safest and more effective method for elimination of Iron and Manganese from water.

Activated carbon is widely employed as a highly effective adsorbent because of its large surface area, high adsorption capacity and special surface chemical properties (Swistock, 2016).

Adsorbent	Maximum Adsorption Capacity (mg/g)	Surface Area (m^2/g)	References
Activated carbon prepared from chitosan flakes	143.53	318.4	(Marrakchi et al., 2017)
Activated carbon of rottan hydrochar	359	1135	(Islam et al., 2017)
Activated carbon from Fox nutshell	75.37	2869	(Kumar and jena, 2016)
Commercial activated carbon	221	514	(Martin and Nunes, 2015)

Understanding the Adsorption Process through Adsorption Isotherms:

Adsorption process is generally studied through adsorption isotherms. Adsorption isotherms are the graphs which describe the interaction of adsorbates with adsorbents i.e. the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. One can say that more information on the mechanism of adsorption can be obtained through the isotherm. The other parameter which can be used to quantify adsorption is percentage removal.

Two materials, having the exact same surface chemistry and the similar shapes of pore size distributions but with different specific surface areas should exhibit, in the same condition (T, pH), isotherms with similar shapes but with different capacities (higher surfaces gives higher capacities but the adsorption process remains the same). To deal with this, you should calculate enthalpies of adsorption using, for instance, a network of different isotherms that were realized at different temperatures.

The Freundlich isotherm was commonly used to describe the adsorption characteristics of the activated carbon in water and waste- water treatment. The empirically derived Freundlich isotherm is defined as:

$$q_e = k_f\, C_e^{1/n}$$

q_e =Amount of dye adsorbed per gram of activated carbon
C_e = Equilibrium concentration
k_f = Adsorption capacity in mg/g for Freundlich adsorption isotherm
n = empirical constant

The Freundlich adsorption isotherm can be expressed in the linear form as:

$$\log q_e = \left[\frac{1}{n}\right] \log C_e + \log k_f$$

The constants in the Freundlich isotherm can be determined by plotting log q_e V/s log C_e. The Langmuir adsorption isotherm was developed by assuming that a fix number of accessible sites are available on the adsorbent surface, all of which have the same energy, adsorption is reversible, and there is no transmigration of adsorbate in the plane of the surface. From these rational considerations, the Langmuir adsorption isotherm is defined as:

$$q_e = \frac{abC_e}{1 + bC_e}$$

a =Adsorption capacity in mg/g for Langmuir adsorption isotherm
b = Langmuir constant

After rearrangement, The Langmuir adsorption isotherm can be expressed in the linear form as:

$$\frac{1}{q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{a}$$

By plotting a graph ($1/q_e$) V/s ($1/C_e$), a straight line will be obtained. From the graph the empirical constant can be obtained where the slope is 1/ab and the linear line will intercept the vertical axis is 1/a (Jusoh, 2005).

Breakthrough Curve:

Adsorption is a transient process. The amount of material adsorbed within a bed depends both on position and time. Consider the time dependence. As fluid enters the bed, it comes in contact with the first few layers of absorbent. Solute adsorbs, filling up some of the available sites. Soon, the adsorbent near the entrance is saturated and the fluid penetrates farther into the bed before all solute is removed. Thus, the active region shifts down through the bed as time goes on.

The fluid emerging from the bed will have little or no solute remaining -- at least until the bulk of the bed becomes saturated. The break point occurs when the concentration of the fluid leaving the bed spikes as unadsorbed solute begins to emerge. The bed has become ineffective. Usually, a breakpoint composition is set to be the maximum amount of solute that can be acceptably lost, typically something between 1 and 5 percent.

As the concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region. This mass transfer zone moves down the bed until it "breaks through". The shape of the mass transfer zone depends on the adsorption isotherm (equilibrium expression), flow rate, and the diffusion characteristics. Usually, the shape must be determined experimentally.

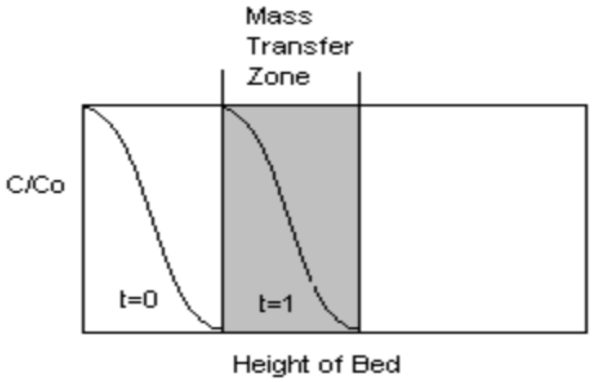


Figure 2: Adsorption Bed

Source:http://facstaff.cbu.edu/rprice/lectures/figures/adsorb4.gif

The wave front may change shape as it moves through the bed, and the mass transfer zone may broaden or diminish. Unfavorable and linear isotherms tend to broaden. Favorable Langmuir and Freundlich isotherms may broaden at first, but quickly achieve a constant pattern front, an asymptotic shape. This means that the mass transfer zone is constant with respect to both position and time. When dealing with a constant pattern front, one can make measurements on a small-scale apparatus and scale-up the results to a full-size adsorber bed (Geankoplis, 2002).

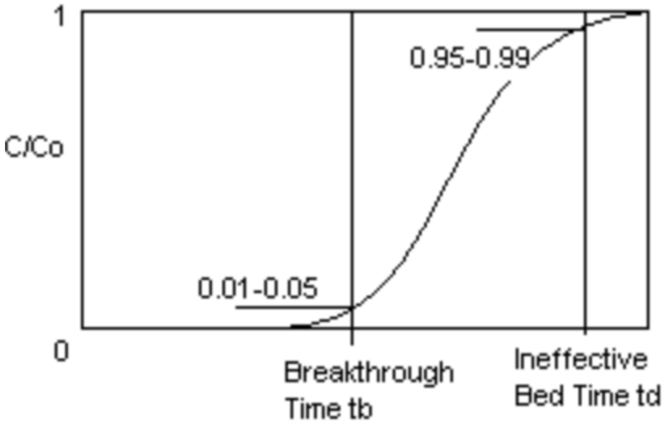


Figure 3: Breakthrough Curve

Source:http://facstaff.cbu.edu/rprice/lectures/figures/adsorb5.gif

C = Concentration of adsorbate

C_o = Concentration of incoming solution

Surface Modification of Adsorbent:

Surface modification of activated carbons is recognized as an attractive approach for enhancement of heavy metal removal. Different heavy metal ions have different affinities for different surface functional groups. It has been reported that the affinities between heavy metals and organic functional groups are different. Modification can be performed by adsorbing foreign organic compounds on the surfaces of carbons. It is well known that activated carbons are able to effectively adsorb organic compounds in aqueous solutions. This chemical behavior leads to immobilization of organic compounds on the carbon surface.

It has been reported that citric acid has a higher binding affinity towards heavy metal ions. It is biodegradable and widely used in the food and pharmaceutical industries. As a result, it was selected for the modification of a commercially available granular activated carbon in this study. The adsorption equilibrium and kinetics can be determined using Langmuir and Freundlich isotherm to quantify the adsorption equilibrium (Chen, Kai-Hau Chon, & Shunnian Wu, 2003).

Characterization of Adsorbent:

1. The methylene blue number is defined as the maximum amount of dye adsorbed on 1.0 g of adsorbent. Adsorption experiments of the molecules of methylene blue are easy and habitually done to characterize activated carbons with the purpose of obtaining information on the adsorption capacity of the materials. According to the dimensions of the methylene blue molecule, it is mainly adsorbed in mesopores, however, a small portion is also found in larger micropore (Hussain, 2017).

2. The point of zero charge is the pH at which the surface of your adsorbent is globally neutral, i.e., contains as much positively charged as negatively charged surface functions. Below this value, the surface is positively charged; beyond this value, it is negatively charged. So normally, it is always easier to adsorb a cation on a negatively charged surface, and an anion on a positively charged surface. However, other interactions may be stronger than purely electrostatic forces, making the effect of surface charge not so important. Additionally, a cation is often complexed with ligands, some of them being possibly negatively charged. Therefore, in such a case, the cation is in fact a negative complex, which may adsorb very well on a positively charged surface (Celzard, 2015).

3. Infrared spectroscopy in organic chemistry is most often used to identify chemical structures from the characteristic adsorption of IR light by different organic functional groups. Thus, the existence of hydroxyl groups, double bonds, and other active parts of a molecule can be deduced. IR-frequency light is passed through a compound. The amount and frequencies of the light absorbed is related to the functional groups and structure of the compound. This helps us to identify the compound (Cooke, 2016).

4. A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector (Everhart-Thornley detector). The number of

secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography. SEM can achieve resolution better than 1 nanometer.

Energy Dispersive X-rays Spectroscopy (EDX or EDS) is an analytical capability were element specific radiation is used for chemical characterisation of the surface near volume. With the aid of proper detectors, the energy or the X-rays is determined. It can be coupled with several applications including Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM).

EDX, when combined with SEM, provides elemental analysis on areas as small as nanometers in diameter. The impact of the electron beam on the sample produces x-rays that are characteristic of the elements found on the sample. The measured intensities yield quantitative information on the element composition and distribution. The depth from where the X-rays originate depends on the material and the used primary electron beam energy. For typical primary energies of 10 to 20 keV it is in the µm range.

Samples for SEM and/or EDX need to be high vacuum compatible. However, for some applications like moisturous or non-conductive samples Environmental SEM (ESEM) is also possible allowing chamber pressures up to 1 mbar (Nanakoudis, 2019).

Regeneration of Adsorbent:

Once adsorption process is over adsorbent is to be discarded as waste. Generation of waste adsorbent is a serious environmental problem. Adsorbents can be regenerated and put to reuse in the same process line. Steam is well known in process industry and can be utilized for regeneration of spent adsorbents. Use of steam for regeneration has multiple benefits however regeneration as a whole process is less studied. Many methods of regeneration are currently being researched which include, thermal regeneration, steam regeneration, pressure swing regeneration, vacuum regeneration, microwave regeneration, ultrasound regeneration, chemical regeneration, oxidative regeneration, ozone regeneration, bio-regeneration. Apart from these regeneration methods combined effects of these methods have been also explored e.g. thermo chemical regeneration, electro-chemical etc. (Shah, 2013).

Chapter 2: Literature Review

Preliminary literature search was carried out to select appropriate adsorbent from the reported one. The review of various adsorbents used is given below.

Adsorbent	**Analyte**	**Conditions**	**Adsorption Capacity/ Adsorption Efficiency**	**Reference**
Granular activated carbon (produced from coconut shell)	Fe(II) and Mn(II)	Contact time: 6 hours Adsorbent dose: 0.1 and 0.6 g and 0.2–0.9 g for Fe(II) and Mn(II) respectively with 200 mL sample solution	Adsorption capacity: 3.6010 and 2.5451 mg/g for Fe(II) and Mn(II) respectively.	(Jusoha, et al., 2015)
Fe impregnated Pumice composite	Mn(II)	Contact time: 24 hours Adsorbent dose: 0.5 to 2.0 g Mn(II) Standard solutions (20-100 mg/L)	Removal efficiencies: 52.3, 60.0 and 33 % for 20, 40 and 60 mg/L of initial Mn(II) concentrations respectively for 0.5 g adsorbent dose	(İzlen, Deniz, & Çifçi, 2017)
Natural zeolite (NZ) modified by NaOH aqueous solutions	Mn(II)	Contact Time: 2 hours Modified by NaOH aqueous solutions (0.5- 2.0 mol /dm^3)	Adsorption capacity: 51.5 mg/g with 1.5 M NaOH	(Ates., Ayten, & Gökçen, 2015)
Durian leaves (Agriculture waste)	Fe(II)	Contact Time: 60 minutes pH = 6	Adsorption capacity: 3.914 mg/g.	(Manal, Mohsen, Jeyaletchumy, Nik, & Azhari, 2015)

Olive stones-derived activated carbons (Agricultural Waste)	Fe(III) and Mn(II)	pH = 5.0 – 6.0	Adsorption capacities for Fe (III) and Mn (II) increased along with an increase of activated carbon dosage	(Akl, Yousef, & AbdElnasser", 2013)
Moringa oleifera leaf, Borassus flabellifer and Mangifera indica	Mn(II)	pH = 6 Contact time = 120 minutes Adsorbent dose = 0.2 g/L	Adsorption Efficiency: 99%, 96%, 93% of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica respectively	(A., Saranya, Sasikala, & Muthuraman, 2017)
Hydroxyapatite Prepared from Cow Bone	Fe(II) and Mn(II)	Contact time = 60 minutes Adsorbent dose = 0.1 – 1 g	Adsorption capacity: 14.68 mg/g and 2.54 mg/g for Mn and Fe respectively	(Olabiyi, OG, & FA, 2018)

I. Adsorbent = Granular activated carbon (produced from coconut shell)

- Batch test had been carried out to determine the potential and the effectiveness of granular activated carbon (GAC) in removal of ferrous and manganese from water. The test was conducted by mixing certain amount of GAC with 200 mL sample solution and shook for 6 hours in room temperature to achieve an equilibrium. This test was conducted using various dosages of GAC, between 0.1 and 0.6 g and 0.2–0.9 g for Fe(II) and Mn(II) respectively. The classical Langmuir and Freundlich adsorption isotherm were applied to evaluate the experimental data and it was found that the experimental data could better fit the Langmuir isotherm. The adsorption capacity of Fe(II) and Mn(II) were 3.6010 and 2.5451 mg/g, respectively. The adsorption capacity for Fe(II) was higher than Mn(II). The main factors that contribute to difference adsorption capacity of Fe(II) and Mn(II) onto GAC are due to ionic radius and electronegativity of metal ions (Jusoha, et al., 2015).

II. Adsorbent = Fe impregnated Pumice composite

- Fe-pumice composite were monitored using scanning electron microscopy (SEM)-energy dispersive X-ray analyser (EDX). Removal of Mn(II) by adsorption process was assessed using pumice and Fe-pumice composite comparatively. Adsorption efficiency was affected by the initial concentration of Mn(II) and adsorbent dose of pumice and Fe-pumice composite. Mn(II) Standard solutions (20-100 mg/L), Fe-pumice composite doses varying from 0.5 to 2.0 g, Contact time = 24 hours. The removal of Mn(II) significantly increased in the Fe-pumice composite system. The removal efficiency of 20 mg/L initial Mn(II) concentration increased from 52.3% to almost 100% when the dose of Fe-pumice composite was increased from 0.5 to 1.5 g. The efficiency of Mn(II) adsorption increased in both system in parallel up to 40 mg/L Mn(II) initial concentration and 0.5 g adsorbent use. However, a drastically drop was observed in the Mn(II) removal efficiency after 40 mg/L initial Mn(II) concentration and it continued to gradually decrease up to 100 mg/L initial Mn(II) concentration. The removal trend of Mn(II) could be explained that metal ions were initially fixed on the active sites of Fe-pumice composite, but further increasing initial Mn(II) concentration caused to decrease of Mn(II) removal due to the saturated active sites on the composite. The removal efficiencies of Mn(II) to be 52.3, 60.0 and 33 % for 20, 40 and 60 mg/L of initial Mn(II) concentrations respectively in the Fe-pumice composite system after 24 hours adsorption time and 0.5 g adsorbent dose.The stability of Fe-pumice composite was evaluated by monitoring of the released Fe concentration. The release of iron was found to be higher in the Fe-pumice composite system than pumice system. (İzlen, Deniz, & Çifçi, 2017).

III. Adsorbent = Natural zeolite (NZ) modified by NaOH aqueous solutions

- Natural zeolite (NZ) modified by NaOH aqueous solutions (0.5- 2.0 mol /dm^3) and the adsorption capacity of natural and modified forms was determined for Mn(II) removal. The characterisations of the zeolites were carried out by XRD, N_2 sorption, FTIR, NH_3-TPD and SEM-EDS. Treatment with NaOH has the effect of multiply by two the Mn(II) adsorption capacity of the natural zeolite. NaOH aqueous solutions (0.5- 2.0 mol /dm^3) Contact Time: 2 hours. The maximum Mn(II) adsorption capacity was achieved with the zeolite treated with 1.5 M of NaOH(51.5 mg/g). More than this concentration of

NaOH leads not only to a decrease in adsorption capacity of natural zeolite for Mn(II), but also to a significant deformation of the zeolite structure. Langmuir isotherm fitted well with results obtained from the Mn(II) adsorption of natural zeolite, the Freundlich isotherm model is more appropriate for the results obtained on NaOH-modified zeolites. (Ates., Ayten, & Gökçen, 2015).

IV. Adsorbent = Durian leaves (Agriculture waste)

- The removal of Fe (II) ions from solution is highly influenced and affected by pH of the solution, contact time and initial metal ion concentration, mixing rate and the particle size of adsorbent. Equilibrium is reached at the 60th minute of batch mixing process and the optimum pH for adsorption is found to be pH 6. The increase in contact time and a decrease in Fe (II) ion concentration tends to increase the rate of removal of Fe (II) ion. The equilibrium data adjusted well with the Langmuir isotherm model by giving out a correlation coefficient of 0.7736. This indicates that a monolayer pattern is followed by the adsorption mechanism of Fe (II) ion onto durian leaves. The maximum adsorption capacity determined using the Langmuir isotherm model is 3.914 mg/g. (Manal, Mohsen, Jeyaletchumy, Nik, & Azhari, 2015).

V. Adsorbent = Olive stones-derived activated carbons (Agricultural Waste)

The optimum pH corresponding to the maximum adsorption was found to lie between 5.0 and 6.0. The results obtained revealed that the sample activated by HNO_3 has the highest adsorption capacity followed by ammonium persulphate and steam activated samples. The amount of Fe (Ш) and Mn (П) adsorbed increased with the increase of concentration. The extent of adsorption for Fe (Ш) and Mn (П) increased along with an increase of activated carbon dosage (Akl, Yousef, & AbdElnasser", 2013).

VI. Adsorbent = Moringa oleifera leaf, Borassus flabellifer and Mangifera indica

- The percentage of removal efficiency of Mn(II) decreased when increases adsorbent dosage where as it was reverse when decreased dosage. When comparing both natural adsorbents the manganese removals from Moringa oleifera leaf, Borassus flabellifer are higher than Mangifera indica activated carbon. The percentage removals [99%, 96%, 93%] of Moringa oleifera leaf, Borassus flabellifer and Mangifera indica were optimum conditions for the removal of manganese is at pH 6, contact time 120min and adsorbent dosage of 0.2 g/L for Moringa oleifera leaf, 0.2 g/L Borassus flabellifer, 0.2 g/L Mangifera indica were studied. The Moringa oleifera leaf activated carbon was highest removal of Mn(II) compared to Borassus flabellifer, Mangifera indica activated carbon (A., Saranya, Sasikala, & Muthuraman, 2017).

VII. Adsorbent = Hydroxyapatite Prepared from Cow Bone

- The adsorption behaviour was studied by batch method. Prepared adsorbent was characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), and X-ray Fluorescence. The effect of initial concentration, pH value of aqueous solution, contact time, adsorbent dose and temperature were the parameters used in determining the optimum conditions of the adsorption process. 60 minutes was established to be the adsorption equilibrium time and the equilibrium adsorption experimental data for the metals were establish to suit the Langmuir adsorption isotherms best and the maximum adsorption capacity was 14.68 mg/g and 2.54 mg/g for Mn(II) and Fe(II) respectively. The adsorption kinetics for the adsorbates was defined best by the pseudo second order kinetic model. The adsorption process is endothermic as revealed by the thermodynamic experiment and the reaction is spontaneous as shown from the values of the free energy change. The hydroxyapatite (adsorbent) was applied to typical raw water with 1.52 mg/l and 3.89 mg/l as the initial concentration of manganese and iron respectively and the removal efficiency for Mn(II) and Fe(II) was 91% and 48% respectively (Olabiyi, OG, & FA, 2018).

Our objective was to propose the adsorbent which can used on the larger scale which usually involves column studies. Hence choosing a powdered form of adsorbent will lead the blockage/clogging of column. So we thought of working with some granular material.

From preliminary literature search it was clear that adsorption on activated carbon is promising technique for Fe and Mn removal. The low adsorption capacity of bare granular activated carbon at low concentration is observed to be one of the significant limitation. Thus literature search was carried out in second phase to in depth study of chemical modification of granular activated carbon. The summery of this study is as follows:

Chemical used for Modification	Analyte	Conditions for Modification	Characterization of Chemically Modified Material	Change in Adsorption Capacity	Reference
Citric Acid	Cu(II)	GAC was reacted with a 1 M citric acid solution at a ratio of 4 g activated carbon to 25 mL citric acid solution.	Specific surface areas determined by NOVA 300 BET analyser. Surface morphology visualized by scanning electron microscopy	Increased adsorption capacity to 14.92 mg Cu/g, which was 140% higher than the unmodified carbon	(J, Paul Chena, Wub, & Chonga)
Nitric Acid	Cu(II)	GAC treated with concentrated nitric acid at a ratio of 10 g of activated carbon to 100 ml of nitric acid.	Surface morphology visualized by scanning electron microscopy. Functional groups detected by FTIR spectra	Adsorption efficiency increased by 125%	(D. Sataphathy & Natarajan, 2005)

I. Adsorbent = Granular Activated Carbon modified by Citric Acid.

- In this study, citric acid was used to modify a commercially available activated carbon to improve copper ion adsorption from aqueous solutions. The carbon was modified with 1.0 M citric acid, followed by an optional step of reaction with 1.0 M sodium hydroxide. It was found that the surface modification reduced the specific surface area by 34% and point of zero charge (pH_{pzc}) of carbon by 0.5 units. Equilibrium results showed that citric acid modification increased the adsorption capacity to 14.92 mg Cu/g, which was 140% higher than the unmodified carbon. Higher initial solution pH resulted in higher copper adsorption. The chemical surface modification adversely affected the copper adsorption rate. Adsorption kinetic mechanisms were investigated with an intraparticle diffusion model. It was found that the modification did not change both external diffusion and intraparticle diffusion (J, Paul Chena, Wub, & Chonga).

II. Adsorbent = Granular Activated Carbon modified by Nitric Acid.

- Concentrated nitric acid, a very powerful oxidizing agent which has been used for modifying the surface of commercial grade carbon. Scavenging of copper ions from aqueous solutions onto both raw as well as modified granular activated carbon has been carried out. Equilibrium results show that surface modification increases the copper ion adsorption by 125% in comparison to that of raw granular activated carbon. FTIR spectra suggest that oxidation of granular activated carbon by nitric acid results in the formation of several functional groups at the carbon surface. The pH studies for both raw and oxidised granular activated carbon show that higher initial solution pH results in higher copper ion adsorption. The surface modification with nitric acid not only enhances the copper adsorption but helps in regeneration of carbon (D. Sataphathy & Natarajan, 2005).

From the above study and literature search we could find out gaps in the existing research. From the identified gaps the following objectives were decided for the project work:

1. **Study water quality of selected site**
2. **Perform Batch adsorption / Column adsorption studies.**
3. **Perform chemical modification and report change in adsorption capacity.**
4. **Characterization of Adsorbent**
5. **Predict mechanism**
6. **Regeneration of Adsorbent**

Chapter 3:
Methodology

Monitoring Basic Water Quality Parameters at selected site

Water quality monitoring is the sampling and analysis of water constituents and conditions. Water quality monitoring is generally considered the primary way of identifying water pollution problems. Combination of chemical and physical monitoring methods helps to achieve the best picture of water quality conditions.

Water quality monitoring can be used for many purposes:

1. To identify whether selected water sample meet guidelines:
2. To identify specific pollutants and sources of pollution.
3. To determine trends. Chemical constituents that are properly monitored (i.e., consistent time of day and on a regular basis, using consistent methods) can be analyzed for trends over time.
4. To screen for impairment. Finding excessive levels of one or more chemical constituents can serve as an early warning "screen" of potential pollution problems.

Acid Wash Procedure for Preparing Sampling Containers:
Each sample bottle was washed with a brush and phosphate-free detergent followed by cold tap water. It was then rinsed with 10% HCl solution and finally rinsed with distilled water.

Sampling of Water Sample:
Whirl-pak bag was rinsed twice with the sample water prior to filling and closing. The mouth of the Whirl-pak Bags was dipped into the running water and the bag was filled fully with sample water. (Half-filling the bottle leaves more room for oxygen which will promote degradation of your sample).

Preservation and Storage of Water Sample:
Raw water sample was filtered and stored in refrigerator at 4 ºC.

The parameters studied are:

1. **Color**

   Hach DR/4000 spectrophotometer sample bottle was filled with filtered Deionised water and was denoted as blank. Another DR/4000 sample bottle was filled with the sample. Blank was placed in cell holder and made zero till the display showed "0" units on Pt-Co scale (Platinum Cobalt Scale). Later the sample was placed in the cell holder and the corresponding value on Pt-CO was recorded.

2. **Turbidity**

   Nephelometer was calibrated using 100 NTU Calibration standard.

   The sample was agitated until air bubbles disappeared and poured into cell. Turbidity reading (NTU) was recorded from the instrument.

3. **pH**

   The pH meter was calibrated using different buffer solutions (i.e. pH = 4, 7 ,and 9). The electrodes were then washed with distilled water and placed in sample solution. The sample was thoroughly stirred, and the corresponding pH was recorded.

4. **Specific Conductivity**

   The conductance of 0.1 N KCl solution was determined using a conductometer. The cell constant of the conductivity cell was determined using the value of observed conductance.

   The conductance of sample was determined, and specific conductance was calculated.

5. **Total Solids (TS)**

   Evaporating dish was dried at 104 ±1°C for 1 hour, cooled, weighed and stored in a desiccator. The sample was stirred with a magnetic stirrer and while stirring, a measured volume was pipetted into the pre-weighed evaporating dish using a wide bore pipette. Evaporated to dryness in an oven at 104 ±1°C.

6. **Total Suspended Solids (TSS)**

   Filter paper was placed on filtration assembly and filtered with 3 successive 20 mL portions of distilled water. Filter paper was then placed in an aluminium dish and dried in oven at 104 ± 1^{o}C for 1 hour. Cooled in desiccator and weighed.

Weighed filter paper was assembled in filtration apparatus. Sample was stirred with a magnetic stirrer and while stirring measured volume was pipetted on to the filter using a wide bore pipette. Washed with 3 successive 10 mL volumes of distilled water, dried and carefully transferred to the aluminium-weighing dish. Dried, cooled and weighed.

7. **Total Hardness as $CaCO_3$**

Standardization of Standardized 0.01M EDTA solution:

10 mL of 0.01 M $ZnSO_4$ solution was pipetted out into conical flask, followed by addition of 2 mL buffer and Eriochrome Black T indicator. This solution was titrated against EDTA solution from burette till the color changed from wine red to blue

Estimation of Total Hardness:

100 mL of the sample was taken into conical flask, followed by addition of 2 mL buffer solution, 2-3 drops of Eriochrome Black T. This solution titrated with standardized EDTA solution (with continuous stirring) until the last reddish color disappeared. At the end point the solution turned blue.

8. **Calcium as Ca^{2+}**

Standardization of Standardized 0.01M EDTA solution:

10 mL of 0.01 M $ZnSO_4$ solution was pipetted out into conical flask, followed by addition 2 mL buffer, Eriochrome Black T indicator. This solution was titrated against EDTA solution from burette till the color changed from wine red to blue

Estimation of Ca^{2+}:

50 mL of the sample was taken and 1 mL Sodium Hydroxide solution (8%) add pinch of Mercurex Powder were added. This solution was titrated with standardized EDTA solution from the burette until the light pink color of solution turned into light blue color.

9. **Total Alkalinity as $CaCO_3$**

Standardization of ~0.02 N H_2SO_4:

10 mL of 0.02 N Na_2CO_3 solution was pipetted into conical flask, followed by addition methyl orange indicator. This solution was titrated against H_2SO_4 solution from burette till the color changed from yellow to wine red.

Estimation of Total Alkalinity:

50 mL water sample was taken, to which 3 drops of phenolphthalein indicator were added. This sample was titrated with 0.02 N sulfuric acid till color changed from pink to clear. To the same sample 3 drops of bromcresol green indicator were added. This solution was then titrated with 0.02N sulfuric acid till color changed from blue to yellow.

10. Chloride as Cl^-

25mL sample was taken in a conical flask and titrated with standardized 0.0141 N $AgNO_3$ solution till the colored turned pinkish yellow.

11. Sulphates as SO_4^{2-}

250 mL of the unknown sample is measured and placed into 400 mL beaker. To this 3 mL of 1:1 HCl added. The solution was heated to boiling point and slowly 80 mL of 0.05 M $BaCl_2$ was added with efficient stirring. The mixture solution was left to digest for about 30 minutes. The solution was allowed to settle. A few drops of $BaCl_2$ was added to the clear solution at the top of the precipitate to check for complete precipitation. The precipitated $BaSO_4$ was filtered using the previously weighed filter paper and drained in a suction pump.

The Barium sulphate precipitate was washed with warm distilled water to free the Cl^- ion in the precipitate. The precipitate freeness of Cl^- ion was tested by performing qualitative test of Cl^-. This was done by adding 1mL of 0.1M HNO_3 into the filtrate collected during the washing and drops of $AgNO_3$ was added in drop wise, if AgCl precipitate formed then it indicates that the Barium sulphate precipitate needs further washing. The filter paper and the residue ($BaSO_4$) were dried and weighed.

12. Nitrate as NO_3^-

10 mL of nitrate stock solution was pipetted out to a beaker, 5 mL of Concentrated HCl and 2 mL of Zn/NaCl granular mixture were added and was allowed to stand for 30 minutes with occasionally stirring to form nitrite. Then the solution was filtered to 100 mL standard flask using Whatman No 41-filter paper and diluted up to the mark. Aliquots of stock solution containing 1- 10 µg/mL of reduced nitrate were transferred into series of 10 mL standard flask. 1 mL of 0.5% sulfanilic acid and 1 mL of 2 M HCl solution were added, shaken thoroughly for 5 minutes for the diazotization reaction to

go to completion. Then, 1 mL of 0.5% methyl anthranilate and 2 mL of 2 M sodium hydroxide solution were added to form an azo dye and the contents were diluted to 10 mL with water. After dilution to 10 mL with water, the absorbance of the red colored dye was measured at 493 nm.

13. Fluorides as F^-

Calibration diagrams were obtained by measuring of potential of six different sets of fluoride standard solutions ordered from low to high concentration. The concentration range is from 0.07 to 1.0 mg/L.

14. Manganese as Mn^{2+}

The sample cell was filled with 10 mL of deionized water. Second sample cell was filled with 10 mL of sample. The contents of Ascorbic Acid Powder Pillow were added to each sample cell. The mixture was shaken to dissolve the contents. Then 12 drops of Alkaline Cyanide Reagent Solution were added to each cell and the mixture was swirled followed by addition of 12 drops of PAN Indicator Solution, 0.1% to each cell. The mixture was well swirled and allowed to stand for 2 minutes. The absorbance of the solution was recorded on spectrophotometer at 520 nm.

15. Iron as Fe^{2+}

The sample cell was filled with 10 mL of deionized water. Second sample cell was filled with 10 mL of sample. The contents of FerroVer Iron Reagent Powder Pillow were added to each sample cell. The mixture was well swirled and allowed to stand for 3 minutes. The absorbance of the solution was recorded on spectrophotometer at 560 nm.

16. Chemical Oxygen Demand (COD)

Standardization of Ferrous Ammonium Sulphate Solution (FAS):

10 mL of FAS was pipetted out into the conical flask, followed by 30 mL of 2 N H_2SO_4,3 mL concentrated H_3PO_4 and Sodium diphenyl amine sulphonate indicator. This solution was titrated against 0.25 N $K_2Cr_2O_7$ from the burette till the color changed from colorless to purple

Estimation of COD:

20 mL of sample was taken in the flask. To that 10 mL of Potassium dichromate solution, a pinch of each silver sulphate and mercuric sulphate and 30 mL of sulphuric acid were added. The mixture was refluxed for 2 hours .The contents were cooled diluted to 150 mL by adding distilled water. To this solution 2-3 drops of Ferroin indicator solution was added and titrated against ferrous ammonium sulphate solution. At the end point blue green color of contents changed to reddish blue. A blank sample of distilled water was carried through the same COD testing procedure as the sample.

17. Dissolved oxygen (DO)

Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

10 mL of 0.025 N $K_2Cr_2O_7$ solution was pipetted out into 250 mL conical flask and 2 mL concentrated HCl solution was added followed by 5 mL 5% KI solution. Conical flask was covered with watch glass and kept in dark for 5 minutes. After 5 minutes the flask solution was titrated against $Na_2S_2O_3$ solution from burette till the solution attained pale yellow color. Then starch indicator was added, and the titration was continued till the color of solution changed from blue to colorless.

Estimation of dissolved oxygen

BOD bottle (300 ml volume) was filled bottle with water sample. 1 mL $MnSO_4$ solution and 1mL alkali azide iodide solution were added. The precipitated formed was allowed to settle. To this solution 1 mL Concentrated H_2SO_4 was added and shaken for about 8 times.

200 mL of this water sample was taken in a titration flask and titrated with 0.025 N $Na_2S_2O_3$ till light-yellow color appeared. To this 1 mL of starch solution was added and again, titrated with 0.025N $Na_2S_2O_3$ till the blue color disappeared.

18. Biological Oxygen demand (BOD)

Estimation of BOD:

With the help of pH meter, the pH of the water sample was adjusted to neutrality by adding 1 N NaOH or 1 N sulphuric acid. The water samples were filled in all the six BOD bottles and 1 mL allylthiourea was added to each bottle. The amount of dissolved oxygen in three and mean of three readings were taken and treats as D_1.

The remaining three BOD bottles were incubated at 20°C in a BOD incubator for 3 days. After 3 days, the amount of dissolved oxygen concentration was estimated in all these three incubated samples of water. The mean of these three readings were taken and treated as D_3.

From the reported studies, the concentration of Fe2+ and Mn2+ were found to be as high as 6 ppm. Hence 10 ppm Mn2+ ions and Fe2+ ions were used throughout the experiment (As we are focusing on drinking water and considering high removal efficiency of activated carbon after adsorption the amount of analyte after adsorption should be measurable)

Batch Adsorption Studies

Adsorption Experiment Based On Adsorbent Dose

Granular Activated Carbon (GAC) was activated by keeping it in an oven at 150 ºC for one hour. 100 mL of the adsorbate solution was measured and contacted with varied masses (1, 2, 3, 4, 5, 6, 7 and 8 g) of the adsorbent (Granular Activated Carbon) for an equilibrium adsorption time of 1 hour at room temperature followed by intermittent stirring. The solution was filtered with Whatmann filter paper and the filtrate solution was taken for Spectrophotometer analysis.

Adsorption Experiment Based on Contact Time

Granular Activated Carbon (GAC) was activated by keeping it in an oven at 150 ºC for one hour. The effect of contact time on adsorption was studied. 2 g of GAC was added to water sample 100 mL at pH 6.8. The mixture was shaken at room temperature.

Surface Modification of Granular Activated Carbon (GAC)

Preparation of citric acid-modified and base- extracted activated carbons

The Granular activated carbon was washed with deionised (DI) water . It was then left to dry in an oven at 110 ºC for 2 hours and was denoted by GAC.

The GAC was reacted with 1 M citric acid solution at a ratio of 4 g activated carbon to 25 mL citric acid solution. It was shaken for 30 minutes before being dried at 50 ºC overnight. The citric acid modified activated carbon was then washed with DI water until no turbidity could be observed when a 0.1 M $Pb(NO_3)_2$ solution was added to the washed liquid. The modified activated carbon was dried at 110 ºC for 2 hours and referred to as CAC.

A fraction of CAC was continuously washed with a 1 M NaOH solution for at least 2 hours. It was then washed with DI water to remove the excess sodium hydroxide until no pH variation in the washed liquid could be detected. This base-extracted CAC was then dried at 110 ºC for 2 hours and referred to as SAC.

Effect of pH

Granular Activated Carbon (GAC) was activated by keeping it in an oven at 150 ºC for one hour. During the pH effect, the parameters of temperature, solution volume, adsorbent dosage, shaking time and initial metals ion concentration were fixed at 25 °C, 100 mL, 1 g, 24 hours and 10 mg/L respectively. Effects of pH were tested at pH 3, 4, 5, 6, 7 and 8. pH values ranging from 3 to 8 were adjusted by adding 0.5 M HCl solution or 0.5 M NaOH solution.

Adsorption Experiment Based On Adsorbent Dose

Granular Activated Carbon (GAC) was activated by keeping it in an oven at 150 ºC for one hour. 100 mL of the adsorbate solution was measured and contacted with varied masses (1, 2, 3, 4, 5, 6, 7 and 8 g) of the different adsorbents (i.e. GAC, CAC, SAC) for an equilibrium adsorption time of 1hour at room temperature followed by intermittent stirring. The solution was filtered with Whatmann filter paper and the filtrate solution was taken for Spectrophotometer analysis.

Column Studies

The column packed with different adsorbents (i.e. GAC, SAC,CAC) in the absorbent: adsorbate ratio of 1:100 and 1:1000. The flow rate of 2 mL/minute was maintained throughout the experiment. Metal ion solution (initial concentration =10 mg/L) was passed onto the column and different aliquots of eluate solution were collected and tested for the concentration of metal ion using spectrophotometry.

Characterization of Adsorbent

Point of Zero Charge (pHpzc)

50 mL of 0.01 M NaCl solution was taken and bubbled with nitrogen gas for few minutes to expel the dissolved CO_2 . pH was then adjusted to 2 by using 0.5 M HCl or 0.5 M NaOH solutions. 0.5 g of Granular Activated carbon (GAC) was added into the flask containing 50 ml of NaCl solution already adjusted to pH 2 and kept for shaking for 24 hours in an airtight condition at 200 rpm at room temperature. Same process was repeated to get Initial pH of 4, 6, 8, 10 and 12, and then 0.5 g of GAC was added after the pH adjustment , and kept for shaking at 200 rpm for 24 hours .After 24 hours of shaking, it was filtered and the final pH for each set was measured. Graph of final pH V/s Initial pH was plotted .The point where initial pH curve crosses final pH curve (Initial pH = Final pH) indicated pHpzc.

Methylene Blue Number

In order to determine the methylene blue number of activated carbons 0.02 g of activated carbon were stirred with 100 mL of MB concentration of 100 ppm for 3 hours at 200 rpm. The solution was then filtered through Whatman 41 filter paper and the remaining concentration of methylene blue was determined by measuring the absorbance at 664 nm using a UV/ Visible spectrophotometer.

Regeneration of Adsorbent

For desorption of M^{2+} ions: (M^{2+} = Mn^{2+} or Fe^{2+})

100 mL of 10 ppm M^{2+} solution was taken in the beaker. 1 g of Granular Activated Carbon (GAC) was added to the beaker, the beaker was covered and kept in dark for 24 hours. The solution filtered and the filtrate was discarded. The adsorbent (GAC) containing adsorbed M^{2+} ions was kept in contact with 1 M HNO_3 solution and kept on shaker for 16 hours. Then the solution was filtered and filtrate solution was subjected to spectrophotometric analysis for the determination of concentration of M^{2+} ions. The % desorption efficiency of 1 M HNO_3 solution was calculated. The regenerated adsorbent was again subjected to above procedure for various cycles and % desorption efficiency at each cycle was calculated.

The above experiment was repeat using 0.1 M HNO_3 and its % desorption efficiency was compared with % desorption efficiency of 1 M HNO_3.

Chapter 3:

Results and Discussions

Monitoring Basic Water Quality Parameters at selected site

I. Physical Analysis

i. Color

The display showed “1” units on Pt-Co scale (Platinum Cobalt Scale).

ii. Odour

The odour was reported as Odourless.

iii. Taste

The taste was reported as unobjectionable

iv. Turbidity

The turbidity was displayed as 1.2 NTU.

v. pH

The pH was displayed as 6.5

vi. Specific Conductivity

Observations and Calculations:

1. Room Temperature: 25 °C
2. Observed conductance of 0.1 N KCl = 11.47 $\mu\ siemens$
3. Cell Constant = $\frac{Specific\ Conductane\ at\ 25\ °C}{Observed\ Conductance} = \frac{12.88}{11.47}$ = 1.123
4. Observed Conductance of sample = 46.8 $\mu\ siemens$
5. Specific Conductance of sample = Observed Conductance × Cell Constant

   = 46.8 × 1.123

   = 52.56 $\mu\ siemens$

Result: Specific Conductance of sample = 52.56 $\mu\ siemens$

II. Chemical Analysis

i. **Total Solids (TS)**

Observations:

Weight of dish = 38820 mg

weight of dish + residue = 38820.291mg

Calculation:

mg Total Solids/L = $\frac{A-B}{mL\ sample} \times 1000$

where: A = weight of dish + residue (mg)

B = weight of dish (mg)

mg Total Solids/L = $\frac{38820.291-38.820}{10} \times 1000$

= 29.1 mg/L

Result: Total Solids = 29.1 mg/L

ii. **Total Suspended Solids (TSS)**

Observations:

Weight of filter = 0.1 mg

Weight of filter + residue = 0.103 mg

Calculations:

mg Total Suspended Solids/L = $\frac{A-B}{mL\ sample} \times 1000$

where: A = weight of filter + residue (mg)

B = weight of filter (mg)

mg Total Suspended Solids/L = $\frac{0.103-0.1}{10} \times 1000$

= 0.3 mg/L

Result:

Total Suspended Solids = 0.3 mg/L

iii. **Total Dissolved Solids (TDS)**

Calculation:

$TDS = TS - TSS$

where:

TDS = Total Dissolved Solids (mg/L)

TS = Total solids (mg/L)

TSS = Total Suspended Solids (mg/L)

$TDS = 29.1 - 0.3$

= 28.8 mg/L

Result: Total Dissolved Solids = 28.8 mg/L

iv. **Total Hardness as $CaCO_3$**

Observation:

Part I: Standardization of ~ 0.01 M EDTA Solution

Burette solution: Standardized 0.01M EDTA solution

Flask Solution: 10 mL of 0.01 M $ZnSO_4$ solution + 2 mL buffer

Indicator: Eriochrome Black T

Color change: Wine red to blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	10.0 -11.0 mL	I	II	III
Final		10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact molarity of EDTA solution:

$$M_1V_1(EDTA) = M_2V_2(\mathrm{ZnSO_4})$$

$$M_1 \times 10 = 0.01 \times 10$$

$$M_1 = 0.01\ M$$

Part II: Estimation of Total Hardness

Burette solution: Standardized 0.01M EDTA solution

Flask Solution: 100 mL sample + 2 mL buffer

Indicator: Eriochrome Black T

Color change: Wine red to blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	2.0 – 3.0 mL	I	II	III
Final		2.8	2.8	2.8
Initial		0	0	0
Difference		2.8	2.8	2.8

Calculations:

$$Hardness\ as\ CaCO_3\ (mg/L) = \frac{V \times N \times 50 \times 1000}{SV}$$

Where V = Volume of titrant (mL)

N = Normality of EDTA

50 = Equivalent weight of $CaCO_3$

SV = sample volume

$$Hardness\ as\ CaCO_3\ (mg/L) = \frac{2.8 \times 0.01 \times 50 \times 1000}{100}$$

= 14.0 mg/L

Result: Hardness as $CaCO_3$ (mg/L) = 14.0 mg/L

v. **Calcium as Ca^{2+}**

Observation:

Part I: Standardization of ~ 0.01 M EDTA Solution

Burette solution: Standardized 0.01M EDTA solution

Flask Solution: 10 mL of 0.01 M $ZnSO_4$ solution + 2 mL buffer

Indicator: Eriochrome Black T

Color change: Wine red to blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	10.0 -11.0 mL	I	II	III
Final		10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact molarity of EDTA solution:

$$M_1V_1(EDTA) = M_2V_2(\mathrm{ZnSO_4})$$

$$M_1 \times 10 = 0.01 \times 10$$

$$M_1 = 0.01\ M$$

Part II: Estimation of Ca^{2+}

Burette solution: Standardized 0.01M EDTA solution

Flask Solution: 50 mL sample + 1 mL Sodium Hydroxide solution

Indicator: Mercurex Powder.

Color change: Light pink to light blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	0 – 1.0 mL	I	II	III
Final		0.5	0.5	0.5
Initial		0	0	0
Difference		0.5	0.5	0.5

Calculations:

$$Calcium\ as\ Ca^{2+}(mg/L) = \frac{V \times N \times 50 \times 1000}{SV}$$

Where V = Volume of titrant (mL)

N = Normality of EDTA

50 = Equivalent weight of $CaCO_3$

SV = sample volume

$$Calcium\ as\ Ca^{2+}(mg/L) = \frac{0.5 \times 0.01 \times 50 \times 1000}{50}$$

= 5.0 mg/L

Result: Calcium as Ca^{2+} = 5.0 mg/L

vi. Magnesium as Mg^{2+}

Calculations:

$$Magnesium\ as\ Mg^{2+}(mg/L)$$

$$= (Total\ Hardness\ as\ CaCO_3 - Ca\ Hardness) \times 0.243$$

$$= (14 - 5) \times 0.243$$

= 2.19 mg/L

Result: Magnesium as Mg^{2+} = 2.19 mg/L

vii. Total Alkalinity as $CaCO_3$

Observation:

Part I: Standardization 0.02 N H_2SO_4

Burette solution: 0.02 N H_2SO_4 solution

Flask Solution: 10 mL of 0.02 N Na_2CO_3

Indicator: Methyl orange

Color change: Yellow to wine red

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	10.0 – 11.0 mL	I	II	III
Final		10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact normality of H_2SO_4 solution:

$$N_1V_1(\mathrm{H}_2SO_4) = N_2V_2(\mathrm{Na}_2CO_3)$$

$$N_1 \times 10 = 0.02 \times 10$$

$$N_1 = 0.02\ N$$

Part II: Determination of Total alkalinity

Burette solution: 0.02 N H_2SO_4 solution

Flask Solution: 50 mL sample + 3 drops of phenolphthalein indicator

Indicator: bromcresol green

Color change: Blue to yellow

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	0 – 1.0 mL	I	II	III
Final		0.8	0.8	0.8
Initial		0	0	0
Difference		0.8	0.8	0.8

Calculations:

$$Total\ Alkalinity\ \ as\ CaCO_3\ (mg/L) = \frac{A \times N \times 50000}{V}$$

Where: A= volume of sulfuric acid used in mL; N = normality of acid used to titrate; V= volume of sample used in mL

$$Total\ Alkalinity\ \ as\ CaCO_3\ (mg/L) = \frac{0.8 \times 0.02 \times 50000}{50}$$

= 16.0 mg/L

Result: Total Alkalinity as $CaCO_3$ (mg/L) = 16.0 mg/L

viii. Chloride as Cl^-

Observation:

Burette solution: Standard 0.0141 N $AgNO_3$ solution

Flask Solution: 25 mL sample

Indicator: Potassium chromate indicator

Color change: Yellow to pinkish yellow

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	0 – 1.0 mL	I	II	III
Final		0.3	0.3	0.3
Initial		0	0	0
Difference		0.3	0.3	0.3

Calculations:

$$Chloride\ ion\ concentration\ (mg/L) = \frac{A \times N \times 35.45 \times 1000}{V_{sample}}$$

Where: A = volume of titrant used (mL) , N is normality of silver nitrate

V_{sample} is volume of sample used (mL).

$$Chloride\ ion\ concentration\ (mg/L) = \frac{0.3 \times 0.0141 \times 35.45 \times 1000}{25}$$

= 6.0 mg/L

Result: Chloride ion concentration = 6.0 mg/L

ix. Sulphates as SO_4^{2-}

Observations and Calculations:

Mass of filter paper = 1.048g

Mass of precipitate and fitter paper = 3.685g

Mass of precipitate $BaSO_4$ is = 3.685 - 2.048 = 0.637g

$$Weight\ of\ SO_4^{2-} = Weight\ of\ BaSO_4 \times\ Gravimetic\ factor$$

$$Weight\ of\ SO_4^{2-} = Weight\ of\ BaSO_4 \times \frac{gram\ formula\ weight\ of\ SO_4^{2-}}{gram\ formula\ weight\ of\ BaSO_4}$$

$$Weight\ of\ SO_4^{2-} = 0.637 \times \frac{32.066 + 4 \times 16}{137.33 +\ 32.066 + 4 \times 16}$$

$$Weight\ of\ SO_4^{2-} = 0.637 \times\ 0.4116$$

$$SO_4^{2-}(mg/L) = \frac{Weight\ of\ BaSO_4\ in\ mg}{Sample\ taken\ (mL)}$$

$$SO_4^{2-}(mg/L) = \frac{0.637 \times\ 0.4116\ \times\ 10^3}{250}$$

= 1.048 mg/L

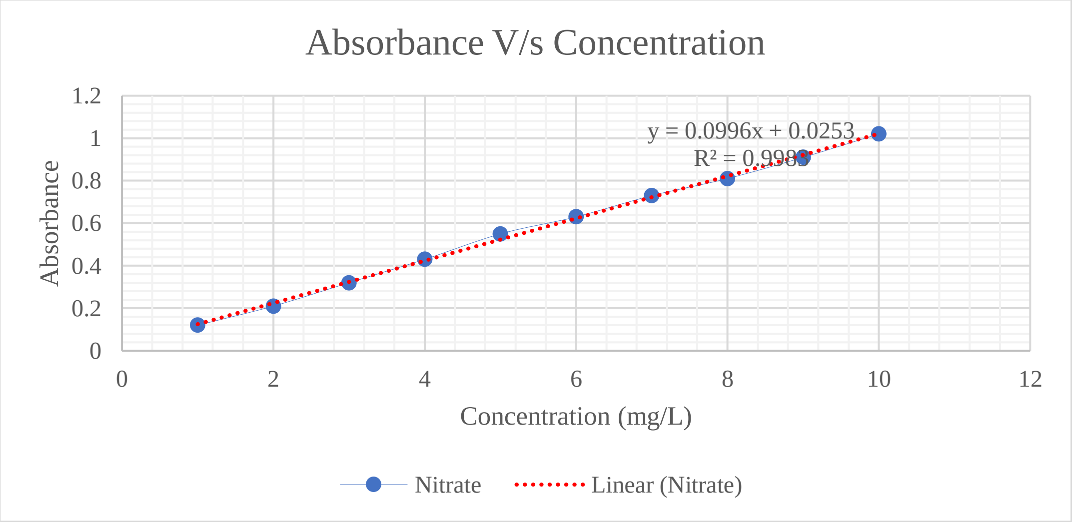
Result: Sulphates as SO_4^{2-} = 1.048 mg/L

x. Nitrate as NO_3^-

Observation:

Concentration of solution containing reduced nitrate μg/L	Volume of stock solution added (mL)	Volume of 0.5% sulfanilic acid added (mL)	Volume of 2 M HCl added (mL)	Volume of 0.5% methyl anthranilate added (mL)	Volume of 2M NaOH added (mL)	Total volume (mL)	Absorbance
1	0.1	1	1	1	2	10	0.12
2	0.2	1	1	1	2	10	0.21
3	0.3	1	1	1	2	10	0.32
4	0.4	1	1	1	2	10	0.43
5	0.5	1	1	1	2	10	0.55
6	0.6	1	1	1	2	10	0.63
7	0.7	1	1	1	2	10	0.73
8	0.8	1	1	1	2	10	0.81
9	0.9	1	1	1	2	10	0.91
10	1.0	1	1	1	2	10	1.02
Sample	-	1	1	1	2	10	0.2

Calibration curve for determination of nitrate in water



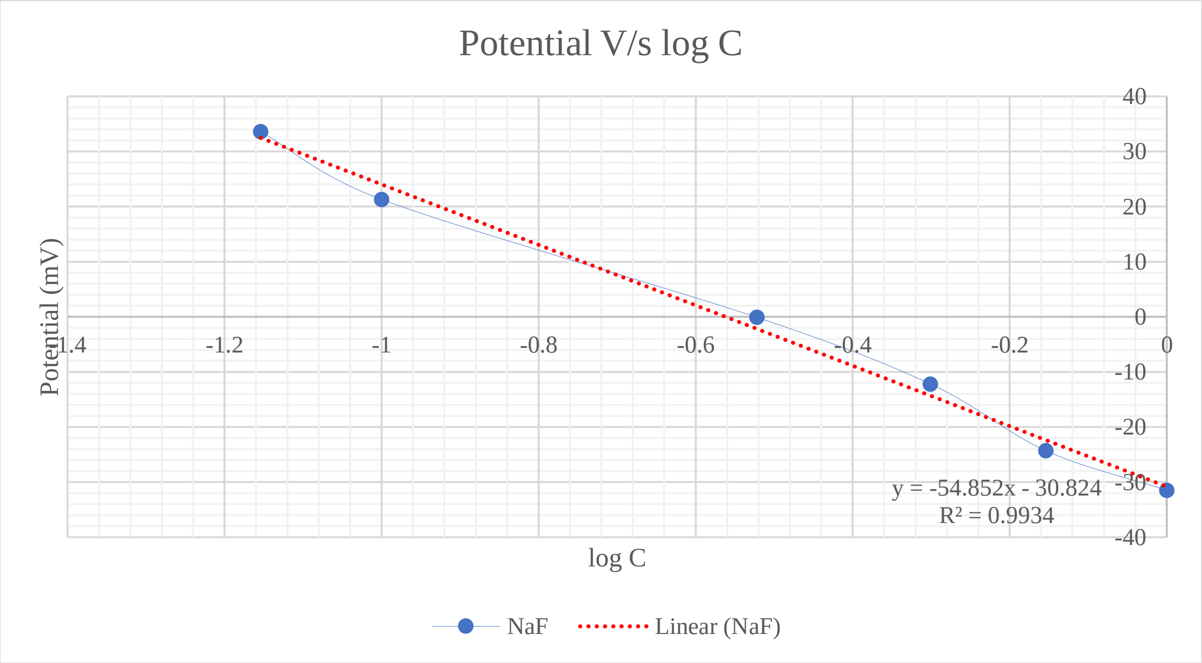
Result: The absorbance of sample solution was found to be 0.2 hence from the calibration curve, the corresponding concentration of nitrate ions in sample = 2 mg/L.

xi. Fluorides as F^-

Observation:

Concentration of F^- (mg/L)	$\log C_{F^-}$	Potential (mV)
0.07	-1.154	33.6
0.1	-1.0	21.3
0.3	-0.522	-0.1
0.5	-0.301	-12.2
0.7	-0.154	-24.3
1.0	0.0	-31.5
Sample	-	15.2

Potentiometric responses of the membrane towards different concentrations of fluoride ion:



Calculations

The electrode potential produced by sample = 15.2 mV corresponding to

log C = -0.823

C = Antilog (-0.823) = 0.150 mg/L

Result

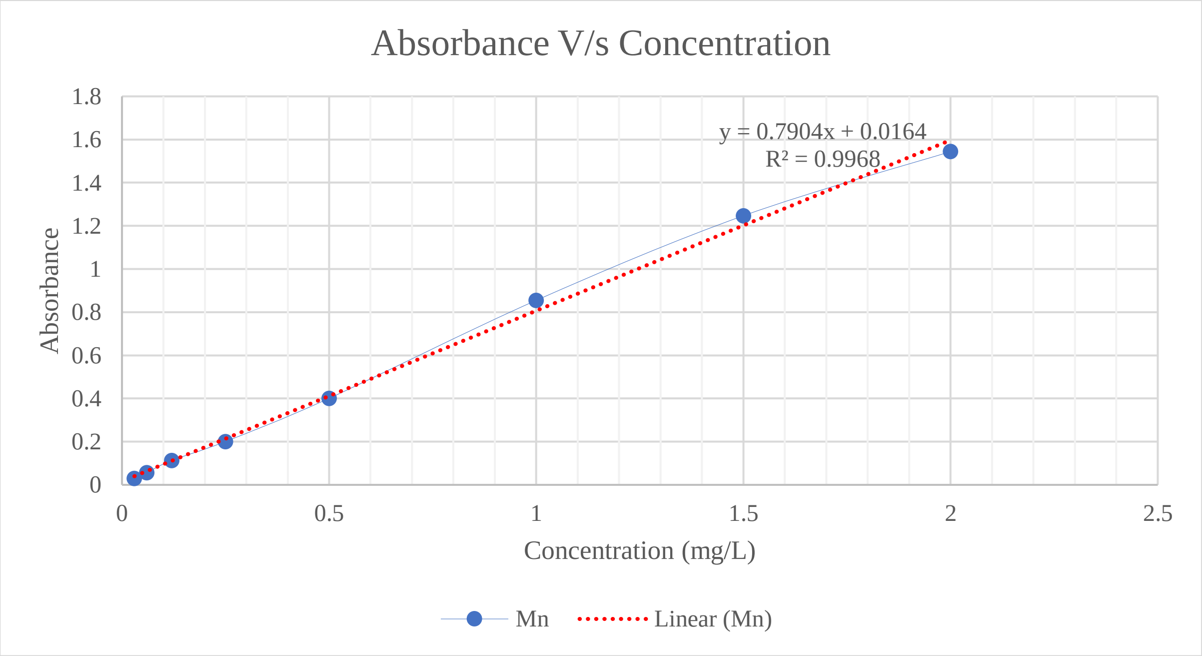
Concentration of fluoride ions in the sample = 0.15 mg/L

xii. Manganese as Mn^{2+}

Observation:

Concentration of Standard Manganese solution (mg/L)	Volume of stock solution (10 mg/L) added (mL)	Total Volume	Absorbance
0.03	0.15	50	0.0291
0.06	0.3	50	0.0569
0.12	0.6	50	0.113
0.25	1.25	50	0.201
0.5	2.5	50	0.401
1.0	5.0	50	0.855
1.5	7.5	50	1.247
2.0	10.0	50	1.544
Sample	-	50	0.321

Calibration Curve for determination Mn^{2+} in water



Result:

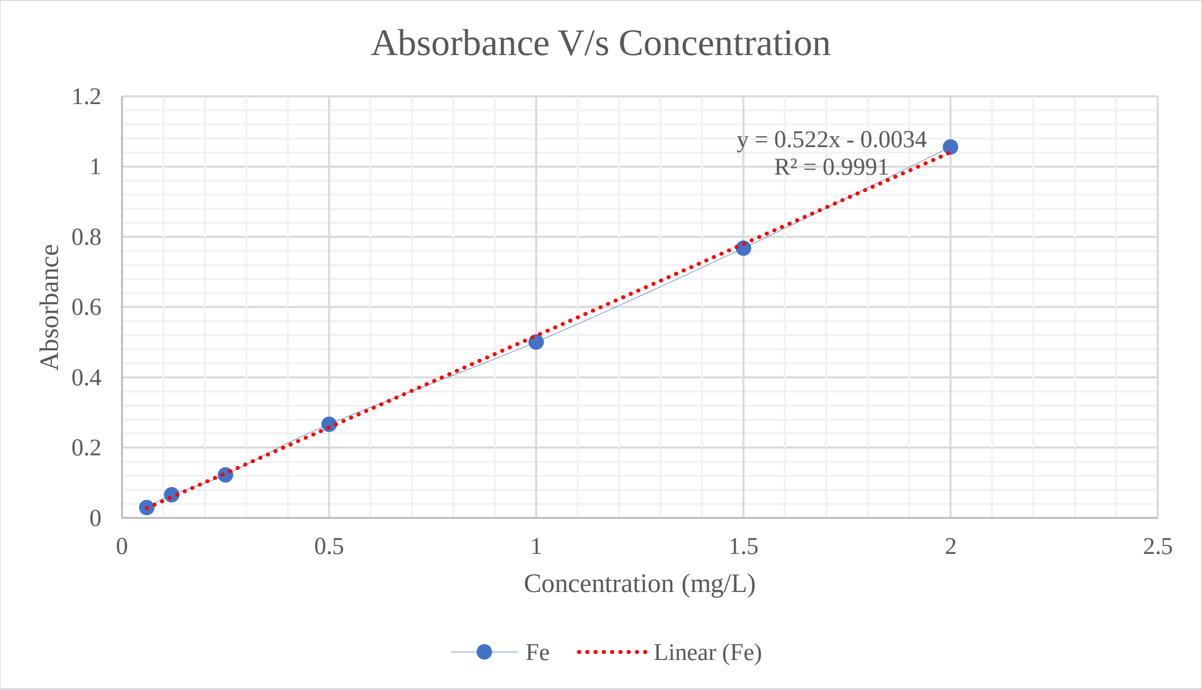
The absorbance of sample was found to be 0.321 hence from the calibration curve, the corresponding concentration of Mn^{2+} ions in the sample = 0.35 mg/L

xiii. Iron as Fe^{2+}

Observation:

Concentration of Standard Fe solution (mg/L)	Volume of stock solution (10 mg/L) added (mL)	Total Volume	Absorbance
0.06	0.3	50	0.030
0.12	0.6	50	0.066
0.25	1.25	50	0.123
0.5	2.5	50	0.267
1.0	5.0	50	0.501
1.5	7.5	50	0.768
2.0	10.0	50	1.056
Sample	-	50	0.04

Calibration Curve for determination Fe^{2+} in water



Result:

The absorbance of sample was found to be 0.04 hence from the calibration curve, the corresponding concentration of Fe^{2+} ions in the sample = 0.09 mg/L

xiv. Chemical Oxygen Demand (COD)

Observation:

Part I: Standardization of ~ 0.25 N FAS solution

Burette solution: 0.25 N $K_2Cr_2O_7$ Solution

Flask Solution: 10 mL FAS + 30 mL of 2 N H_2SO_4 + 3 mL Concentrated H_3PO_4

Indicator: Sodium diphenyl amine sulphonate indicator

Color change: Colorless to purple

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
		I	II	III
Final	10.0 -11.0 mL	10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact normality of FAS solution:

$$N_1V_1(\mathrm{K_2}Cr_2O_7) = N_2V_2(\mathrm{FAS})$$

$$0.25 \times 10 = N_2 \times 10$$

$$N_2 = 0.25\ N$$

Part II: Blank titration

Burette solution: 0.25 N Ferrous Ammonium Sulphate Solution

Flask Solution: 20 mL distilled water + 10 mL of Potassium dichromate solution + pinch of each silver sulphate and mercuric sulphate + 30 mL of sulphuric acid + 150 mL of distilled water

Indicator: Ferroin indicator

Color change: Blue green to reddish blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	25.0 – 26.0 mL	I	II	III
Final		25.6	25.6	25.6
Initial		0	0	0
Difference		25.6	25.6	25.6

Part III: Estimation of COD

Burette solution: 0.25 N Ferrous Ammonium Sulphate Solution

Flask Solution: 20 mL sample + 10 mL of Potassium dichromate solution + pinch of each silver sulphate and mercuric sulphate + 30 mL of sulphuric acid + 150 mL of distilled water

Indicator: Ferroin indicator

Color change: Blue green to reddish blue

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	23.0 – 24.0 mL	I	II	III
Final		25.5	25.5	25.5
Initial		0	0	0
Difference		25.5	25.5	25.5

Calculations:

$$COD\ (mg/L) = \frac{(B-A)\times\ N\ \times 1000 \times 8}{V}$$

where, **A** = Volume of titrant used against sample (in ml)

B = Volume of titrant used against Blank (in ml)

N = Normality of titrant (0.25N)

V = Volume of Sample taken (in ml).

$$COD\ (mg/L) = \frac{(25.6 - 25.5) \times 0.25 \times 1000 \times 8}{20}$$

= 10.0 mg/L

Result:

Chemical Oxygen Demand (COD) = 10.0 mg/L

xv. Dissolved oxygen (DO)

Observation

Part I: Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

Burette solution: ~ 0.025 N $Na_2S_2O_3$ solution

Flask Solution: 10 mL of 0.025 N $K_2Cr_2O_7$ + 2 mL Concentrated HCl solution + 5 mL 5% KI solution

Indicator: Starch indicator

Color change: Blue to colorless

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
		I	II	III
Final	10.0 -11.0 mL	10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact normality of $Na_2S_2O_3$ solution:

$$N_1V_1(K_2Cr_2O_7) = N_2V_2(Na_2S_2O_3)$$

$$0.025 \times 10 = N_2 \times 10$$

$$N_2 = 0.025\ N$$

Part II: Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

Burette solution: 0.025 N $Na_2S_2O_3$ solution

Flask Solution: 200 ml of water sample + 1 mL $MnSO_4$ solution + 1mL alkali azide iodide solution + 1 mL Concentrated H_2SO_4

Indicator: Starch indicator

Color change: Blue to colorless

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	7.0 – 8.0 mL	I	II	III
Final		7.3	7.3	7.3
Initial		0	0	0
Difference		7.3	7.3	7.3

Calculation:

$$DO\ in\, mg/L = \frac{V \times N}{0.025}$$

Where V = mL thiosulphate solution used and N = molarity of thiosulphate titrant

$$DO\ in\, mg/L = \frac{7.3 \times 0.025}{0.025}$$

= 7.3 mg/L

Result:

Dissolved Oxygen (DO) = 7.3 mg/L

xvi. Biological Oxygen Demand (BOD) at 27 ºC (3 days)

Observation

Part I: Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

Burette solution: ~ 0.025 N $Na_2S_2O_3$ solution

Flask Solution: 10 mL of 0.025 N $K_2Cr_2O_7$ + 2 mL Concentrated HCl solution + 5 mL 5% KI solution

Indicator: Starch indicator

Color change: Blue to colorless

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	10.0 -11.0 mL	I	II	III
Final		10.0	10.0	10.0
Initial		0	0	0
Difference		10.0	10.0	10.0

Exact normality of $Na_2S_2O_3$ solution:

$$N_1V_1(\mathrm{K}_2\mathrm{C}r_2O_7) = N_2V_2(\mathrm{N}a_2S_2\mathrm{O}_3)$$

$$0.025 \times 10 = N_2 \times 10$$

$$N_2 = 0.025\ N$$

Day 1

Part II: Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

Burette solution: 0.025 N $Na_2S_2O_3$ solution

Flask Solution: 200 ml of water sample + 1 mL $MnSO_4$ solution + 1mL alkali azide iodide solution + 1 mL Concentrated H_2SO_4

Indicator: Starch indicator

Color change: Blue to colorless

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
	7.0 – 8.0 mL	I	II	III
Final		7.3	7.3	7.3
Initial		0	0	0
Difference		7.3	7.3	7.3

Calculation:

$$DO\ in\, mg/L = \frac{V \times N}{0.025}$$

Where V = mL thiosulphate solution used and N = molarity of thiosulphate titrant

$$DO\ in\, mg/L = \frac{7.3 \times 0.025}{0.025}$$

= 7.3 mg/L

Day 3

Part II: Standardization of ~ 0.025 N $Na_2S_2O_3$ solution

Burette solution: 0.025 N $Na_2S_2O_3$ solution

Flask Solution: 200 ml of water sample + 1 mL $MnSO_4$ solution + 1mL alkali azide iodide solution + 1 mL Concentrated H_2SO_4

Indicator: Starch indicator

Color change: Blue to colorless

Observation table:

Burette Reading	Pilot Reading (mL)	Constant Reading (mL)		
		I	II	III
Final	7.0 – 8.0 mL	7.0	7.0	7.0
Initial		0	0	0
Difference		7.0	7.0	7.0

Calculation:

$$DO\ in\, mg/L = \frac{V \times N}{0.025}$$

Where V = mL thiosulphate solution used and N = molarity of thiosulphate titrant

$$DO\ in\, mg/L = \frac{7.0 \times 0.025}{0.025}$$

= 7.0 mg/L

$$Biological\ oxygen\ demand\ (BOD)\ in\ mg/L = D_1 - D_3$$

Where D_1 = Initial dissolved oxygen (mg/1) in sample.

D_3 = Dissolved oxygen (mg/1) after 5 days incubation.

$$Biological\ oxygen\ demand\ (BOD)\ in\ mg/L = D_1 - D_3$$

= 7.3 – 7.0

= 0.3 mg/L

Results

Biological oxygen demand (BOD) = 0.3 mg/L

Basic Water Quality Parameter:

	Results for Raw Water	Permissible limit in drinking water as per WHO
Physical Analysis		
1. Color (Units on PT. Co. Scale)	1	5
2. Odour	Unobjectionable	Unobjectionable
3. Taste	Unobjectionable	Unobjectionable
4. Turbidity (NTU)	1.2	5
5. pH	6.3	6.5– 8.5
6. Specific Conductivity ($\mu\ seimens$)	52.56	-
Chemical Analysis		
1. Total Solids (mg/L)	29.1	-
2. Suspended Solids (mg/L)	0.3	-
3. Total Dissolved Solids (mg/L)	28.8	500
4. Total Hardness as $CaCO_3$ (mg/L)	14.0	300

5. Calcium as Ca^{2+} (mg/L)	5	75
6. Magnesium as Mg^{2+} (mg/L)	2.19	30
7. Total Alkalinity as $CaCO_3$ (mg/L)	16.0	200
8. Chlorides as Cl^- (mg/L)	6.0	250
9. Sulphates as SO_4^{2-} (mg/L)	1.048	200
10. Nitrates as NO_3^- (mg/L)	2.0	45
11. Fluorides as F^- (mg/L)	0.15	1
12. Manganese as Mn^{2+} (mg/L)	0.35	0.05
13. Iron as Fe^{2+} (mg/L)	0.09	0.1
14. COD (mg/L)	10	-
15. DO (mg/L)	7.3	-
16. BOD at 27 ºC (3 days) (mg/L)	0.3	-

Batch Adsorption Studies

Initial concentrations of Fe^{2+} solution and Mn^{2+} solution are 10.0 mg/L and 10.0 mg/L respectively.

$$\%\ Removal\ Efficiency = \frac{C_o - C_t}{C_o} \times 100$$

Where C_o and C_t are the concentrations of iron and manganese before and after adsorption for a period of time t respectively.

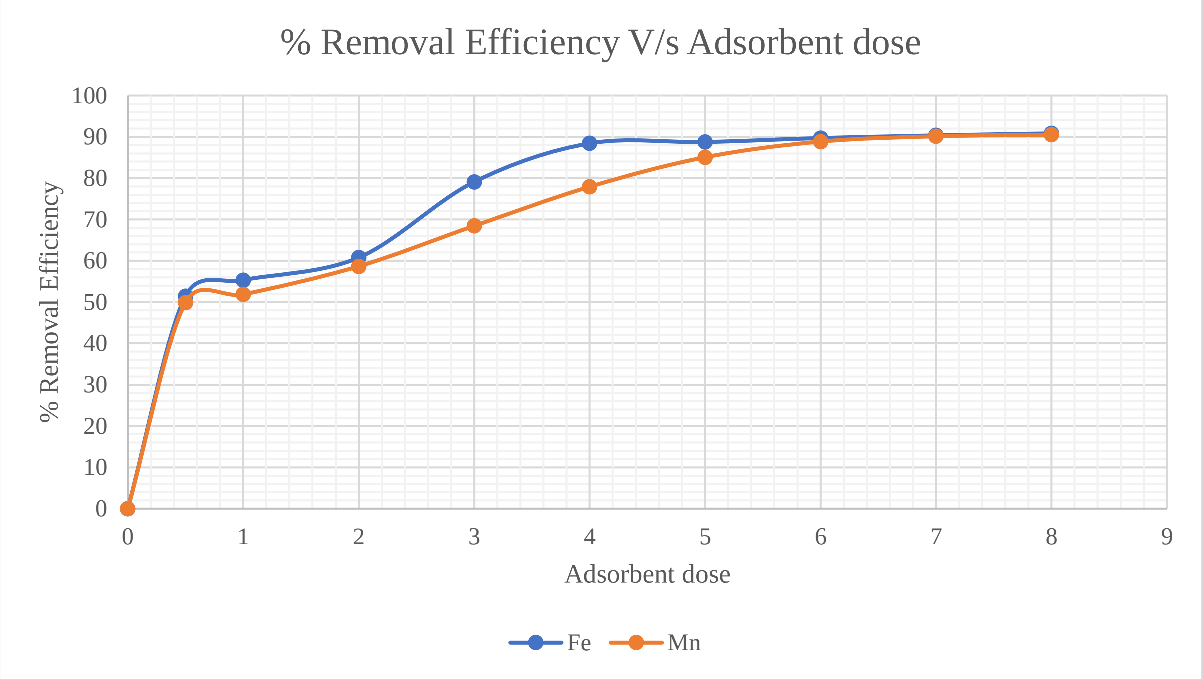
Percentage Removal Efficiency of Iron (Fe^{2+}) in relation to Adsorbent Dose:

Serial Number	Adsorbent dose (g)	Initial concentration (mg/L)	Final concentration (mg/L)	% Removal Efficiency
1	0	10.0	10.0	0
2	0.5	10.0	4.855	51.45
3	1.0	10.0	4.77	55.30
4	2.0	10.0	3.923	60.77
5	3.0	10.0	2.091	79.09
6	4.0	10.0	1.158	88.42
7	5.0	10.0	1.125	88.75
8	6.0	10.0	1.029	89.71
9	7.0	10.0	0.965	90.35
10	8.0	10.0	0.915	90.85

$$\%\,Removal\ Efficiency = \frac{10.0 - 4.855}{10.0} \times\ 100 = 51.45\%$$

Percentage Removal Efficiency of Manganese (Mn^{2+}) in relation to Adsorbent Dose:

Serial Number	Adsorbent dose (g)	Initial concentration (mg/L)	Final concentration (mg/L)	% Removal Efficiency
1	0	10.0	10.0	0
2	0.5	10.0	5.012	49.88
3	1.0	10.0	4.814	51.86
4	2.0	10.0	4.134	58.66
5	3.0	10.0	3.156	68.44
6	4.0	10.0	2.208	77.92
7	5.0	10.0	1.494	85.06
8	6.0	10.0	1.114	88.86
9	7.0	10.0	0.986	90.14
10	8.0	10.0	0.946	90.54



From the above tables, it clear that the removal efficiency of Iron and Manganese by Granular Activated Carbon (GAC) increases with adsorbent dosage. The results indicate that a greater number of ions was removed from the solution with increasing amount of the adsorbent in the system. This effect may be explained in terms of the availability of a greater surface area.

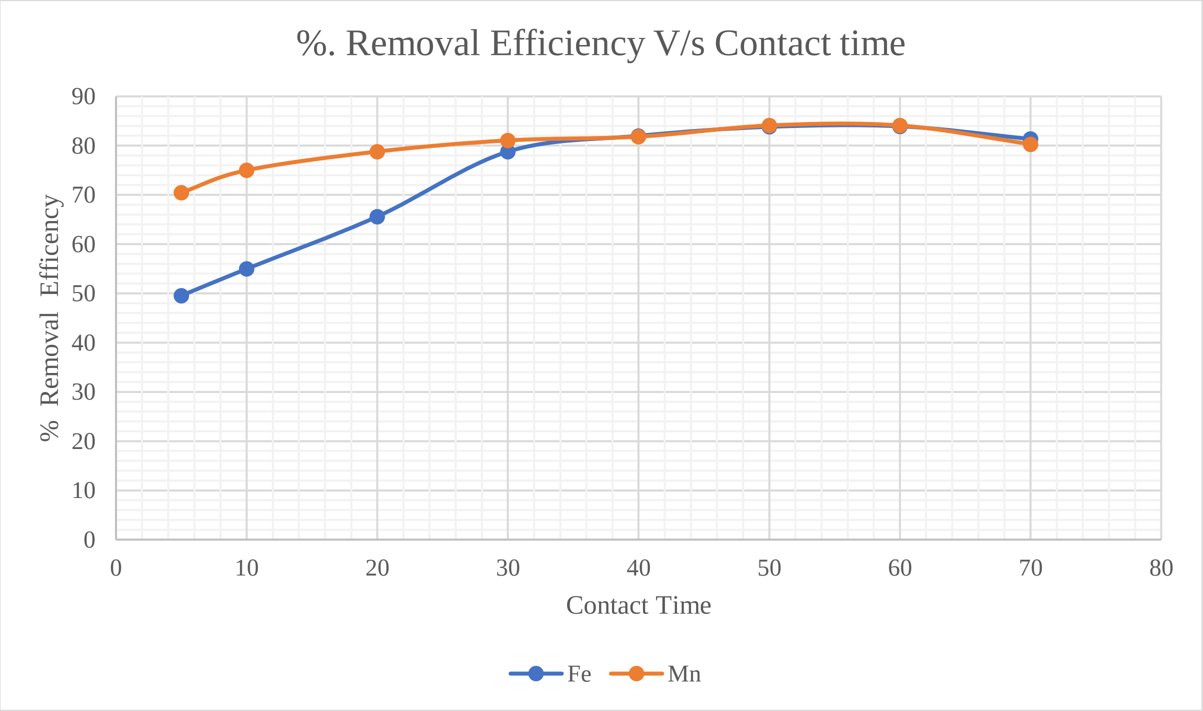
It was also observed that sharp increase in removal efficiency was observed with just 0.5 gm of dose. Considering this minimum amount of adsorbent and extension of this work for chemical modification for future experiments, 0.5 g was optimized as dose for experiments.

Percent Removal Efficiency of Iron (Fe^{2+}) based on Contact Time:

Serial Number	Contact time (minute)	Initial concentration (mg/L)	Final concentration (mg/L)	% Removal Efficiency
1	5	10.0	5.046	49.54
2	10	10.0	4.502	54.98
3	20	10.0	3.441	65.59
4	30	10.0	2.122	78.78
5	40	10.0	1.801	81.99
6	50	10.0	1.608	83.92
7	60	10.0	1.608	83.92
8	70	10.0	1.865	81.35

Percent Removal Efficiency of Manganese (Mn^{2+}) based on Contact Time:

Serial Number	Contact time (minute)	Initial concentration (mg/L)	Final concentration (mg/L)	% Removal Efficiency
1	5	10.0	2.955	70.45
2	10	10.0	2.5	75.00
3	20	10.0	2.121	78.79
4	30	10.0	1.892	81.08
5	40	10.0	1.818	81.82
6	50	10.0	1.591	84.09
7	60	10.0	1.591	84.09
8	70	10.0	1.97	80.30



The data obtained show that the metal ion uptake by the activated carbon increased with increasing contact time, with equilibrium being established in less than one hour. This equilibrium time was considered, but more time was allowed particularly in determining the equilibrium adsorption isotherms to ensure the attainment of equilibrium conditions.

Using optimized data, Langmuir and Freundlich isotherm were plotted.

Parameters for Langmuir and Freundlich isotherm:

$$q_e = \frac{C_o - C_e}{m} \times V$$

Where

q_e =Amount of dye adsorbed per gram of activated carbon

C_o = Initial Concentration before adsorption

C_e = Final Concentration after adsorption

V = Volume of solution in L

m = mass of adsorbent in g

The Freundlich adsorption isotherm can be expressed in the linear form as:

$$\log q_e = \left[\frac{1}{n}\right] \log C_e + \log k_f$$

The Langmuir adsorption isotherm can be expressed in the linear form as:

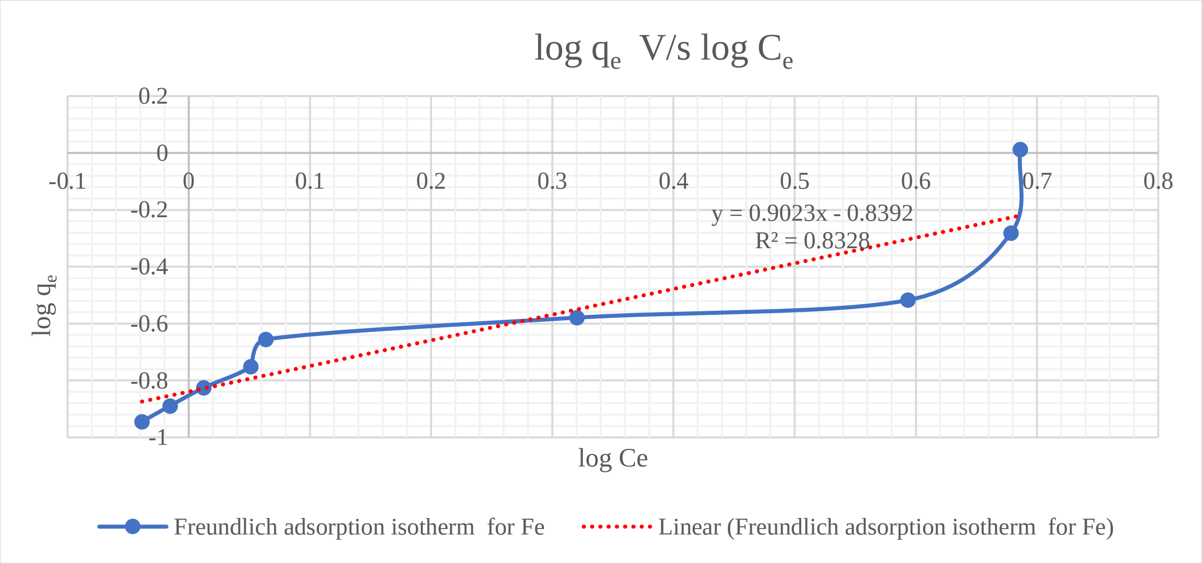
$$\frac{1}{q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{a}$$

For Fe^{2+}:

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
1.029	4.855	0.9718173	0.20597322	0.01241537	0.68618923
0.523	4.77	1.91204589	0.20964361	-0.2814983	0.67851838
0.30385	3.923	3.29109758	0.25490696	-0.5173408	0.59361831
0.263633333	2.091	3.79314705	0.47824008	-0.5789997	0.32035403
0.22105	1.158	4.52386338	0.86355786	-0.6555095	0.06370856
0.1775	1.125	5.63380282	0.88888889	-0.7508016	0.05115252
0.149516667	1.029	6.68821759	0.9718173	-0.8253104	0.01241537
0.129071429	0.965	7.74764804	1.03626943	-0.8891699	-0.0154727
0.1135625	0.915	8.80572372	1.09289617	-0.9447651	-0.0385789

$q_e = \frac{10.0-4.855}{0.5} \times 0.1 = 1.029$

Freundlich adsorption isotherm for Fe^{2+}:



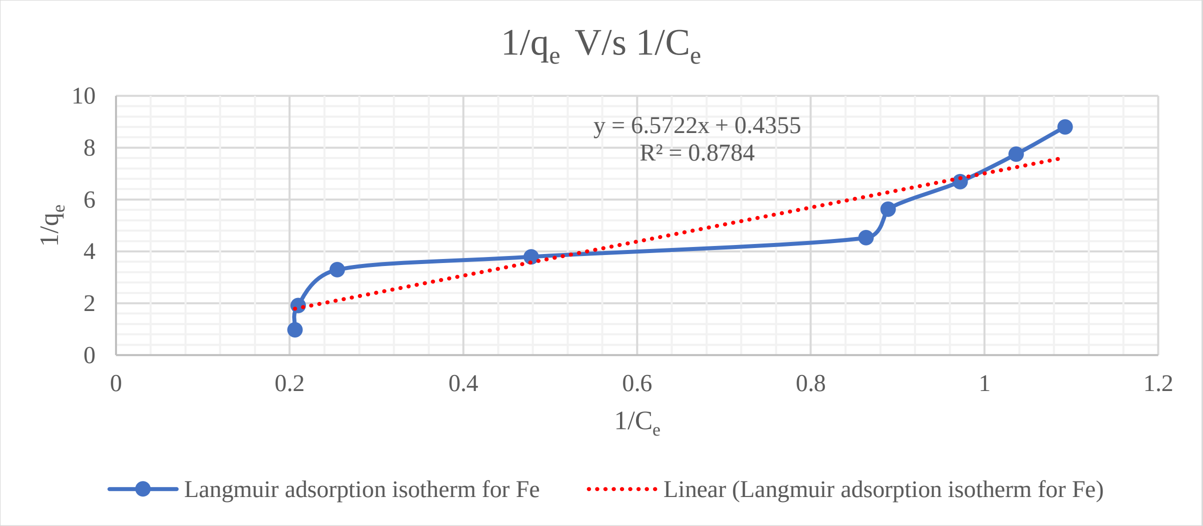
Calculation:

1/n = slope = 0.9023

log k_f = intercept = -0.8392

$k_f = 10^{(-0.8392)}$ = 0.1448

Langmuir adsorption isotherm for Fe^{2+}:



Calculation:

Intercept = 1/a = 0.4355

a = 1/0.4355 = 2.2962

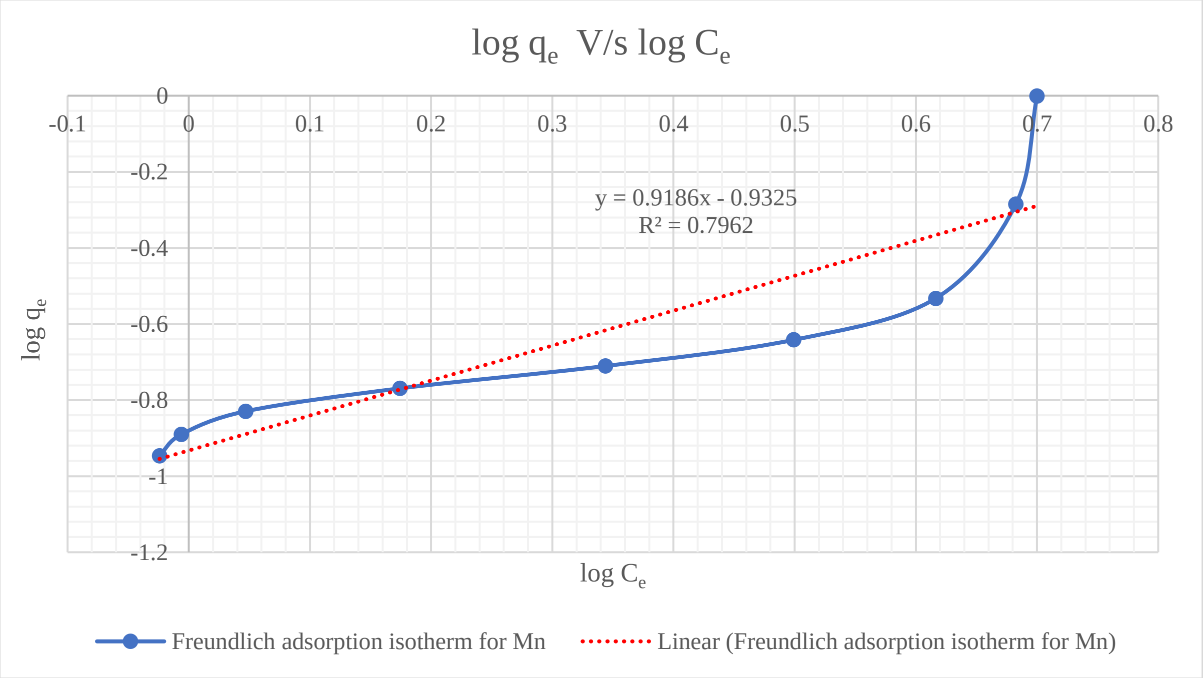
Slope = 1/ab = 6.5722

b = 1/ (a × 6.5722) = 1/ (2.2962× 6.5722) = 0.0666

For Mn^{2+}:

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
0.9976	5.012	1.00240577	0.19952115	-0.0010436	0.70001106
0.5186	4.814	1.92826841	0.20772746	-0.2851675	0.68250609
0.2933	4.134	3.40947835	0.24189647	-0.5326879	0.61637047
0.228133333	3.156	4.38340152	0.31685678	-0.6418113	0.49913699
0.1948	2.208	5.13347023	0.45289855	-0.710411	0.34399907
0.17012	1.494	5.87820362	0.66934404	-0.7692446	0.1743506
0.1481	1.114	6.75219446	0.89766607	-0.8294449	0.04688519
0.128771429	0.986	7.7656978	1.01419878	-0.8901805	-0.0061231
0.113175	0.946	8.83587365	1.05708245	-0.9462495	-0.0241089

Freundlich adsorption isotherm for Mn^{2+}:



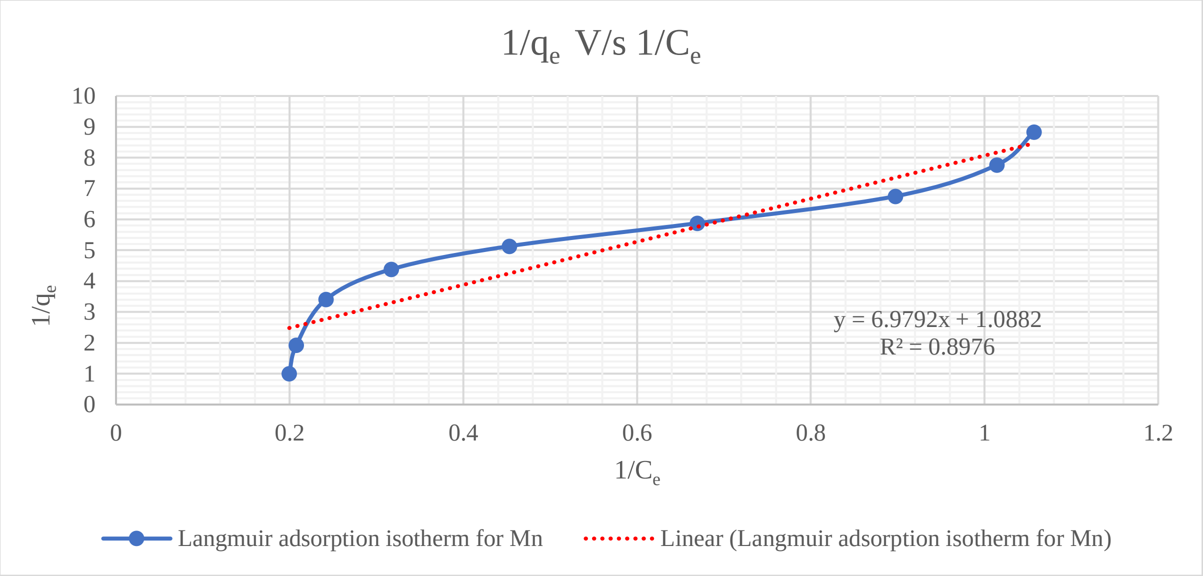
Calculation:

1/n = slope = 0.9186

$\log k_f$ = intercept = -0.9325

$k_f = 10^{(-0.9325)}$ = 0.1168

Langmuir adsorption isotherm for Mn^{2+}:



Calculation:

Intercept = 1/a = 1.0882

a = 1/1.0882= 0.9189

Slope = 1/ab = 6.9792

b = 1/ (a × 6.9792) = 1/ (0.9189 × 6.9792) = 0.1159

Adsorption Isotherm Constants at pH 7:

Metals	Freundlich Constants			Langmuir Constants		
	1/n	k_f	R^2	a	b	R^2
Fe^{2+}	0.9023	0.1448	0.8328	2.2962	0.0666	0.8784
Mn^{2+}	0.9186	0.1168	0.7962	0.9189	0.1159	0.8976

k_f = Adsorption capacity in mg/g for Freundlich adsorption isotherm

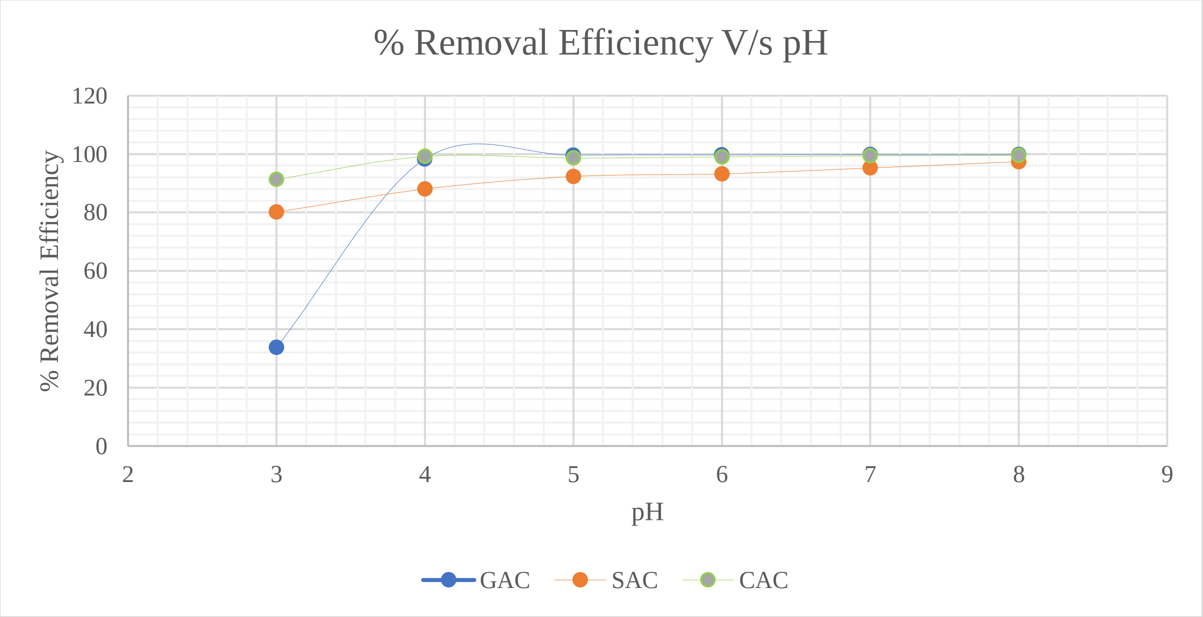
a =Adsorption capacity in mg/g for Langmuir adsorption isotherm

The value of 1/n and b can ran range from 0 to +1

Surface Modification of Granular Activated Carbon (GAC) for Enhancement of Metal Ion Adsorption

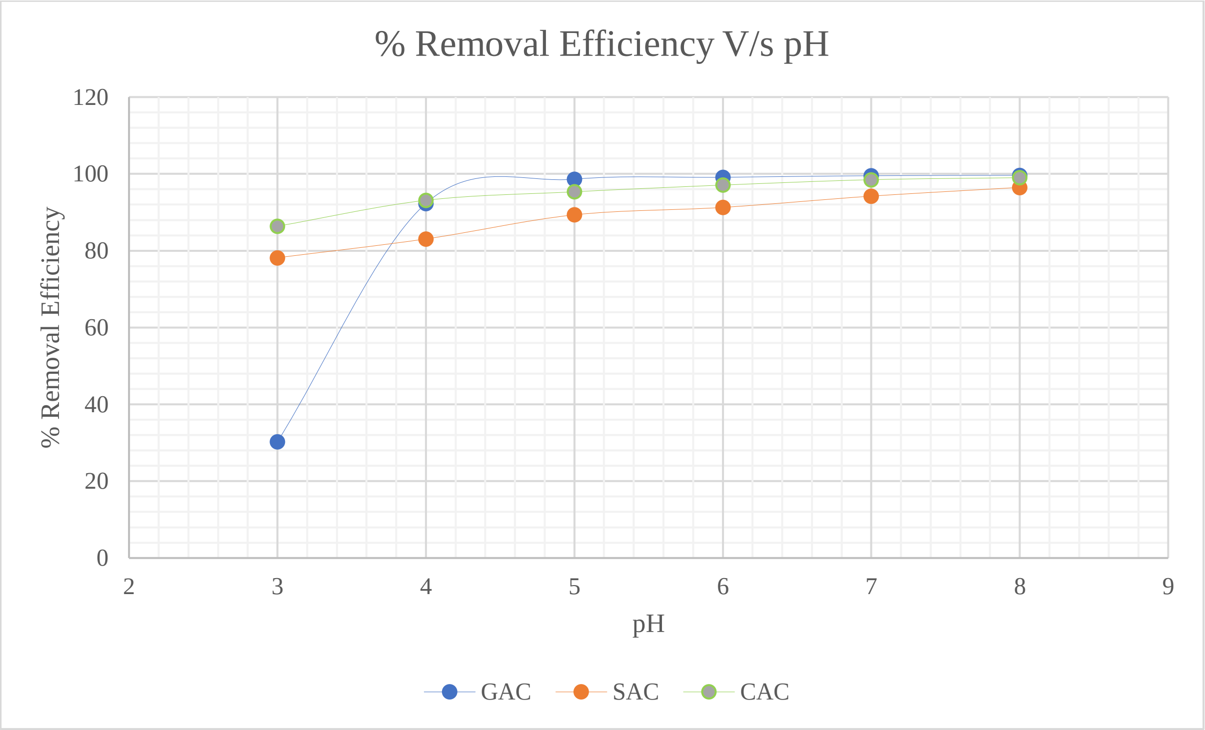
Percentage Removal Efficiency of Iron (Fe^{2+}) in relation to pH:

Serial Number	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)			% Removal Efficiency		
			GAC	CAC	SAC	GAC	CAC	SAC
1	3	10	6.624	0.866	1.988	33.76	91.34	80.12
2	4	10	0.168	0.081	1.197	98.32	99.19	88.03
3	5	10	0.038	0.136	0.766	99.62	98.64	92.34
4	6	10	0.028	0.096	0.678	99.72	99.04	93.22
5	7	10	0.018	0.06	0.476	99.82	99.40	95.24
6	8	10	0.017	0.049	0.26	99.83	99.51	97.40



Percentage Removal Efficiency of Manganese (Mn^{2+}) in relation to pH:

Serial Number	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)			% Removal Efficiency		
			GAC	CAC	SAC	GAC	CAC	SAC
1	3	10	6.974	1.361	2.183	30.26	86.39	78.17
2	4	10	0.768	0.687	1.693	92.32	93.13	83.07
3	5	10	0.138	0.466	1.066	98.62	95.34	89.34
4	6	10	0.088	0.291	0.872	99.12	97.09	91.28
5	7	10	0.048	0.151	0.579	99.52	98.49	94.21
6	8	10	0.037	0.099	0.351	99.63	99.01	96.49



It demonstrates that the metal adsorption by the WAC is strongly pH dependent. The adsorption sharply increases when the solution pH is increased from 3 to 4, which is in consistence with the observations reported in the literature. The metal ion adsorption is mainly due to the strong dependence of dissociation of surface functional groups on the pH of solution. As pH increases, more surface functional groups dissociate to provide metal binding sites, which results in higher metal ion adsorption. The interaction of metal ions with activated carbon can be described as:

$SOH + M^{2+} \longrightarrow SOM^{+} + H^{+}$

$SOH + M^{2+} + H_2O \longrightarrow SOMOH + 2H^{+}$

where SOH represents a generalized surface functional group.

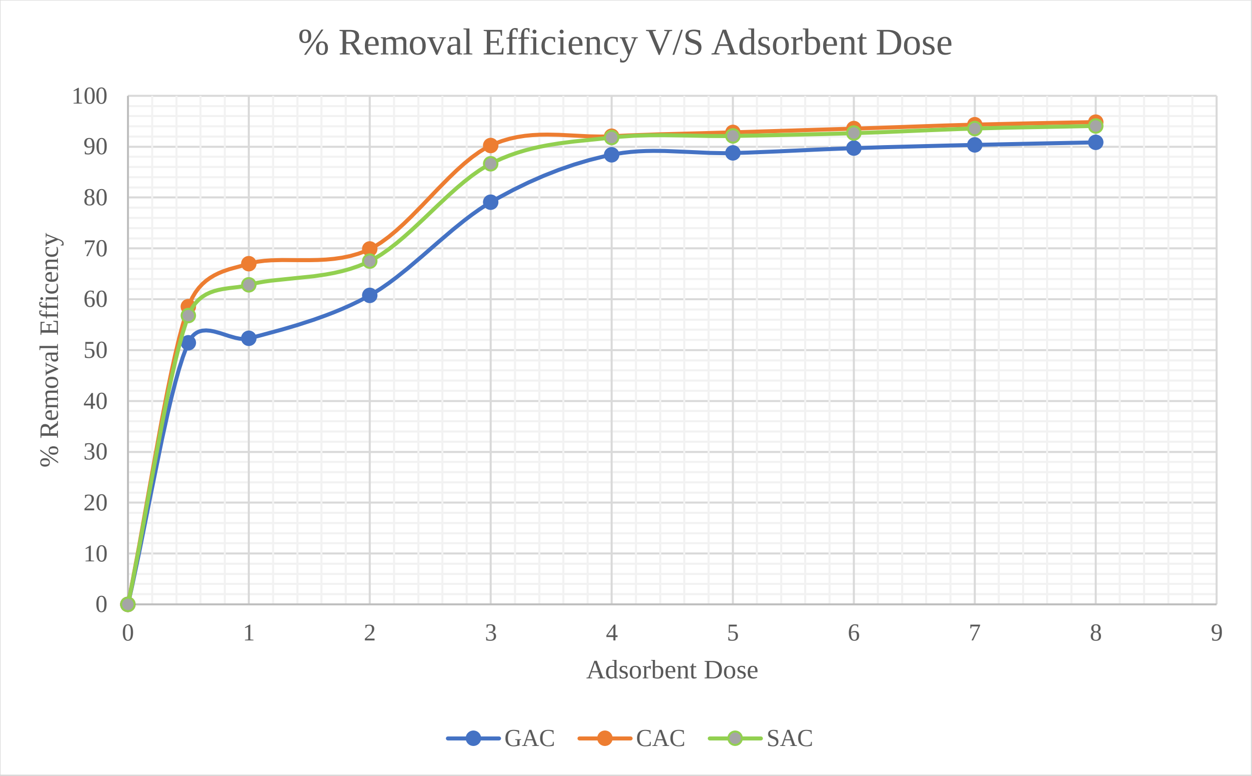
The dissociation constant of citric acid is 3.1, which suggests that citric acid modified activated carbon should show high metal adsorption at solution pH of above 3.1.

This is confirmed in the above graphs, SAC adsorbed nearly 84% Fe^{2+} ions from the aqueous solution even at solution pH of about 3.5, and CAC adsorbed nearly 96% Fe^{2+} ions at the same pH, while SAC adsorbed nearly 80% Mn^{2+} ions from the aqueous solution at solution pH of about 3.5, and CAC adsorbed nearly 90% Mn^{2+} ions at the same pH.

It suggests that citric acid modified activated carbon can be applied efficiently in a wider pH range.

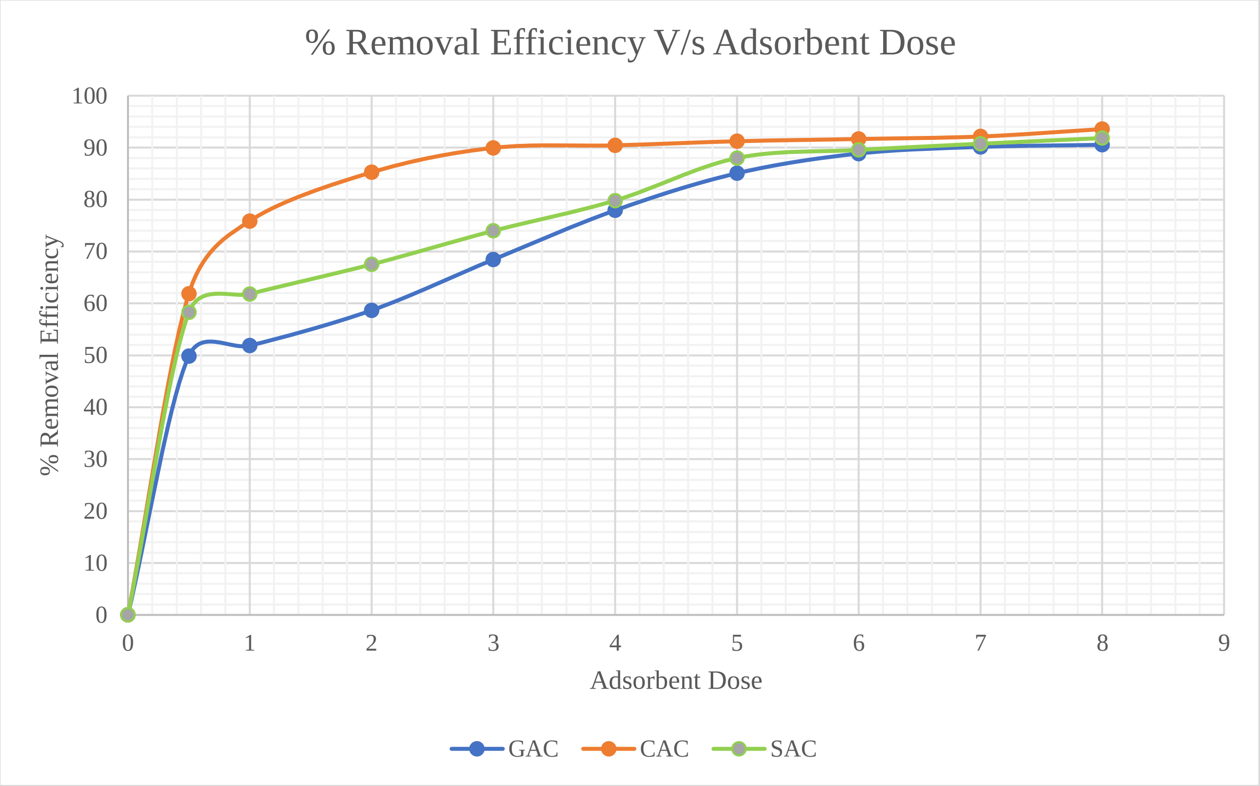
% Removal Efficiency for Iron (Fe^{2+}) in relation to Adsorbent Dose

Serial Number	Adsorbent Dose	Initial Concentration (mg/L)	Final Concentration (mg/L			% Removal Efficiency		
			GAC	CAC	SAC	GAC	CAC	SAC
1	0	10.0	10	10	10	0	0	0
2	0.5	10.0	4.855	4.145	4.323	51.45	58.55	56.77
3	1.0	10.0	4.77	3.302	3.719	52.3	66.98	62.81
4	2.0	10.0	3.923	3.012	3.249	60.77	69.88	67.51
5	3.0	10.0	2.091	0.976	1.334	79.09	90.24	86.66
6	4.0	10.0	1.158	0.795	0.82	88.42	92.05	91.8
7	5.0	10.0	1.125	0.718	0.789	88.75	92.82	92.11
8	6.0	10.0	1.029	0.645	0.734	89.71	93.55	92.66
9	7.0	10.0	0.965	0.566	0.643	90.35	94.34	93.57
10	8.0	10.0	0.915	0.516	0.592	90.85	94.84	94.08



% Removal Efficiency for Manganese (Mn^{2+}) in relation to Adsorbent Dose

Serial Number	Adsorbent Dose	Initial Concentration (mg/L)	Final Concentration (mg/L			% Removal Efficiency		
			GAC	CAC	SAC	GAC	CAC	SAC
1	0	10.0	10	10	10	0	0	0
2	0.5	10.0	5.012	3.813	4.173	49.88	61.87	58.27
3	1.0	10.0	4.814	2.413	3.819	51.86	75.87	61.81
4	2.0	10.0	4.134	1.476	3.249	58.66	85.24	67.51
5	3.0	10.0	3.156	1.005	2.603	68.44	89.95	73.97
6	4.0	10.0	2.208	0.956	2.019	77.92	90.44	79.81
7	5.0	10.0	1.494	0.877	1.201	85.06	91.23	87.99
8	6.0	10.0	1.114	0.834	1.045	88.86	91.66	89.55
9	7.0	10.0	0.986	0.786	0.925	90.14	92.14	90.75
10	8.0	10.0	0.946	0.643	0.816	90.54	93.57	91.84



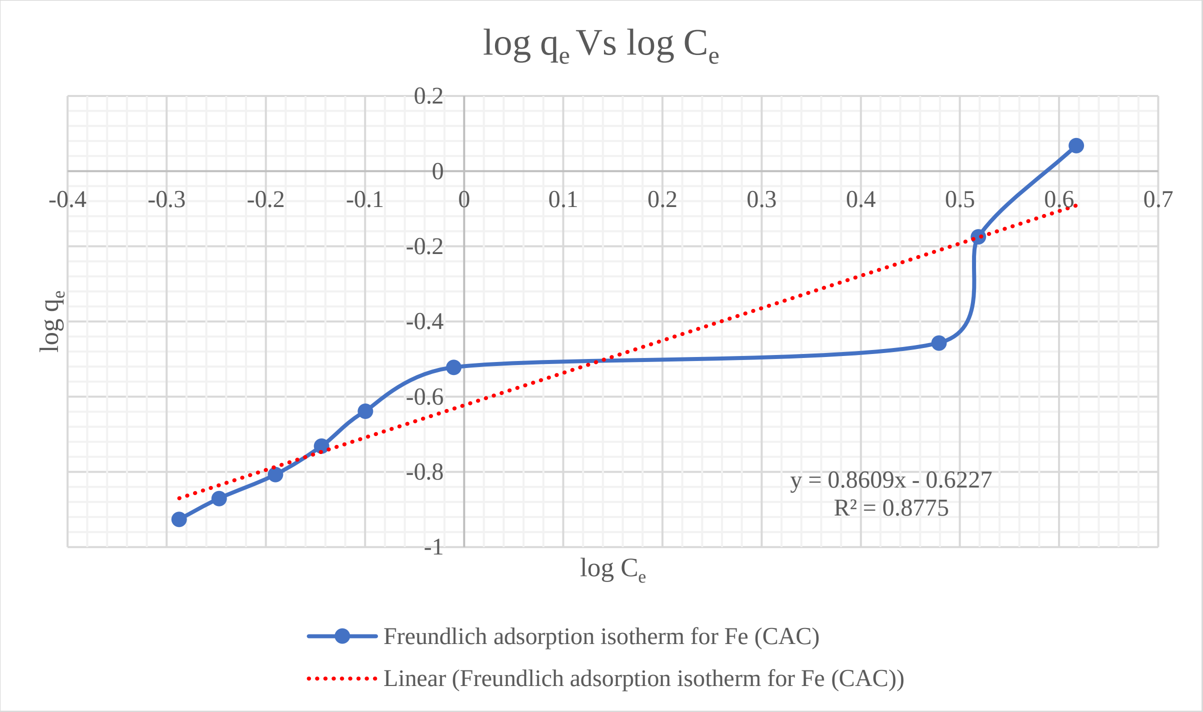
From the above figure it was observed that with CAC for all adsorption, the obtained % removal efficiency is higher followed by SAC and then bare GAC. Thus surface modification has proved to be effective for adsorption.

From the above optimized conditions, the adsorption isotherms were plotted

For Fe^{2+} (CAC):

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
1.171	4.145	0.85397096	0.24125452	0.0685569	0.61752453
0.6698	3.302	1.49298298	0.30284676	-0.1740549	0.51877707
0.3494	3.012	2.86204923	0.33200531	-0.4566771	0.47885497
0.3008	0.976	3.32446809	1.02459016	-0.5217222	-0.0105502
0.230125	0.795	4.34546442	1.25786164	-0.6380362	-0.0996329
0.18564	0.718	5.38677009	1.39275766	-0.7313284	-0.1438756
0.15591667	0.645	6.41368252	1.5503876	-0.8071075	-0.1904403
0.13477143	0.566	7.41997032	1.76678445	-0.8704022	-0.2471836
0.11855	0.516	8.43525938	1.9379845	-0.9260984	-0.2873503

Freundlich Adsorption Isotherm for Fe^{2+} (CAC):



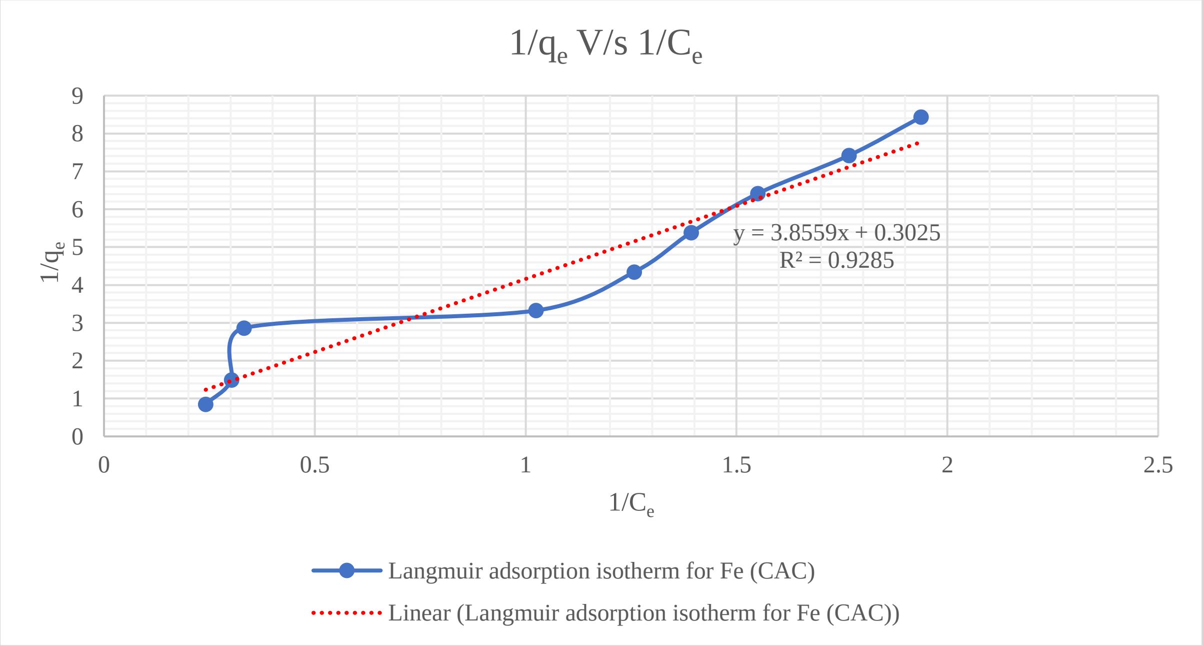
Calculations:

1/n = slope = 0.8609

log k_f = intercept = -0.6277

$k_f = 10^{(-0.6277)} = 0.2357$

Langmuir Adsorption Isotherm for Fe^{2+} (CAC):



Calculation:

Intercept = 1/a = 0.3025

a = 1/0.3025 = 3.3058

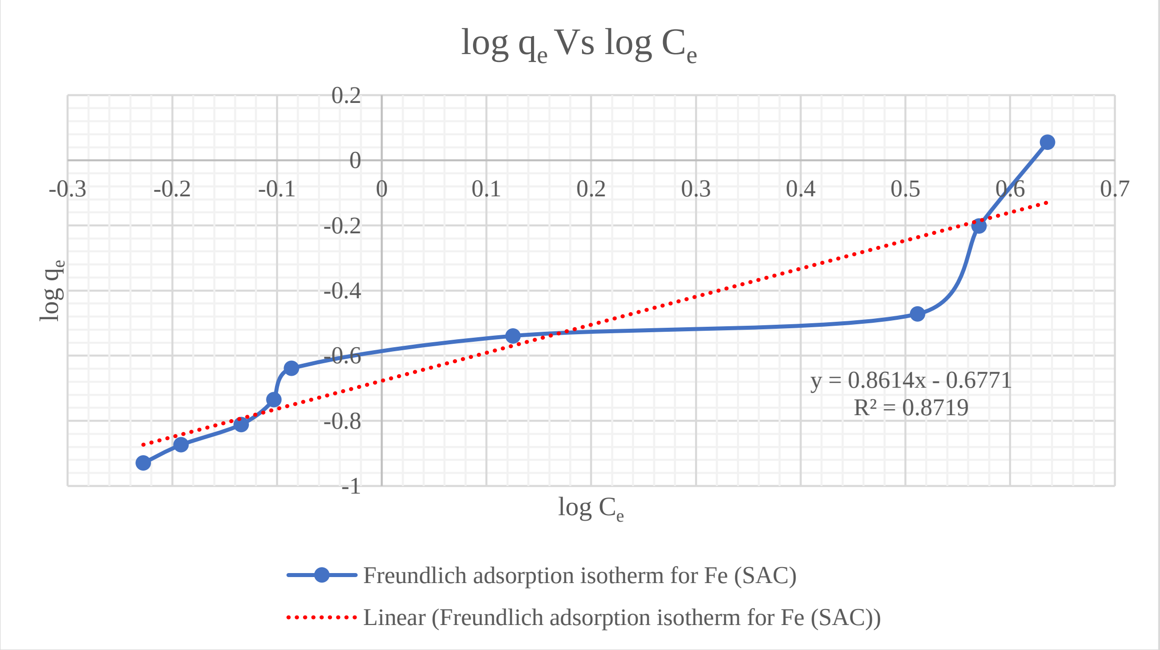
Slope = 1/ab = 3.8559

b = 1/ (a × 3.8559) = 1/ (3.3058× 3.8559) = 0.0784

For Fe^{2+} (SAC):

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
1.1354	4.323	0.88074687	0.23132084	0.05514889	0.63578524
0.6281	3.719	1.59210317	0.26888949	-0.2019712	0.57042618
0.33755	3.249	2.96252407	0.30778701	-0.4716619	0.51174971
0.28886667	1.334	3.46180475	0.74962519	-0.5393026	0.12515583
0.2295	0.82	4.35729847	1.2195122	-0.6392173	-0.0861861
0.18422	0.789	5.42829226	1.26742712	-0.7346632	-0.102923
0.15443333	0.734	6.47528599	1.36239782	-0.811259	-0.1343039
0.13367143	0.643	7.48103024	1.55520995	-0.8739614	-0.191789
0.1176	0.592	8.50340136	1.68918919	-0.9295927	-0.2276783

Freundlich Adsorption Isotherm for Fe^{2+} (SAC):



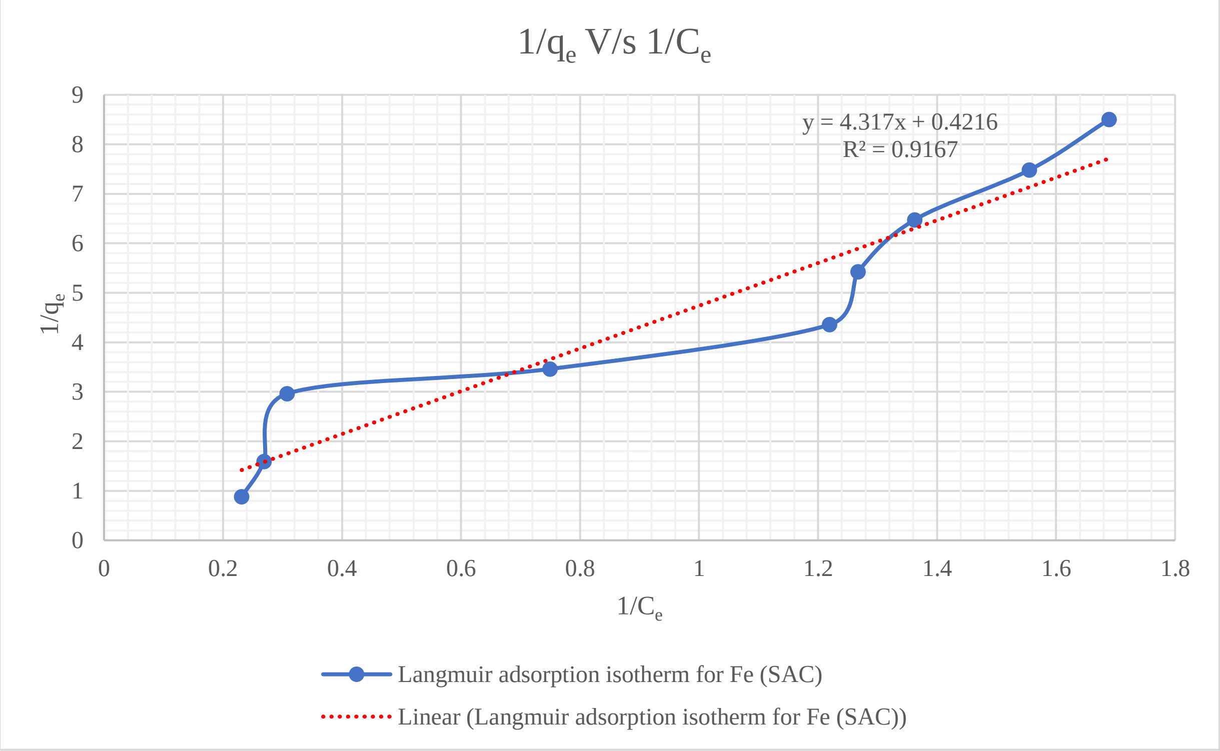
Calculations:

1/n = slope = 0.8614

log k_f = intercept = -0.6771

$k_f = 10^{(-0.6771)}$ = 0.2103

Langmuir Adsorption Isotherm for Fe^{2+} (SAC):



Calculation:

Intercept = 1/a = 0.4216

a = 1/0.4216 = 2.3719

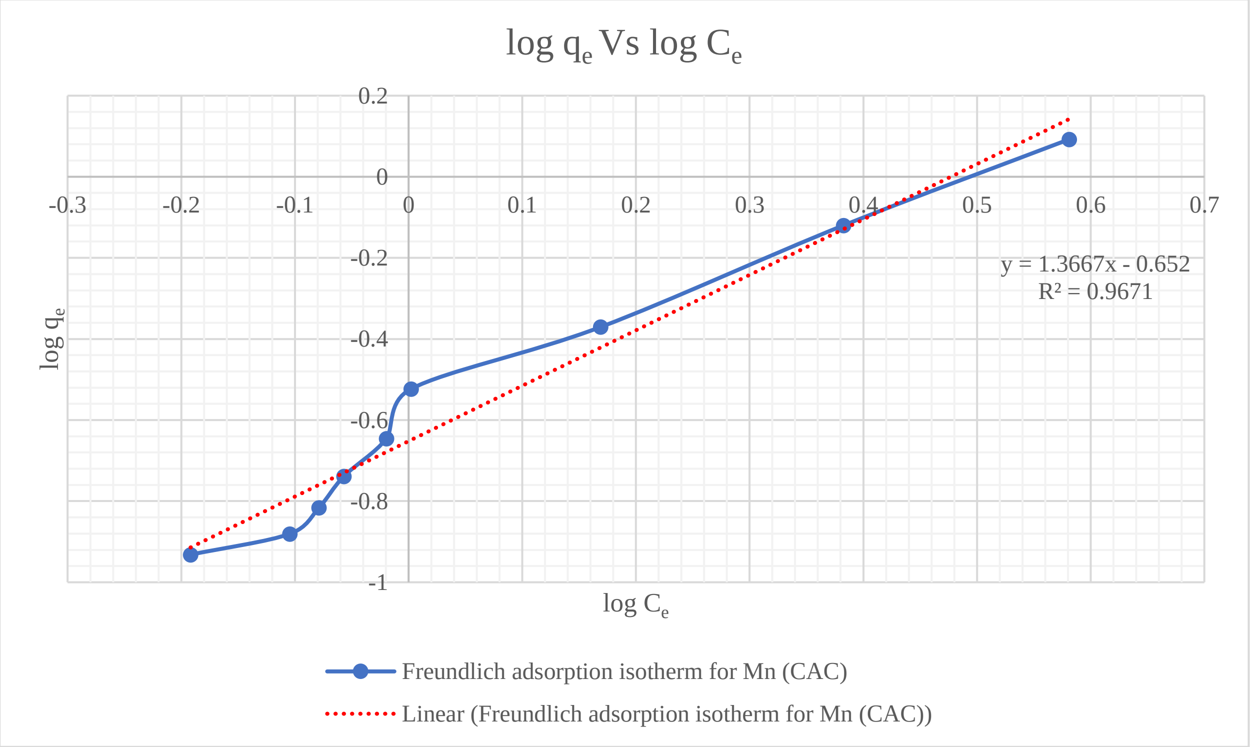
Slope = 1/ab = 4.317

b = 1/ (a × 4.317) = 1/ (2.3719× 4.317) = 0.0977

For Mn^{2+} (CAC):

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
1.2374	3.813	0.80814611	0.26226069	0.09251011	0.58126681
0.7587	2.413	1.31804402	0.41442188	-0.1199299	0.38255732
0.4262	1.476	2.34631628	0.67750678	-0.3703866	0.16908636
0.29983333	1.005	3.33518621	0.99502488	-0.5231201	0.00216606
0.2261	0.956	4.42282176	1.0460251	-0.6456994	-0.0195421
0.18246	0.877	5.48065329	1.14025086	-0.7388323	-0.0570004
0.15276667	0.834	6.54593061	1.19904077	-0.8159714	-0.0788339
0.13162857	0.786	7.59713479	1.27226463	-0.8806498	-0.1045775
0.1169625	0.643	8.54974885	1.55520995	-0.9319534	-0.191789

Freundlich Adsorption Isotherm for Mn^{2+} (CAC):



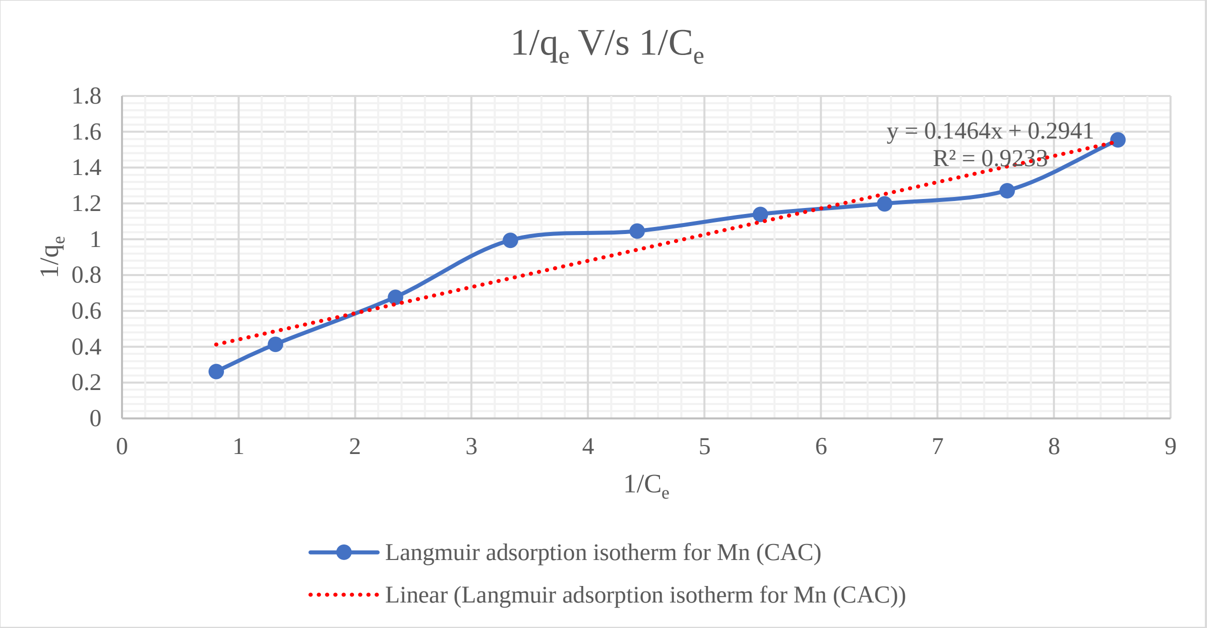
Calculations:

1/n = slope =1.3667

log k_f = intercept = -0.652

$k_f = 10^{(-0.652)}$ = 0.2228

Langmuir Adsorption Isotherm for Mn^{2+} (CAC):



Calculation:

Intercept = 1/a = 0.2941

a = 1/0.2941 = 3.4002

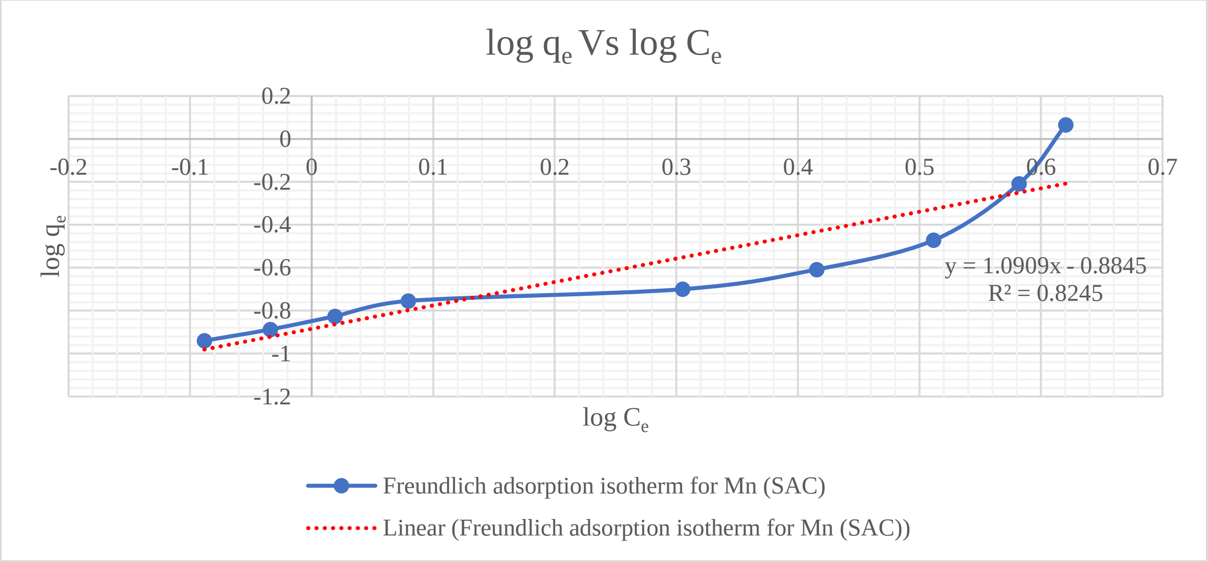
Slope = 1/ab = 0.1464

b = 1/ (a × 0.1464) = 1/ (3.4002× 0.1464) = 2.0089

For Mn^{2+} (SAC):

q_e	C_e	$1/q_e$	$1/C_e$	$\log q_e$	$\log C_e$
1.1654	4.173	0.85807448	0.23963575	0.06647501	0.62044838
0.6181	3.819	1.61786119	0.26184865	-0.2089413	0.58194966
0.33755	3.249	2.96252407	0.30778701	-0.4716619	0.51174971
0.24656667	2.603	4.05569826	0.38417211	-0.6080656	0.41547417
0.199525	2.019	5.01190327	0.4952947	-0.7000027	0.30513632
0.17598	1.201	5.68246392	0.83263947	-0.7545367	0.07954301
0.14925	1.045	6.7001675	0.9569378	-0.8260857	0.01911629
0.12964286	0.925	7.71349862	1.08108108	-0.8872514	-0.0338583
0.1148	0.816	8.71080139	1.2254902	-0.9400581	-0.0883098

Freundlich Adsorption Isotherm for Mn^{2+} (SAC):



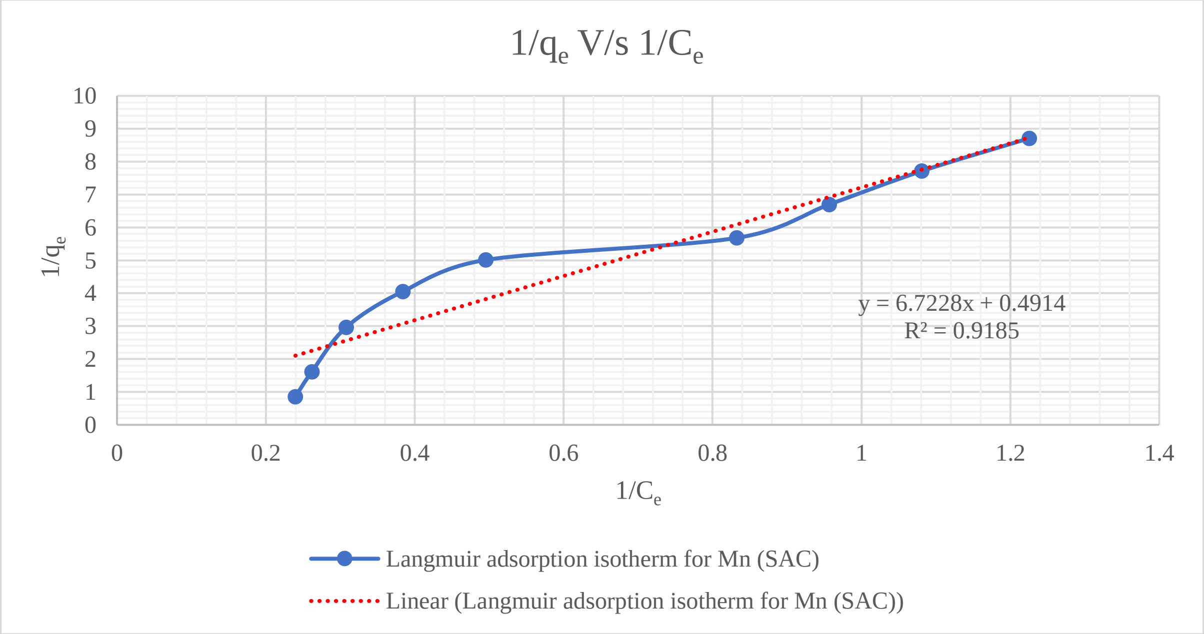
Calculations:

1/n = slope =1.0909

log k_f = intercept = -0.8845

$k_f = 10^{(-0.8845)}$ = 0.1304

Langmuir Adsorption Isotherm for Mn^{2+} (SAC):



Calculation:

Intercept = 1/a = 0.4914

a = 1/0.4914= 2.0350

Slope = 1/ab = 6.7228

$b = 1/(a \times 6.7228) = 1/(2.0350 \times 6.7228) = 0.0731$

Adsorption Isotherm Constants at pH 7:

Metal	Adsorbent	Freundlich Constants			Langmuir Constants		
		1/n	k_f	R^2	a	b	R^2
Fe^{2+}	GAC	0.9023	0.1448	0.8328	2.2962	0.0666	0.8784
	CAC	0.8609	0.2357	0.8775	3.3058	0.0784	0.9285
	SAC	0.8614	0.2103	0.8719	2.3719	0.0977	0.9167
Mn^{2+}	GAC	0.9186	0.1168	0.7962	0.9189	0.1159	0.8976
	CAC	1.3667	0.2228	0.9671	3.4002	2.0089	0.9233
	SAC	1.0909	0.1304	0.8245	2.0350	0.0731	0.9185

k_f = Adsorption capacity in mg/g for Freundlich adsorption isotherm

a =Adsorption capacity in mg/g for Langmuir adsorption isotherm

The adsorption plots for metal isothermal adsorption data at controlled pH demonstrates that the Langmuir adsorptive isothermal equation fits the experimental data well.

Comparison of k_f (Freundlich adsorption capacity) and a (Langmuir adsorption capacity) show that the CAC has higher metal adsorption capacity(i.e. adsorption capacity increased to 143 % for Fe and 370 % for Mn), than WAC which is very consistent with the enhancement in the surface site density. This indicates that the apparent reduction in the surface areas of the carbons does not adversely affect metal adsorption. The immobilization of citric acid on the activated carbon surface introduces more surface adsorptive sites (mainly carboxylic functional groups from the citric acid), which provide additional metal ion binding capacity. The immobilization of citric acid may also change the nature of the carbon surface from hydrophobic to hydrophilic, which facilitates the access of metal ions to surface adsorption sites. The metal adsorptive capacity of SAC is higher (i.e. adsorption capacity increased to 140.3.2 % for Fe and 221.5 % for Mn) than that of the WAC; however, it is lower than that of the CAC. This might result from removal of organic substances by the alkali NaOH solution. These substances can also participate in the metal binding process and contribute to metal adsorption.

Column Studies

Temperature: 30 °C

Column length: 19.5 cm

Column diameter: 1.5 cm

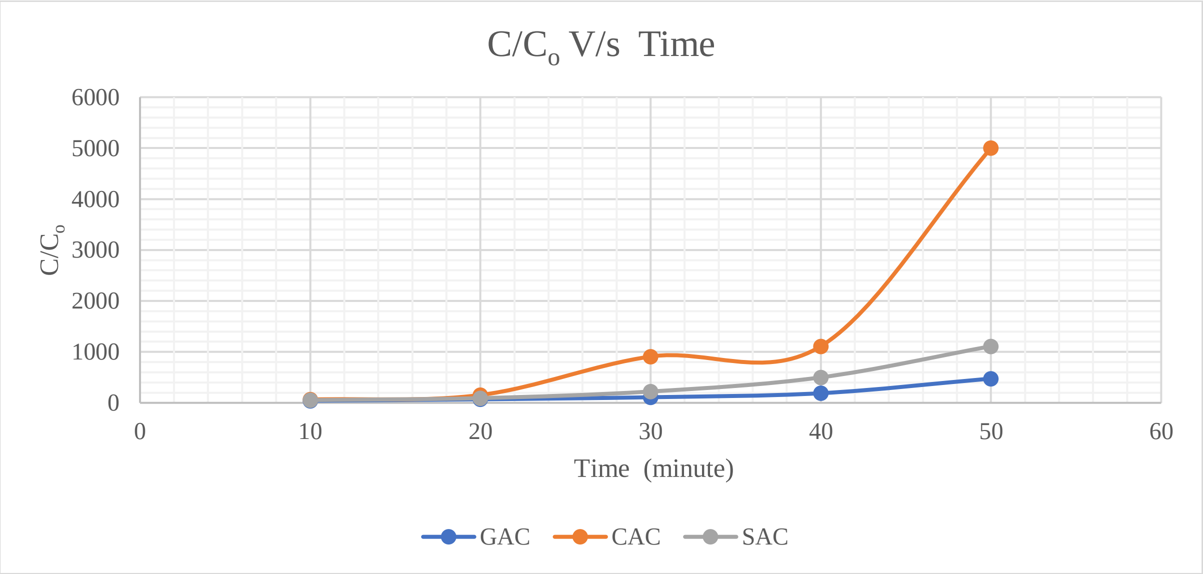
Flow rate: 2 mL/minute

Adsorbent: adsorbate ratio= 1:100

Bed height: 3 cm

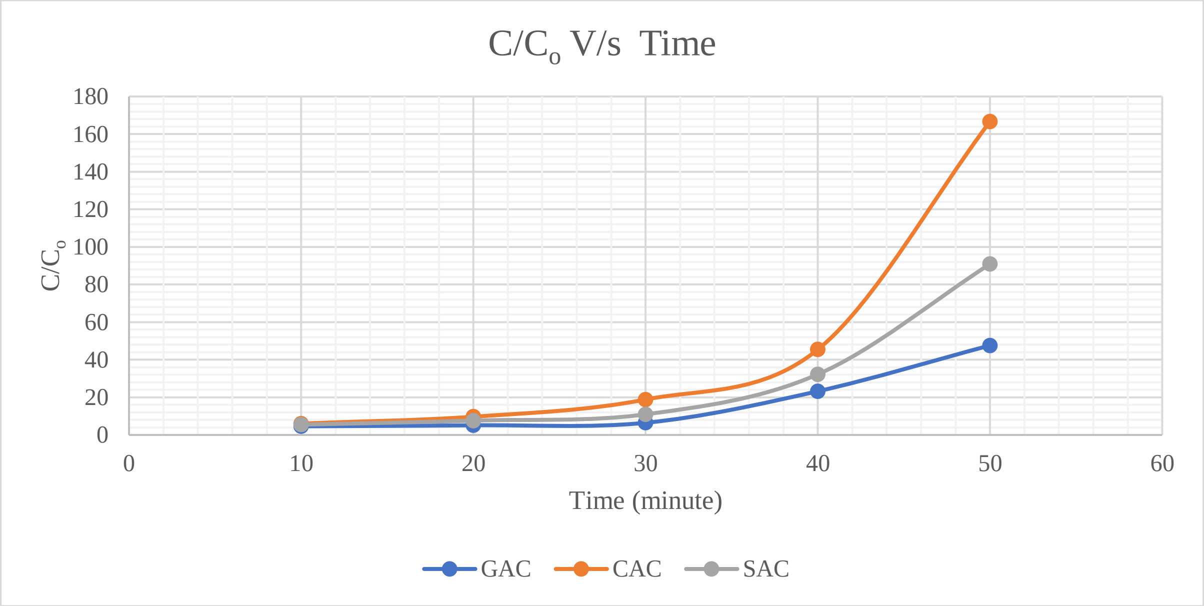
For Mn^{2+}

Aliquots (mL)	Time (minute)	Concentration of Adsorbate Solution (C) (mg/L)	Concentration of Incoming Solution C_o (mg/L)			$\frac{C}{C_o}$		
			GAC	CAC	SAC	GAC	CAC	SAC
20	10	10	0.236	0.156	0.187	42.37288	64.102	53.475
40	20	10	0.144	0.065	0.108	69.44444	153.84	92.592
60	30	10	0.091	0.011	0.045	109.8901	909.09	222.22
80	40	10	0.053	0.009	0.02	188.6792	1111.1	500
100	50	10	0.021	0.002	0.009	476.1904	5000	1111.1



For Fe^{2+}

Aliquots (mL)	Time (minute)	Concentration of Adsorbate Solution (C) (mg/L)	Concentration of Incoming Solution C_o (mg/L)			$\frac{C}{C_o}$		
			GAC	CAC	SAC	GAC	CAC	SAC
20	10	10	2.17	1.65	1.83	4.608294	6.0606	5.4644
40	20	10	1.94	1.03	1.31	5.154639	9.7087	7.6335
60	30	10	1.54	0.53	0.91	6.493506	18.867	10.989
80	40	10	0.43	0.22	0.31	23.25581	45.454	32.258
100	50	10	0.21	0.06	0.11	47.61904	166.66	90.909



When studies were carried out with 100 mL it was observed that as compare to GAC and SAC, CAC shows significantly high adsorption. Similar trend was observed for Fe^{2+} and Mn^{2+}. Although the shape obtained is not S shape indicating that saturation is not attained further studies will definitely support applicability of CAC as better adsorbent among the studied on using column studies.

Also, observations obtained through column studies supports the data obtained through batch studies.

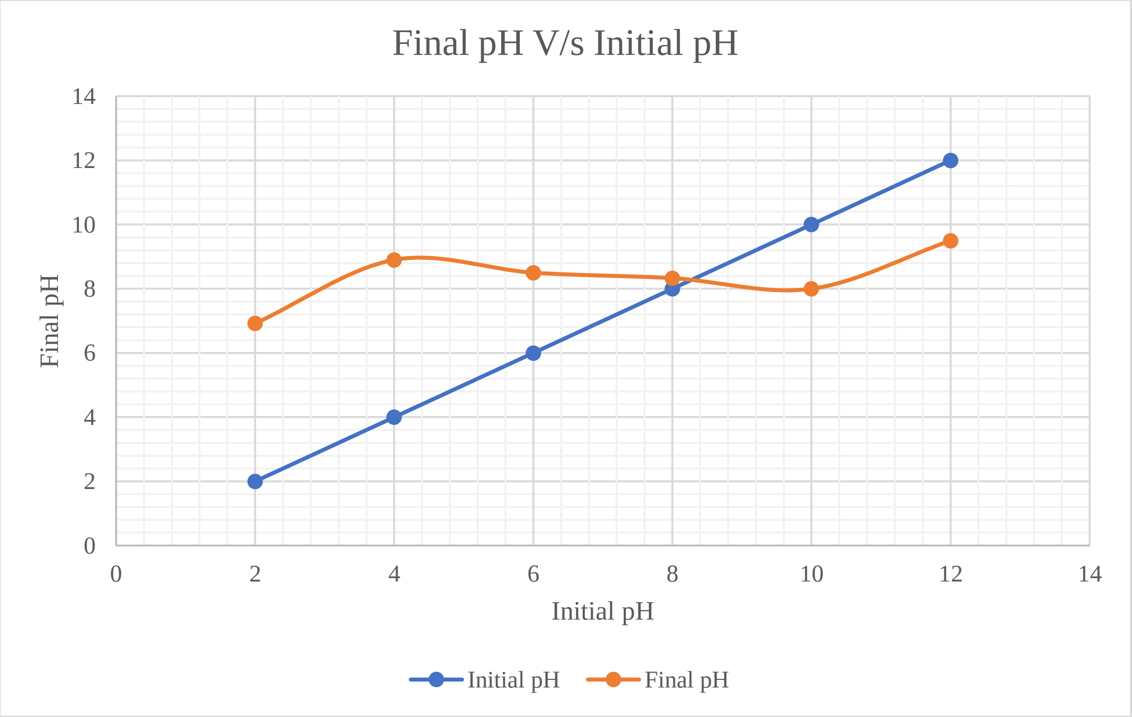
The studies were carried out with Initial metal ion concentration 10 mg/L which has a significant effect on breakthrough curve pattern as shown in figures above . Initial metal ion concentration was fixed to 10 mg/L considering the reported metal ion concentration of drinking water (at trace level) and adsorption capacity of CAC obtained by batch adsorption studies. Curves demonstrate that as the time increases columns get saturated.

Characterization of Adsorbent

Point of Zero Charge (pHpzc)

Observations:

Initial pH	Final pH
2	6.92
4	8.9
6	8.5
8	8.33
10	8
12	9.5



Result:

Point of Zero Charge (pHpzc) for GAC = 8.2

Methylene Blue Number

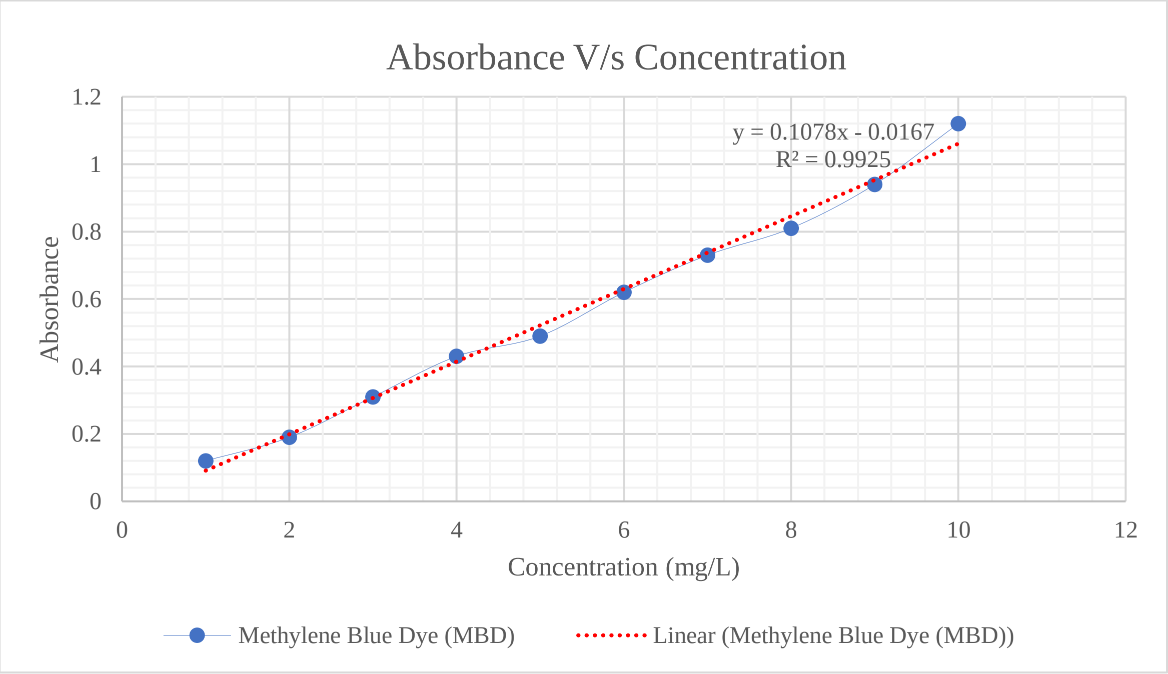
Observation:

The obtained filtered solution was subjected to 10 times dilution as the absorbance of filtered solution was very high.

Observation Table:

Concentration (mg/L) of Methylene Blue Dye Solution	Absorbance
1	0.12
2	0.19
3	0.31
4	0.43
5	0.49
6	0.62
7	0.73
8	0.81
9	0.94
10	1.12
Filtered Solution of MBD	

Calibration Curve for Methylene Blue Dye (MBD):



From the calibration curve, the absorbance of filtered solution was found to be 0.48, hence the corresponding concentration of filtered MBD solution was found to 4.6 mg/L

Hence actual concentration of filtered MBD solution = 4.6 × 10 = 46 mg/L

Calculations:

$$MB_N = \frac{(C_0 - C_e) \times V}{M}$$

Where C_o and C_e are initial and equilibrium concentration of MB (mg/L) respectively, M is the mass of adsorbent in gram (g) and V is the volume of the solution in liter (L) and MB_N is Methylene blue number.

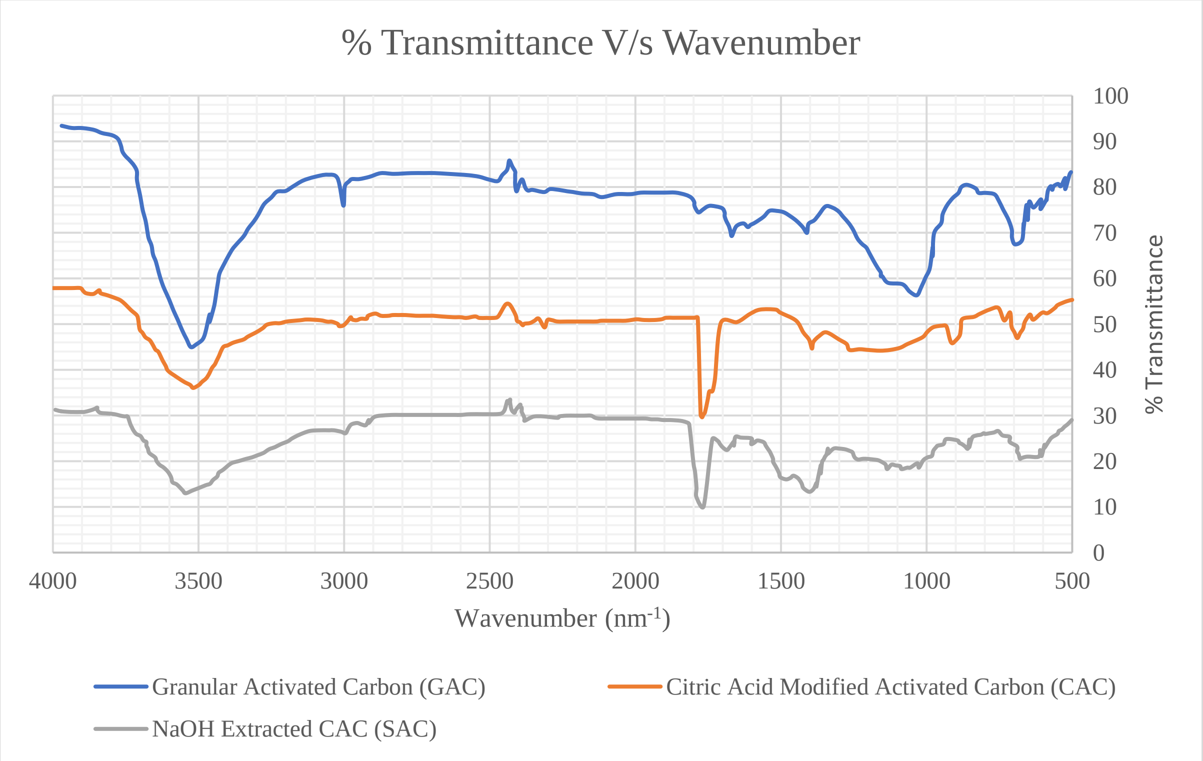
$$MB_N = \frac{(100 - 46) \times 0.1}{0.02}$$

$$MB_N = 270 \text{ mg/g}$$

Result:

Methylene blue number (MB_N) for GAC = 260 mg/g

IR Spectra



According to FTIR spectra, all materials show the broad peak at 3500 cm^{-1} indicating O–H stretching vibration mode of OH^{-} groups or adsorbed water.

Considering the IR spectra of Granular Activated Carbon (GAC), the band at 3000 cm^{-1} is attributed to C–H interaction with the surface of the carbon. The bands around 1033 cm^{-1} are confirmed to pertain to ring vibration in a large aromatic skeleton generally found in carbonaceous material.

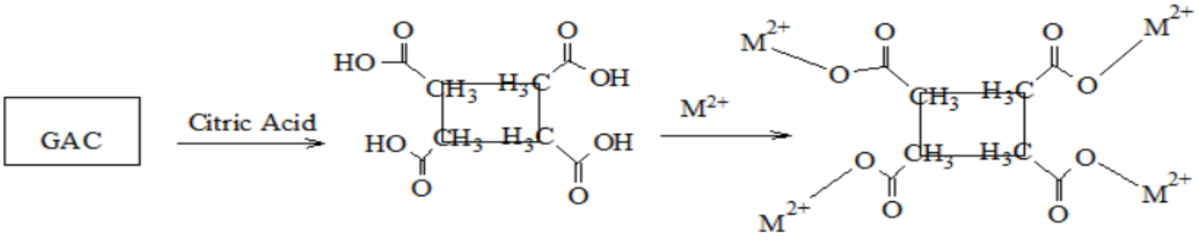
In the IR spectra of Citric Acid Modified Activated Carbon (CAC), an addition peak at 1760 cm^{-1} appear, which due to C=O stretching vibration which a characteristic peak for acid.

Considering the spectra of NaOH Extracted CAC (SAC), The bands between 1384 and 1450 cm^{-1} are observed, assigned to -OH bending vibration that present strong peak when NaOH was added.

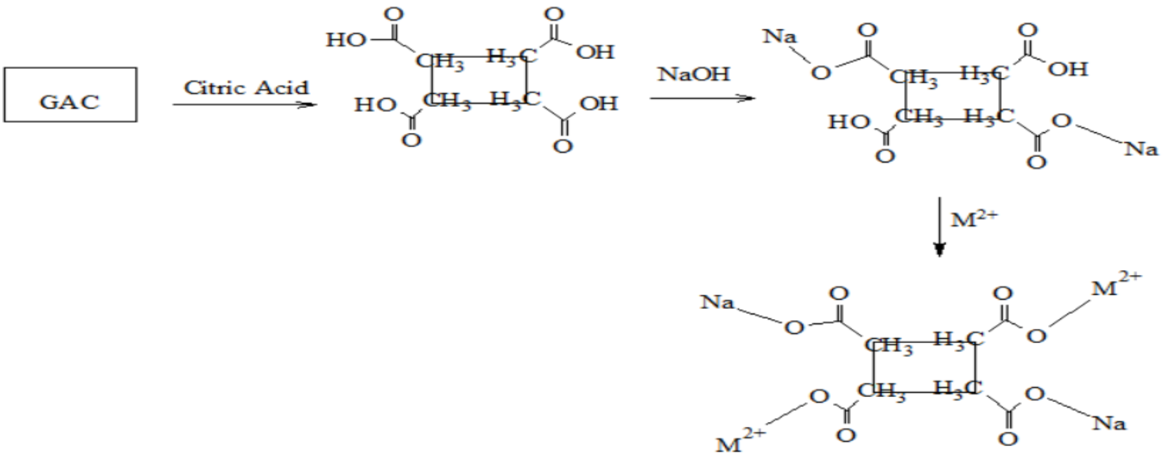
Proposed mechanism for adsorption:

$M^{2+} = Mn^{2+}, Fe^{2+}$

For CAC:



For SAC:



Regeneration of Adsorbent

Observation:

Initial Concentration (C_o) of Mn^{2+} solution (mg/L)	Number of Cycle	With 1 M HNO_3 solution		With 0.1 M HNO_3 solution	
		Concentration (C_f) of Mn^{2+} ion in the filtrate solution (mg/L)	% desorption efficiency	Concentration (C_f) of Mn^{2+} ion in the filtrate solution (mg/L)	% desorption efficiency
10	1	8.4	84.0	9.2	92.0
10	2	7.8	78.0	8.8	88.0
10	3	7.3	73.0	8.2	82.0
10	4	6.8	68.0	7.8	78.0
10	5	6.4	64.0	7.3	73.0

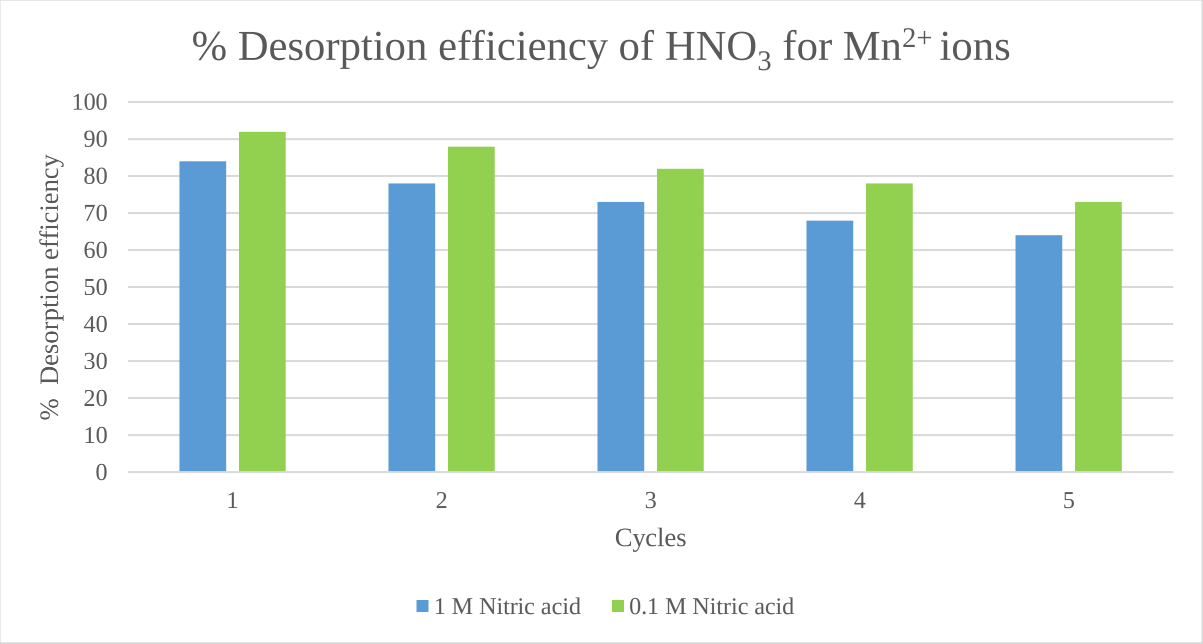
$$\%\ desorption\ efficiency = \frac{C_f}{C_0} \times 100$$

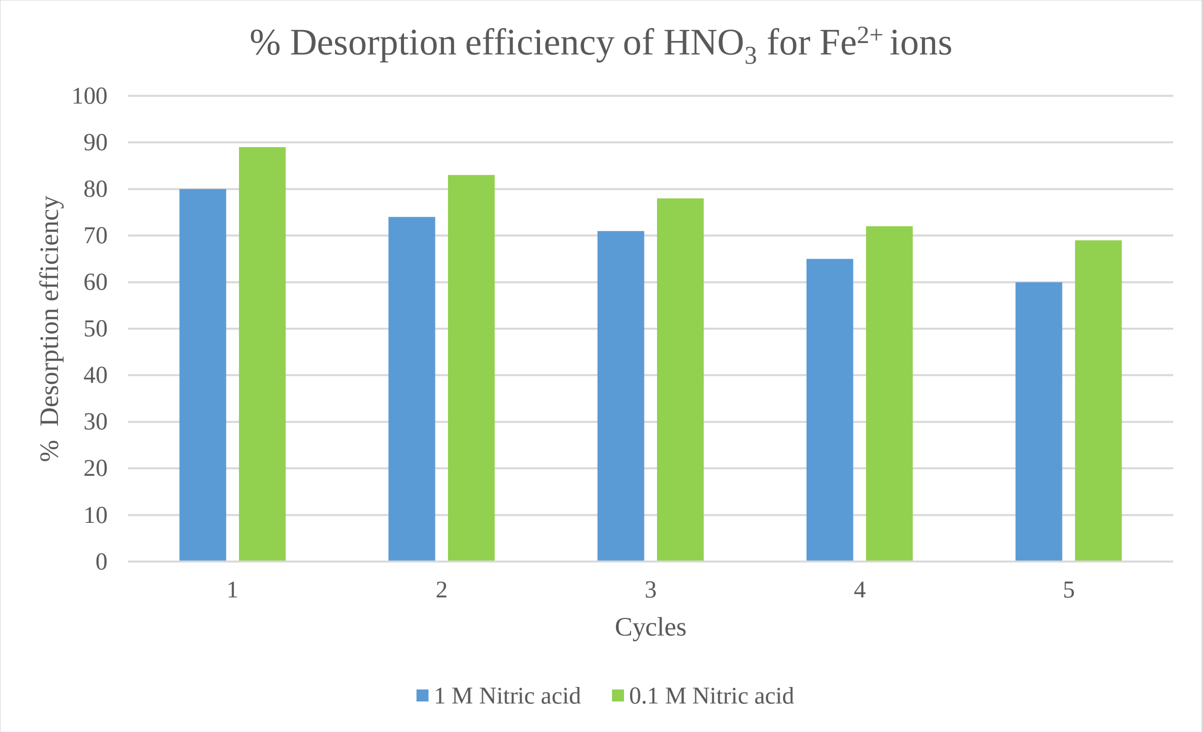
C_o = Concentration of initial solution

C_f = Concentration of filtrate solution

$\%\ desorption\ efficiency = \frac{8.4}{10} \times 100$ = 84.0 %

Initial Concentration (C_o) of Fe^{2+} solution (mg/L)	Number of Cycle	With 1 M HNO_3 solution		With 0.1 M HNO_3 solution	
		Concentration (C_f) of Fe^{2+} ion in the filtrate solution (mg/L)	% desorption efficiency	Concentration (C_f) of Fe^{2+} ion in the filtrate solution (mg/L)	% desorption efficiency
10	1	8.0	80.0	8.9	89.0
10	2	7.4	74.0	8.3	83.0
10	3	7.1	71.0	7.8	78.0
10	4	6.6	65.0	7.2	72.0
10	5	6.0	60.0	6.9	69.0





Result:

% desorption efficiency of 0.1 M HNO_3 for Mn^{2+} ions as well as for Fe^{2+} ions were found to be higher than % desorption efficiency of 1 M HNO_3.

Using 0.1 M HNO_3, in first cycle, 92 % removal was achieved for Mn^{2+} in fourth cycle the removal efficiency of 78 % was achieved. In first cycle, 89 % removal was achieved for Fe^{2+} and in fourth cycle the removal efficiency of 72 % was achieved

Removal efficiency decreases as cycle proceeds because the use of acid solution may destroy the binding sites of the CAC or insufficient acid solution may allow the metal ion to remain in the binding sites.

Chapter 4:
Conclusion

Water Quality Monitoring revealed that all the basic water quality parameters were found in the permissible limits as per WHO.

Activated carbon modification by citric acid significantly improves its metal ion adsorption capacity. The maximum adsorption capacity increased from 2.29 mg Fe^{2+}/g WAC to 3.30 mg Fe^{2+}/g CAC and 2.37 mg Fe^{2+}/g SAC, respectively. The maximum adsorption capacity increased from 0.91 mg Mn^{2+}/g WAC to 3.40 mg Mn^{2+}/g CAC and 2.03 mg Mn^{2+}/g SAC, respectively.

Effect of initial solution pH on the metal adsorption onto the citric acid modified carbons was insignificant; however, it became important when the unmodified carbon was used. These modified carbons were able to maintain high metal adsorption capacity in very wide pH range. Therefore, they can be useful in treating wastewater with a wider pH range.

We can also conclude that removal of metal ion in a packed bed system using CAC is an effective and feasible method. Behaviour of breakthrough curve and the metal adsorption capacity is strongly influenced by flow rate, bed depth, influent concentration, and pH. We observed higher adsorption capacities at the flow rate of 2 mL/min, bed depth of 3 cm, influent concentration of 10 mg/L, and pH of 7.

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Appendix

Preparation of Solutions:

Turbidity:

Solution I: 1.000 g of hydrazine sulphate, $(NH_2)_2.H_2SO_4$ was dissolved in minimum quantity of distilled water and diluted with distilled water in 100 mL standard volumetric flask.

Solution II: 10.00 g of hexamethylenetetramine, $(CH_2)_6N_4$, was dissolved in minimum quantity of distilled water and diluted with distilled water in 100 mL standard volumetric flask.

4000 NTU suspension: In a flask mix 5.0 mL of Solution I and 5.0 mL of Solution II. Let stand for 24 h at 25 ±3°C. This results in a 4000 NTU suspension.

Dilute 4000 NTU stock solution with distilled water to prepare dilute standards just before use and discard after use.

pH:

0.05 M Potassium hydrogen phthalate buffer (pH 4.00): 10.12 g of $KHC_8H_4O_4$ (potassium hydrogen phthalate) were dissolved in 1000 mL freshly boiled and cooled distilled water

0.025M Potassium dihydrogen phosphate + 0.025M disodium hydrogen phosphate buffer, (pH 6.86): 3.387 g of KH_2PO_4 + 3.533 g of Na_2HPO_4 were dissolved in 1000 mL freshly boiled and cooled distilled water

0.01M sodium borate decahydrate (borax buffer), (pH = 9.18): 3.80 g of $Na_2B_4O_7.10H_2O$ was dissolved in 1000 mL freshly boiled and cooled distilled water.

Specific Conductivity:

0.1 N KCl solution: 0.3725g of KCl was dissolved in minimum quantity of deionized water and diluted up to the mark with deionized water in 50 mL standard volumetric flask.

Total Hardness as $CaCO_3$:

Buffer 10 : 5.4 g of ammonium chloride was dissolved in 20 mL of water, 35 mL of 10 M ammonia was added and diluted with water to 100 mL.

Standardized 0.01M EDTA solution: 3.362g EDTA was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

0.01 M $ZnSO_4$ solution: 0.08071 g of $ZnSO_4$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 50 mL standard volumetric flask.

Calcium as Ca^{2+}

8% NaOH solution: 8 g of NaOH is dissolved in 100 mL distilled water.

Standardized 0.01M EDTA solution: 3.362g EDTA was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

0.01 M $ZnSO_4$ solution: 0.08071 g of $ZnSO_4$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 50 mL standard volumetric flask

Total Alkalinity as $CaCO_3$

0.02 N H_2SO_4: Pipette out 0.4 mL of concentrated H_2SO_4 into 250 mL standard volumetric flask and diluted it up to the mark with distilled water.

Phenolphthalein indicator: 0.5 g phenolphthalein was dissolved in 50 mL 95% ethyl alcohol and 50 mL water was added.

Bromcresol green indicator: 100 mg bromcresol green sodium salt was dissolved in 100 mL distilled water.

0.02 N Na_2CO_3: 0.053 g of Na_2CO_3 was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 50 mL standard volumetric flask.

Chloride as Cl^-

Standard 0.0141 N $AgNO_3$: 0.2397g of $AgNO_3$ was dissolved in minimum quantity of distilled water and diluted up to the mark in 100 mL standard volumetric flask.

Sulphates as SO_4^{2-}

1:1 HCl: 10 mL of HCl mixed with 10 mL of water.

0.05 M $BaCl_2$: 1.041 g of $BaCl_2$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

0.1 M HNO_3: Pipette out 0.6 mL of concentrated HNO_3 in 100 mL standard volumetric flask and diluted up to the mark with distilled water.

Nitrate as NO_3^-

Nitrate solution (100 μg/mL) was prepared by dissolving 0.0258 g potassium nitrate in water and diluting to 100 mL.

Working standard solutions 1- 10 μg/mL were prepared by appropriate dilution 0.1 – 1.0 mL respectively).

Sulfanilic acid (0.5 g in 100 mL water) and methyl anthranilate (0.5 mL in 100 mL of alcohol) were used.

2 M HCl: Pipette out 17.69 mL of concentrated HCl into 100 mL standard measuring flask and diluted up to the mark with distilled water.

2 M NaOH: 8 g of NaOH was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard measuring flask.

Fluorides as F^-

1000 mg/L sodium fluoride stock solution was prepared by dissolving 2.21 g NaF in a 1000 mL polystyrene volumetric flask with deionised water. Sodium fluoride has been previously oven-dried at 105 °C for 1 hour and stored in a dessicator. The concentration of this stock solution is 1000 mg/L

Standards at the required concentration (0.07 – 1.0 mg/L) were prepared by appropriate dilution of the stock solution. Equal volume of buffer was added to each solution.

Manganese as Mn^{2+}

Manganese stock solution (10 mg/L): 0.02876 g of $KMnO_4$ was dissolved in distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

Calibration standard solutions (0.03- 2.0 mg/L) were prepared by appropriate dilutions.

Iron as Fe^{2+}

Stock Ferrous Ammonium sulphate (10 mg/L): 0.07022 g of Ferrous Ammonium sulphate was dissolved in distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

Calibration standard solutions (0.06 - 2.0 mg/L) were prepared by appropriate dilutions.

Chemical Oxygen Demand (COD)

Potassium Dichromate Solution (0.25 N) $K_2Cr_20_7$: 12.258 g of $K_2Cr_20_7$ was dissolved in minimum quantity of distilled water and diluted up to mark with distilled water in 1000 ml standard volumetric flask.

Ferrous Ammonium Sulphate Solution (0.25 N): 98.026 g of ferrous ammonium sulphate was dissolved in minimum quantity of distilled water and 20 mL of concentrated H_2SO_4 was added and diluted with distilled water in 1000 mL standard volumetric flask.

0.25 N $K_2Cr_2O_7$ solution: 0.6128 g of $K_2Cr_2O_7$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 50 mL standard volumetric flask.

2 N H_2SO_4 : Pipette out 5.55 mL of concentrated H_2SO_4 into 100 mL standard volumetric flask and dilute it up to the mark with distilled water.

Dissolved oxygen (DO)

0.025 N $Na_2S_2O_3$ solution: 0.395 g of $Na_2S_2O_3$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

0.025 N $K_2Cr_2O_7$ solution: 0.06128 g of $K_2Cr_2O_7$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 50 mL standard volumetric flask.

$MnSO_4$ solution: 4.8 g $MnSO_4$ was dissolved in 10 mL distilled water

Alkali- azide iodide solution: 50 g of NaOH and 13.5 g of NaI were dissolved in distilled water and diluted to 100 mL then, 10 g NaN_3 dissolved in 40 mL distilled water was added.

5% KI solution: 5 g of KI dissolved in 100 mL of distilled water

Adsorption Experiments

Fe^{2+} solution (10 ppm): 0.07020 g of Ferrous Ammonium Sulphate (FAS) was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

Mn^{2+} solution (10 ppm): 0.02749 g of $MnSO_4$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

1 M Citric acid solution: 192.13 g of Citric acid was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

0.1 M $Pb(NO_3)_2$ solution: 3.312 g of $Pb(NO_3)_2$ was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

1 M NaOH solution: 4 g of NaOH was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 100 mL standard volumetric flask.

Point of Zero charge

0.01 M NaCl solution: 0.1461 g of NaCl was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 250 mL standard volumetric flask.

0.5 M NaOH solution: 5 g of NaOH was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 250 mL standard volumetric flask.

0.5 M HCl solution: 11.1 mL of concentrated HCl was pipetted out into 250 mL standard volumetric flask and diluted up to the mark with distilled water.

Methylene Blue Number:

100 ppm Stock Methylene Blue solution: 100 mg of Methylene Blue Dye (MBD) was dissolved in minimum quantity of distilled water and diluted up to the mark with distilled water in 1000 mL standard volumetric flask.

Standard solution (1-10 mg/L) were prepared by pipetting 0.1-1 mL of 100 ppm Stock Methylene Blue solution into the respective 10 mL standard volumetric flask.

Regeneration of Adsorbent

1 M HNO_3 solution: 62.5 mL of concentration HNO_3 solution was pipetted out into 1000 mL standard volumetric flask and diluted up to the mark with distilled water.

0.1 M HNO_3 solution: 6.25 mL of concentration HNO_3 solution was pipetted out into 1000 mL standard volumetric flask and diluted up to the mark with distilled water.