

## EFFECT OF DOSAGE OF ADSORBENT (MANGANESE DIOXIDE) ON THE REMOVAL OF IRON FROM WATER

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**Received 26-02-17; Revised & Accepted: 30-03-17**

### ABSTRACT

Adsorption of iron in water by manganese dioxide was studied using different adsorbent dosages. The research work was restricted to laboratory scale whereby the iron in water was complexed with ethylene diaminetetraacetic acid (EDTA). The amount of iron adsorbed was determined by varying the amount of manganese dioxide adsorbent to see its effect on the removal of iron. The removal of iron was found to have resulted from; adsorption and oxidation/filtration by the manganese dioxide. The complexation titration of the water sample was treated with 2.00, 2.50, 3.00, 3.50, 4.00, 5.00, 8.00 and 10.00g adsorbents of manganese dioxide at volumetric flow rates of; 1.90, 2.00, 3.50, 3.60, and 10.00ml/min. at varying time intervals. The work showed that, at the same volumetric flow rate with varying dosage adsorbents, the higher dosage removed iron better than the lower adsorbents. The research proved that even at increased volumetric flow rate of 10.00ml/min. with 10.00g adsorbent there was no detection of iron in the treated water sample. Therefore increased adsorbent dosages increased the rate of iron adsorption from water and hence its removal.

**Keywords:** complexometric titration, dosage adsorbent, EDTA-volumetric method, treated water sample, manganese dioxide, iron

### INTRODUCTION

Iron finds its way as impurities in water because it has been found that, it is one of the most abundant naturally occurring elements within the soil and possibly the rock formations and may be up to about 5% of the earth crust. Common sources of iron in groundwater are; the weathering of iron bearing minerals and rocks and some other man-made sources which include, acid-mine drainage, sewage landfill leachate and industrial effluents [1]. Iron is found in many sources of water as one of the major impurities and it promotes the growth of microorganisms leading to high contamination in drinking water [2]. Iron is also known to infiltrate the soil and the underlying geologic rock formations during rainfall causing it to seep into the aquifers which serves as groundwater, it is found to be one of the most troublesome elements in water [3].

Iron is an essential mineral in the body. It helps in the transportation of oxygen in the blood, but its presence in water above 0.3mg/L makes water unsuitable for use due to its metallic taste, discoloration, odour, turbidity, and staining of laundry. Iron is readily found in most drinking water supplies and imparts a strong metallic taste to the water and staining [4,5]. The stains (rusty

or brown) on fabrics, plumbing fixtures, dishes etc, cannot be removed by soaps and detergents. Iron deposits can build up overtime in water tanks, pressure tanks, pipelines and even ordinary water heaters, thereby reducing the quantity and pressure level of the water supply [6] and the system being put in place for the water supply.

The presence of iron in water is mainly in two forms; soluble ferrous iron or insoluble ferric iron. The ferrous iron ( $\text{Fe}^{2+}$ ) is in the dissolved form, while the ferric iron ( $\text{Fe}^{3+}$ ) is in the particulate form. Iron in groundwater often naturally co-exists with low dissolved oxygen (DO), favouring the  $\text{Fe}^{2+}$  form; but the surface water favours the  $\text{Fe}^{3+}$  form or the particulate ferric hydroxide,  $\text{Fe}(\text{OH})_3$  because it is more oxygenated [6]. Water containing ferrous iron is always clear and colourless, since the iron is completely dissolved, but when it is being exposed to air, oxidation takes place, the water turns cloudy and a reddish brown substance is being formed. The sediment being formed is the ferric form of iron that will not dissolve in water [7].

The presence of iron in drinking water is objectionable taste, and there are many problems that may result in iron toxicity in man [8]. Iron toxicity may result in anorexia, diarrhea, diphasic shock, oliguria etc and even death, and that much damage can be experienced by the patient such as vascular congestion of the gastrointestinal tract, liver, heart, etc, under acute poisoning of iron [9]. As a result of these, the determination of iron in drinking or even industrial water is very necessary in exploring new ways of water supplies, especially from boreholes and other surface water sources which may be used by man. A chemical treatment program which can remove the excess iron should be put in place for which course this research is all about.

This present research work is aimed at developing a method of removal of iron from potable water using manganese dioxide as the adsorbent under varying dosage, to see how change in adsorbent dosage (concentration) affects the removal of iron in water.

## **MATERIALS AND METHODS**

### **Sample Collection and Simulation**

A 20 litre water sample was collected in a plastic container from the Rivers State School of Health Technology, Port Harcourt. Plastic or glass containers made from Kimax or Pyrex brand borosilicate glass have the advantage of being sterilizable, easy to clean and inert to all solutions except those that are, strongly alkaline [10].

To simulate water condition as in the field,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  added to deionised water obtained from the Chemistry Laboratory of the Rivers State University of Science and Technology to give iron concentration approximately equal to that of the sample.

### **Preparation of Stock Solutions for the Determination of Iron in Water Sample**

All the reagents used in this work were of analytical grade and were used without further purification. All weighing were done using Mettler-Toledo GmbH 2004 Analytical balance, type PL203, SNR1228410965.

Sodium acetate solution was prepared by weighing 408g of it, and dissolved in water and diluted to 1 litre to obtain 3 molar sodium acetate solution. A 1.0g salicylic acid was dissolved in 100ml 99.7 – 100% v/v ethanol to prepare 1% salicylic acid solution. A 3.721 (0.01M) of ethylenediamine tetraacetic acid (EDTA) disodium salt was weighed and dissolved in distilled water in a 1000ml

volumetric flask and made up to the 1000ml mark. A 36.38% HCl of specific gravity 1.18 was used for the work, and a 50% w/w aqueous solution of hydrogen peroxide was used. Portions of 10.0g, 8.0g, 5.0g, 4.0g, 3.5g, 2.5g and 2.0g of manganese dioxide (MnO<sub>2</sub>) were weighed. Then each portion was tested under volumetric flow rates of 1.9ml/min., 2.0ml/min., 3.60ml/min., and 10.0ml/min. obtained from the different sizes of sintered glass funnels.

### Materials required for the Determination and Adsorption of Iron in water

Sintered glass funnels of various sizes, retort stand and clamp, burette, pipette, 100ml conical flask, 150ml beakers, 100ml measuring cylinders, 600mm sieve to form the sand bed gravels, a thermometer and a digital clock.

### Experimental Procedure for the Determination of Iron in Water

The EDTA-volumetric method was used to determine the concentration of iron in the raw sample by passing the water through the sintered glass funnel to produce clean water as follows:

A 100ml water sample was put into a beaker with the aid of a pipette and 4 – 5 drops of concentrated HCl was added. The water was boiled to remove hydrogen sulphide (H<sub>2</sub>S) if present. Then 50ml of water was collected for further procedure. A 0.5ml hydrogen peroxide was added and a faint yellow to bright yellow colour was developed depending on the iron content present. Two drops of sodium acetate was added into the solution, and a purple colour was developed depending on the iron content present. When there is no colour change the process is stopped, but if colour change, titrate with the EDTA solution in the burette until the purple colour disappears and the colour of the sample is the yellow colour that developed before the salicylic acid solution was added. The end point is noted. The amount of iron in the water sample was calculated using the formula;

$$Fe \left( \frac{\text{mg}}{\text{L}} \right) = \frac{(M \times ml) \text{ EDTA} \times 55850}{ml \text{ sample}} \quad [11]$$

### Adsorption of iron in Manganese dioxide Media with Varying Flow Rates

In order to get 600mm coarse particles, gravels are sieved using a sieve and the coarse particles washed thoroughly in order to prevent dust and other impurities from interfering with the experiment. The washed coarse particles was then dried and placed on top of the filtering tube as packed bed. Manganese dioxide which is the adsorbent was then placed on the packed bed to form the third layer for absolute purification. The filtering tube (sintered glass funnel) was then fixed to the retort stand with a 100ml measuring cylinder under it. Each sintered glass funnel has a specific flow rate. The temperature of the sample was taken using a thermometer before proceeding. Water was poured into the sintered glass funnel and allowed until 100ml water has drained from the lower end of the tube into the measuring cylinder. The time (minutes) taken to obtain 100ml of treated water was taken for that particular flow rate. This procedure was repeated for all the portions of the different masses of adsorbents used. The resulting data are shown as tabulated below.

### RESULTS AND DISCUSSION

Table 1 and 2 showed the results obtained from complexometric titration of water sample treated with 2.0g of adsorbent with volumetric flow rate of 1.9ml/min. and 3.50ml/min. The data showed that the lower volumetric flow rate of 1.9ml/min. of table 1 produced better result of iron adsorption by manganese dioxide. At 54 and 108 minutes, there was no detection of iron in water sample with volumetric flow rate of 1.9ml/min. Detection of iron was found at 162 minutes and 208 minutes of

0.33mg/L and 1.12mg/L respectively. While in table 2, with volumetric flow rate of 3.50ml/min., detection of iron in water sample was found at 58 minutes which amounted to 1,12mg/L and increased to 3.35mg/L at 114 minutes.

In tables 1, 3, 4 and 5, the volumetric flow rate was kept at 1.96ml/min., since it produced better result when compared to the volumetric flow rate of 3.50ml/min. of table 2. The results showed that increase in adsorbent dosage to 2.50g, 3.00g and 3.50g produced better results in terms of iron adsorption by the manganese dioxide. The rate of adsorption increases with increase in adsorbent dosage. At adsorbent dosage of 2.50g of table 3 at 107 minutes iron was not detected in the water sample, with 3.00g adsorbent dosage, at time 159 minutes, presence of iron was not detected, and when further increased to 3.50g adsorbent dosage in table 5, even at 206 minutes iron was not detected in the water sample. Also in tables 2, 3, 4, and 5, detection of iron in treated water sample was found to be 2.23mg/L at 85, 258, 307, and 308 minutes respectively.

In tables 6 and 7, volumetric flow rate was increase to 2.0ml/min with adsorbent dosage of 4.0g and 5.0g respectively. Detection of 1.12mg/L of iron in water occurred at 246 minutes under adsorbent dosage of 4.0g, while at adsorbent dosage of 5.0g, at 245 minutes no iron was detected. In table 6, at time 26 minutes and 300 minutes iron level was found to be 1.12mg/L, in which the adsorption of iron has reached an equilibrium or saturation point, whereby it cannot be adsorbed any more by the manganese dioxide as compared to table 5, where at 253 to 308 minutes adsorption of iron by manganese dioxide has stopped taken place and there is a record in the increase in the presence of iron in water sample.

To further confirm that increase in adsorbent dosage increases the rate of adsorption of iron water, tables 2 and 8 compared. There was no detection of iron in table 8 at 3.60ml/min. volumetric flow rate with adsorbent dosage of 5.0g even at 139 minutes, while in table 2, at volumetric flow rate of 3.50ml/min. with adsorbent dosage of 2.0g at 114 minutes, iron present in water sample was detected to be 3.35mg/L in a scale of 4.47mg/L, which shows that only very little amount of iron was removed under this condition. The results showed that increase in adsorbent dosage, even under increased volumetric flow rate causes more iron to be adsorbed to the manganese dioxide.

In tables 9 and 10, the volumetric flow rate was increased to 10ml/min. with adsorbent dosage of 8.0g and 10.0g respectively. The results showed that at 60minutes there was no detection of iron in the water sample. While in table 2 detection of iron occurred at 58 minutes to the tune of 1.12mg/L at volumetric flow rate of 3.50ml/min. This is a pointer to the fact to the fact that increase in dosage of manganese dioxide adsorbent increases the rate of adsorption of iron from water. It can be seen from tables 7 and 8 that when the amount of adsorbent is 5.0g and the volumetric flow rate is  $\leq$  3.60ml/min., that the iron concentration in the treated water sample is either zero or very low, such that the EDTA-volumetric method cannot be used for detection of iron in the sample. Also when the amount of adsorbent is 8.0g and 10.0g with volumetric flow rate of 10ml/min., the iron concentration in the treated water sample is zero or very low ( $< 0.15$ mg/L). EDTA-volumetric method has the detection limit of 0.15mg/L

The results from tables 1 to 10 showed that; increase in dosage of manganese dioxide adsorbent under various volumetric flow rates increased the rate of iron adsorption in the water sample by the media. This clearly indicates that increase in adsorbent dosages increases the rate of adsorption by the adsorbent all other conditions being the same.

Table 1: Data obtained from complexometric titration of water sample treated with 2.0g of adsorbent with volumetric flow rate of 1.9ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	54	Undetected
2	108	Undetected
3	162	0.33
4	208	1.33

Table 2: Data obtained from complexometric titration of water sample treated with 2.0g of adsorbent with volumetric flow rate of 3.50ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	31	Undetected
2	58	1.12
3	85	2.23
4	114	3.35

Table 3: Data obtained from complexometric titration of water sample treated with 2.50g adsorbent with volumetric flow rate of 1.96ml/min

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	53	Undetected
2	107	Undetected
3	154	0.22
4	206	0.56
5	258	2.23
6	305	2.23

Table 4: Data obtained from complexometric titration of water sample treated with 3.00g adsorbent with volumetric flow rate of 1.96ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	53	Undetected
2	107	Undetected
3	159	Undetected
4	204	0.33
5	253	1.68
6	307	2.23

Table 5: Data obtained from complexometric titration of water sample treated with 3.50g adsorbent with volumetric flow rate of 1.96ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	52	Undetected
2	104	Undetected
3	156	Undetected
4	206	Undetected
5	253	1.68

6	308	2.23
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Table 6: Data obtained from complexometric titration of water sample treated with 4.0g adsorbent with volumetric flow rate of 2.0ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	50	Undetected
2	100	Undetected
3	148	Undetected
4	196	Undetected
5	246	1.12
6	300	1.12

Table 7: Data obtained from complexometric titration of water sample treated with 5.0g adsorbent with volumetric flow rate of 2.0ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	50	Undetected
2	97	Undetected
3	144	Undetected
4	200	Undetected
5	245	Undetected

Table 8: Data obtained from complexometric titration of water sample treated with 5.0g adsorbent with volumetric flow rate of 3.60ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	32	Undetected
2	61	Undetected
3	87	Undetected
4	111	Undetected
5	139	Undetected

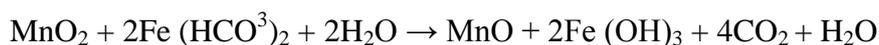
Table 9: Data obtained from complexometric titration of water sample treated with 8.0g adsorbent with volumetric flow rate of 10.0ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	10	Undetected
2	20	Undetected
3	30	Undetected
4	40	Undetected
5	50	Undetected
6	60	Undetected

Table 10: Data obtained from complexometric titration of water sample treated with 10.0g adsorbent with volumetric flow rate of 10.0ml/min.

Sample No	Time (Minutes)	Concentration of Fe (mg/L)
1	10	Undetected
2	20	Undetected
3	30	Undetected
4	40	Undetected
5	50	Undetected
	60	Undetected

The treatment procedure for the effective removal of iron in this research work is the adsorption of iron in manganese dioxide media. Iron in the ferrous form contains no oxygen, such as water from deep wells or groundwater. Since it lacks oxygen, the dissolved carbon dioxide reacts with iron in the ground to form ferrous ion in the bicarbonate form known as iron bicarbonate  $\text{Fe}(\text{HCO}_3)_2$  which produces  $\text{Fe}^{2+}$  ions in water when it reacts with oxygen to form  $\text{Fe}^{3+}$  ions, in the presence of manganese dioxide according to the equation:



In this research work, two major factors have been found to influence the effective removal of iron, viz: (a) dosage of adsorbent ( $\text{MnO}_2$ ) and (b) volumetric flow rate.

The amount of iron removed from the treated water sample was increased as a result of the increase in dosage of manganese dioxide, under the same volumetric flow rate. This is as a result of the increase the number of available adsorption sites of the adsorbent, hence increase in adsorption capacity, and therefore enhanced removal of iron from the treated water [12]. According to the increase in concentration of coconut shell charcoal led to greater amount of iron removal in water, hence increase in residence time for oxidation/ filtration between the iron in water and the manganese dioxide which acts as both adsorbent and an oxidizing agent. There was increased level of adsorption at every level of increased dosage, and at the outer surface of the manganese dioxide there existed both adsorption and diffusion into the pores as observed by [13], under adsorption studies of Cd(II) on polymer grafted sawdust. Since the bulk and surface metal concentration started to decrease, there is also the possibility of decrease in diffusion and a point of equilibrium will be reached [14]. Increasing the dose of the adsorbent ( $\text{MnO}_2$ ), the driving force of the metal ions ( $\text{Fe}^{2+}$ ) from the bulk phase on to the adsorbent.

Under a fixed adsorbent dose, the total sites of adsorption may be very limited, hence resulting in the decrease in the removal of iron from the treated water, since increased concentration (dosage) will result in increased sites of adsorption. The research work showed that increased manganese dioxide adsorbent, also increased the surface area for adsorption and oxidation of iron in water.

From the work, it was observed that increased flow rate decreased the rate of adsorption of iron by  $\text{MnO}_2$ . This agreed with the work of [15], that flow rate influenced the rate of iron removal and that lower flow rate gave better results due to contact time. Hence under the same adsorbent dosage lower flow rate gave better results. Therefore iron removal from water using manganese dioxide as

the adsorbent, there should be a calculated dose at a particular flow rate in order to achieve a better result.

Based on the research work, it was observed that the rate of iron adsorption increases with dosage increase. The point where the volumetric flow rate and the dosage adsorbent produced the maximum adsorption of iron is the equilibrium point. A further increase in dosage adsorbent or volumetric flow rate will amount to waste. Finally it has been shown that increase in dosage of  $\text{MnO}_2$  adsorbent increases the rate of iron adsorption and hence effective removal of iron from water.

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