# Reduce The Amount of Potassium Permanganate (KMnO₄) Used In The Disposal Of Manganese In The Water By Using (MnO₂) Generated In The Reaction Medium

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## ABSTRACT

*A primary use of permanganate is iron and manganese removal. Permanganate will oxidize iron and manganese to convert ferrous (2+) iron into the ferric (3+) state and (2+) manganese to the (4+) state. Disadvantages of Potassium Permanganate Use Long contact time is required. Potassium permanganate has a tendency to give water a pink color. Potassium permanganate is toxic and irritating to skin and mucous membranes. No byproducts are generated when preparing the feed solution, however this dark purple/black crystalline solid can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed. Over-dosing is dangerous and may cause health problems such as chemical jaundice and drop in blood pressure. From this point been thinking about the same efficiency and alternative fading all the previous defects. This alternative is MnO₂ resulting from the reduction of KMnO₄ iron and manganese removal and without external additions .Use MnO₂ in iron and manganese removal save a lot of money and save processing units, which were closed because of the high cost of treatment. As it can fade all KMnO₄ defects and can be used continuously without extra additives and can be re-generated to ensure the continued effectiveness and quality of results.*

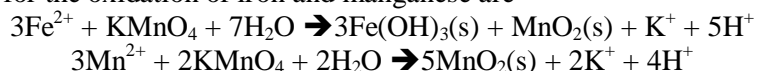**Keywords:** KMnO₄, MnO₂, Manganese in water, Iron and Manganese removal.

## INTRODUCTION

Manganese (Mn) is the first element in Group VIIB in the periodic table; it has an atomic number of 25, an atomic weight of 54.94, and common valences of 2, 4, and 7 (and more rarely, valences of 1, 3, 5, and 6). The average abundance of Mn in the earth's crust is 1060 mg $L^{-1}$, in soils it is 61 to 1010 mg $L^{-1}$, in streams it is 7 μg $L^{-1}$ and in ground waters it is <0.1 mg $L^{-1}$. Manganese is associated with iron minerals and occurs in nodules in ocean, fresh waters, and soils. The common ores are pyrolusite (MnO2) and psilomelane. Manganese is used in steel alloys, batteries and food additives. The common aqueous species are the reduced $Mn^{2+}$ and the oxidized $Mn^{4+}$. The aqueous chemistry of manganese is similar to that of iron. Since groundwater is often anoxic, any soluble manganese in groundwater is usually in the reduced state ($Mn^{2+}$). Upon exposure to air or other oxidants, groundwater containing manganese usually will precipitate black $MnO_2$. Elevated manganese levels therefore can cause stains in plumbing/laundry, and cooking utensils. It is considered an essential trace element for plants and animals. The United Nations

Food and Agriculture Organization recommended maximum level for manganese in irrigation waters is 0.2 mg $L^{-1}$. The U.S. EPA secondary drinking water standard MCL is 50 µg $L^{-1}$.

Manganese may exist in a soluble form in neutral water when first collected, but it oxidizes to a higher oxidation state and precipitates or becomes adsorbed on the container walls. Determine manganese very soon after sample collection. When delay is unavoidable, total manganese can be determined if the sample is acidified at the time of collection with $HNO_3$ to pH <2 [1]. A primary use of permanganate is iron and manganese removal. Permanganate will oxidize iron and manganese to convert ferrous (2+) iron into the ferric (3+) state and 2+ manganese to the 4+ state. The oxidized forms will precipitate as ferric hydroxide and manganese hydroxide [2]. The precise chemical composition of the precipitate will depend on the nature of the water, temperature, and pH.

The classic reactions for the oxidation of iron and manganese are -
$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2(s) + K^+ + 5H^+$$
$$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 2K^+ + 4H^+$$

The potassium permanganate dose required for oxidation is 0.94 mg $mg^{-1}$ iron and 1.92 mg $mg^{-1}$ manganese [3]. In practice, the actual amount of potassium permanganate used has been found to be less than that indicated by stoichiometry. It is thought that this is because of the catalytic influence of $MnO_2$ on the reactions [4]. The oxidation time ranges from 5 to 10 minutes, provided that the pH is over 7.0 [5]. In utilizing potassium permanganate in water treatment, caution should be taken to prevent overdosing, in which case, excess manganese will pass through the treatment plant. Proper dosing should be maintained to ensure that all of the permanganate is reduced (i.e., forming $MnO_2$ solids) and removed from the plant upstream of, or within, the filters. If residual manganese is reduced downstream of the filters, the resulting solids can turn the finished water a brown/black color and precipitate in the homes of consumers on heat exchange surfaces such as hot water heaters and dishwashers. Use of potassium permanganate can also be a source of manganese in the finished water, which is regulated in drinking water with a secondary maximum contaminant level of 0.05 mg $L^{-1}$. Under reducing conditions, the $MnO_2$ solids accumulated in filter backwash water and settling basins can be reduced to soluble Mn2+ and pass through the filters thereby remaining in the finished water. Also, under these conditions, soluble $Mn^{2+}$ in return water from settling basin dewatering facilities and filter backwash water recycled to the head of the plant are potential sources of manganese that will have to be treated and/or controlled to minimize finished water manganese levels [6]. Overdosing of permanganate in conventional plants is generally corrected by settling the excess $MnO_2$ solids in the settling basin. Removal of the excess permanganate can be monitored qualitatively by observing the disappearance of the pink color characteristic of permanganate. In plants that do not utilize flocculation and sedimentation processes permanganate dosing should be closely monitored [7].

**Disadvantages of Potassium Permanganate Use-**
a. Long contact time is required.
b. Potassium permanganate has a tendency to give water a pink color.
c. Potassium permanganate is toxic and irritating to skin and mucous membranes.
d. No byproducts are generated when preparing the feed solution, however this dark purple/black crystalline solid can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed. Over-dosing is dangerous and may cause health problems such as chemical jaundice and drop in blood pressure [8].
So we will use manganese dioxide resulting from the reduction of *potassium permanganate* by water to get rid of the metal ions, particularly iron and manganese (by adsorption).

## MATERIALS AND METHODS

The appropriate dose is calculated from the necessary potassium permanganate for chemical treatment of raw water based on the concentration of manganese in the raw water pre-treatment as follows in the classic reaction of potassium permanganate to remove $Mn^{+2}$ the numbers of moles is

$$3Mn^{2+} \rightarrow 2KMnO_4$$
$$3mol \rightarrow 2\ mol$$
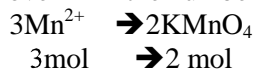
That mean when the concentration of$(Mn^{+2})$ is 1.2 mg $L^{-1}$ that mean we need (0.0023 g) $KMnO_4$ for one liter that mean 2.3 Kg per one $m^3$ of raw water.
This dose is added to the raw water through pump earmarked for permanganate and flow rate is adjusted based on
1 - concentration of manganese in the raw water
2 - flow rate of permanganate pump
For example, if the concentration of manganese in the raw water (0.8 mg $L^{-1}$) and the flow rate of permanganate pump unit L $S^{-1}$ that required permanganate exactly 95.4 g $h^{-1}$ .
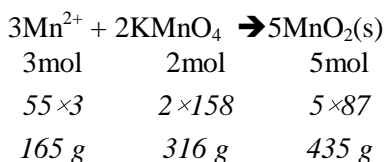Based on the flow rate of water treatment unit adjust pump rate of permanganate pump unit After adding a dose of the required permanganate ,manganese will turn this dose to manganese dioxide as follows

$$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 2K^+ + 4H^+$$
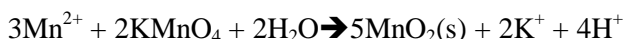
As can be seen every 2 moles of permanganate given 3 moles of manganese dioxide which is adsorbed material in question.

**Laboratory Practical Experience:** Manganese concentration is calculated by the persulfate method (B) is preferred because the use of mercuric ion can control interference from a limited chloride ion concentration.
**Experiment:** 5 ml of manganese standard 1ml = 0.1 mg $L^{-1}$ manganese and complete to 500 ml. That produce manganese 1 mg $L^{-1}$. From this equation

$$3Mn^{2+} + 2KMnO_4 \rightarrow 5MnO_2(s)$$

| 3mol | 2mol | 5mol |
|------|------|------|
| *55×3* | *2×158* | *5×87* |
| *165 g* | *316 g* | *435 g* |

Add 0.00192 g of $KMnO_4$ to 500 ml of 1 mg $L^{-1}$ manganese and mix them well as we know that the oxidation time ranges from 5 to 10 minutes, provided that the pH is over 7.0 [9]. That will produce 0.00261 g of $MnO_2$ (calculated from upper equation).
**The second step:** 0.00261 g of $MnO_2$ + 500 ml of 1mg $L^{-1}$ manganese and mix them well for 10 min.
After that filter and determine the conc. of manganese. We found it 0 mg $L^{-1.}$
**The third step:** Add another 500 ml of 1 mg $L^{-1}$ manganese and mix well for 10 minute. After that filter and determine the concentration of manganese. We found it 0.28 mg $L^{-1}$

## RESULTS AND DISCUSSION

From practical Experiment, which proved that the amount of manganese dioxide resulting from the interaction of $KMnO_4$ with a known concentration of manganese This quantity is enough for adsorption of the same concentration of manganese and more than that, as in the third step of the experiment.
**Deduction Mathematical Equation:**
mg of Manganese (Mn) Adsorbed = mg (Mn) before adding $MnO_2$– mg (Mn) after adding $MNO_2$.
mg of (Mn) Adsorbed = mg (Mn) before – mg (Mn) after .
If we know mg = mg $L^{-1} \times$ volume by liter (L)

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mg of (Mn)  Adsorbed= (mg $L^{-1}$ of (Mn)  before- mg $L^{-1}$ of (Mn)  after ) $\times$ L
dividing the two sides by   [g of ($MnO_2$)]
mg of (Mn)  Adsorbed / g of ($MnO_2$)= (mg $L^{-1}$ of (Mn)  before- mg $L^{-1}$ of (Mn)  after ) $\times$ L/ g of ($MnO_2$).
imposing that     G=mg of (Mn)  Adsorbed / g of ($MnO_2$)
G=( mg $L^{-1}$ of (Mn)  before- mg $L^{-1}$ of (Mn)  after ) $\times$ L/ g of ($MnO_2$).

**Past experience in application**   G=(1-0.28) mg $L^{-1}$ $\times$1 / 0.00261 g = 275.86  mg $g^{-1}$
That mean we every one gram of $MnO_2$ can adsorb 275.86 mg manganese.
and then we can say
$\quad$ $3Mn^{2+}$ + $2KMnO_4$ $\rightarrow$ $5MnO_2(s)$
$\quad$ and $\qquad$ $5MnO_2(s)$ $\longrightarrow$ x mol Mn
$\quad$ 1/87 mol $MnO_2$ $\longrightarrow$ 0.275/55 mol Mn
$\qquad$ so x= 2.17 mol Mn
that mean  $5MnO_2(s)$ adsorb $\longrightarrow$ 2.177 mol Mn  which is  119.625 g of manganese
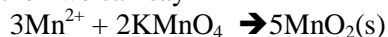
## APPLICATIONS

From practical experience above, which proved that the amount of( $MnO_2$) resulting from the interaction of ($KMnO_4$) with a known concentration of manganese This quantity is enough to adsorption of the same concentration of manganese . Next application was designed, which we will explain as follows in figure 1.
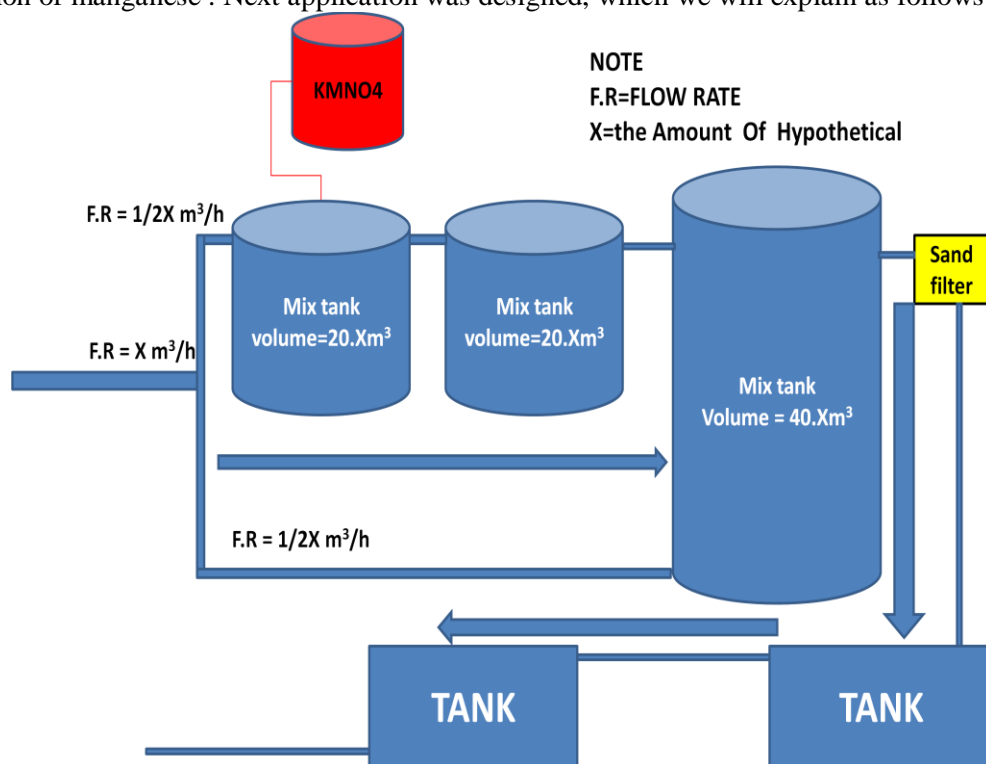


**Figure 1.** The proposed processing unit

1. If the rate of pumping and processing unit(X $m^3$ $h^{-1}$),( **X=**the amount  of  Hypothetical**)**   for example, this rate is distributed into two equal parts (1/2X $m^3$ $h^{-1}$).
2. Upper part is pumped by $KMnO_4$ according to manganese concentration as previously in tank capacity 20 $m^3$ with rapid mixing.
3. After the first tank water flow to the second tank equivalent of the first tank. With the rapid mixing well.

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4. After it is collected half treated water with half untreated water in his third tank capacity 40 m$^3$ with the rapid mixing well.

5. After that water flow on the sand filter and then water tank and then another and then abroad for consumption

6. The resulting water be completely free of manganese and half only KMnO$_4$ amount, providing 50%

Note: By adding treated water to untreated water we avoid all defects of the use of KMnO$_4$ in water treatment

## CONCLUSIONS

Clear from the foregoing that it can use MnO$_2$ output of KMnO$_4$ used in treatment gives better results and fading all the disadvantages of using KMnO$_4$ and gives better results and reduce consumption to nearly half the cost without affecting the efficiency of the treatment process or incurring big money in the construction of expensive treatment units

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