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Removal of Iron and Manganese from Groundwater: A Study of Using Potassium Permanganate and Sedimentation.

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Removal of Iron and Manganese from Groundwater: A Study of Using Potassium Permanganate and Sedimentation

إزالة الحديد والمنجنيز من المياه الجوفية : دراسة إستخدام برمنجنات البوتاسيوم والترسيب

M. A. Elsheikh, H. S. Guirguis and A. Fathy

KEYWORDS:
Iron, Manganese, Potassium Permanganate, Alum, Filtration, Sedimentation.

الملخص العربي:- **تدرس هذه الورقة البحثية كفاءة إزالة الحديد والمنجنيز من المياه الجوفية بإستخدام الأكسدة بواسطة برمنجنات البوتاسيوم متبوعا بالترشيح وكذلك إستخدام المعالجة التقليدية التي تشمل الترويب والترسيب والترشيح. تم إجراء التجارب لتركيزات مختلفة من الحديد والمنجنيز. وقد اوضحت النتائج ان برمنجنات البوتاسيوم يعطي نتائج جيدة فعند استخدام جرعات مقاربة لنصف الجرعة المحسوبة نظريا فيمكن إزالة حتي 100 % من الحديد و 90% من المنجنيز وذلك للتركيزات المختلفة التى تم إختبارها عند الأس الهيدروجيني 7.0. وكذلك تقل نسبة الإزالة للمنجنيز بشكل كبير عند زيادة معدل الترشيح. بالنسبة للترسيب فيجب إستخدامه عندما تزداد تركيزات الحديد والمنجنيز مجتمعة عن 5.0 مجم/لتر وذلك لتقليل معدل إنسداد المرشح. وعند إستخدام المعالجة التقليدية بإضافة الشبة والترويب والترسيب والترشيح فانها تزيل حتي 97% و 18% من الحديد والمنجنيزعلى التوالي. أما عند إستخدام برمنجنات البوتاسيوم مع الشبة فانها تحسن من إزالة المنجنيز ولكنها تقلل من كفاءة إزالة الحديد. وعند إستخدام الشبة مع زيادة الأس الهيدروجيني حتى 10 فيمكن إزالة 100% و 95% من الحديد والمنجنيز على التوالى وكذلك زيادة فترة عمل المرشح.**

***Abstract*— This paper studies the efficiency of iron (Fe^{+2}) and manganese (Mn^{+2}) removal from groundwater using oxidation by potassium permanganate followed by filtration and using conventional treatment consisting of flocculation, sedimentation and filtration. Experiments were done for different combinations of Fe^{+2} and Mn^{+2} concentrations. The obtained results show that Potassium Permanganate (PP) gives good results. By using PP dose equals to half of the theoretically required one, it can remove up to 100% and 90% of iron and manganese respectively over different tested concentrations at pH=7.0. Increasing rate of filtration decreases the Mn^{+2} removal efficiency obviously. Sedimentation is required when combined concentrations of iron and manganese are greater than 5.0 ppm to reduce filter rapid clogging. Using conventional treatment with adding Alum, flocculation, sedimentation and filtration can remove up to 97% and 18% of iron and manganese respectively. Using PP in addition to alum enhances manganese removal but decreases iron removal. However, using Alum with raising pH to 10 leads to 100% and 95% of Fe^{+2} and Mn^{+2} removal and increases filter working period.**

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I. INTRODUCTION

GROUNDWATER sources in Egypt can be divided into renewable aquifers like Nile Valley and Delta and non-renewable aquifers like the aquifer of the western desert in the Nubian sandstone [1]. Iron and Manganese are usually present in groundwater as dissolved minerals or associated with other components [2]. Existence of iron and manganese in water causes many problems like water coloring and taste, clothes staining and encouraging bacterial growth in water distribution networks which affect the pipes transfer efficiency [3] but in general they don't cause health problems [4]. The secondary maximum contaminant levels for Iron and Manganese are 0.3 mg/l and 0.05 mg/l respectively [5]. The most common methods used to remove iron and manganese include oxidation by Aeration, Chlorine, Chlorine dioxide, Potassium Permanganate and/or Ozone followed by Filtration alone or Sedimentation and Filtration [6,7]. There are other methods that can be used also like using filters with special media like green sand, using Ion exchange, Biological methods or membrane filtration [8].

Potassium Permanganate (PP) is considered a stronger oxidant and has many advantages over other oxidants. Oxidation chemistry of iron and manganese by PP can be described as following [9]:

$$3Mn^{+2} + 2KMnO_4 + 2H_2O \longrightarrow 5MnO_4 + 2K^+ + 4H^+ \qquad (1)$$

$$3Fe^{+2} + KMnO_4 + 7H_2O \longrightarrow 3Fe(OH)_3 + K^+ + MnO_2 + 5H^+ \qquad (2)$$

To oxidize one mg of iron and one mg of manganese, about 0.94 mg and 1.92 mg of PP are required respectively [9].

When iron and manganese exist in high concentrations, they cause filter to run less than 24 hours so a clarification step is needed before filtration to increase the filtration period [10]. Therefore, treatment method would there include flocculation, sedimentation and filtration stages [11].

This paper studies using of PP followed by filtration only or using PP and/or alum (Al) followed by flocculation, sedimentation and filtration for Fe^{+2} and Mn^{+2} oxidation and removal.

II. MATERIALS AND METHODS

A. Study Method

Simulated groundwater was prepared by adding salts of iron and manganese to tap water. The study consists of three stages of experiments: the first one discusses the different factors (e.g. dosages, detention time or pH) that affect the oxidation of Fe^{+2} and Mn^{+2} by using PP followed by direct filtration. Experiments were done for Fe^{+2} and Mn^{+2} = 1.50 and 1.0 mg/l respectively which act the iron and manganese concentration in the Delta region, Egypt. The second stage investigates the results of the first one on other combined concentrations of Fe^{+2} and Mn^{+2} by using direct filtration alone also. The third one discusses the efficiency of using sedimentation if high concentrations of Fe^{+2} and Mn^{+2} exist. This phase includes flocculation, sedimentation and filtration.

B. The Pilot plant

Fig. 1 shows the pilot plant which is constructed for the study. It consists of feeding tank, process tank for adding and mixing chemicals, Flocculation and Sedimentation tanks and a Rapid Sand Filter (RSF). For 1st and 2nd phase experiments, the flocculation and sedimentation tanks aren't included. The RSF is made of PVC pipe of internal Diameter = 100 mm and includes 35 cm gravel layer with diameter 6:25 mm and 75 cm of coarse sand with Diameter 1.18:1.60 mm. The Rate of Filtration is obtained by controlling the outlet filter valve.

C. Chemicals

The Simulated groundwater containing iron and manganese is made by adding ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) and manganese sulfate mono-hydrate ($MnSO_4.H_2O$) to tap water. They are obtained from Alnasr company for chemicals, Cairo. Potassium permanganate ($KMnO_4$) with 99.90% purity and aluminum Sulphate Hexadecahydrate $Al2(So_4)_3.16H_2O$) were obtained from a Local supplier. Also, Sodium hydroxide (NaOH) was used to adjust pH.

D. Devices and Analyses

Iron and manganese measuring devices were used to measure Iron and Manganese concentrations (Hanna, USA). Portable pH device was used to measure water pH. The devices were calibrated before the study.

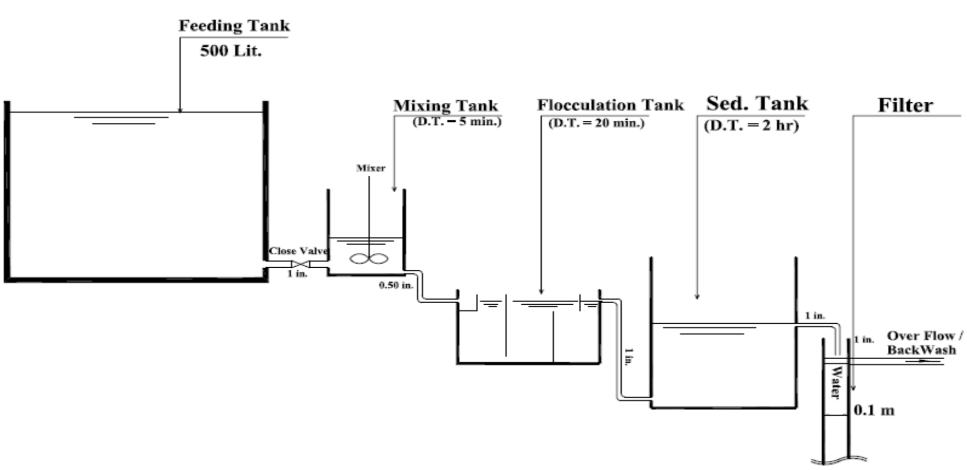

Fig. 1. Pilot Plant with Mixing, Flocculation, Sedimentation and Filtration Tanks. (When direct filtration mode is used, the flocculation and sedimentation tanks are removed.)

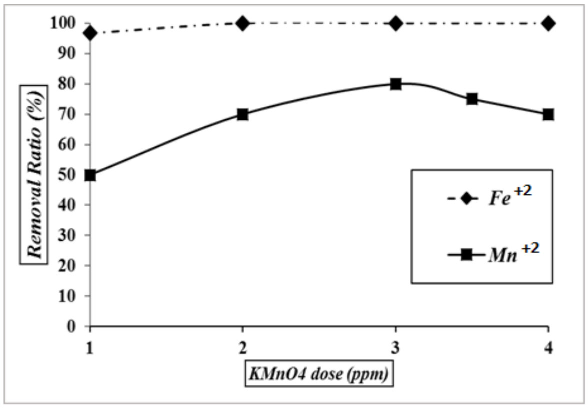

Fig. 2. Effect of using different P.P. doses on Fe^{+2} and Mn^{+2} removal (Initial Fe^{+2} and Mn^{+2} concentrations are 1.50 and 1.0 mg/l, pH=7.0, ROF=150 m/d and RT=10 mins).

III. RESULTS AND DISCUSSIONS

A. Stage 1: Study using Potassium Permanganate

In this stage, the experiments are done for Fe^{+2} and Mn^{+2} concentrations = 1.50 and 1.0 mg/l respectively at constant R.O.F.= 150 m3/m2/d. These experiments discuss the removal efficiency of iron and manganese by using potassium permanganate under different conditions like different dosages of PP, retention time, effect of pH and ROF effect.

1) Effect of PP dosages

Fig. 2 shows the results of using different PP dosages for Fe^{+2} and Mn^{+2} removal. Using a dosage of 1 ppm of PP can remove up to 97% of iron just after 10 minutes. For Manganese, using PP enhances the removal process greatly at pH=7.0. Using PP dose = 2.0 ppm -which is near to half of the theoretically calculated dose- can remove 66% of Manganese after 10 minutes. Using doses near to the theoretical dose remove up to 80% of Manganese in just 10 minutes. Increasing PP dosage than the theoretical one has a bad effect on water. When the dosage of 4 ppm is used, the water is colored pink from the effect of increased PP dosage. The increased PP quantity contains Manganese according to the following equation [12]:

$$KMnO_4 + 8H^+ + 5e^- \rightarrow Mn^{+2} + K^+ + 4H_2O \quad \text{.......... ....(3)}$$

Therefore, a special care should be taken into consideration when choosing the PP dosage. These results agree with other studies that recommend using PP dosages near the theoretical ones [12].

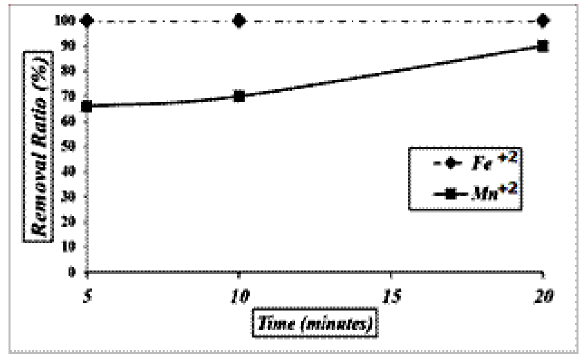

Fig. 3. Effect of Retention time on Fe^{+2} and Mn^{+2} removal by P.P. (Initial Fe^{+2} and Mn^{+2} conc. are 1.50 and 1.0 mg/l, pH=7.0, PP=2.0 ppm and ROF=150 m/d)

2) Effect of Retention Time

The results for using PP dose =2.0 ppm for R.T.=5:20 mins are shown in fig. 3. The oxidation process of iron using PP happens very fast. Complete Iron oxidation needs less than 5 minutes. The oxidation process of Manganese using PP also happens fast and is enhanced by increasing R.T. Using R.T. less than 5 minutes, about 66 % of Manganese is oxidized. Using R.T. equals to 20 minutes increases the R.R. to 90%.

3) Effect of pH

Fig. 4 shows the results of pH effect on Fe^{+2} and Mn^{+2} oxidation by PP dose = 2.0 ppm and R.T. = 10 mins It's shown that Iron is oxidized at pH greater than 7.0 and much of Manganese oxidation by using PP happens also at pH near to 7.0. Increasing pH to 8 and 9, increases the R.R. to 75% and 85% respectively. Therefore, it's concluded that pH affects the process of Fe^{+2} and Mn^{+2} oxidation by PP slightly or by other words, they need pH greater than 7.0.

The obtained results agree with others which found that the required dose of PP to oxidize Mn^{+2} was less than that the indicated by the stoichiometry. It is thought that when Mn^{+2} is separated on the filter, it coats the filter sands and make the filter work as a green sand one, therefore, the required dose becomes smaller [10]. The oxidation time ranges from 5 to 10 minutes, provided that the pH is over 7.0 [11]. On the other hand, some studies found that the required dosage is slightly more than the required theoretical dose at pH less than 8.0 [12] and therefore, the required dose should be determined accurately.

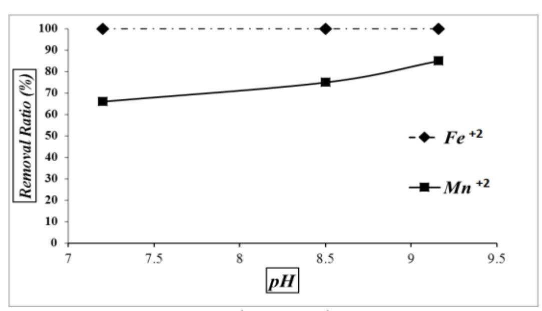

Fig. 4. Effect of pH on Fe^{+2} and Mn^{+2} removal by PP (Initial Fe^{+2} and Mn^{+2} conc. are 1.50 and 1.0 mg/l, P.P.=2.0 ppm, ROF=150 m/d and RT=10 mins)

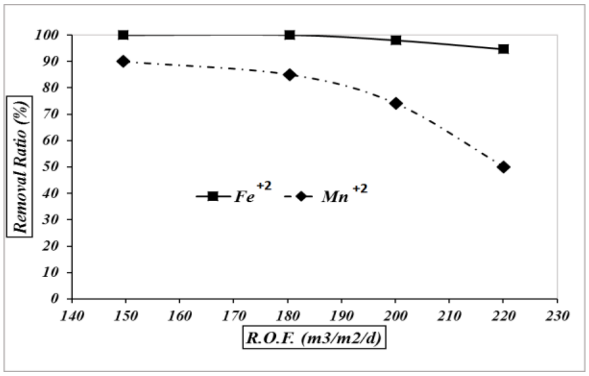

Fig. 5. Effect of R.O.F. on Fe^{+2}/Mn^{+2} removal (Initial Fe^{+2}/Mn^{+2} conc. is 1.50/1.0 mg/l, pH=7.0, PP=2.0 ppm and RT=20 min)

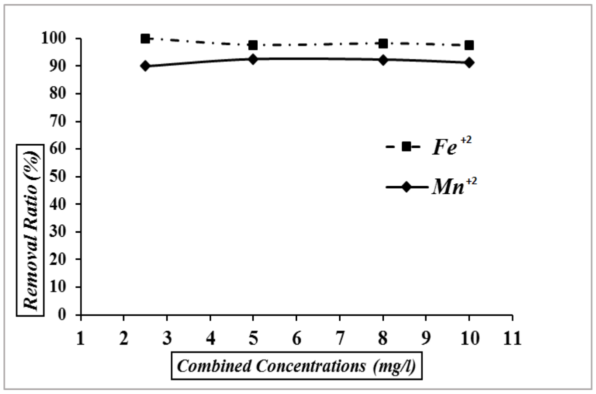

Fig. 6. Effect of using half dose of P.P. on different concentrations of Fe^{+2} and Mn^{+2} (Initial pH=7.0, R.T.=20 min. Samples are taken and analyzed after 8 hours from filter run start).

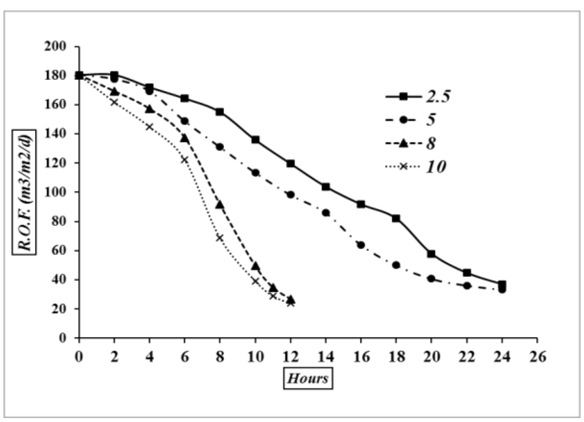

Fig. 7. Change in R.O.F. of different concentrations of Fe^{+2} and Mn^{+2} (Initial pH=7.0, R.T.=20 min. All exp. Started at R.O.F.=180 m/d).

4) Rate Of Filtration (ROF) effect

The effect of increasing ROF on Fe^{+2} and Mn^{+2} removal is shown in fig. 5. PP dose = 2.0 ppm was used for R.T. = 20 mins. For Iron: increasing ROF from 150 to 180 m/d doesn't affect the removal efficiency. At ROF=220 m/d, R.R. becomes 95%. But in general, it's seen that Iron removal is slightly affected by increasing ROF. For Manganese: Biggest R.R. is obtained at ROF equals 150 m/d. At ROF equals 220 m/d, the removal ratio becomes 50% only. Therefore, it's obvious that

TABLE I
FE^{+2}/MN^{+2} CONCENTRATIONS OF PHASE 2 EXPERIMENTS

FE^{+2} (MG/L)	MN^{+2} (MG/L)	COMBINED CONC. (MG/L)	P.P. DOSE (PPM)
1.5	1	2.5	2
3	2	5	3.5
5	3	8	5.5
6	4	10	7

removal ratio of Manganese depends on ROF in contrast to Iron. Therefore, ROF of 150-180 m/d -(6.25-7.5 m/h)- is recommended for Mn^{+2} and 150-220 m/d (6.25-9.17) for iron. However, it's reported that recommended ROF for Mn^{+2} removal is about 15-18 m/hr where for iron is 6-7.5 which is considered totally different from this study results [11].

E. Stage 2: Study results of Phase 1 on other Fe^{+2} and Mn^{+2} concentrations

In this stage, the experiments were done for different concentrations of Iron and Manganese with using half of the calculated stoichiometric doses of PP. Table I shows these concentrations and the used PP doses. The experiments started with R.O.F. equals to 180 $m^3/m^2/d$, pH=7.0 and R.T. equals 20 minutes. The experiments lasted for 24 hours or until ROF became less than 30 m/d.

1) Effect of using the Half dose of PP

Fig. 6 shows the results of using Half of PP dose on the removal of Fe^{+2} and Mn^{+2} different concentrations. The figure shows that using PP is very efficient to oxidize and remove Fe^{+2} and Mn^{+2} at different concentrations. Using half of stoichiometric dose of PP can remove about 98% of Fe^{+2} and more than 90% of Mn^{+2} despite increasing combined concentrations to 10 mg/l.

2) Filter Clogging Rate

Fig. 7 shows the change in ROF with time (in hours) for experiments of stage 2. The change in ROF expresses the velocity of filter clogging at different concentrations. The figure shows that the R.O.F. is decreased with time. This occurs as removed iron and manganese accumulate on filter media and start to clog the filter. It's shown that increasing Fe^{+2} and Mn^{+2} Concentrations lead to rapid filter clogging. when concentrations of iron and manganese exceed 5.0 mg/l, the removed particles cause rapid clogging of filters and decrease the period of filter run to be less than 12 hours. This period isn't practical nor economical to be applied to water treatment plants as the ratio of backwash water will increase. Therefore, it's recommended that when the combined concentrations exceed 5.0 mg/l to use sedimentation before filtration. other studies suggest using sedimentation when combined concentrations of Fe^{+2} and Mn^{+2} exceed 8.0 mg/l [8] or when iron concentration is greater than 5.0 mg/l [11].

F. Stage 3: Study using Conventional treatment to remove Fe^{+2} and Mn^{+2}:

This set of experiments deals with using Conventional treatment to remove Fe^{+2} and Mn^{+2} when they are found in high concentrations.

The treatment includes adding alum (with/without other chemicals), mixing with water for 5 mins, flocculation for 25 mins, sedimentation for 2.0 hrs and then filtration. This set discusses using alum alone, Alum with PP and Alum with increasing pH followed by filtration and sedimentation.

Fig. 8 shows the results obtained from these experiments. It is shown that using alum alone can remove high ratio of Fe^{+2}. By using alum dose=60 ppm, about 97% of Fe^{+2} can be removed. However, the R.R. of Mn^{+2} doesn't exceed 18%. Using PP with Alum enhanced Mn^{+2} R.R. to reach about 63% but decreased Fe^{+2} R.R. to 79% when PP dose=5.0 ppm used with Alum dose=40 ppm. Using alum alone with increasing water pH to over 10 leads to complete removal of Iron and about 95% of Mn^{+2}.

Another study found that Fe^{+2}/Mn^{+2} removal ratios by Coagulation and Clarification were about 18:75% and 8:24% for Fe^{+2}/Mn^{+2} respectively for different concentrations of iron and manganese. However, when PP was used, Fe^{+2} R.R. was about 99% which is greater than our study results and Mn^{+2} R.R. was 72% which is similar to the above results [13].

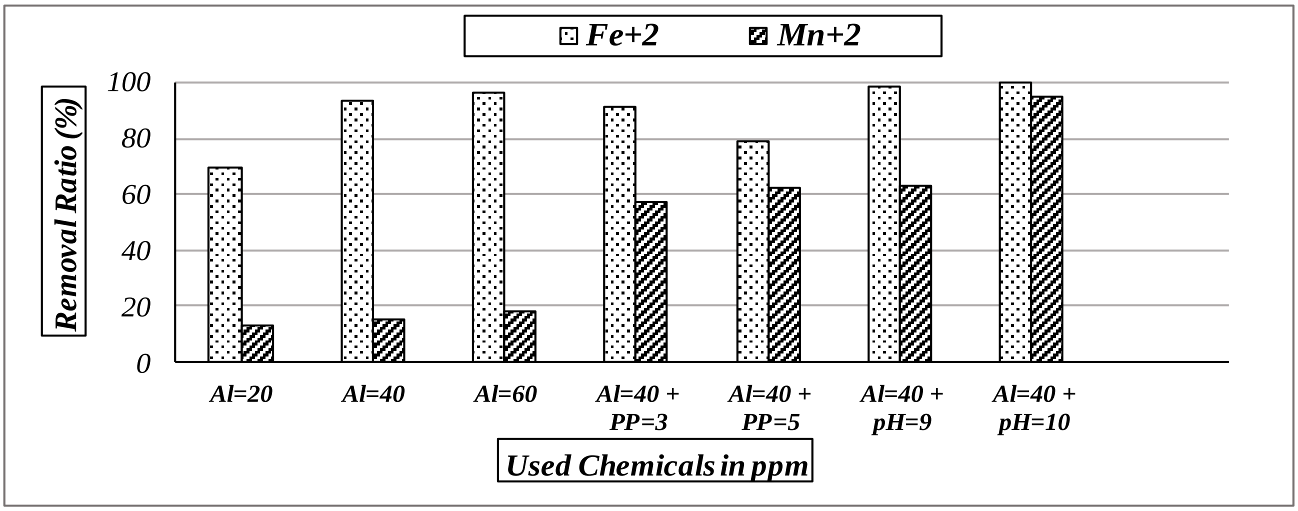

Fig. 8. Results of using conventional treatment for removal of Fe^{+2}=5.0 mg/l and Mn^{+2}=3.0 mg/l (Initial pH=7.0, All exp. Started at ROF=150 m/d and samples are taken after 10 hours from filtration start).

G. Recommendations

1) Using PP

PP is considered a good selection for the process of iron and manganese removal. The experiments show that using dosages near to half of the required theoretical dose at pH=7.0 and retention time of 20 minutes can remove iron completely and 90% of manganese. However, the applied dose should be determined very accurately to prevent water coloring.

2) Using sedimentation

Sedimentation is required when iron and manganese combined concentrations exceed 5.0 mg/l to allow longer filtration periods.

3) Using Alum

Using alum with sedimentation alone can't remove high ratio of manganese. However, using alum with raising pH to 10 leads to remove high ratio of both Fe^{+2}/Mn^{+2} concentrations.

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