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Influence of ageing on the catalytic activity of MnO_2 sludge for oxidation of Mn(II)

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ABSTRACT

Manganese can be present in natural water in concentrations exceeding 10 mg/l. If not treated well, Mn(II) ions can easily escape through the water treatment systems. Mn(II) in the distribution systems could form manganese dioxide, which is insoluble in water, causing several problems such as water discoloration, turbidity, metallic taste, odour, corrosion and biofouling. Oxidation is a common method for Mn(II) removal. Oxidation process can become more efficient with catalytic effects of several substances. High Mn(IV) concentrations can be maintained only by sludge recycle which eventually leads to sludge ages as high as 10 days. The aim of this study was to determine whether ageing of MnO_2 sludge affects its catalytic effect on the oxidation of manganese by aeration. In order to reach this aim, five different groups of experiments were carried out by MnO_2 sludge aged for a period of 0–10 days. It has been demonstrated that the catalytic effect of MnO_2 sludge on the oxidation of manganese, contrary to what is commonly expected, aeration increases with increasing sludge age. It has been concluded that, catalytic oxidation rate constant, k_{cat} obtained from the batch systems can safely be used in design of continuous flow Mn(II) oxidation reactors with sludge recycle. As a result, the catalytic effect of MnO_2 sludge on the Mn(II) oxidation by aeration increases with increasing sludge age up to approximately fourth day.

Keywords: Autocatalytic oxidation; Catalytic effect; Manganese oxidation; Sludge age

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1. Introduction

Manganese is one of the most common contaminants found in both surface and ground water, but predominantly in the latter. Generally, big, great amounts of metals such as manganese and iron are present in fresh waters from weathering of rocks and soils. Manganese can be present in natural water in concentrations exceeding 10 mg/l [1]. Manganese in natural waters can exist in truly dissolved, colloidal and suspended forms, for example Mn(II), Mn(IV). Soluble manganese (Mn(II)) is typically found in all water supplies, with higher concentrations usually

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present in water obtained from groundwater sources or reservoir hypolimnions [2,3]. The oxidation of manganese is affected by several factors such as Mn(II) and oxygen concentration, pH, temperature, organic matter and other ions [4–7].

Manganese removal methods generally require the use of strong oxidizing agents such as oxygen, potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone [2]. The oxidation of manganese by air alone is usually slow process unless the pH is raised above neutral level. However, the oxidation rates are much higher at elevated pHs than those of the pHs values less than 8.0. Manganese (II) oxidation aeration is not commonly practised because the process is slow kinetically slow and pH dependent. The oxidation is considered acceptable at above pH 9.5. The removal of manganese from aqueous solution by oxidation with dissolved molecular oxygen at pH of 9.0 has been shown previously as an autocatalytic in nature [4]. The rate equation for the conversion of Mn (II)–Mn(IV) includes an autocatalytic term in addition to the proportional term of the reduced metal ion concentration. However, Pankow and Morgan also concluded that an auto-oxidative reaction does not take place between Mn(II) and MnO_2 at pH values below 9.0 [8].

In order to apply these results obtained in batch systems of the continuous flow systems with MnO_2 sludge recycle, one has to know that the effect of the sludge age on the catalytic effect of MnO_2 [9].

Previous research suggested that the presence of manganese oxides may exert a pseudo-catalytic effect on further precipitation of the metal from the liquid phase [10–12]. A two-reaction mechanism has been proposed, where a relatively rapid adsorption is followed by a slower oxidation [13].

$$\mathrm{Mn}^{2+} + \mathrm{MnO_2} \xrightarrow{k} \mathrm{MnO_2Mn}^{2+}$$

$$\mathrm{O_2} + \mathrm{MnO_2Mn}^{2+} \xrightarrow{k_1} 2\mathrm{MnO_2}$$

Since the reaction product is solid, the autocatalysis is heterogeneous and the exact kinetic analysis of the reaction is difficult. Nevertheless, at constant pH and under constant partial pressure of oxygen, an autocatalytic rate type of expression was shown to be obeyed during the initial stages of the oxidation.

$$\frac{-\mathrm{d}[\mathrm{Mn(II)}]}{\mathrm{d}t} = k[\mathrm{Mn(II)}] + k_1[\mathrm{Mn(II)}][\mathrm{Mn(IV)}] \qquad (1)$$

$$k_{\mathrm{cat}} = (k + k_1[\mathrm{Mn(IV)}]) \qquad (2)$$

The aim of the study was to determine whether ageing of MnO_2 sludge affect its catalytic effect on the oxidation of Mn(II) by aeration.

2. Materials and methods

2.1. Experimental procedure

The oxidation of Mn(II) was studied in a batch reactor of one litre volume under the constant pH, temperature and O_2 concentration. The experimental setup is illustrated in Fig. 1. The reaction vessel was intensely mixed using Wisestir HS-50A type of mixer. $NaHCO_3$ was added into the distilled water in order to obtain a solution with an alkalinity equal to 8×10^{-3} eq/l. Air was given into the solution using fine bubble diffusers. The pH of the solution was controlled by adding 0.1 N NaOH and 0.1 N HNO_3. The pH of the solution was measured by Schott lab 850 type of ion analyser with sensitivity of ±0.01 pH unit. The dissolved oxygen levels were monitored using Armfield oxygen meter. Constant temperature (25°C) was maintained by immersing the reaction vessel into GN 111-200 Gastronorm water bath.

Mn(II) stock solution was prepared by dissolving $MnSO_4.H_2O$ (Manganese sulphate monohydrate) in one litre demineralized water. The samples taken at pre-decided times as measured from the start of the experiments were immediately filtered and acidified after filtration with 2 ml HNO_3. In the beginning, the samples were taken in every 2–3 min, after the 20th minutes of the experiment, in every 10 min, and since most of the manganese is oxidized in 20 min.

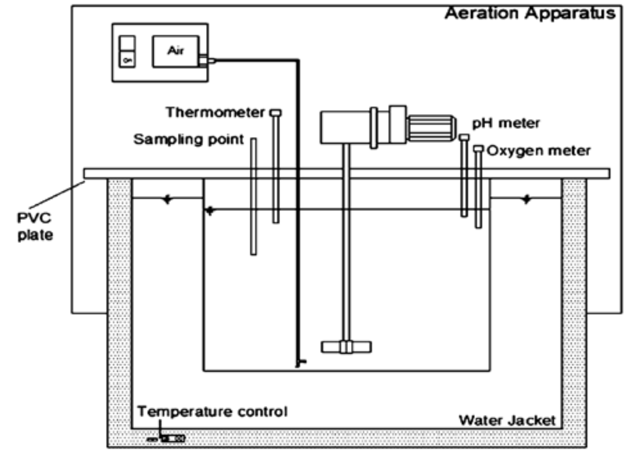

Fig. 1. The experimental set-up.

Filtration through a 0.22 μm membrane filter is accepted procedure defined in Standard Methods (3010A) for the determination of dissolved manganese. Residual Mn(II) concentrations were determined by Atomic Absorption Spectrometer (AAS) [14]. The detection limit for manganese was 0.015 mg/l in AAS measurement. All experiments were conducted at 25°C and pH 9.5 and 10.

Appropriate amount of $MnCl_2.2H_2O$ is added to 1 litre distilled water by adjusting the pH and alkalinity, and then it is aerated during 24 h. pH of MnO_2 sludge samples at different concentrations is adjusted to 9.5 after addition of 8×10^{-3} eq/l alkalinity. MnO_2 sludge aged for a period within the range of 0–10 days was added to reach pre-determined concentrations. pH of the sludge samples did not change during aging up to 10 days. Aged MnO_2 sludge was added into the reaction vessel after dropping their pH to 9.5–10. Initial Mn(II) concentration was chosen as 10 mg/l. In the beginning, the manganese concentration of the prepared solution was confirmed by several measurements.

2.2. Experiment steps

Oxygenation experiments were carried out of five different groups of experiments as summarized in Table 1.

The average k_{cat} values were obtained for these groups of experiments.

3. Results and analysis

3.1. The effects of pH on Mn(II) oxidation

The experimental results which were obtained from different pH (9.0, 9.5 and 10) were given in Fig. 2. The pH value studied in this article was predicted by assessing the oxidation time for different pH values. This is why three different pH values were used in this article. Mn(IV) were not initially added in these experiments. Linear relationship between the Mn(II) concentration and time on a semi-logarithmic plot indicates the first order kinetics in line, with the results given in the literature. Reproducibility of the results is good in the homogenous systems. When pH was increased by keeping all other experimental conditions the same, the reaction was accelerated due to increasing pH. On the other hand, at pH=10, it is obvious that Mn(II) removal is caused not only by oxidation but also by precipitation. Because at pH=10, approximately 32% of the added HCO_3 is converted into CO_3 causing precipitation of $MnCO_3$ because of the low solubility product (K_{sp}) of $MnCO_3$ ($\approx 1.76 \times 10^{-11}$). Even at pH=9.5, about 13% CO_3 can be formed. At pH=9, less than 5% of the added HCO_3 will be converted into CO_3. Oxidation process is followed by a precipitation process in the drinking water treatment plants. So precipitation plays a significant role in the Mn(II) oxidation with MnO_2 sludge recycle [15].

Table 1
Groups of the experiments used in this study

Run no	$Mn(II)_0$ (mg/l)	$Mn(IV)_0$ (mg/l)	pH
1	10	50	10
2	10	100	10
3	10	50	9.5
4	10	100	9.5
5	10	200	9.5

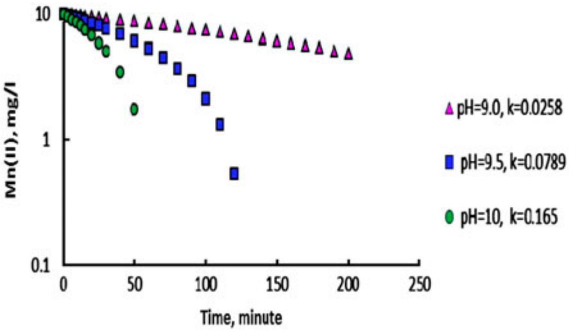

Fig. 2. Variation of Mn(II) with time for different pH values (Mn(II): 10 mg/l, alkalinity: 8×10^{-3} eq/l, T: 25°C, pO_2: 0.21 atm.).

It is evident from Fig. 2 that increasing pH causes decreasing reaction time in oxidation of Mn(II) with air. Reaction time in which the oxidation is completed,

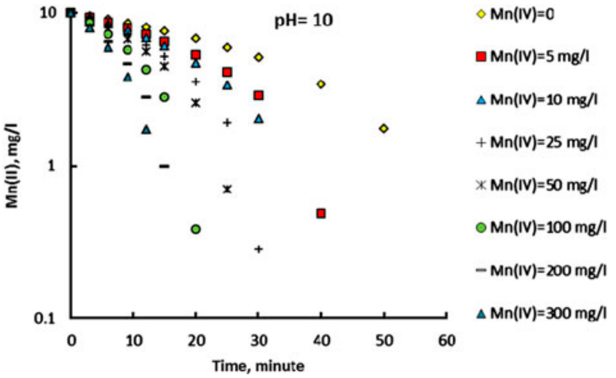

Fig. 3. Variation of Mn(II) with time for different initial Mn(IV) concentrations (Mn(II): 10 mg/l, pH: 10, alkalinity: 8×10^{-3} eq/l, T: 25°C, pO_2: 0.21 atm.).

Table 2
k, k_{cat} and reaction time values for different Mn(IV) concentrations and pH

pH	$[Mn(II)]_0$ mg/l	$[Mn(IV)]_0$ mg/l	k, k_{cat}, min^{-1}	Reaction time, t, min
10	10	0	0.165	61
10	10	5	0.238	42
10	10	10	0.266	38
10	10	25	0.324	31
10	10	50	0.372	27
10	10	100	0.481	21
10	10	200	0.601	17
10	10	300	0.689	15
9.5	10	0	0.0789	127
9.5	10	5	0.0821	122
9.5	10	10	0.0856	117
9.5	10	25	0.0897	111
9.5	10	50	0.0952	105
9.5	10	100	0.128	78
9.5	10	200	0.167	60
9.5	10	300	0.213	47

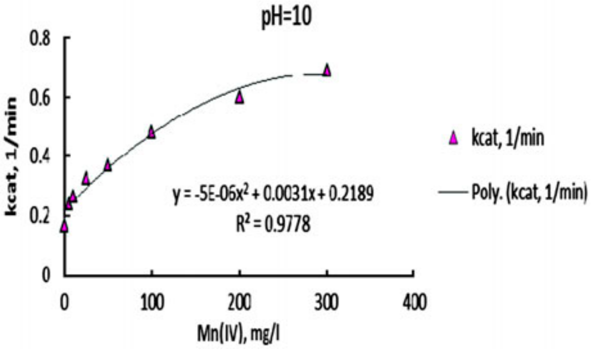

Fig. 4. The relationship between the k_{cat} and $[Mn(IV)]_o$(pH 10).

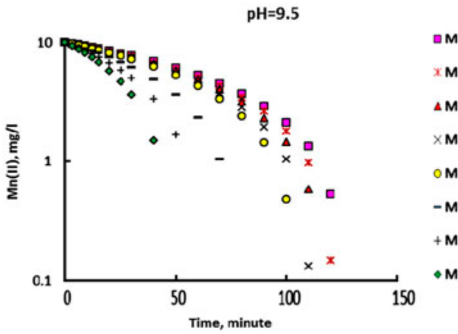

Fig. 5. Variation of Mn(II) with time for different initial Mn(IV) concentrations (Mn(II): 10 mg/l, pH: 9.5, alkalinity: 8×10^{-3} eq/l, T: 25°C, pO_2: 0.21 atm.).

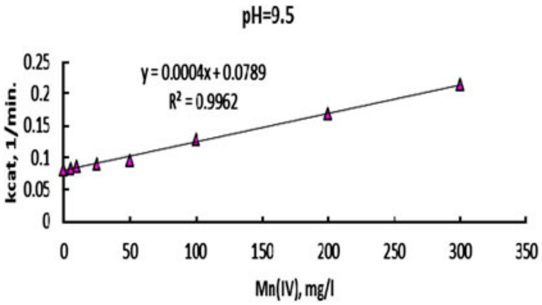

Fig. 6. The relationship between the k_{cat} and $[Mn(IV)]_0$ (pH: 9.5).

t, pH 9.0 was found to be 387 min. The corresponding t value for pH 9.5 and 10 were found as 127 and 61 min, respectively.

3.2. The effects of MnO_2 on Mn(II) oxidation

The results of the experiments with initial Mn(II) concentration of 10 mg/l and with varying initial Mn (IV) concentrations for pH:10 are given in Fig. 3.

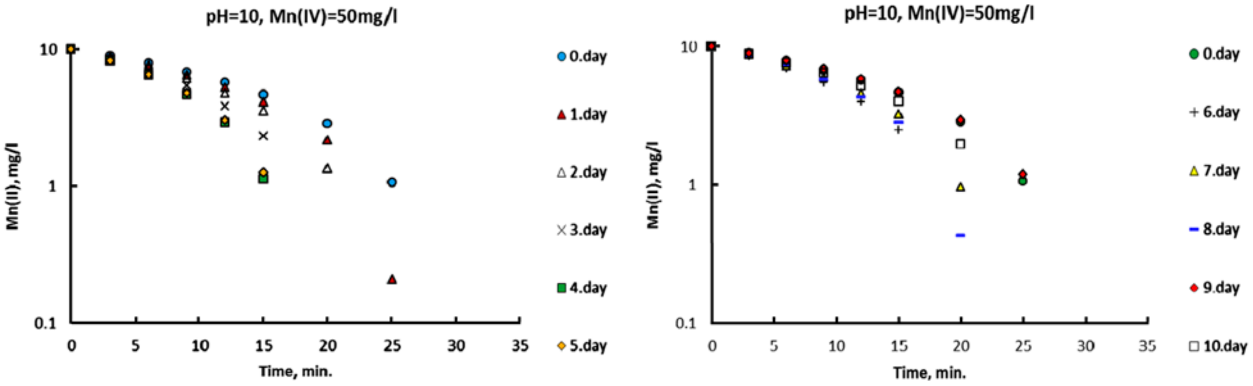

Fig. 7. Manganese concentration vs. time for different aging periods of manganese sludge (Mn(II): 10 mg/l, Mn(IV): 50 mg/l, pH: 10, alkalinity: 8×10^{-3} eq/l, T: 25°C, pO_2: 0.21 atm.).

Table 3
Variation of average k_{cat} with θ_c

First group		Second group		Third group		Fourth group		Fifth group	
θ_c day	k_{cat} average min^{-1}	θ_c day	k_{cat} average min^{-1}	θ_c day	k_{cat} average min^{-1}	θ_c day	k_{cat} average min^{-1}	θ_c day	k_{cat} average min^{-1}
0	0.3577	0	0.481	0	0.0952	0	0.128	0	0.167
1	0.3916	1	0.5611	1	0.0987	1	0.2316	1	0.2391
2	0.4325	2	0.6312	2	0.1871	2	0.2871	2	0.3564
3	0.5129	3	0.6715	3	0.2654	3	0.3012	3	0.3968
4	0.5914	4	0.6024	4	0.2742	4	0.3318	4	0.4372
5	0.5826	5	0.5845	5	0.3284	5	0.3594	5	0.3529
6	0.5013	6	0.5584	6	0.2647	6	0.3612	6	0.3281
7	0.4514	7	0.5187	7	0.2581	7	0.3417	7	0.3613
8	0.4785	8	0.5289	8	0.2361	8	0.3065	8	0.3395
9	0.3524	9	0.5632	9	0.2015	9	0.3217	9	0.3128
10	0.4015	10	0.5421	10	0.2264	10	0.3158	10	0.3418

Catalytic rate constant, k_{cat} was calculated from the slopes of the lines on semi—logarithmic plots of Mn (II) and time. It is evident from these figures that the Mn(II) oxidation is in accordance with the first order kinetics. Needed time for the completion of the reaction was about 61 min when no Mn(IV) was present in the reactor, whereas, the reaction time was reduced to about 15 min when 300 mg/l of Mn(IV) was added initially into the reactor. Thus, the reaction time is reduced with increasing initial Mn(IV) concentrations. k and k_{cat} values obtained through the experiments in homogenous and heterogeneous systems, respectively, are given in Table 2. The relationship between k_{cat} and Mn(IV) at pH 10, is shown in Fig. 4.

As it can be seen from Fig. 4, k_{cat} or catalytic oxidation rate is polynomial increasing with increasing initial Mn(IV) concentration up to 300 mg/l. This means that there is a catalytic effect of Mn(IV) on the Mn(II) of oxidation at Mn(IV) concentrations up to 300 mg/l. MnO_2 accelerates the oxidation rate of Mn (II) by adsorption, oxidation and precipitation processes.

In Fig. 5, various Mn(IV) values were investigated at pH 9.5. As the initial concentrations of Mn(IV) increased, oxidation of Mn(II) was increased.

Comparison of k_{cat} values given at pH 10 and pH 9.5 clearly indicates the significant affect of pH on the oxidation rate. The relationship between k_{cat} and Mn (IV) concentration at pH 9.5 is presented in Fig. 6. A linear increase in k_{cat} with Mn(IV) is obtained. This relationship is linear, but the same relationship at pH 10 is polynomial. This might indicate that besides the (initial) adsorption of Mn(II)–MnO_2 also precipitation of $MnCO_3$ might play a significant role at this pH. So part of the "removal" of Mn(II) is most likely obtained by adsorption, even under anaerobic conditions, and another part by precipitation and oxidation. As the effect of precipitation of $MnCO_3$, is less at pH 9.5 compared with 10, And it is also known that adsorptive capacity and pH of MnO_2 are low.

At pH value of 9.5 and 10, most of the Mn(IV) will be in the form of MnO_2 precipitate. The zero point of charge for hydrous MnO_2 is in the range of pH 2.8–4.5. In the absence of other ions, the overall surface charge is largely determined by the pH of the solution. The sorptive and ion-exchange characteristics of MnO_2 solutions, as well as the parameters controlling coagulation, must be studied some details. Total surface area of MnO_2 precipitate does not only depend on the MnO_2 concentration but it also depends on the size of the flocks, which is function of the mixing intensity or stirring speed [14].

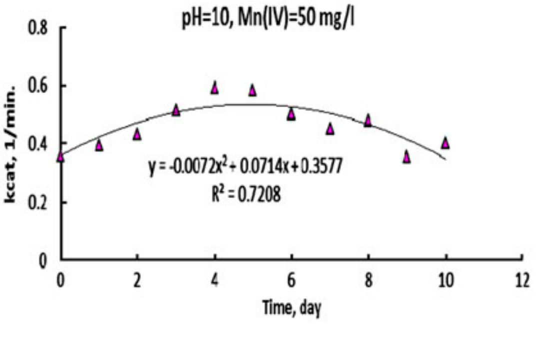

Fig. 8. The relationship between the k_{cat} and sludge age (θ_c), (Mn(IV): 50 mg/l, pH: 10).

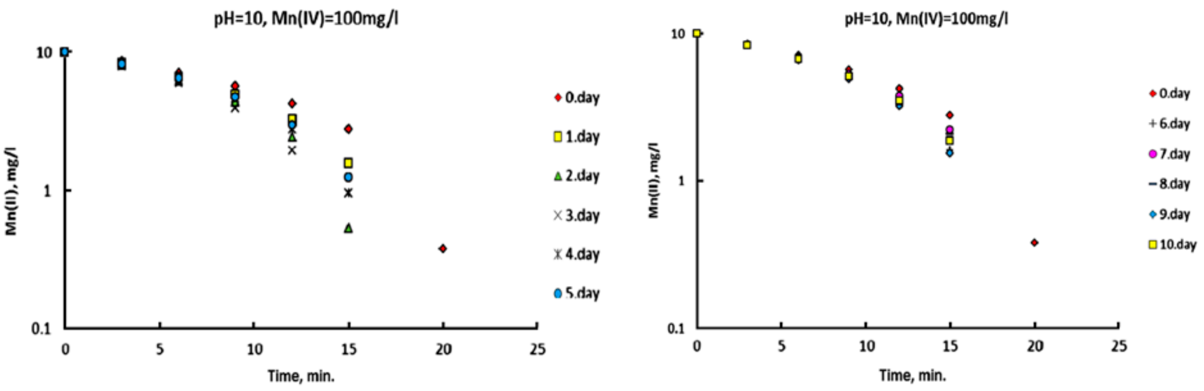

Fig. 9. Manganese concentration vs. time for different aging periods of manganese sludge (Mn(II): 10 mg/l, Mn(IV): 100 mg/l, pH: 10, alkalinity: 8×10^{-3} eq/l, T: 25ºC, pO_2: 0.21 atm.).

3.3. *The effects of sludge age on Mn(II) oxidation*

3.3.1. *First group experiments*

The linear plots of manganese concentrations vs. time for different manganese sludge aging periods (0–10 days) are illustrated in Fig. 7.

The slopes of the data denote catalytic reaction rate constant k_{cat}. The average k_{cat} values obtained for this group of experiments are given in Table 3.

The relationship between the k_{cat} and the sludge age, θ_c is shown in Fig. 8. It is evident from Fig. 8 that k_{cat} increased with increasing θ_c up to about four days. There was slight decrease in k_{cat} for sludge ages greater than four days. It is predicted that activated surface of MnO_2 decreases with sludge ageing.

3.3.2. *Second group experiments*

Initial Mn(IV) concentration was increased to 100 mg/l and sludge age was varied within the range of 0–10 days. Semi-logarithmic plots of Mn(II) vs. time are given Fig. 9.

The slopes of k_{cat} vs. sludge age are shown in Fig. 10. According to Fig. 10, k_{cat} increased with increasing θ_c up to about four days, like first group. Comparison of the k_{cat} values given in Group 1 and Group 2 of Table 3 reveals that k_{cat} values obtained for 100 mg/l of manganese concentration are greater than the k_{cat} values obtained for 50 mg/l of Mn(IV) concentration as expected.

3.3.3. *Third group experiments*

pH was reduced to 9.5 in order to reduce the reaction rate and in order to have better differentiation of the effect of sludge age. Arithmetic plots of k_{cat} vs. time are given in Fig. 11 for sludge ages from 0 to 10 days. Average k_{cat} values are given Table 3.

The comparison of k_{cat} values of each groups were shown in Table 3. According to Table 3, as pH increase, enhancement of the oxidation rate can be seen significantly. For example, when pH was 10 (Group 1) $k_{cat} = 0.3577$ but when pH was 9.5 (Group 3) k_{cat} was decreased to 0.0952, and this situation valid until $\theta_c = 5$. The relationship between k_{cat} and the sludge age is presented in Fig. 12. It is evident from Fig. 12 that k_{cat} increased with increasing θ_c up to about five days. But after five days, as polynomial-plots, a decreasing was observed for k_{cat}.

3.3.4. *Fourth group experiments*

pH was reduced to 9.5 for 100 mg/l in order to reduce the reaction rate and effect of sludge age. Arithmetic plots of k_{cat} vs. time are given in Fig. 13 for sludge ages from 0 to 10 days. Average k_{cat} values are given Table 3.

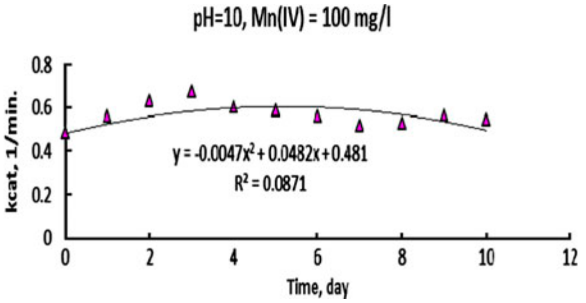

Fig. 10. Relationship between the k_{cat} and sludge age (θ_c), (Mn(IV): 100 mg/l, pH: 10).

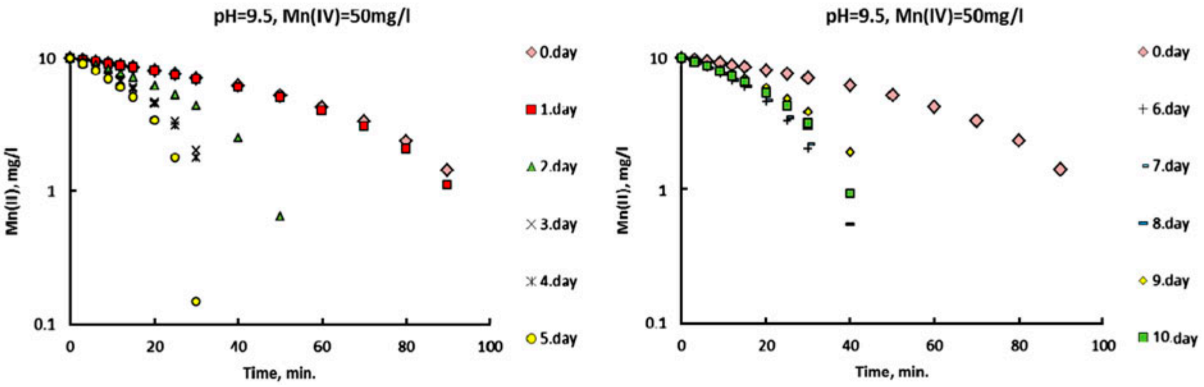

Fig. 11. Manganese concentration vs. time for different aging periods of manganese sludge (Mn(II): 10 mg/l, Mn(IV): 50 mg/l, pH: 9.5, alkalinity: 8×10^{-3} eq/l, T: 25ºC, pO_2: 0.21 atm.).

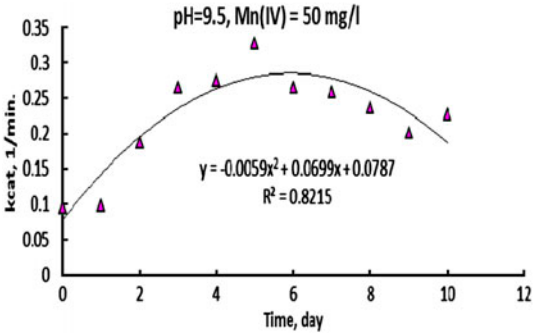

Fig. 12. The relationship between the k_{cat} and sludge age (θ_c), (Mn(IV): 50 mg/l, pH: 9.5).

Comparison of k_{cat} values given in Groups 3 and 4 of Table 3 reveals that k_{cat} values obtained 100 mg/l of manganese concentration are greater than the k_{cat} values obtained for 50 mg/l of manganese concentration. The variation of k_{cat} with sludge age is illustrated in Fig. 14.

Comparison of k_{cat} values in Groups 2 and 4 of Table 3 reveals that k_{cat} values indicates the significant affect of pH on the oxidation rate. Also, as mentioned before, it might be an additional effect of more precipitation at higher pH. k_{cat} values are at pH 10 are greater than pH 9.5.

3.3.5. Fifth group experiments

Manganese concentration was raised to 200 mg/l sludge age was varied within the range of 0–10 days at pH 9.5. Arithmetic logarithmic plots of Mn(II) vs. time are given in Fig. 15.

Initial Mn(IV) concentration was raised to 200 mg/l at pH 9.5. The variation of k_{cat} with sludge age is illustrated in Fig. 16. The results are given at Table 3. It can be concluded from the comparison of the data given Groups 3–5 of Table 3 that k_{cat} values obtained for initial manganese concentration of 200 mg/l are generally greater the k_{cat} values obtained for 50 mg/l of initial manganese concentration. But it is similar for 100 mg/l of initial manganese concentration. Collective evaluation of the results of the experiments

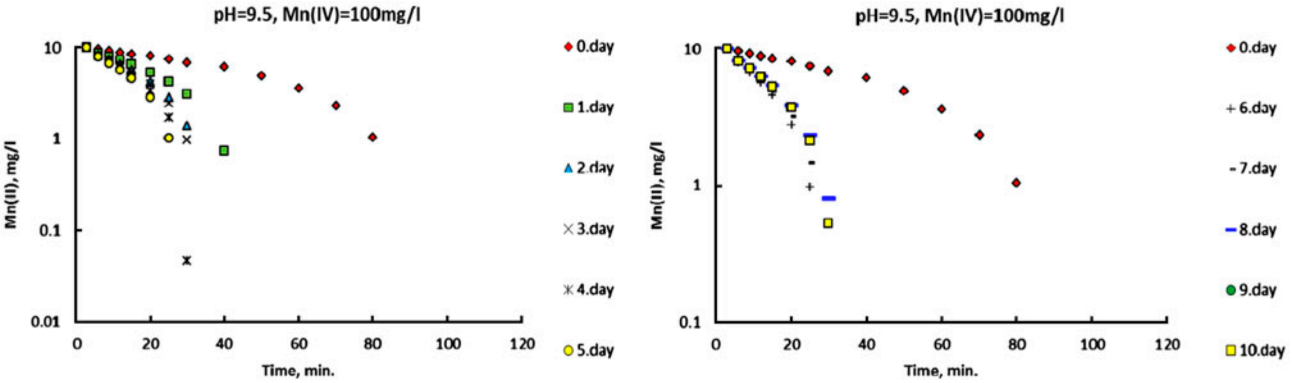

Fig. 13. Manganese concentration vs. time for different aging periods of manganese sludge (Mn(II): 10 mg/l, Mn(IV): 100 mg/l, pH: 9.5, alkalinity: 8×10^{-3} eq/l, T: 25ºC, pO_2: 0.21 atm.).

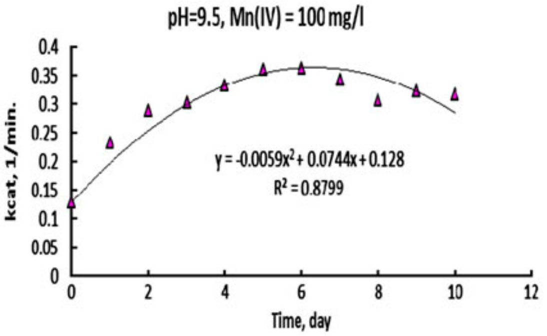

Fig. 14. The relationship between the k_{cat} and sludge age (θ_c), (Mn(IV): 100 mg/l, pH: 9.5).

indicates that k_{cat} increased with sludge age for five days. The effect of sludge age was more distinct for smaller sludge ages (up to about five days). But generally, 5–10 days there is a decreasing for k_{cat} values.

Prior to this study it was expected that catalytic effect of MnO_2 would be reduced with ageing due to the reduced active sites of MnO_2 precipitate. But the results did not verify this expectation and demonstrated that catalytic effect is increased with sludge age up to approximately fourth day. This is a very important and practically useful conclusion in application of continuous flow oxygenation system with MnO_2 recycle. Tufekci and Sarikaya have demonstrated the significant effect of ferric concentration in the aeration tank maintained by sludge recycle reduced the required aeration tank volume [9,16]. Sludge recycle may result in high sludge ages which also help to increase the oxidation rate.

To be on the safe side, continuous flow manganese oxygenation reactors with sludge recycle can be designed using the catalytic oxidation rate constants obtained from the batch systems. Authors do not have definite and clear explanations for the increased catalytic effect with sludge age. However, it was observed by O'Connor [17] that the adsorption capacity of the $Fe(OH)_3$ on Fe(II) removal is very robust, and his effect can be well expressed by high removal concentrations of Fe(II) particularly on the filters which are covered with $Fe(OH)_3$ and on contact filters. In addition, it was mentioned that it is conductive to have an aging process in the filter for the residue which will grow [17–19]. This circumstance is similar to the oxidation of manganese.

4. Conclusion

This study has demonstrated that the catalytic effect of MnO_2 sludge on the Mn(II) oxidation by aeration increases with increasing sludge age up to approximately fourth day, contrary to what is commonly expected. Catalytic oxidation rate constant k_{cat} obtained from the batch systems can safely be used in design of the continuous flow manganese oxidation reactors with MnO_2 sludge recycle.

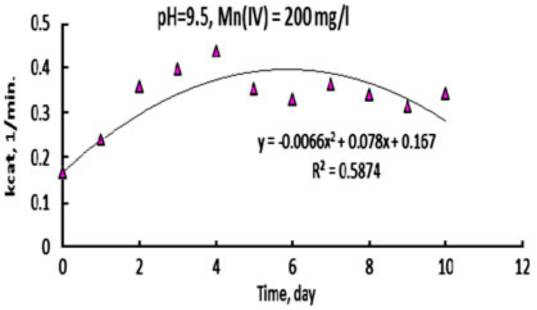

Fig. 16. The relationship between the k_{cat} and sludge age (θ_c), (Mn(IV): 200 mg/l, pH: 9.5).

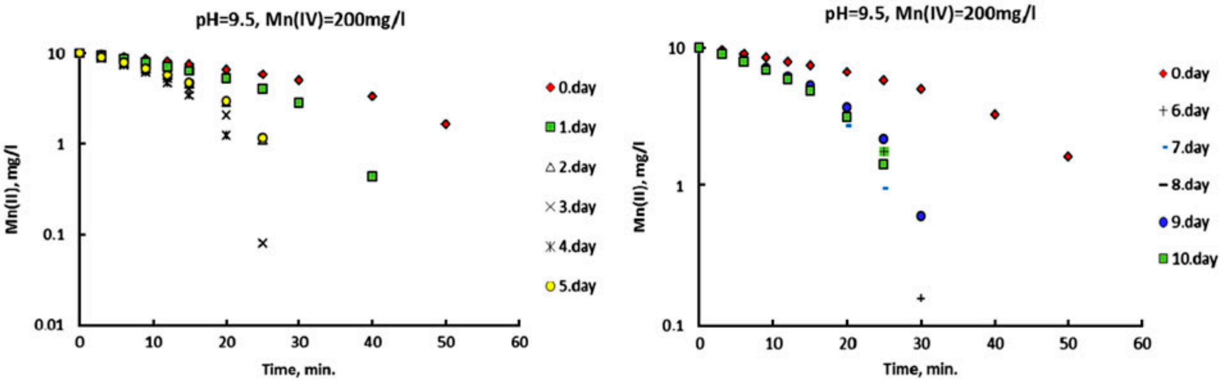

Fig. 15. Manganese concentration vs. time for different aging periods of manganese sludge (Mn(II): 10 mg/l, Mn(IV): 200 mg/l, pH: 9.5, alkalinity: 8×10^{-3} eq/l, T: 25°C, pO_2: 0.21 atm.).

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