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PHOTO-REDUCTION KINETICS OF MnO$_2$ IN AQUATIC ENVIRONMENTS CONTAINING HUMIC ACIDS

Narsito[1,*], Sri Juari Santosa[1], and Setya Lastuti[2]

[1] *Graduate Studies in Environmental Chemistry, Department of Chemistry, Gadjah Mada University, Sekip Utara, Yogyakarta, 55281, INDONESIA*

[2] *Institute for Environmental Health Engineering, Yogyakarta, INDONESIA*

ABSTRACT

The kinetics of photo-reduction of manganese(IV) oxide, MnO$_2$ in aqueous medium, in the presence of humic acid has been investigated, including the possibility for the involvement of such radicals in the reduction. Results showed that in aqueous medium, the efficiency of the photo-reduction of MnO$_2$ producing a soluble ionic Mn(II) was governed strongly by an internal electron transfer within an intermediate of HA-MnO$_2$ anion complex, resulted in the chemical adsorption of humic acid on MnO$_2$ surface. It was observed that under solar radiation and atmosphere containing oxygen, the rate of MnO$_2$ reduction increased considerably, by factors of about 46 and 2 respectively. Moreover, there was evidence that some radicals certainly played a role in the photo-reduction of MnO$_2$, since radical scavenger addition significantly decreased the reduction efficiency of MnO$_2$. In the present of an excess of propanol-2, however, which was expected to remove all OH radicals present, only about 60 % decrease in reduction efficiency were observed, suggesting that radicals other than OH radical are involved in the reduction of MnO$_2$. It was observed further that the presence of iron(III) in MnO$_2$ up to 1 % (w/w) did not alter the reduction efficiency of MnO$_2$.

INTRODUCTION

From biochemical point of view, manganese is of special important. It is usually considered as one of trace elements essentially important for plant; it plays a key role in the enzymatic synthesis of chlorophyll, required in photosynthesis, i.e. the conversion of CO$_2$ and H$_2$O to form carbohydrates [1, 2]. In addition to their well established functions in photosynthesis, the divalent forms of both magnesium and manganese are important as centers of hydrolytic and phosphate transferring enzymes [3].

In aquatic environments, manganese usually exists in 3 (three) possible oxidation states, i.e.: Mn(II), Mn(III), and Mn(IV). The concentration of manganese species is often used to determine the redox condition of aquatic environments. The [Mn(IV)]/[Mn(II)] ratio could be used as an indicator for the redox condition of the environments. Aquatic environments in a reduced state are characterized by high Mn(II) and low Mn(IV) concentrations, giving low values of [Mn(IV)]/[Mn(II)] ratios. An oxidized aquatic environment is characterized by low Mn(II) and high Mn(IV) concentrations, giving high values of [Mn(IV)]/[Mn(II)] ratios.

Naturally, most of manganese exists in the high oxidation state, Mn(IV), as MnO$_2$, which has very low water solubility [4]. This is probably the reason why in most aquatic environment, the availability of manganese is usually very low (less than 1.0 mg/L). Although, it is widely known that in such condition of well aerated, and of high acidity, containing humic materials, tends to have relatively high manganese concentration; the fundamental aspects, governing the level of manganese bioavailability in aquatic and soil environments, have not fully understood [5, 6].

EXPERIMENTAL SECTION

Materials

All chemicals used in the present work were *analytical grade*, including : (1) Mn(IV) Oxide, MnO$_2$, (2) Acids: hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid, acetic acid, oxalic acid, (3) Bases: sodium hydroxide, potassium hydroxide, barium hydroxide, (4) Salts: potassium chloride, silver nitrate, magnesium acetate, and potassium permanganate, and (5) Others: standards solutions (pH = 4,0; pH = 7,0; and pH = 10,0). In this work, humic acids used were isolated from peat soils, which were obtained from Sambutan Village, the District of Samarinda Ilir, the Province East Kalimantan, Indonesia.

Instrumentation

In the present work, an open narrow mouth beaker glass served as reactors for photo-reduction of (suspended in water medium) MnO$_2$, producing water a soluble manganese of Mn(II), which is quantitatively analyzed by an air-acetylene flame AAS, employing an Atomic Absorption Spectrometer of Shimadzu Model AA-6501.

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* Corresponding author. Tel/Fax : +62-274-545188

Procedures

An extraction technique developed by Schnitzer [7] was used in the isolation of humic acids from raw peat soils. The International Humic Substances Society, IHS, which could be summarized as follows, has recommended the technique. About 1 L of 0.1 M NaOH was added into a portion of 100 g raw peat soils. After 24 hours shaking under a nitrogen atmosphere, the alkaline supernatant, containing humic and fulvic acids, was acidified with 6 M HCl up to pH = 10, and then stored under nitrogen atmosphere for another 24 hours. Separation of the humic acids (as solid residue) from the soluble fulvic acid (in the supernatant) was done by centrifugation at a speed of 12 000 rpm for about 10 minutes. After purification steps, the humic acids separated was then freeze-dried, and a brownish black solid was obtained [8].

In this work, a series of experiments was directed to study the kinetics of MnO_2 photo-reduction, especially the reduction rates and factors influencing the reduction efficiency, including the influence of the presence of free oxygen in the reaction atmosphere, the presence of iron(III) in the reaction vessels, the presence of OH radical's scavenger on the reduction efficiency.

RESULT AND DISCUSSION

In the previous work [9], it was pointed out that during MnO_2 photo-reduction in aqueous medium, after absorption of solar energy, humic acids may play an important role as photo-sensitizer followed by the formation of some reactive intermediates. Considering the chemical structure of humic acids, it is reasonable to expect that the MnO_2 photo-reduction proceeds in a mechanism, involving three steps, as proposed in [9], i.e.:

1. The soluble humic acid (HA) was first adsorbed on the surface of MnO_2 particles suspended in the solution to form such intermediate complex of HA-MnO_2.
2. Under solar radiation exposure, the delocalized π electrons in the aromatic system of the intermediate complex HA-MnO_2, would be excited through an electronic transition of π - π*, as shown in Fig 1.
3. Since all functional groups in humic acids are negatively charged (deprotonated) in alkaline medium, the probability of the π - π* transition considerably increases in alkaline medium. In this condition, it is reasonable to expect an internal electron transfer from oxygen center to the manganese center of intermediate complex, giving possibility for reductive dissociation of Mn(IV) → Mn(II), as shown in Fig 2.

In strongly acidic medium, the formation of such stable intermediate complex of HA-MnO_2 could not be expected, since in this condition, all functional groups of the humic acids, both carboxyl, ∃-COOH, and hydroxyl, ∃-OH groups are positively charged (protonated), which are not attractive for such covalent bond formation with manganese atom in MnO_2. Consequently, no MnO_2 reduction could be observed in this condition.

The Rate of MnO_2 Photo-reduction

It is interesting that data in Table 1 show that MnO_2 reduction also occurs without any stimulation of solar radiation. In a dark condition, the intermediate complex HA-MnO_2 formed is relatively stable (unexcited), resulting in an unfavourable condition for such reductive dissociation of Mn(IV) → Mn(II). Similar results have been reported by Scott *et al.* [6] for soil samples containing MnO_2 minerals. They observed a significant amount of MnO_2 that was solubilized producing Mn(II), when the samples were stored in dark condition.
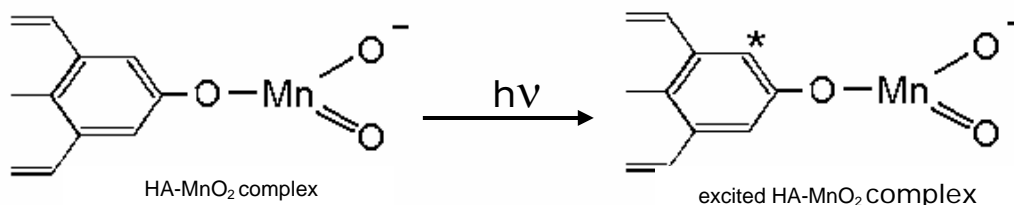

Fig 1. Excitation of the humic acids aromatic system in the intermediate HA-MnO_2 complex through π-π* transition.
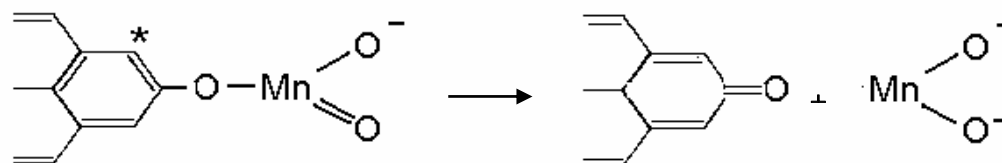

Fig 2. Reductive dissociation of exited intermediate of HA-MnO_2 complex, producing water soluble Mn(II) of MnO_2^{2-}.

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Table 1. The Influence of solar radiation on the efficiency of MnO_2 reduction in the presence of 1.0 g/L humic acids in aqueous medium (under N_2 atmosphere at pH = 10)

Radiation (hours)	No Radiation*)			Under Solar Radiation		
	mmol/L of Mn		E **)	mmol/L of Mn		E **)
	Added	Obtained	(%)	Added	Obtained	(%)
0	0.43	0.000	0.00	0.43	0.000	0.00
1	0.43	0.003	0.70	0.44	0.015	3.46
2	0.42	0.004	0.95	0.41	0.038	9.27
3	0.43	0.004	0.93	0.41	0.052	12.89
4	0.44	0.007	1.59	0.43	0.120	27.26
5	0.44	0.007	1.59	0.41	0.130	31.36
6	0.43	0.007	1.63	0.45	0.210	46.93
7	0.43	0.008	1.86	0.45	0.220	49.33
8	0.43	0.010	2.33	0.42	0.260	62.18
k_1 (h^{-1})	$(4.22 \pm 0.44) \times 10^{-5}$			$(1.93 \pm 0.19) \times 10^{-3}$		
R	0.9644			0.9763		

*) : Stored in dark   *** : E = the reduction efficiency

Table 2. MnO_2 photo-reduction in aqueous medium in the presence of 1.0 g/L HA at pH = 10 under two different atmospheres (nitrogen and air)

Time (hours)	Under N_2 atmosphere			Under O_2 atmosphere		
	mmol/L Mn		Efficiency	mmol/L Mn		Efficiency
	added	obtained		added	obtained	
0	0.43	0.000	0.00	0.43	0.000	0.00
1	0.43	0.054	12.73	0.43	0.134	31.37
2	0.43	0.082	19.33	0.43	0.189	44.21
3	0.43	0.129	30.33	0.45	0.282	63.07
4	0.43	0.161	37.73	0.43	0.286	67.05
5	0.41	0.164	40.06	0.41	0.29	71.56
6	0.43	0.194	45.47	0.43	0.324	75.86
k_1 (h^{-1})	$(1.68 \pm 0.10) \times 10^{-3}$			$(3.52 \pm 0.37) \times 10^{-3}$		
R	0.9917			0.9790		

Assuming the dissociation of the $HA-MnO_2$ intermediate complex is the rate determining step of the MnO_2 reduction, simple estimation on the overeall rate constants for the reduction could be made. A regression analysis made on data in Table 1, assuming the MnO_2 overall reduction was kinetically first order reaction, shows that MnO_2 reduction under solar radiation, with a rate constant, $k_1 = (1.93 \pm 0.19) \times 10^{-3}$ h^{-1}, proceeds in about 46 times faster that in dark, with a rate constant, $k_1 = (4.22 \pm 0.44) \times 10^{-5}$ h^{-1}.

Since functional groups of fulvic acids and of humic acids are the same, the proposed mechanism for MnO_2 reduction could also be used to explain metal reduction by fulvic acid reported earlier [6,10]. For a mixture containing chromium(VI) and fulvic acids stored in dark condition (without radiation), Wittbrodt and Palmer [10] observed that chromium(VI) was reduced to chromium(III).

The Influence of Free O_2 on MnO_2 Photoreduction

Essentially, free molecular oxygen (O_2) is an oxidizing agent. Before the experiment, it was expected that the efficiency of MnO_2 reduction would decrease substantially, when considerable amount of free oxygen was added. Surprisingly, data in Table 2 show that free oxygen addition, (replacing N_2 with air) into the reaction atmosphere, increases (about doubled) the reduction efficiency significantly, indicating that oksigen plays a role in MnO_2 photo-reduction.

This phenomenon is probably related to the fact that in alkaline medium, humic acids relatively strongly absorbs ultraviolet radiation [9], which is equivalent to a radiant energy of about 600 kJ/mol. Since under solar radiation, this amount of energy should be used in the π - π^* electronik transition of humic acids, it is not too difficult to understand that in the excited state, humic acids would be in an energy level of about 600 kJ/mol, giving possibility for the humic acids to act as photo-sensitizer in the MnO_2 photo-reduction.

It should be noted that in the ground state ($^3\Sigma_g$), molecular oxygen is a reactive species, as a consequence of its paramagnetic property. Since molecular oxsygen has 2 (two) excited states [3], i.e. the first excited state, ($^1\Delta_g$), and second excited state, ($^1\Sigma^*_g$), having energies of 92 kJ/mol and 155 kJ/mol

respectively, the energy content in the excited humic acids (600 kJ/mol) should be more than enough to make molecular oxygen excited. Such interaction between the excited molelecular oxygen and the manganese center of the excited intermediate complex $HA-MnO_2^*$ should be highly favourable, utilizing empty manganese d orbitals, forming an highly reactive short lived transition state.

Moreover, the interaction would increase the density of the π electron of the Mn–O double bond in the intermediate complex $HA-MnO_2$, promoting charge separation and therefore increase the polarizability of the Mn–O bond. The increase of the Mn–O bond polarizability would result in a better condition for such electron transfer from oxygen to manganese center of the intermediate complex $HA-MnO_2$ [3]. This is probably the reason why in atmosphere containing free oxygen (air), Mn(IV) $\rightarrow$ Mn(II) conversion proceeds significantly faster than in nitrogen atmosphere, as shown in Table 2 by rate constants of $k_1 = (3.52 \pm 0.37) \times 10^{-3}$ h^{-1} and of $k_1 = (1.68 \pm 0.10) \times 10^{-3}$ h^{-1} respectively.

The Role of Free Radicals on MnO_2 Photo-reduction

It seems justified to conclude that under solar radiation, in alkaline medium (pH = 10) used in the present experiment, humic acids were in its excited state, having energy of about 600 kJ/mol. In this condition, the formation of such radicals, like hydroxyl, OH, and peroxide, HOOH, radicals seem possible [11]. In aqueous medium, the radicals is relatively stable, as shown by the electrolytic dissociation constants of $k = 1 \times 10^{-10}$ for hydroxyl radicals and of $k_1 = 2.5 \times 10^{-12}$ for peroxide radicals [3].

Since molecular oxygen, in both the ground state and the excited state, is principally a radical, similar effects of hydroxyl and peroxide radicals in MnO_2 photo-reduction in the presence of humic acids could be expected. Under the absence of molecular oxygen (in nitrogen atmosphere), it is reasonable to expect that hydroxyl radical plays a role in MnO_2 photo-reduction, provided humic acids are present. An experimental results presented in Fig 3 confirmed this expectation, the addition of propanol-2, a specific radical scavenger for OH radicals [12, 13], into the reactor considerably decreases the efficiency of the MnO_2 photo-reduction. Data in Figure 3 clearly show that OH radical certainly plays an important role in the MnO_2 photo-reduction.

In Fig 3, it is also observed, however, that an excess addition of propanol-2 into the reactor, which was expected to remove all OH radical present in the solution, was not effective enough to prevent completely the MnO_2 photo-reduction. It suggests that OH radical is not the main cause of the MnO_2 photo-reduction.

This phenomenon confirmed further the hypothesis proposed that the formation of a reactive intermediate complex, $HA-MnO_2$ is a reaction step has to be follow in MnO_2 photo-reduction, and the presence of radicals, like OH and HOOH radicals, as well as molecular oxygen, is just promotes the electron transfer from the oxygen to manganese centers in the intermediate complex, $HA-MnO_2$ producing soluble Mn(II).

The Effects of Iron(III) on MnO_2 Photo-reduction

In the trivalent state, it is known that iron plays an important role in the degradation of humic substances, i.e. : humin, humic acids, and fulvic acids. In 1996, Stumm and Morgan [14] observed that in the presence of iron(III), as both Fe_2O_3 or as $Fe(OH)_3$, humic acids and fulvic were decomposed into smaller organic molecules with lower molecular weight. Since during the degradation, iron(III) was reduced into besi(II), they concluded that the humic acids and fulvic acids degradation are oxidation. For this reason, it is reasonable to expect that in the present of iron(III), the efficiency of MnO_2 photo-reduction would substatially altered.

In the present work, it was not experimentally confirmed, however. The efficiency of MnO_2 photo-reduction was hardly altered, even when the photo-reduction was performed in the presence of up to 1 %(w/w) of iron(III) added into the MnO_2. The expected degradation product of humic acids probably plays similarly with humic acids, to serve as photo-sensitizer, producing similar intermediate complex $HA-MnO_2$, required for MnO_2 photo-reduction.

Since in this experiment, all MnO_2 photo-reduction were performrd at alkaline medium (pH = 10), iron(III), which was expected to oxidize humic acids as suggested by Stumm and Morgan [14], was not available in an enough concentration. The amount of iron available in solution is limited by the solubility of iron(III) hydroxide, $Fe(OH)_3$, which is relatively very low, (K_{sp} $Fe(OH)_3 = 4 \times 10^{-38}$). Under the experimental condition applied in this experiment (pH = 10), iron(III) concentration available in solution was only about 4×10^{-23} mmol/L, which is much too low as compared with the MnO_2 used (0.43 mmol/L).
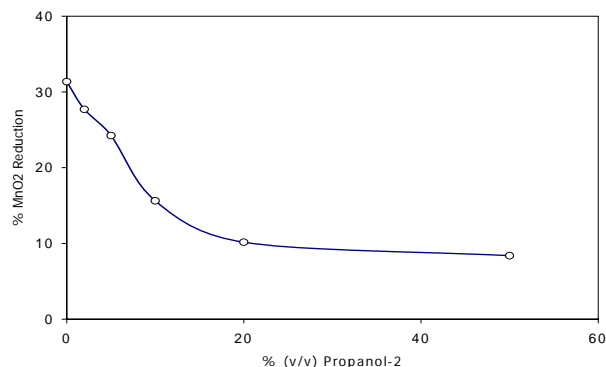

Fig 3. Effect of propanol-2 (OH radical's scavenger) in MnO_2 photore-duction in 1 %(w/v) HA at pH = 10, under N_2 and solar radiation for 5 hours.

CONCLUSION

All data obained in the present investigation are consistent with an assumption that during the MnO_2 reduction, the soluble humic acids was first adsorbed on the surface of MnO_2 particles suspended in the solution, forming an intermediate complex of HA-MnO_2. The intermediate complex, HA-MnO_2, is subject to π - π^* electronic transition, giving possibility for an internal electron transfer from the oxygen center of the humic acids part to the manganese center of the MnO_2 in the intermediate complex, HA-MnO_2, to produce water soluble Mn(II).

Under ultraviolet (solar) radiation, the MnO_2 reduction increases considerably, due to the more favourable condition for π - π^* electronic transition within the interme-diate HA-MnO_2 complex, resulting in a higher possibility for an internal electron transfer from the oxygen to the manganese centers of the intermediate HA-MnO_2 complex. Under solar radiation, the rate of the MnO_2 reduction considerably increases, as shown by an increase in the rate constants from a value of $k_1 = (4.22 \pm 0.44) \times 10^{-5}$ h^{-1} for experiment in dark condition to a value of $k_1 = (1.93 \pm 0.19) \times 10^{-3}$ h^{-1} for experiment under an exposure of solar radiation.

The present work confirms that some radicals play important roles in the MnO_2 photo-reduction, providing humic acids are present. The presence of molecular oxygen (substantially radicals) increases the reduction rate from a rate constant of $k_1 = (1.68 \pm 0.10) \times 10^{-3}$ h^{-1} in N_2 atmosphere to a rate constant of $k_1 = (3.52 \pm 0.37) \times 10^{-3}$ h^{-1} in air atmosphere.

It was also observed that an excess addition of propanol-2 into the reactor, which was expected to remove the OH radical present in the solution, was not effective enough to prevent completely the MnO_2 photo-reduction. It suggests that OH radical is not the main cause of the MnO_2 photo-reduction.

Humic acid degradation into smaller size organic molecules, caused by the presence of iron(III) reported by Stumm and Morgan [14], was not confirmed in the present work. No alteration in the reduction efficiency of MnO_2, was observed, even when the MnO_2 photo-reduction was performed in the presence of up to 1 % (w/w) of iron(III) added into the MnO_2. The expected degradation product of humic acids probably plays similarly with humic acids, to serve as photo-sensitizer, producing similar intermediate complex HA-MnO_2, required for MnO_2 photo-reduction.

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