THE KINETICS ON MnO_2 PHOTOREDUCTION IN THE PRESENCE OF HUMIC ACIDS

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The kinetics of MnO_2 photoreduction, in the presence of humic acids, has been investigated. The humic acids was isolated from peat soils of Samarinda, East Kalimantan. In this work, the role of humic acid as photosensitizer in the photoreduction of MnO_2 producing a water-soluble form of manganese, Mn^{2+}, was evaluated. Moreover, the kinetics of the reduction was studied, focusing on the identification of the intermediate formed during the reduction, and the possibility for the involvement of such radicals in the photoinductive reduction of MnO_2.

The work was started with isolation and characterization of humic acid used, especially for the qualitative and quantitative composition of the functional groups presence and the absorption pattern of humic acid toward electromagnetic radiation. The work was then followed by a series of experiments related to factors, influencing the conversion efficiency of MnO_2 to Mn^{2+}, such as acidity of the medium and the effectiveness of the humic acid used. Finally, the reduction rate was determined, and the role of conditions influencing the reduction, such as the influence of the use of air (instead of nitrogen), as atmosphere containing oxygen, effect of propanol-2 addition, as a radical scavenger, and iron (III) addition, as an oxidizing agent for humic acid, were evaluated.

Results showed that in aqueous medium, humic acids play important role in photoreduction of MnO_2. In media with low acidity, the efficiency of MnO_2 photoreduction increases significantly as the pH increases, It was observed, however, the application of such medium of high pH could not be realized in practice, to increase the enviromental availability of manganese, since at pH > 10, the Mn^{2+} produced by the photo reduction

would be precipitated as $Mn(OH)_2$. Moreover, the results showed that in aqueous medium, the MnO_2 photoreduction producing a soluble form of Mn^{2+} was governed strongly by an internal electron transfer within an intermediate of $HA-MnO_2^-$ complex anion, formed by chemical adsorption of the humic acid on the MnO_2 surfaces. It was observed that under solar radiation, the rate of MnO_2 reduction increased considerably.

It was several evidence that some radicals certainly plays a role in MnO_2 the photoreduction, since radical scavenger addition significantly decreases the reduction efficiency of MnO_2. In the presence of an exsess of propanol-2, however, which was expected to remove all OH radicals present, may decrease only about 60 % of the reduction efficiency, suggesting that radicals other than OH radical are probably involved in the reduction. It was observed further that the presence of iron (III) in MnO_2 up to 1 % (w/w) does not alter the reduction efficiency significantly.

Key words: Kinetics, photoinductive reduction, manganese (IV) oxide, MnO_2, humic acids