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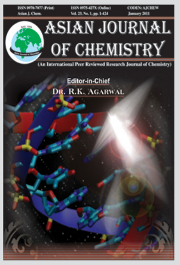

Catalytic Decomposition of Hydrogen Peroxide Using Heat Treated Sea Nodule Residue

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The kinetics of the decomposition of aqueous hydrogen peroxide by heat-treated sea nodule residue has been studied with varying catalyst loading, concentration of hydrogen peroxide and initial pH of the solution. The rate of decomposition increases with increasing amount of catalyst and the reaction followed first order kinetics with respect to [H_2O_2].

Key Words: Hydrogen peroxide, Sea nodule residue, Washed sea nodule residue.

INTRODUCTION

Although manganese nodules or manganese oxides have been extensively used for studying their adsorptive properties and catalytic activities for adsorptive removal of various cationic, anionic pollutants and degradation of organic substrates[1-8], the use of leached residue is scanty[9,10]. The selective extraction of strategic metals like Cu, Co and Ni along with Mn and Fe leaves behind more than 70 % residue as wastes for disposal. Due to increasingly stringent disposal rules it has become imperative to develop methods for proper utilization of such a huge quantity of leached residues. These leached residues containing oxides/oxyhydroxides of Fe, Mn, Al and Si showed reasonable high porosity and surface area. The adsorption properties of variety of species, cationic and anionic, have been carried out recently[9-12]. Moreover, Fe and Mn in these residues are present in variable oxidation states. In view of above characteristics, one can envisage the use of leached residues as an effective oxidation catalyst for a variety of organic contaminants.

Since hydrogen peroxide is very often used as oxidant along with small amount of catalysts for oxidation of variety of organic substrates, it is essential to undertake a study of decomposition ability of leached residue and heat-treated leached residue for decomposition of hydrogen peroxide alone.

EXPERIMENTAL

Leached residue sample (SNR), generated after reduction roast-ammoniacal leaching process were collected from Pilot plant operated at Hindustan Zinc Limited, Udaipur, India. The parent Indian Ocean manganese nodule (SN), which generates the residue after leaching process, was also collected for comparison of activity. The samples were air dried for several days, mixed thoroughly and kept in airtight bottles for characterization and further use. In order to remove loosely associated metal ions/anions, the leached residue was washed with distilled water. In a typical lot 50 g of the leached residue was dispersed in 500 mL distilled water (solid:liquid ratio = 1:10) and stirred for 2 h at room temperature. The content was filtered, washed with distilled water for further removal of sulphate and then air dried to get the washed sea nodule residue (WSNR). The air-dried samples are further heated at 300 and 400 ºC for 5 h using a tubular furnace fitted with programmable temperature controller. These heat-treated samples are designated as WSNR-300 and WSNR-400, respectively and studied for their characterization and catalytic decomposition of hydrogen peroxide.

The hydrogen peroxide solution was prepared by proper dilution and standardized by standard $KMnO_4$ solution.

Characterization of samples: Particle size of sea nodule residue and washed sea nodule residue was determined using Malvern SA-CP3 particle size analyzer. The XRD patterns of samples were recorded on a Sidemen's D 500 X-ray diffractometer using CuK$_\alpha$ ($\lambda = 1.5418$) radiations. FT-IR spectra of different samples in KBr pellets were recorded using a Thermo-Nicolet 870 FT-IR in absorption mode averaging 32 scans and at a resolution of 4 cm^{-1}. Surface areas of the samples were determined by N_2/BET method using a Quantasorb (Quantachrome, Novawin). All pH measurements were carried out by a Toshniwal CL 54 pH meter using a combined glass electrode.

Catalytic decomposition of hydrogen peroxide: The catalytic decomposition of aqueous H_2O_2 (AR) was studied by conventional gasometrical method. The volume of the oxygen liberated at different time (V_1) was determined in a glass burette at atmospheric pressure and room temperature.

RESULTS AND DISCUSSION

Characterisation of leached residue: Particle size analyses showed the leached residue contained very fine particles with mean particle diameter of 17.8 μm. The BET surface areas of sea nodule, sea nodule residue and washed sea nodule residue were found to be 130, 60.9 and 66.7 $m^2 g^{-1}$, respectively. Decrease of surface area of sea nodule residue is presumably due to loss of porosity of sea nodule and formation of manganese carbonate and silicate on roasting of sea nodule with coal. Marginally higher surface area of washed sea nodule residue is presumably due to increased number of accessible pores on washing of adsorbed species from sea nodule residue. The average pore diameter, however practically remains same (*ca.* 40 Å) in all three samples.

The XRD of air-dried sea nodule, sea nodule residue and washed sea nodule residue are given in Fig. 1. It is noted that sea nodule is mostly amorphous in nature with a few low intensity peaks corresponding mainly to quartz todorokite. After reduction roasting followed by leaching, the XRD peaks due to todorokite disappear because of its consumption in the formation of metal, especially Mn silicates. In addition formation of $MnCO_3$ is also evident from the appearance of its characteristic peaks in sea nodule residue. On washing with distilled water, no change in the characteristic peak positions is observed from that of sea nodule residue. On calcinations the intensity of characteristic peaks of $MnCO_3$ decreases due to its decomposition and almost disappear at around 500 ºC.

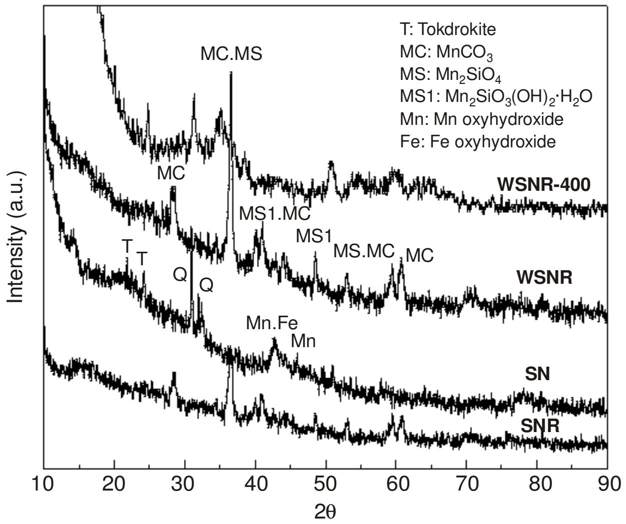

Fig. 1. Powder X-ray diffraction of sea nodule (SN), Sea nodule residue (SNR), washed sea nodule residue (WSNR) and WSNR heated at 400 ºC

FT-IR spectra of air-dried sea nodule, sea nodule residue and washed sea nodule residue (untreated and that of heat treated) are presented in Fig. 2. The broad absorption band at *ca.* 3445 cm^{-1} and moderately intense band at *ca.* 1650 cm^{-1} in all samples are attributed to O-H stretching and bending modes of vibrations[12]. On washing the sea nodule residue with distilled water, the position of majority bands retained same except disappearance of absorption band at 1072 cm^{-1} presumably due to loss of small amount loosely bound NH_3 or sulphate on washing[10]. The sulphate is most likely generated from the impurities of coal during reduction roasting with sea nodules. The calcinations of washed sea nodule residue at 300 ºC in air for 3 h leads to decrease of characteristic absorption bands for carbonate which practically disappear on calcinations at 400 ºC.

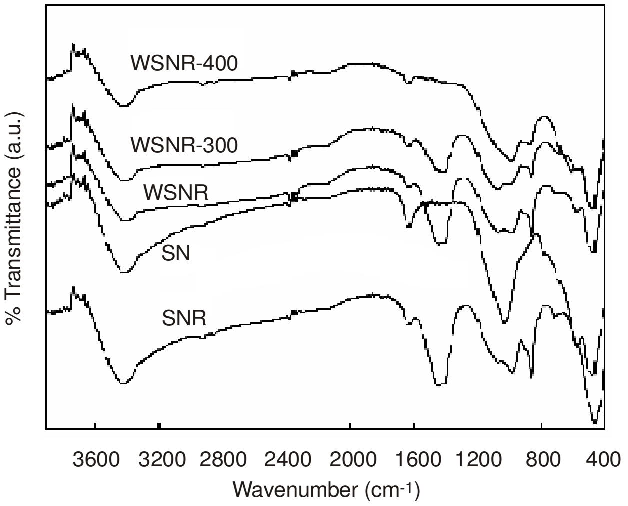

Fig. 2. FT-IR spectra of sea nodule (SN), Sea nodule residue (SNR), washed sea nodule residue (WSNR) and WSNR heated at 300 and 400 ºC

Decomposition of hydrogen peroxide: In order to evaluate the catalytic efficiency of leached residue (WSNR-400), the decomposition of hydrogen peroxide was studied at room temperature at constant stirring but varying concentration of hydrogen peroxide ($0.05 \leq [H_2O_2]$ mol $dm^{-3} \leq 0.10$) and amount of leached residue (20-50 mg).

Effect of catalyst amount for decomposition of H_2O_2: The plots of log ($V_\infty - V_t$) *versus* time (Fig. 3) at constant concentration of hydrogen peroxide (0.05 mol dm^{-3}) are linear with varying amount of catalyst in the range (20 - 50 mg) indicating first order kinetics for the decomposition reaction. The rate constant are, however, relatively lower than those obtained with manganese nodule presumably due to decrease of Mn(IV) content in the leached residue during reduction-roasting process[8]. Further, it is evident that the rate constant (k) increases with increasing catalyst amount (Table-1) due to

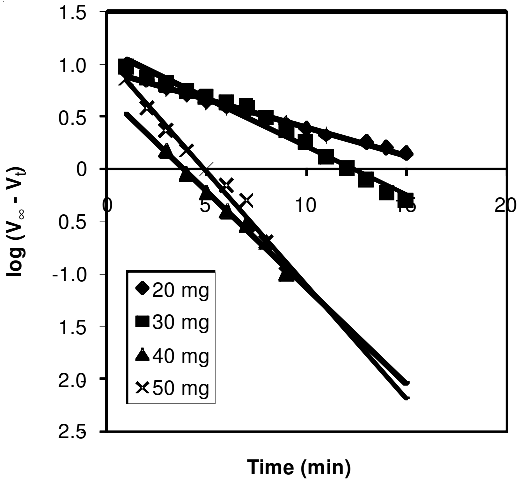

Fig. 3. Plots of ln ($V_\infty - V_t$) *versus* time for decomposition of H_2O_2 at varying catalyst dose

TABLE-1
EFFECT OF CATALYST DOSE ON RATE OF HYDROGEN PEROXIDE DECOMPOSITION, $[H_2O_2] = 0.05$ mol dm^{-3}

Catalyst dose (mg)	Rate constant k (s^{-1})
20	0.00197
30	0.00363
40	0.00703
50	0.00828

increasing amount of catalytically active sites at higher dose of catalyst (Fig. 4). The linear plot of decomposition rate *versus* amount of catalyst with relatively less intercept indicates that the auto-decomposition of H_2O_2 is negligible under the experimental conditions.

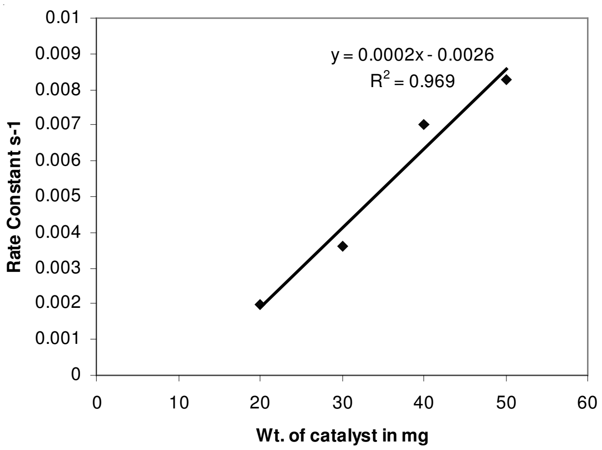

Fig. 4. Effect of catalyst amount for decomposition of H_2O_2

Effect of concentration of H_2O_2: The plots of log (V_∞ - V_t) *versus* time with varying concentration of hydrogen peroxide (0.05 - 0.10 mol dm^{-3}) are also linear. The rate constant increases with increase of hydrogen peroxide concentration.

The log-log plots drawn between rate constant and concentration of hydrogen peroxide (Fig. 5) is found to be linear with slope 1.03 indicating the rate of decomposition is first order dependence with concentration of the hydrogen peroxide.

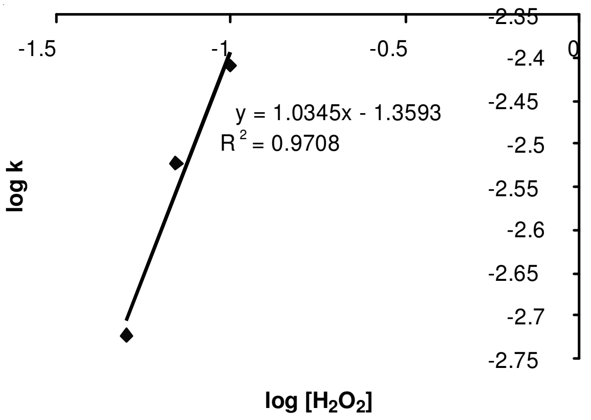

Fig. 5. Plot of log $[H_2O_2]$ *versus* log k

Effect of initial pH on decomposition of H_2O_2: Rate of decomposition of hydrogen peroxide also depends upon initial pH of the solution. Rate of the reaction increases with increasing pH of the solution (Fig. 6).

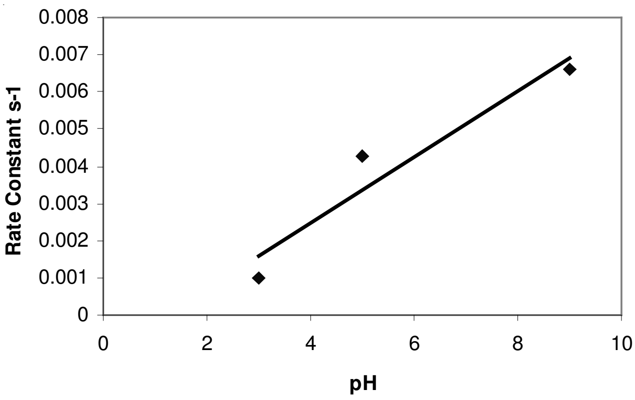

Fig. 6. Plot of rate constant *versus* pH of the solution

Conclusion

The leached residue is heated at 400 ºC (WSNR-400) is active for decomposition of hydrogen peroxide which indicated its possible utilization as oxidation catalyst for decomposition of organic substrates. The rate of decomposition is increased with increase of catalyst dose, increase of H_2O_2 concentration and increase of initial pH.

REFERENCES

1. K.M. Parida, S. Mallick and S.S. Dash, *J. Colloid Interf. Sci.*, **290**, 22 (2005).
2. K.M. Parida, P.K. Satapathy and N.N. Das, *J. Colloid Interf. Sci.*, **181**, 456 (1996).
3. S. Bhattacharjee, S. Chakrabarty, S. Maity, S. Kar, P. Thakur, G. Bhattacharyya, *Water Res.*, **37**, 3954 (2003).
4. R. Liu and H. Tang, *Water Res.*, **34**, 4029 (2000).
5. M.X. Zhu, Z. Wang and L.Y. Zhou, *J. Hazard. Mater.*, **150**, 37 (2008).
6. A.H. Gemeay, R.G. El-Sharkawy, I.A. Mansour and A.B. Zaki, *Appl. Catal. Environ.*, **80**, 106 (2008).
7. W. Zhang, Z. Yang, X. Wang, Y. Zhang, X. Wen and S. Yang, *Catal. Commun.*, **7**, 408 (2006).
8. K.M. Parida, N.N. Das and P.K. Satapathy, *J. Colloid Interf. Sci.*, **173**, 112 (1995).
9. A. Agrawal, K.K. Sahu and B.D. Pandey, *Colloids Surf. A*, **237**, 133 (2004).
10. N.N. Das and R.K. Jana, *J. Colloid Interf. Sci.*, **293**, 253 (2006).
11. C.P. Huang and F.G. Ostavic, *J. Environ. Eng. Div.*, **104**, 863 (1978).
12. K. Nakamato, Infrared Spectra of Inorganic and Coordination Compounds, Part B, John Wiley & Sons, New York, edn. 5 (1997).