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CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE ON MANGANESE DIOXIDE NANOPARTICLES AT DIFFERENT PH VALUES

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ABSTRACT

Catalytic decomposition of hydrogen peroxide on manganese dioxide nanoparticles was studying under different experimental conditions such as pH (1, 6.5 and14) and at 15°C Temp. The kinetics of the reaction was analyzed by first order equation and rate constants were determined from the slopes of the straight lines. It was observed from the experimental results that the decomposition rate constant was found to be dependent on pH. MnO_2 nanoparticles used as a catalyst for decomposition H_2O_2 were synthesized by chemical co-precipitation method. The as-prepared MnO_2 nanoparticles were systematically characterized by X-Ray diffraction (XRD), FTIR and SEM - EDX analysis techniques. The average particle size of manganese dioxide nanoparticles was calculated from the XRD study. The average particle size of MnO_2 nanoparticles was 14 nm. The resulting MnO_2 nanoparticles were found to exhibit remarkable environmental catalytic performance in the catalytic decomposition of hydrogen peroxide in aqueous solution.

KEYWORDS: Chemical Co-Precipitation, MnO_2 Nanoparticles, H_2O_2, Catalytic Decomposition

INTRODUCTION

In recent years nanoscale materials have proved to have unique properties than its bulk due to large surface to volume ratio. Among many transition metal oxide, MnO_2 nanoparticles as the one of the most attractive oxide due to its unique properties manganese dioxide nanoparticle is a low band gap, high optical constant semiconductor that exhibits ferroelectric and catalytic properties, it has wide applications, particularly as reversible-cathode for lithium batteries [1], a catalyst for purification of air[2], in removal of CO from hydrogen rich fuel cell[3].

MnO_2 nanoparticles were prepared by chemical co-precipitation method because having several advantages like, simple and rapid preparative method, easy control of particle size and composition can be made in this method and also there are various possibilities to modify the particle surface state and overall homogeneity. Co-precipitation of various salts (nitrates, sulfates, chlorides, perchlorates etc.) under a fine control PH by using NaOH solution yields corresponding spinal oxide nanoparticles.

In the present study, MnO_2 nanoparticles were synthesized by chemical co-precipitation method. As an important functional metal oxide, manganese oxide nanoparticles are one of the most attractive inorganic materials because of its physical and chemical properties and wide application in catalysis[4], ion exchange[5], molecular adsorption[6], biosensor, and particularly, energy storage[7]. A catalyst provides an alternative reaction pathway to the reaction product, the rate of the reaction is increased as this alternative route has lower activation energy than the reaction route in the absence if the catalyst. The decomposition of H_2O_2 is used by different scientists and research workers as a well-like indicator reaction [8] as the conversion of H_2O_2 to water and oxygen is strongly affected by the catalyst[9]. An effort has been made in the

present research to investigate the catalytic decomposition of hydrogen peroxide on MnO_2 nanoparticles at different conditions.

EXPERIMENTAL

Synthesis of Manganese Dioxide Nanoparticles

The Co-precipitation method was performed by using manganese salt for synthesis of MnO_2 nanoparticles, which was prepared by dissolving 4.925 mg of manganese dichloride tetrahydrate in 250ml of distilled water. The pH of the reaction volume was brought to 12 with hydroxide sodium and the reaction was stirred 300 rpm for 18 hours, settling down for one day and separation of supernatant, then washed with distilled water for several times to remove any soluble products. After that the precipitate was dried at 100°C in the air for 7 hours, which was obtained MnO_2 nanoparticles.

Decomposition of Hydrogen Peroxide

Manganese dioxide nanoparticles used as a catalyst which are lead to the decomposition of peroxide under acidic and alkaline conditions. Manganese dioxide nanoparticles are one of the more stable species among the different oxidation states of manganese.

The decomposition of hydrogen peroxide was studied in the presence of MnO_2 nanoparticles at different pH values and 15°C temperature. As H_2O_2 is sensitive to light, therefore, all the experiments were performed in the absence of light by wrapping the black paper around the beaker to minimize the error. The amount of solid catalyst used in each experiment was 0.03 g/100ml. The 0.3M H_2O_2 was used in all cases. The pH of the mixture was set to the desired value by using dilute solutions of HCl or NaOH. The content of the beaker was stirred uniformly by means of a magnetic stirrer using magnetic bar. After an interval of 5 min about 5ml of the reaction mixture was withdrawn from the beaker and was rapidly added to 5ml 9M H_2SO_4 solutions. The solid was separated from a mixture by filtrations, and the filtrate was then titrated against 0.025 M of $KMnO_4$ solution. From this, the amount of the decomposed H_2O_2 was estimated. In all cases, blank experiments were also performed in the absence of the solid in order to investigate the effect, if any of the experimental conditions on the decomposition of H_2O_2. The schematic of the experimental setup is shown in Figure (1).

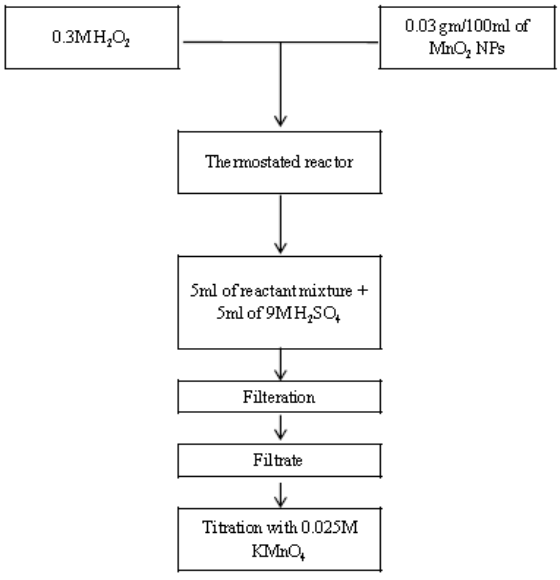

Figure 1: Schematics of Experimental Setups

RESULTS AND DISCUSSIONS

FT-IR Analysis of Manganese Dioxide Nanoparticles

Figure (2) shows FT-IR spectrum of prepared MnO_2 nanoparticles at room temperature. The spectrum was recorded in the range of 4000-800 cm^{-1}. The FT-IR spectrum shows characteristic peaks. The two significant absorption peaks observed at 611.96 and 487.75 cm^{-1} are corresponded to characteristic stretching bonds O-Mn-O, which demonstrated the presence of the MnO_2 nanoparticles in the sample.

The broad absorption peak observed at 3414.83 cm^{-1} reveals the stretching band of H-O-H caused by absorbing water molecules, while the absorption peak at 1616.74 cm^{-1} symbolized the bending band of adsorbed water and absorption peak at 1384.45 cm^{-1} is associated with the hydration water of MnO_2 nanoparticles.

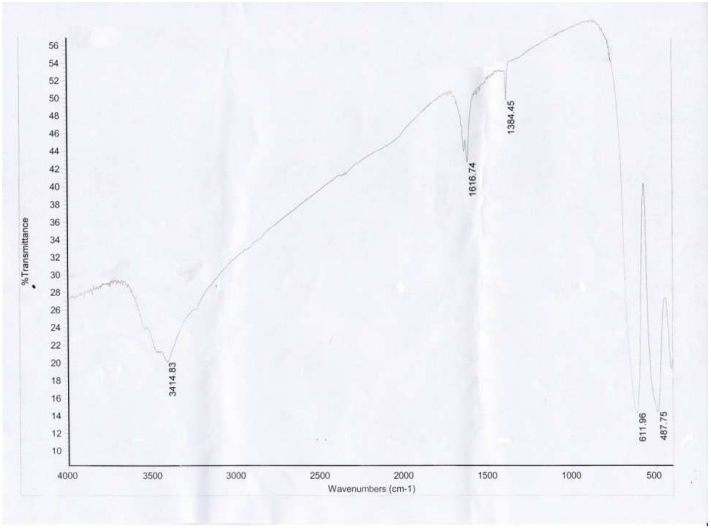

Figure 2: FT-IR Spectrum for Prepared MnO_2 Nanoparticle

SEM Analysis of Manganese Dioxide Nanoparticles

The surface morphology of the synthesized manganese dioxide nanoparticles is studied by scanning electron micrograph. Figure (3a-3b) as shown below the SEM images MnO_2 nanoparticles with magnification of 5,000 and 3,500. The instrumental parameters, accelerating voltage, spot size, magnification and working distances are indicated SEM image.

Figure (3a-3b) exhibits the agglomeration occurred during the synthesis process. The particles are mostly circular and irregular in shape with a nanosized range. Some of the particles are shaped in flakes of agglomerates of manganese dioxide nanoparticles.

EDX Analysis of Manganese Dioxide Nanoparticles

The chemical composition of synthesized manganese dioxide nanoparticles was studied by using EDX analysis. Table 1, shows the ratio of elements which contains weight % and atomic % for all elements and their total ratio equal to 100. Figure (4) EDX results confirm that the presence of Mn and O in the sample.

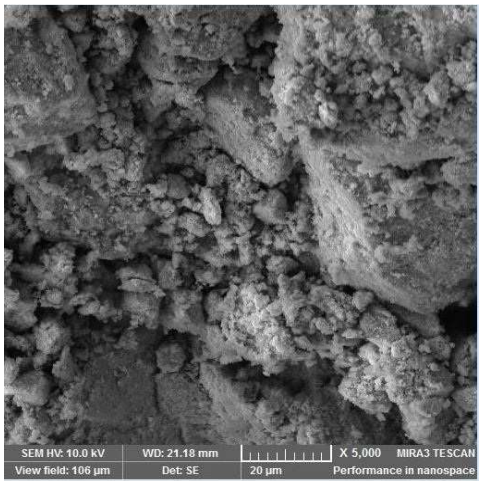

Figure 3a: SEM for Prepared MnO_2 Nanoparticle at 5, 000 Magnification

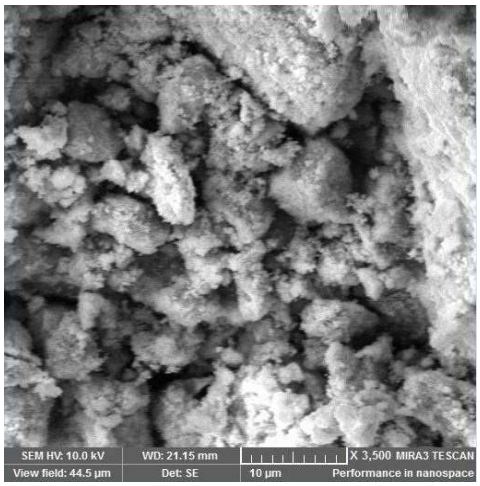

Figure 3b: SEM for Prepared MnO_2 Nanoparticle at 3, 500 Magnification

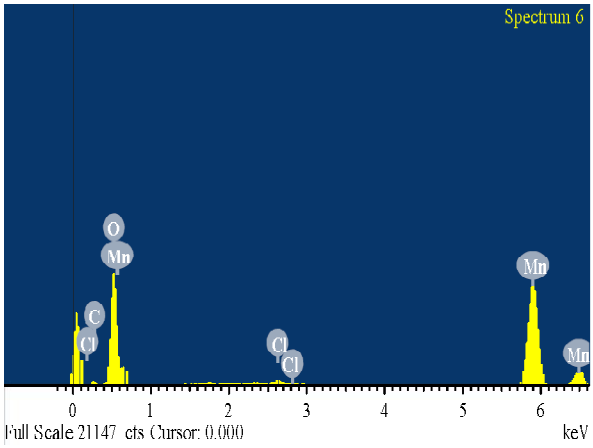

Figure 4: EDX Spectra of MnO_2 nanoparticle

Table 1: Chemical Composition of MnO_2 Nanoparticle

Element	Weight %	Atomic %
C K	4.43	10
O K	35.56	60.23
Cl K	0.62	0.48
Mn K	59.38	29.29
Total	**100**	

XRD Analysis of MnO_2 Nanoparticles

The Structure of the MnO_2 nanoparticles was characterized by using X-ray diffraction (XRD). XRD was collected by using a Rigaku Mini with Cu Kα radiation (λ = 0.1541 nm). The diffractograms were recorded in range of 10-80°. Figure (5) shows X-ray diffraction study of manganese dioxide nanoparticles synthesized by chemical co-precipitation method. From the XRD pattern it is clear that MnO_2 nanoparticles synthesized purely crystalline in nature. All the peaks found to be the broadened and indicating the formation of small crystallites. The average MnO_2 nanoparticles size was calculated by using Debye-Scherer formula.

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where 'D' is the particle diameter size, 'K' is the shape factor, 'λ' the X-ray wavelength (0.1541nm), 'θ' the Bragg's angle in radians and 'β' the full width at half maximum in radians. The particle size is calculated by using the above formula is 14 nm.

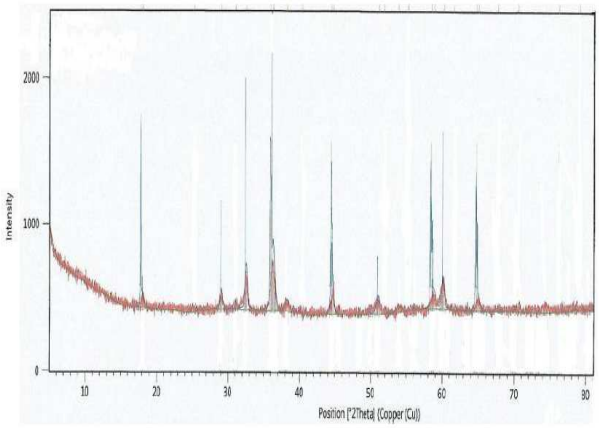

Figure 5: XRD Pattern of MnO_2 Nanoparticle

Study of Catalytic Decomposition of Hydrogen Peroxide

The hydrogen peroxide decomposed with time at different pH values and at 15°C temperature in the presence of Manganese dioxide nanoparticles. During the decomposition processes, the MnO_2 nanoparticles is reduced by H_2O_2 to manganese ion and then Manganous ion in hydroxide form $Mn(OH)_2$ is oxidized to MnO_2 nanoparticles.

The decomposition of H_2O_2 solution by MnO_2 suggested [10] as follows mechanism for H_2O_2- MnO_2 system:

$$MnO_2 + H_2O_2 \rightarrow Mn^{2+} + 2HO^- + O_2$$

$$Mn^{2+} + 2HO^- \rightarrow Mn(OH)_2$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

The experimental data were plotted in the form of percent concentration of H_2O_2 vs. Time. The Figure (6) illustrates that the concentration of hydrogen peroxide decreases with time at different pH values and constant temperature. Then the decomposition of hydrogen peroxide was measurable at the pH values higher than the PZC (zero point charge) and increased with the increases in pH, whereas at the pH values less than PZC the decomposition was negligible. This suggested the fact that only the negative surface sites were catalytically active for the decomposition of hydrogen peroxide and the positive surface sites were passive[11]. At higher pH values above PZC the surface carried a high negative surface charge which caused enhanced decomposition as shown in the Figure (7). Thus on the basis of the above observation, it is assumed that the decomposition of hydrogen peroxide over the negative surface sites adopted the following mechanism [12].

$$SO^- + H_2O_2 \rightarrow SO\text{-}H^+ + HO_2^-$$

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^-$$

$$SO\text{-}H_+ + OH^- \rightarrow SO^- + H_2O$$

Where, SO^- represents the surface negative sites and SOH^+ represents the surface positive sites.

The net result of these reactions is the generation of oxygen, which was observed in the form of bubble formation during the decomposition reaction.

The Figure (8) shows that the decomposition of H_2O_2 proceeds through first order kinetics. In order to investigate the kinetics of the reaction, the experimental data were analyzed with first order kinetics. The straight lines obtained from the relationship between log (a-x) vs. t. it reveals that the kinetics of the decomposition reaction on the surface of the MnO2 nanoparticles catalyst are also following first order behaviour.

Furthermore, the rate constants observed in the acidic medium were higher than that in the alkaline medium as shown in the Table 2. It may be due to the fact that oxides and hydroxides develop surface electrical charges by the protonation and deprotonation of the surface groups when in the acidic medium. Therefore, decomposition of H_2O_2 enhanced in the alkaline medium as compared to acidic medium.

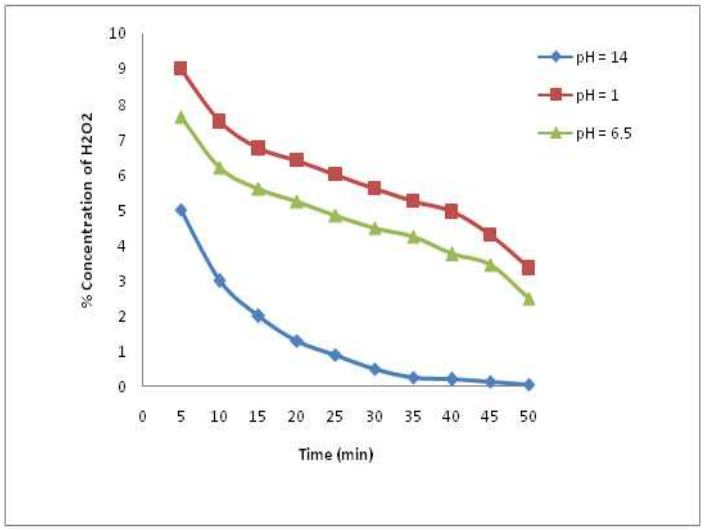

Figure 6: % Concentration of H_2O_2 on MnO_2 Nanoparticles vs Time at Different pH Values

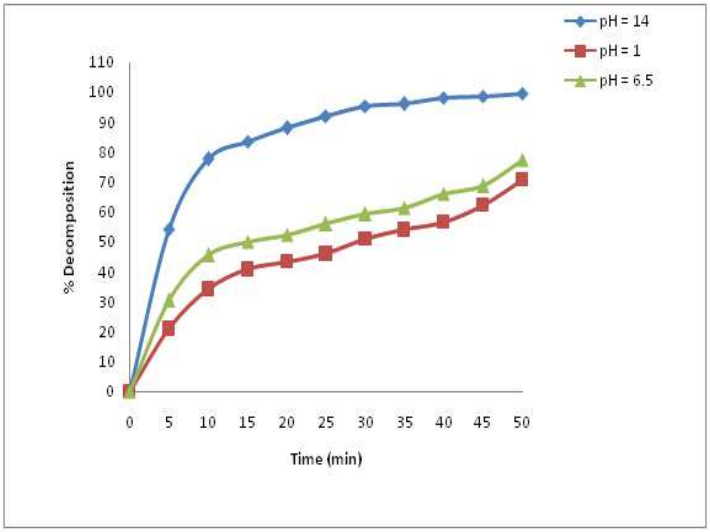

Figure 7: % Decomposition of H_2O_2 on MnO_2 Nanoparticles vs Time at Different pH Values

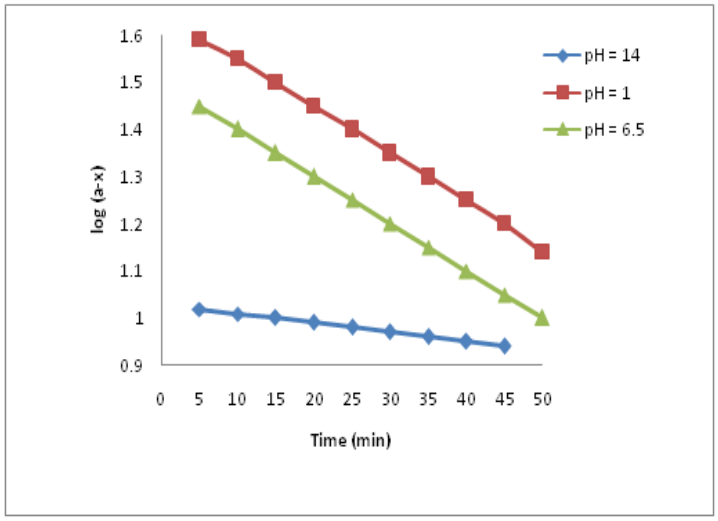

Figure 8: Log (a-x) versus Time for Decomposition of H_2O_2 on MnO_2 Nanoparticles at Different pH Values

Table 2: Rate Constant K (min^{-1}) for Decomposition of H_2O_2 on MnO_2 Nanoparticles at Different pH Values

No.	pH	K (min^{-1})
1	1	0.02303
2	6.5	0.01474
3	14	0.00444

CONCLUSIONS

Nanoparticles of MnO_2 have been successfully synthesized through chemical Co-precipitation method. The FT-IR spectral analysis shows the characteristic peaks of Mn-O is stretching. SEM image reveals that the most of the nanoparticles are circular, irregular in shape and agglomerates. EDX confirms that the total ratio of manganese dioxide nanoparticles and their chemical composition. XRD analysis reveals that the average size of MnO_2 nanoparticle as 14 nm.

MnO_2 nanoparticles potentially were applied as a catalyst to decomposition of H_2O_2 at different pH values and 15°C temperature. Clearly observed as increases pH value the decomposition of H_2O_2 increases, especially in alkaline medium due to the negative surface sites, which responsible for the decomposition of hydrogen peroxide and increases in alkaline medium. The decomposition reaction on the surface of MnO_2 nanoparticles shows the First-Order behaviour. The rate constants observed in acidic medium were higher than alkaline medium due to the protonation of surface group in an acidic medium and deprotonation in alkaline medium.

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