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Catalytic Decomposition of Hydrogen Peroxide in the Presence of Synthesized Iron-Manganese oxide Nanocomposites via Different Methods

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Abstract

The special application of iron-manganese oxide nanocatalysts has been investigated in decomposition of hydrogen peroxide. In this research, iron-manganese oxide nanocomposites were synthesized by co-precipitation, sol-gel and mechanochemical methods using iron (III) nitrate, iron (II) sulfate and manganese (II) nitrate as starting materials. These nanocomposites were prepared on the various catalyst beds. The polyvinyl pyrrolidon was used as a capping agent to control the agglomeration of the nanoparticles. Nanocatalysts were identified by FT-IR, XRD and SEM. The sizes of nanoparticles were determined by XRD data and Scherer equation. Catalytic activity of prepared samples by co-precipitation method was higher than the samples prepared by other methods. Based on surface area analysis and BET data, using of sodium metasilicate bed led to the high surface area and catalytic activity. To optimize the catalytic activity of nanoparticles factors such as concentration, cations ratio, pH and calcination temperature were investigated.

Keywords: *Hydrogen peroxide, Nanocatalyst, Iron-manganese oxide, Catalyst bed, Infrared spectroscopy, X-Ray diffraction, Electron microscopy, Catalytic property.*

1. INTRODUCTION

Decomposition of hydrogen peroxide to supply oxygen for the atmosphere is a suitable method. For the decomposition of hydrogen peroxide the active inorganic metal oxides of manganese, iron, cobalt and lead are used. If these metal-oxides are prepared at nanoscales their performance can accelerate the catalytic decomposition of hydrogen peroxide [1]. Catalytic substrates or beds such as zeolites increase the surface area of the nanoparticles and their uniform size distribution that improve the catalytic activity in the decomposition of hydrogen peroxide.

Ahmed et al [2] synthesized iron-manganese oxides by combustion and sol-gel methods. In combustion method, stoicheiometric amount of manganese acetate Mn $(CH_3CO_2)_2 \cdot 4H_2O$, ferric nitrate Fe $(NO_3)_3 \cdot 9H_2O$ and urea were mixed in an agate mortar for few minutes. Urea was added to the mixture (as fuel) and mixed again thoroughly then transferred to a quartz crucible and heated at 500ºC for 1/2 h. At this temperature, the reaction lasted for 3–5 min. A foamy and highly porous precursor was obtained. The ferrite powder was calcined at 900ºC. In sol-gel method the raw materials, Mn $(CH_3CO_2)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, were first dissolved in ethylene glycol and de-ionized water under stirring until a homogeneous mixture was observed, heated to 70ºC for 12 hours and dried at 80ºC for 24 hours. The resulting gel was calcined at 600ºC [2]. The smallest nanosize was obtained in combustion method (41 nm).

Shin-Liang Kuo et al [3] synthesized $MnFe_2O_4$ - carbon black (CB) composite powders by a co-precipitation method in alkaline aqueous solutions. $MnSO_4$ and $FeCl_3$ were dissolved with a stoicheiometric ratio of 2:1 respectively in 1M HCl aqueous solution in presence of N_2. The solution was added into another solution that contained 1.5M NaOH and suspended activated carbon powder under vigorous stirring. Black precipitate was formed immediately upon mixing. The powder was formed by drying at 50ºC. A subsequent calcination process was carried out at different temperatures for 2 hours in N_2 atmosphere.

The decomposition of hydrogen peroxide by manganese oxide at pH 7 is represented by a pseudo first-order model [4].

Pretty Lahirri et al [5] synthesized a set of ferrites with different compositions by co-precipitation method.

They found that some ferrous spinels act as catalysts for the decomposition of H_2O_2 and their effectiveness is dependent on the composition of the catalyst. The catalytic activity of the ferrous spinels for hydrogen peroxide decomposition was evaluated by the evolution rate of oxygen from the liquid phase. The evolution rate of gaseous O_2 was monitored with a gasometrical assembly.

Nasr-Allah M. Deraz [6, 7] studied the hydrogen peroxide decomposition activity by oxygen gasometry of the reaction kinetics at 20-40 ºC on the pure and ZnO-doped cobalt oxide catalysts. The results revealed that the treatment of Co_3O_4 with ZnO at 400-700ºC brought about a significant increase in the specific surface area of cobalt oxide.

In the present work, iron-manganese oxide nanocomposites were synthesized using different preparation methods to achieve the high surface area and catalytic activity in decomposition of hydrogen peroxide. To improve the H_2O_2 decomposition efficiency, different synthesis methods, catalytic supports and parameters such as concentration, cations ratio, pH and calcination temperatures were investigated to optimize the catalytic activity for increasing the rate of hydrogen peroxide decomposition.

2. EXPERIMENTAL

2.1. Reagents and instruments

Mn $(NO_3)_2.4H_2O$, Fe $(NO_3)_3.4H_2O$, $FeSO_4.7H_2O$ and polyvinyl pyrolidone (PVP) as a capping agent were purchased from Merck company. The IR and UV spectrums were recorded by IR-Perkin Elmer and UV-Shimadzu respectively. The nanocomposites were characterized by XRD and scanning electron microscopy (SEM) analysis.

2.2. Preparation of $MnFe_2O_4$ nano composites

2.2.1. Co-Precipitation method

An appropriate amount of Mn $(NO_3)_2.4H_2O$ and Fe $(NO_3)_3.4H_2O$ were dissolved in water and heated to 40ºC. While the solution was being stirred vigorously, 20 ml of NaOH 0.1M was added to the solution. After 30 minutes the reaction was halted; filtering and washing steps at pH=7 were carried-out. As a result the precursors of $MnFe_2O_4$ i.e. $Mn(OH)_2$ and $Fe(OH)_3$ were produced which were left for 24 hours at 60ºC ±10ºC to get dried. The dried precursors were calcined at 300ºC for 2 hours after which $MnFe_2O_4$ powder was formed. The ionic equation of the reaction is as followed:

$$Mn^{2+} + 2Fe^{3+} + 8OH^- \longrightarrow Mn(OH)_{2\downarrow} + 2Fe(OH)_{3\downarrow} \xrightarrow{\Delta} MnFe_2O_4 + 4H_2O$$

2.2.2. Sol-gel method

$Mn(NO_3)_2.4H_2O$ and $Fe(NO_3)_3.4H_2O$ were dissolved in ethylene glycol or citric acid as a gelling agent. While stirring de-ionized water was added until a homogenous mixture was formed which was heated at 70ºC for 12 hours and dried at 80ºC for 24 hours.

The resulting mixture was ground and reheated at 100ºC for 24 hours and slowly cooled. Final calcination was carried-out at 500ºC for 2 hours at a heating rate of 10ºC/min which was followed by cooling step to room temperature at the same rate.

2.2.3. Mechanochemical method

$Mn(NO_3)_2.4H_2O$ and $Fe(NO_3)_3.4H_2O$ were mixed and ground to have a uniform powder. Addition of some distilled water converted the powder to gel which was dried at 50ºC for 4 hours that was calcined at 300ºC for 2 hours to obtain $MnFe_2O_4$.

To increase the nanoparticles active surfaces in above method an optimized amount of sodium metasilicate and zeolite as catalytic beds were added to metal salts. To have a gel form of the mixture some deionized water was added to the mixture. The obtained mixture was dried at 50ºC and calcined at 300ºC for 2 hours to form the desired phase.

2.2.4. Co-Precipitation method in the presence of PVP

The procedure of this method is similar to the co-precipitation method. The difference is the acting of PVP as a capping agent which controls nanoparticles size and prevent their agglomeration [8] (Figure1).

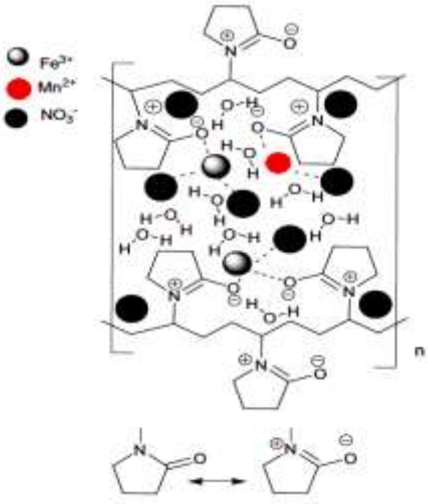

Figure1. *Proposed mechanism of PVP interactions with metal ions*

2.3. Measurement of catalytic activity of the nanocatalysts on decomposition of hydrogen peroxide

The catalytic activity of the nanoparticles on hydrogen peroxide decomposition was evaluated by evolution rate of oxygen from the liquid phase. A measured amount of catalyst (0.1 g) was injected into a thermostatic reaction vessel containing 10 ml of %5 H_2O_2 (pH = 6.64) for each specimen.

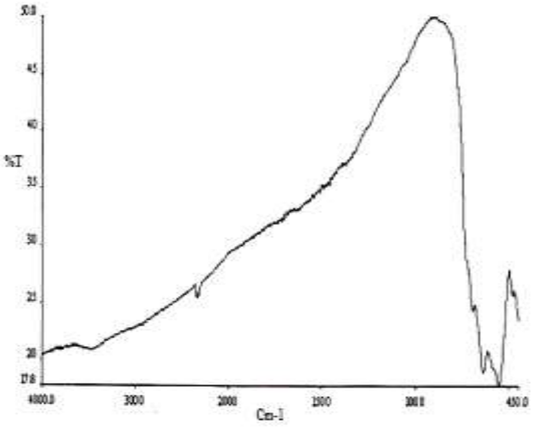

Figure2. *IR spectrum of $MnFe_2O_4$*

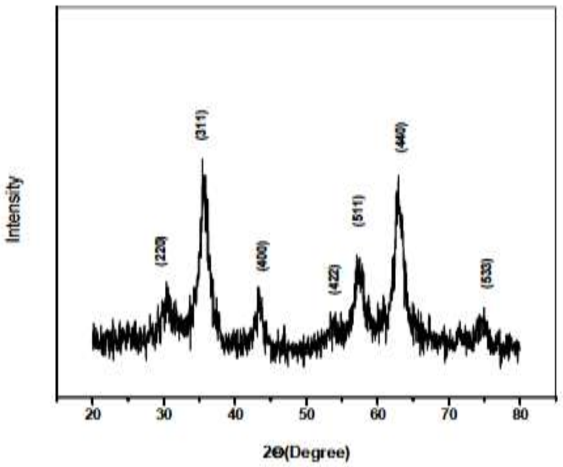

Figure3. *XRD of $MnFe_2O_4$*

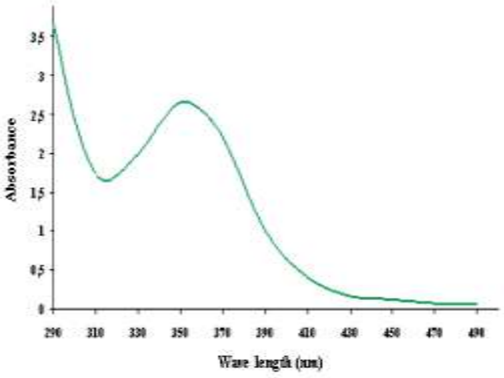

Figure4. *UV spectrum of $MnFe_2O_4$*

H_2O_2 was standardized immediately prior to use by $KMnO_4$ solution. The peroxide decomposition is represented by:

$$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + 1/2\ O_2(g)$$

H_2O_2 undergoes an exothermic reaction to form O_2 and H_2O. The evolution rate of gaseous O_2 was monitored with a gasometric assembly. The time dependent volume (VT) of the evolved oxygen was monitored at 0.5 min intervals in all cases. The catalytic activity was calculated by $a=k/(t\times m)$ equation where a is the activity, k is a constant, t is the reaction time and m is the mass of catalyst (in this experiment it is 0.1 g).

3. RESULT AND DISCUSSION

3.1. IR investigation

The IR transmission spectrums were recorded for sample calcined at 300ºC. Two bands with wave numbers 470 cm^{-1} and 562 cm^{-1} are attributed to Fe-O and Mn-O on octahedral and tetrahedral sites with spinel structure ($MnFe_2O_4$) respectively (Figure2).

3.2. XRD investigation

The peaks that are present and are labeled by codes 220, 311, 400, 422, 511, 440, 553 belong to $MnFe_2O_4$ with spinel structure (Figure. 3). Based on data obtained from JCPDS-JCDD (joint committee for powder diffraction-international center for diffraction data) our sample exhibits a cubic structure and no extra height exists along the peak that implies the sample doesn't contain any impurity. Using Scherer equation the average size of nanoparticles was determined to be 45 nm. The XRD of the sample that was prepared by co-precipitation method and PVP capping agent demonstrates a decrease of 15 nm in particle size that may be related to capping agent.

3.3. Investigating the UV spectrum

Considering the low solubility of transitional elements in organic solvents and water, for analyzing the UV spectrum the sample should be left in suspended and disperse situation in ultrasonic bath. In electromagnetic region, the molecules experience the electronic transition. Charge transition band in maximum wavelength absorptive (347 nm) and observation of broad peaks before and after the incident indicate the formation of ferrite compound [9] (Figure4).

3.4. SEM analysis

Analyzing the morphology of the nanoparticles using the SEM indicates that the synthesized nanoparticles are quasi-spherical and the size is less than 100 nm that means the synthesized catalysts have nanodimension. The information obtained from XRD also confirms the above findings. The results obtained from the calculation of average size of nanoparticles by the aid of SEM images and analytical clemex image software are as follows: The size of samples prepared by co-precipitation method and synthesized in presence of a capping agent are 50 nm and 40 nm respectively (Figures.5a and b). It should be mentioned that the determination of nanoparticle size by the aid of SEM is related to the morphology of the particles that means the reported size of the nanoparticles verified by XRD and SEM techniques are related to uniform distribution of the particle size.

SEM images demonstrate the fact that the morphology of majority of nanoparticle beds is quasi - spherical. Another determination by SEM images is related to the particles size i.e. the formed particles exhibits nano-dimension (less than 100 nm). The size of the Particles formed on silica and porous beds are smaller than those formed on zeolite bed (Figures6a, b and c).

Dispersion and distribution of nanoparticles size in silica and porous beds are more than the other beds, hence it can be concluded that the above results are effective in incrementation of catalytic activities of silica and porous beds.

3.5. The role of catalyst support on surface area and particle size

Presence of catalytic support of sodium metasilicate illustrates various advantages associated with nanoparticles such as simple work-up procedure, short reaction times, reduced particle size, high total surface area (m_2), high specific surface area (m_2/g), high product yield, easy recovery and reusability of the catalyst. The use of sodium metasilicate reduces the size of nanoparticles from 43 nm to 12 nm, increases the catalytic activities and the distribution of nanoparticles on the support. The data that confirms the above claims are listed in table 1 and shown in Figures7a and b. Furthermore presence of catalytic support increments the amount of evolved oxygen (Figure8).

Table1.*Surface area analysis (BET) - iron-manganese oxide nanocamposites in the presence of sodium metasilicate catalyst support.*

Sample	Weight (g)	Adsorb gas	Relative pressure (P/P_0)	Total surface area (m^2)	Specific surface area (m^2/g)
In the absence of support	**0.107**	**Nitrogen**	**0.15**	**0.5407**	**5.0531**
In the presence of support	**0.105**	**Nitrogen**	**0.15**	**11.2864**	**107.4899**

It should be mentioned that three other catalyst beds i.e. mesoporous, molecular sieves and zeolit 13X were also investigated, but none of them had the effectiveness of sodium metasilicate on decomposition of H_2O_2, as a result the amount of evolved oxygen was in excess. Among the catalyst beds the zeolit 13X bed had the less effect (Figure8).

3.6. Investigating the different parameters influencing the H_2O_2 decomposition

3.6.1. Effect of calcination temperature

In order to determine the optimized calcination temperature, different calcination temperatures were implemented on hydroxide precipitation produced via co-precipitation method. Catalytic activity was at maximum when the temperature of calcination reached 300ºC. At this temperature decomposition of hydrogen peroxide occurred at lower temperature which evolved more oxygen. In higher calcination temperature the nanoparticles are agglomerated, so their sizes incremented and the surface area for catalytic activities was reduced. At lower calcination temperature crystalline-phases of metal oxide were not formed (Figure9).

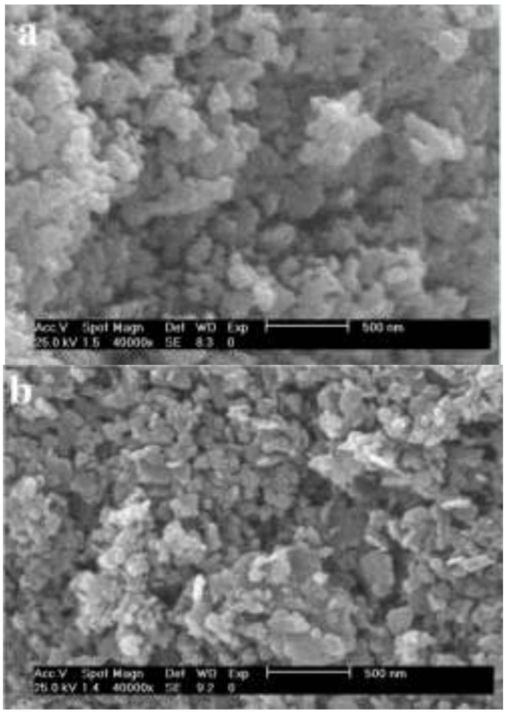

Figure5. *SEM images of $MnFe_2O_4$, a) co-precipitation method, b) in the presence of PVP.*

3.6.2. Optimization of pH in co-precipitation method

Decomposition of hydrogen peroxide is a pH variable. The optimized pH for the maximum catalytic activity of the sample was on the basic region (pH= 9-10).

The sample in acidic region (low pH) had the least catalytic activity (Figure10). Our results suggest that the catalytic activities of $MnFe_2O_4$ in decomposing of H_2O_2 can be modulated by the pH value of the environment, i.e. in acidic environment (low pH) H_2O_2 is decomposed to •OH but in neutral and alkaline conditions (pH= 9-10) H_2O_2 is decomposed to H_2O and O_2.

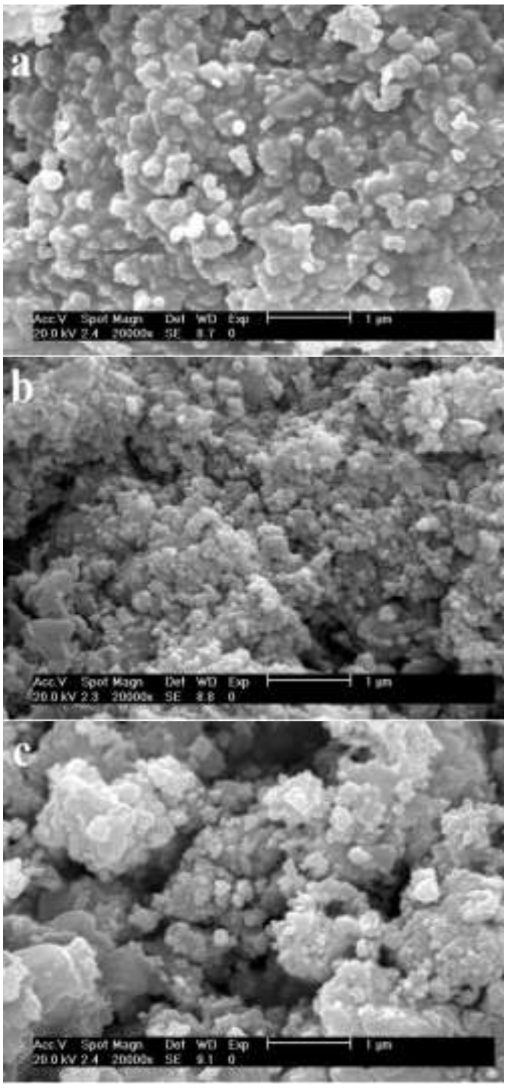

Figure6. *SEM images of nanocomposite a) with sodium metasilicate support, b) with porous beds, c) with zeolite support.*

3.6.3. Effects of various catalyst beds

It was observed that for having the maximum catalytic activity the amount of metal salt should be fourfold catalytic bed (Figure11). In fact the amount of catalytic bed should be optimized because as substrate increases the catalytic active sites are covered as a result the catalytic activities are reduced; furthermore if it is less than the optimized amount the surface activity is not altered.

It was observed that if $FeSO_4$ is used as a reactant instead of $Fe(NO_3)_3$ the surface activity is reduced dramatically, the reason could be related to the poisoning nature of sulfate.

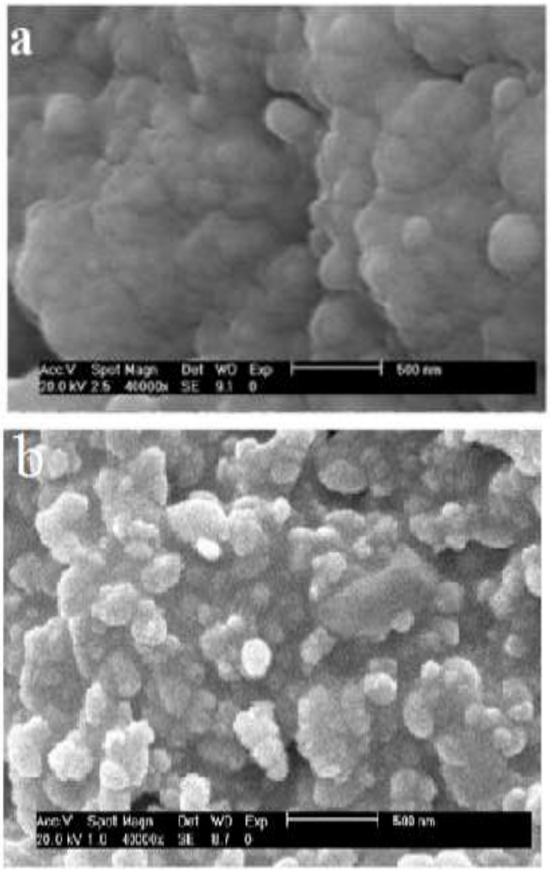

Figure7. *SEM images of iron-manganese oxide nanocomposites a) in absence, b) in presence of sodium metasilicate catalyst support.*

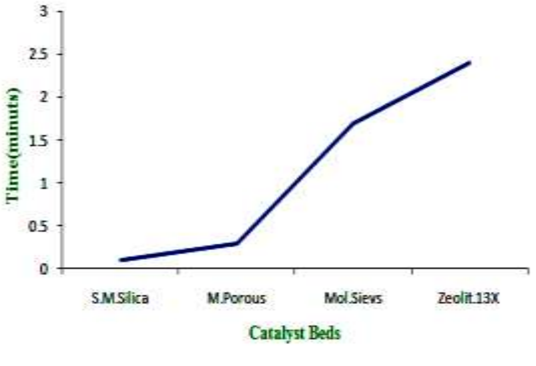

Figure8. *Catalytic activity of iron-manganese oxide nanocomposites in the presence of catalyst beds on hydrogen peroxide decomposition.*

In co-precipitation method, catalytic activity is not poisoned because of the washing and filtering processes. It was confirmed that suitable starting materials are metal nitrates instead of metal hydroxides and metal oxides, the reason is in metal nitrate ions are looser to move about, and therefore; the ion-exchange was carried-out better (Figure12).

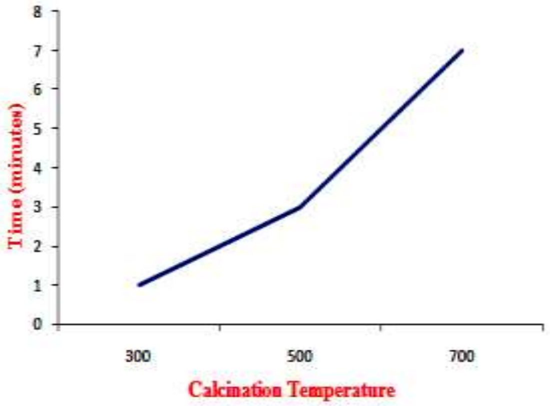

Figure9. *Effect of calcination temperature on catalytic activity of hydrogen peroxide decomposition (samples obtained from co-precipitation method).*

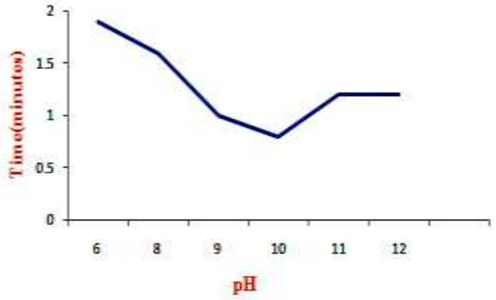

Figure10. *Effect of pH on catalytic activity of hydrogen peroxide decomposition (samples obtained from co-precipitation method).*

3.7. Feasibility of reusing nanocatalysts

In order to examine the reusability of nanocatalysts in decomposition of hydrogen peroxide, a few of synthesized samples were chosen, and catalytic decomposition reaction was carried-out on them. At the end of the reaction the samples were collected, dried, weighted, and then they were reused for the decomposition of hydrogen peroxide. The difference between the catalytic activity and the weight of nanocatalysts were considered. The slight difference in initial and final weights of nanocatalysts indicates that both the primary and consumed nanocatalysts have the same catalytic activity in hydrogen peroxide decomposition. The results are summarized in table 2.

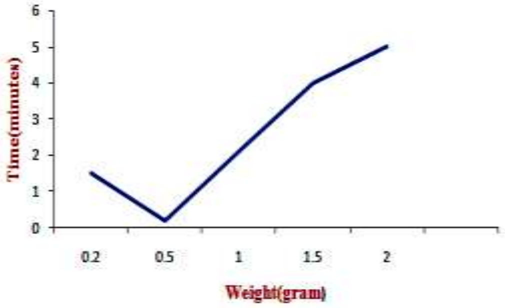

Figure11. *Optimization of support weight in 2g catalyst.*

Figure12. *Effect of starting materials for hydrogen peroxide decomposition.*

Table2.*Feasibility of reusing nanocatalysts*

Sample	Reaction Time (s)	Secondary weight (g)	Reaction Time (s)	Initial weight (g)	Reaction Time (s)
Co-Precipitation method	33	0.098	30	0.1	33
Sol-Gel	155	0.099	150	0.1	155
Silica Support	13	0.091	12	0.1	13
Zeolit 13X	123	0.088	120	0.1	123

4. CONCLUSION

To carry-out the hydrogen peroxide decomposition reaction in short time $MnFe_2O_4$ nanocomposites were used. In order to reach the maximum speed in hydrogen peroxide decomposition reaction, nanocatalysts with the highest catalytic activity should be used. Hence, major variables that were so effective in catalyst synthesis should be considered, and optimized. Conditions of each variable that had a major effect in incrementation of catalytic activity were investigated that caused the augmentation of nanoparticles active surface area and their uniform distribution on catalytic supports that are as followed:

1. The best method for synthesis of nanocatalysts was Co-Precipitation method that provided the maximum catalytic activity for decomposition of H_2O_2. The suitable pH for nanoparticles precipitation was around 9. The optimized calcination temperature was about 300ºC.
2. For controlling the nanoparticle size PVP capping agent was applied by using co-precipitation method. PVP agent caused a 15 nanometer reduction in nanoparticles size.
3. To accelerate hydrogen peroxide decomposition, sodium metasilicate was used as a catalytic support. In presence of sodium metasilicate shorter time was needed to decompose a certain amount of H_2O_2.
4. Investigating the reusability of nanocatalysts indicated that second use of nanocatalyst was accompanied by a slight poisonous that was negligible; therefore the nanocatalysts could be used for a few times.

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