

Oxidation of Hydrogels Based of Sodium Alginate and MnO₂ as Catalyst

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Abstract

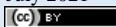
In this study, first a hydrogel based on sodium alginate and acrylamide was prepared by radical polymerization method and then manganese oxide was formed in its lattice structure and nanocomposite hydrogels were obtained. In the next step, Nanocomposite hydrogels were used as catalysts for the oxidation of alcohols. To evaluate the physical properties and confirm the structure of nanocomposite hydrogels, Hydrogel swelling tests, FT-IR infrared conversion spectroscopy, TGA Thermal gravimetric, SEM Scanning electron microscopy and TEM Transmission electron microscopy were used. The amount of manganese was measured using an atomic absorption spectrometer. Also, factors affecting oxidation reactions such as reaction temperature, amount of catalyst and reaction time were optimized to achieve the highest percentage of conversion of alcohols to aldehydes. Under optimal conditions, the highest conversion percentage of benzyl alcohol was 79% for Benz aldehyde at 80 °C for 24 hours.

Keywords: Hydrogel, Sodium Alginate, Nanocomposite Hydrogels, Alcohol Oxidation, Manganese Dioxide.

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Competing Interests: The authors declare that they have no conflict of interests.

Transparency: The authors confirm that the manuscript is an honest, accurate, and transparent account of the study was reported; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained.

Ethical: This study follows all ethical practices during writing.

1. Introduction

Hydrogels are a network of polymer chains, that's sometimes found in liquid. A hydrogel is a three-dimensional solid made of polymer chains, held in place by cross-links. They are insoluble in water due to the presence of covalent, ionic or physical chemical crosslinks [1]. Due to the inherent cross linking, the structural integrity of the hydrogel network does not decompose at high concentration in water. Some of the water in the hydrogel structure is absorbed through hydrophilic interactions, while most of it is free. In a swollen hydrogel, the amount of water depends on the chemical structure of the polymer chains and the density of the crosslinks [2]. The term hydrogel was first used in 1894 [3]. Hydrogels sold under the trademark were approved in 2019 to help with weight loss. Hydrogels can swell and absorb hundreds of times their own weight of water, so they are called superabsorbent or absorbent water. Their ability to swell depends on pH, temperature, ionic strength, and solvent type and polymer structures [4].

One of the important features of synthesized hydrogels is that they do not the absorption of water in their structure and do not become viscous and flowing. To increase the strength of the hydrogels, the percentage of networking of the chains is important. By increasing the concentration of acrylamide crosslinking hydrogel, its strength can be increased [5]. Increased crosslinking reduces the hydrogel water absorption capacity due to the reduction of voids between the chains.

However, the higher size of the acrylamide creates a brittle hydrogel network. The introduction of monolayer to form hydrogen bonds increases the strength of the gels [6]. Hydrogels have many applications in health products, cosmetics, water preservatives, moisturizers, sludge coagulants, thickeners and are used in medicine as eye lenses and artificial muscles. Food industry, photographic technology, as adsorbents in baby diapers, as well as in the agricultural and horticultural industries to improve the capacity and conservation of soil and water, in fire retardant compounds and many other applications are used. These compounds occupy a large part of the world markets due to their economic and technical value [7].

1.1. Nanocomposite Hydrogels

Nanocomposite hydrogels are hydrophilic materials that have improved thermal and mechanical properties compared to conventional hydrogels. Nanocomposite hydrogels have both nanoparticle and hydrogel properties [8]. Like hydrogels, they are flexible, environmentally friendly, and like nanoparticles. The use of nanocomposite hydrogels including metal nanoparticles such as manganese, Copper, Iron, Gold, Silver, etc. has been widely increased due to their unique optical, electrical and catalytic properties, as shown in Figure 1.

1.2. Preparation of Hydrogel with Manganese Dioxide Nanoparticles

Manganese dioxide is widely used in electrodes, catalysts and magnetic materials. Manganese dioxide is used as an active catalyst for oxidation in various organic reactions. For example, this compound is used for the oxidation of methane, alcohol, carbon monoxide. Manganese dioxide is usually prepared at a high temperature, which is calculated to be higher than 100 degrees Celsius. Manganese dioxide nanoparticles can be prepared by various physical and chemical methods. Lijan et al. Reported the synthesis of nanoparticles Mn_3O_4 with Manganese (ii) acetyl acetonate $[Mn(acac)_2]$ and alumina at 180 °C [9].

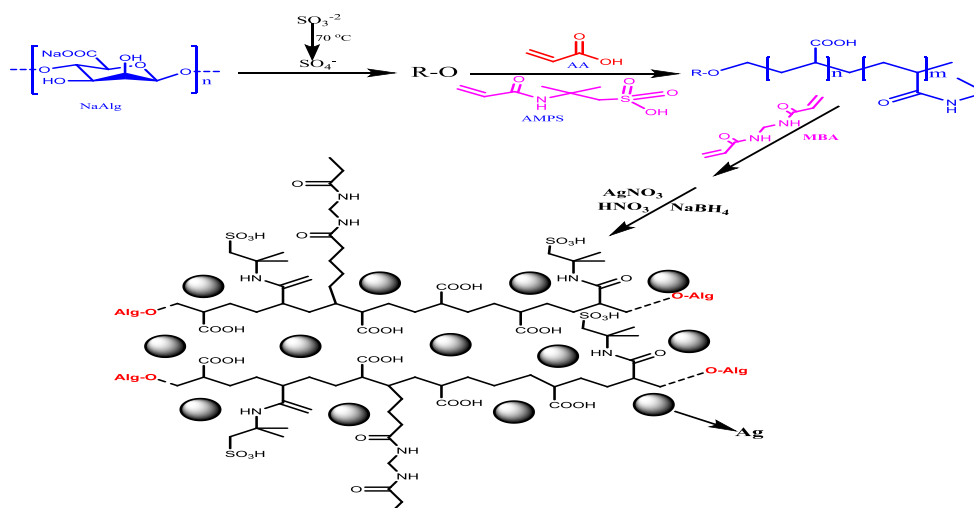


Figure-1. Structure of nanocomposite hydrogels [3].

1.3. Oxidation of Alcohols

Oxidation of alcohols is one of the most important reactions in organic synthesis. The primary alcohol is converted to aldehydes and the secondary alcohols are converted to ketones. Also, the ketones and aldehydes resulting from oxidation. These compounds are valuable today in the pigments, perfumes, vitamins, pharmaceuticals and chemical industries. In many cases, these reactions occur in undesirable solvents in the environment. In the last decade, the development of processes that use safety oxidants economically has attracted the attention of many researchers. Catalytic oxidation with hydrogen peroxide in aqueous solution is an economically and environmentally safe alternative to oxidation reactions performed in synthetic laboratories and the chemical industry [10]. Many methods of alcohol oxidation are known today. Oxidation of alcohols using molecular oxygen (O_2) as an oxidizer has attracted the attention of many researchers due to the cheapness and green nature of this reagent. Oxidation of alcohol by stoichiometric amounts in the previous century was more with chromate and permanganate [11]. But now new methods include the amount of metal catalysts in combination with oxidants such as manganese oxide, replaced by hydrogen peroxide, the previous century [12].

In the alcohol family, the oxidation of secondary alcohols is converted to ketones, and the oxidation of benzyl alcohols of the primary usually results in the production of aldehydes, acids, or mixtures of the two. And the third type of alcohol has no reducing properties and is more resistant to oxidation. This property is due to the fact that in the alcohol family the tertiary of carbon attached to the OH agent is not attached to another hydrogen atom. Therefore, controlled oxidation of alcohols of the primary with selective and mild oxidants, aldehyde and if not controlled, a mixture of aldehyde and carboxylic acid and with strong oxidants and in more severe conditions only carboxylic acid is produced. Ketones, which are the product of the oxidation of secondary alcohols, do not show much tendency for oxidative reactions. Exceptionally, the other two most oxidized ketones are methyl ketones, known as the oxidized Iodoform reaction, which produce the carboxylic acid salt [11]. The second group of ketones that are more capable of oxidation are cyclic ketones.

Which breakdown under harsh conditions and produces acid. For example, the conversion of cyclohexane to adipic acid is shown in Figure 2.

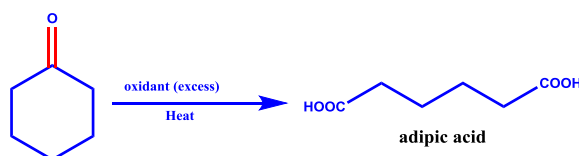


Figure-2.
Oxidation of cyclohexane to adipic acid [4].

2. Materials and Methods

The chemicals used in this study were acrylamide monolayer and N-network builder, 1- methylene Beas acrylamide from Merck company, 99% pure sodium alginate powder, Felucca company, ammonium per sulfate (APS) as a starter from Mark company, and were also used manganese sulfate, sodium boor hydride used in this research was purchased from Merck Company and used. And ethanol was purchased from Bides tan Alcohol Company.

2.1. Preparation of Hydrogel

To prepare the hydrogel, 2g of sodium alginate and 2g of acrylamide (AAM) are used. In this solution, 0.1g of ammonium per sulfate (APS) is used as a thermal initiator and 0.1g of Methylene base acrylamide (MBA) is used as a crosslinking agent. The taken Sodium alginate was first dissolved in 40ml of distilled water and then placed in a water bath at 80 °C and stirred with a mechanical stirrer at 200 rpm to obtain a uniform solution. Methylene base acrylamide (MBA) dissolved in 5 ml of cold distilled water then added and the solution was stirred with a mechanical stirrer for one minute. Acrylamide (AAM) was then added to the reaction vessel and stirred with a mechanical stirrer for one minute to give a uniform solution. Then 0.1g of ammonium per sulfate is solved in 5 ml of distilled water was added to the reaction vessel as a starter and the timer was turned on and the gel time was measured. The reaction to hydrogel lasted 20 m. In the next step, the hydrogel formed from the water bath was removed and then immersed in 80ml of ethanol and replaced with ethanol solvent for 2 to 3 times with fresh solvent so that the obtained gels were dehydrated and unreacted substances were removed from them. The resulting gels were then sliced into ethanol and placed on a watch glass and placed in an oven at 50 °C for 24 hours to dry completely.

2.2. Swelling Rate of the Hydrogel

To measure the swelling of the hydrogel, first 0.1g of solid hydrogel powder made with a particle size of 245-250 micrometers (60-60 mesh) was added to 200ml of distilled water and kept at room temperature for 40 m to complete the swelling of the hydrogel. The swollen hydrogel is poured into a mesh bag and after 40 m the equilibrium swelling is calculated using the Equation 1.

$$Es = \frac{(W_2 - W_1)}{W_1} \quad (1)$$

In this regard, W_1 and W_2 are the weight of dry hydrogel and swollen hydrogel.

2.3. Preparations of the Hydrogel Nano Particles Consists of Manganese Oxide

First, 0.4g of dry hydrogel was added to a container containing distilled water and kept at room temperature for one day to swell completely. After filtering the hydrogel, 0.4g of manganese sulfate salt solution ($MnSO_4$) dissolved in 50ml of water was added to the reaction vessel containing the hydrogel. After 24 hours, this hydrogel was washed with distilled water and then 0.2g of sodium boor hydride ($NaBH_4$) dissolved in 50 ml of water was added to the container containing the hydrogel. The mixture was leave at room temperature for 48 hours to form a dark brown color. The hydrogel is then washed again with distilled water and placed in 100 ml of 96% ethanol to dehydrate. After dewatering, 30ml of 10% nitric acid solution was added to the container containing the hydrogel and after 3-4 minutes until the manganese particles were reactivated, the hydrogel that containing the manganese nanoparticles washed with distilled water and then using ethanol for dehydration. The resulting dark gels were dried in an oven at 105°C for 24 hours and used as a catalyst in oxidation reactions [13]. The advantages of this catalytic system are very easy to separation by a magnet and its high recoverability. This catalyst can also be used as a green catalyst in oxidation reactions in aqueous medium with good efficiency and in a short time range.

3. Results and Discussion

3.1. FTIR spectral analysis

The structure of the samples was studied by infrared spectroscopy. Figure 3 spectrum (A) is for sodium alginate polysaccharide. The peak observed in the wave number 3353 cm^{-1} belongs to the hydroxyl group, the peaks observed in the wave numbers 1625 cm^{-1} and 1421 cm^{-1} belong to the asymmetric and asymmetric carboxylate groups, respectively, and the peak appearing in the ether group in this poly saccharide group is about 621 cm^{-1} Spectrum (B) is related to sodium alginate-based hydrogels. The adsorption in the regions of 3375 cm^{-1} , 2939 cm^{-1} and 3209 cm^{-1} belong to the OH groups of

alginate chains, NH amide and CH of a monogrammed hydrogel network, respectively. Spectrum (C) is related to monogram hydrogels. New spectra in the range of 555 cm^{-1} confirm the presence of manganese in the hydrogel [14].

3.2. Thermogravimetric analysis (TGA)

As can be seen in Figure 4, at 193°C , sodium alginate poly Saccharide 17% hydrogel based on sodium alginate lost 8% and at the same temperature nanocomposite hydrogels lost only 7% by weight. The high thermal stability of hydrogels is due to the network structure of hydrogels and polyacrylamides. And the stability of Nanocomposite hydrogels is due to the presence of manganese oxide in the hydrogel network [15].

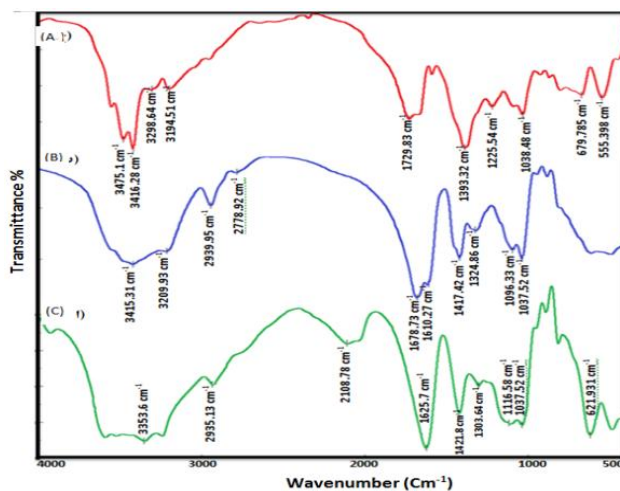


Figure-3. Infrared spectrum (A) Sodium alginate poly Saccharide (B) Sodium alginate-based hydrogel and (C) Nanocomposite hydrogels.

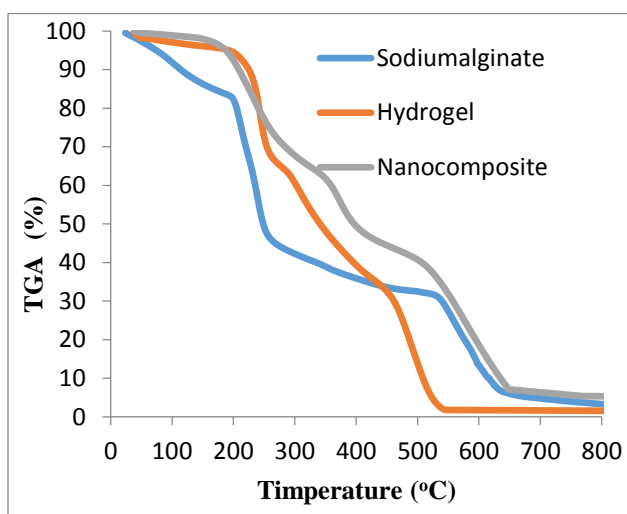


Figure-4. (TGA) thermogram of poly Saccharide sodium alginate, and nanocomposite hydrogels.

3.3. Swelling of Hydrogels and Nanocomposite Hydrogel

According to Figure 5 diagram (a), the amount of water absorption in the hydrogel and the diagram (b) is related to the nanocomposite hydrogels. This swelling has been fixed after 40min, respectively. The reason for the decrease in the swelling of nanocomposite hydrogels is the presence of manganese oxide nanoparticles in the hydrogel bed. Which was mineral filler and could also act as a network builder? Therefore, the water absorption rate in this hydrogel is very high and can be considered as a suitable option for applications that require rapid solvent adsorption. In Figure 5, diagram shows that nanoparticle hydrogels have less water absorption, probably because manganese nano particles can play a networking role to some extent.

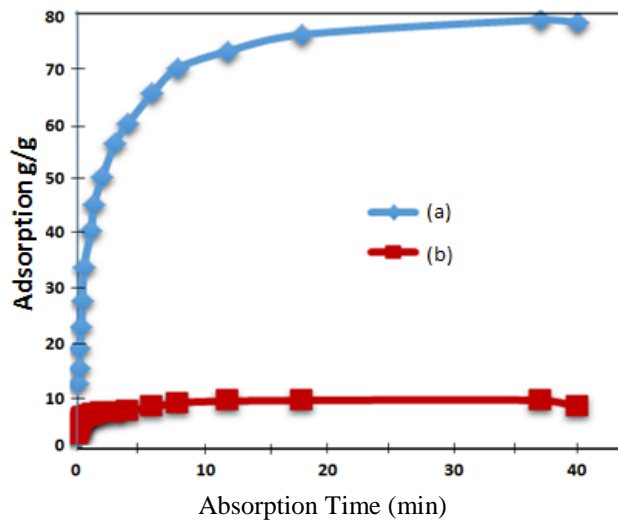


Figure-5. Diagrams (a), the amount of water absorption in the hydrogel and the diagram (b) is related to the nanocomposite hydrogels.

3.4. SEM Analysis

The SEM image of the sodium alginate-based hydrogel sample and nanocomposite hydrogels is shown in Figure 6. In the structure of the hydrogel, there are empty cavities that absorb the water and soluble ions from solution. These cavities are also a good place for nanoparticles to form. The nano composite images show more porosity and pores than the hydrogel [14].

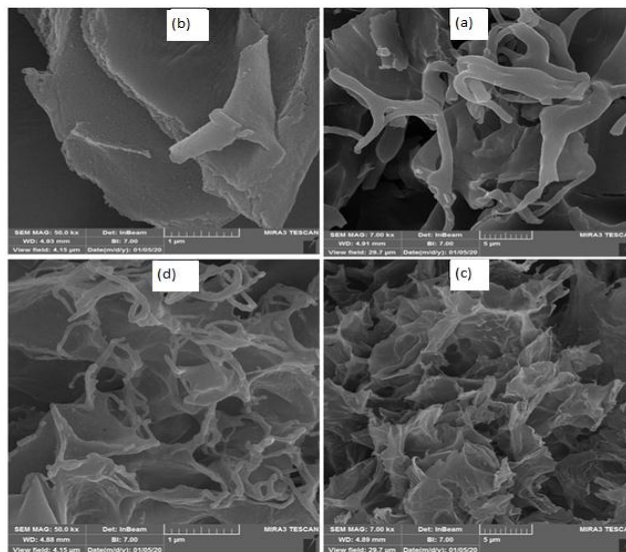


Figure-6. Shows SEM hydrogel images with magnifications of 7,000 (a) 50,000 (b) nanocomposite hydrogels images with magnifications of 7,000 (c) and 50,000 (d).

3.5. TEM analysis

Magnifications a transmission electron microscope was used to determine the exact size of the nanoparticles. Figure 7. shows images of electron microscopes passing through synthesized nano particles at different magnifications. As can be seen, the nanoparticles are well dispersed in the hydrogel bed and their approximate size is 40 to 80 nm.

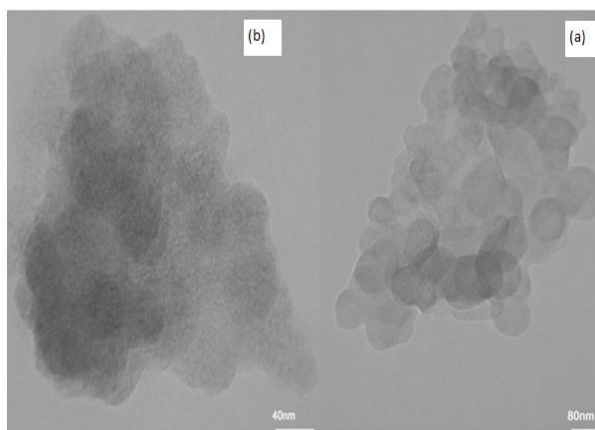


Figure-7.
TEM image of Nanocomposite hydrogels.

3.6. Map analysis of nanocomposite hydrogel

Finally, Figure 8 map analysis (MAP) confirms the relatively uniform dispersion of manganese oxide in the hydrogel containing manganese oxide Nano particles.

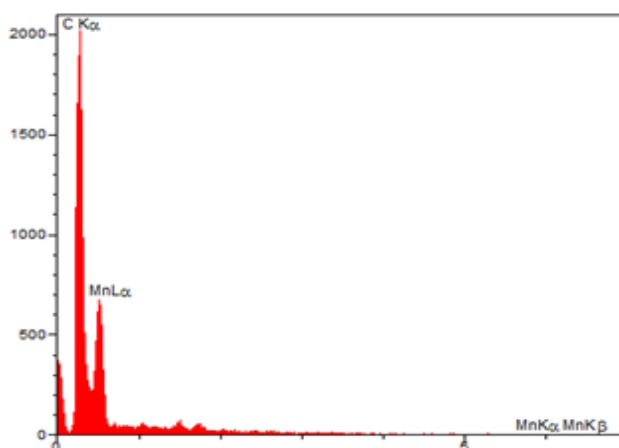


Figure-8.
Elemental composition of Nanocomposite hydrogel.

3.7. XRD Analysis of nanocomposite hydrogels

Figure 9 (a) shows the XRD pattern of Nanocomposite hydrogels and Figure 9 (b) shows the XRD pattern of manganese oxide. The results of XRD analysis show that the adsorption of loaded manganese oxide in approximately one gram of hydrogel is 0.05g, which is about 5% by weight, and TGA analysis shows the same result.

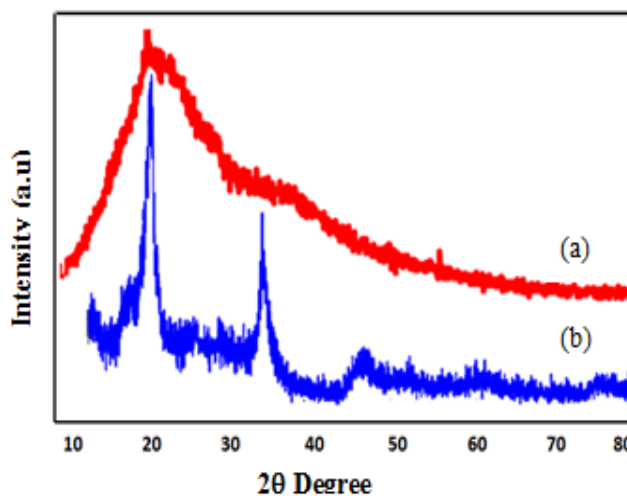


Figure-9.
XRD analysis of absorption manganese oxide.

3.8. Effect of temperature in the oxidation

Oxidation of benzyl alcohol by manganese oxide catalyst at different temperatures was studied for 24 hours. The results are presented in Table 1. As can be seen, the benzyl alcohol oxidation reaction efficiency increased at 80 °C

compared to 25, 40, and 60 °C. The best efficiency of 79% was obtained when manganese oxide nanoparticles were used as a catalyst at 80 °C.

Table-1.

The effect of temperature on the oxidation reaction of benzyl alcohol.

No	Temperature (C°)	Benz aldehyde (%)	Benzoic acid (%)	Others
1	25	-	-	-
2	40	9	-	-
3	60	18	-	-
4	80	79	-	-
5	100	42	26	-

3.9. Effect of amount nanocomposite hydrogel

To study the effect of the amount of catalyst, the oxidation reaction of benzyl alcohol with different amounts of catalyst at 80 °C for 24 hours was performed as shown in [Table 2](#).

Table-2.

Oxidation of benzyl alcohol in acetonitrile solvent at 80 °C for 24 hours.

No	The amount of catalyst (g)	Product (%)
1	0.05	7
2	0.2	31
3	0.5	38
4	0.7	42
5	1	79
6	1.5	76

The results of [Table 2](#) show that by increasing the amount of catalyst from 0.05 to 1g, the reaction efficiency increases and after this amount, the reaction efficiency does not change much.

3.10. Effect of reaction time

Shows the effect of reaction time on the oxidation of benzyl alcohol in the presence of Nanocomposite hydrogels.

As seen in [Table 3](#), the reaction time increases from 12 to 24 hours, the efficiency gradually increases from 37% to 79%, after which time the reaction efficiency remains virtually unchanged.

Table-3.

Investigation of the effect of reaction time on acetonitrile solvent and temperature of 80°C.

No	Time of reaction (h)	Product (%)
1	12	37
2	16	55
3	20	70
4	24	79
5	48	79

As the reaction time increases from 12 to 24 hours, the efficiency gradually increases from 37% to 79%, after which time the reaction efficiency remains virtually unchanged.

3.11. Reuse of nanocomposite hydrogels

Catalyst recovery is one of the important factors in evaluating synthesized catalysts. In this experiment, the catalyst was isolated after the reaction and then used in the next reaction. Reuse of hydrogels containing nanoparticles of manganese oxide in the benzyl alcohol oxidation reaction is shown in [Figure 10](#).

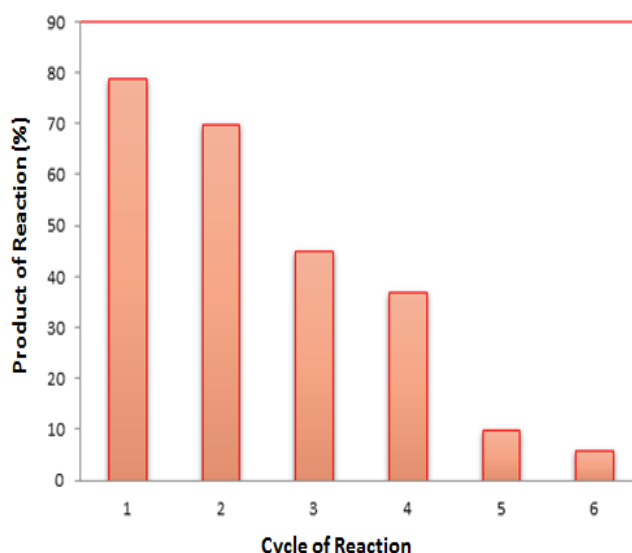


Figure-10. Reuse of Nanocomposite hydrogels catalysts containing manganese oxide nanoparticles in the benzyl alcohol oxidation reaction.

3.12. Effect of solvent on oxidation reactions

In this experiment, the oxidation reaction of benzyl alcohol in different solvents was performed and the result is shown in Figure 11. It is observed that oxidation in acetonitrile solvent shows higher efficiency. The use of toxic and flammable solvents is one of the most important issues in the chemical industry. The introduction of these solvents into the environment creates harmful pollutants and naturally will cost a lot of money to control them. Problems due to the separation of solvents from products complete recycling of solvents and environmental hazards are among the factors that have drawn the attention of researchers to the use of green solvents [5].

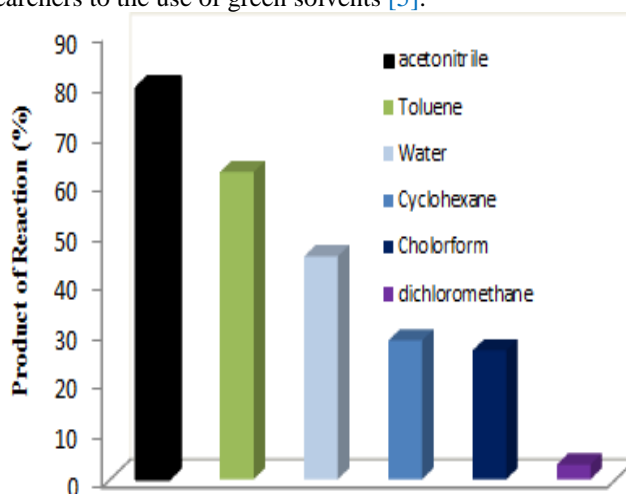


Figure-11. Oxidation of benzyl alcohol in various solutions near the synthesized catalyst

3.13. Oxidation in the different conditions

Different conditions have been used for the oxidation of benzyl alcohol. These conditions are given in Table 4.

Table-4. Investigation of oxidation of benzyl alcohol in different conditions.

No	Temperature (°C)	Atmosphere	Time (h)	Product (%)
1	110	O ₂	15	70
2	110	Air	15	38
3	70	Argon	20	21
4	70	Air	20	9

The results of Table 4 show that the oxidation of benzyl alcohol in the presence of oxygen and different temperatures in which toluene is the solvent was performed at different times, the main reaction efficiency being performed during toluene at 110 °C It is 70%. However, the reaction of benzyl alcohol in the absence of oxygen in the presence of air is less

efficient in the mentioned conditions (its main efficiency is 38%). So, it turned out that oxygen plays a major role in the oxidation of benzyl alcohol.

4. Conclusions

In this study, hydrogels containing manganese oxide nanoparticles were used to oxidize alcohols. The data showed that the active nanoparticles of manganese oxide are well formed in the hydrogel bed and the particle size is less than 80 nm. The efficiency of oxidation reactions was determined by gas chromatography (GC). It was also observed that the benzaldehyde product is the major reaction product, and this product is selectively formed. The selectivity of the benzyl alcohol oxidation reaction in water was 50%. The maximum efficiency of benzyl alcohol oxidation was 79%. Solvent results show that acetonitrile is more efficient than other solvents.

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