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SYNTHESIS AND IDENTIFICATION OF FE3O4/CLINOPTILOLITE MAGNETIC NANOCOMPOSITE

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ABSTRACT

In the present work, magnetic zeolitehave been synthesized by insitu method using combination of iron oxide nanoparticlesFe_3O_4 and clinoptilolite. Fe_3O_4nanoparticleshave been synthesized electrochemically and then clinoptilolitewas added to solution. The Fe_3O_4 nanoparticles synthesized at the temperature of 90° C with applying the potential of 8V for 1800 seconds. The synthesized nanocomposite characterized by IR spectra,scanning electron microscopy (SEM) and XRD methods.Results shows that nanoparticles have uniform spherical shape with an average size of 40 nm.The clinoptilolite and Fe_3O_4 crystallinity were well preserved and showed that the crystallinity of the modified clinoptilolite was slightly reduced, However, the crystal structure is maintained.

Keywords: Nanocomposite, Nanoparticles, Magnetic materials, Clinoptilolite, Electrochemical synthesis.

Contribution/ Originality

In the present study the Electrochemical synthesis has been used for the synthesis of iron oxide nanoparticles The advantage of this method compared to other method is considerably high flexibility under conventional conditions. and for the first time, Fe_3O_4 magnetic nanoparticles were loaded on the surface of natural clinoptilolite via a simple and one step approach. and Use of sorbents for the extraction of organic compounds from environmental samples

1. INTRODUCTION

In the resent years, magnetic adsorbents are widely used for removing the organic contaminants [1], heavy metals [2] and biomolecules [3]. Among the magnetic nanoparticles, iron oxide nanoparticles have been greatly interested because of their unique properties. Co-precipitation [4] and electrochemical [5] synthesis methods are the most important methods formagnetic nanoparticles

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synthesize.To prevent unwanted oxidation and aggregation of particles, however, some compounds are used to protect and coat thesenanoparticles.The most commonlyusedcompound is silica, carbon, various polymers, and zeolites [6, 7].

Zeolites constitute a large family of alumina silicate minerals, including natural and synthetic types [8]. One of the most important natural zeolites isclinoptilolite,which is widely used to adsorb heavy cations and gases, remove radioactive materials from contaminated soils and ammonium from urban wastewater [9, 10]. Use of magnetic adsorbents makes easier separation processing and there is no need for filtration that are common like centrifuging [11].

A common method to synthesize magnetic zeolites is reflux process, however, with disadvantages, in cluding prolonged time and large volumes of organic solvents. The purpose of the present work is preparation of clinoptilolite/iron oxide magnetic nanocomposite. In this study, iron oxide nanoparticles was synthesized by electrochemical method and clinoptilolite is added to the electrochemical cell during the synthesis of iron oxide nanoparticles, therefore nanocomposite can be synthesized in a single-step process. The major advantages of this method are its simplicity, low cost, and no need fororganic solvents

2. EXPERIMENT

The used materials are tetra-methyl ammonium chloride (Merck-Germany), pure iron (Local Market) electrode, clinoptilolite zeolite (NeginPowder-Iran), deionized water and laboratory power supply DC (PS-302D- Zhaoxin- China).

Two pieces the pure iron as anode and cathode electrodeused for synthesis of Fe_3O_4 nanoparticles with the surface ratio of 1:4 respectively.0.04 M tetra-methyl ammonium chloride solution used as an electrolyte.

2.1. Synthesis

The electrodes surface were cleaned completely by ethanol and got free of any contamination. Also for stabilize the temperature the chemical cell was placed in a water bath. For preparation of magnetic nanoparticles with favourable size and shape, some of parameters such as temperature and voltage have been optimized. First, nanoparticles were synthesized under control voltages 8,10 and 15 V by applying an external magnetic field under 60, 70, 80 and 90°C temperatures for 1800s. After analysis of samples the optimum conditions were selected as 8V and 90°C.then, 5g clinoptilolite was added to the electrochemical cell for 4 hours.After the procedures, remaining black precipitate collected and washed with deionized water and methanol. Finally, it was dried in vacuum oven at 65°C.

3. RESULTS AND DISCUSSION

In order to study the formation of nanocomposite, the obtained powder was analysed with FT-IR spectroscopy in the range of 400 to 4000cm^{-1}.Fig. 1presents the FT-IRspectra of Fe_3O_4 nanoparticles, clinoptilolite and magnetic zeolite. As can be seen in Fig1-a the characteristic absorption bands of Fe-O are observed at 442-580cm^{-1} [5]. In the FTIR spectrum of clinoptilolite

zeolite (Fig1-b), the asymmetric stretch at 1250 and symmetric stretch at 750 cm^{-1}andbands at 490 $cm^{-1}$are related to the vibration of Si – O or Al – O bond [12]. The peaks were proven the existence of O-H in3625and1630cm^{-1}related to water [13]. The FTIR spectrum of magnetic zeolite does not significantly differ from the clinoptilolite in the spectral regions 400 to 4000cm^{-1}. Also in comparison with Fe_3O_4, FTIR spectrum of magnetic zeolite in the range of 442-580cm^{-1} shows vibration bands that related to Fe-O functional groups.This fact indicates that Fe_3O_4 structure has not changed in this reaction.

The X-Ray diffraction (XRD) patterns of magnetic zeolite and Fe_3O_4 nano particles are given in Fig.2. The reference pattern of JCPDS no 39-.1383 was selected forclinoptilolite.The XRD pattern of clinoptilolite also showed amounts of anorthite (7%) and cristobalite (14%) phasesasimpurities [13]. The clinoptilolite/Fe_3O_4 pattern shows three crystalline peaks at 2θ° of 35.36°, 59.40° and 61.78° related to the 311, 511 and 440 crystallographic planes of the face-centered cubic (FCC) iron oxide Nano crystals [14]. Fig.3 presents the SEM images of Fe_3O_4 nanoparticles (Fig3a-b), clinoptilolite zeolite (Fig.3c), and magnetic zeolite (Fig3.d). Fig.3a shows the Fe_3O_4 nanoparticlesthat synthesized at 45°C whereas Fig.3 b shows theFe_3O_4nanoparticles that produced at the temperature of 90°C. As can be seen by increasing of temperature, the average size of particles was decreased from 80 nm to 30 nm [14, 15]. Fig.3c presents the clinoptilolite zeolite. Zeolite powder with average size less than 50nm can be recognizedas separated particles or in the form of larger agglomerates [13]. As shown in Fig. 3d, themagnetic zeolite has uniform spherical particles with the average size of 40 nm .Scanning electron microscopic (SEM) images showed that the Fe_3O_4 nanoparticles have spherical shape with average size less than 100 nm.

4. CONCLUSION

In this study, iron oxide nanoparticles were prepared by electrochemical oxidation of metallic iron. For preparation of magnetic nanoparticles with favourable size and shape, the effect of temperature and voltage were optimized. In the potential 8V and temperature 90°C,the prepared nanocomposite has a particle size of 30- 40 nm. The obtained results by FT-IR spectroscopy and scanning electron microscopy (SEM), confirmed the formation of Fe_3O_4 /clinoptilolite. The X-ray diffraction pattern proved that the structure clinoptilolite and Fe_3O_4 are not changed by the modification process.

5. ACKNOWLEDGEMENTS

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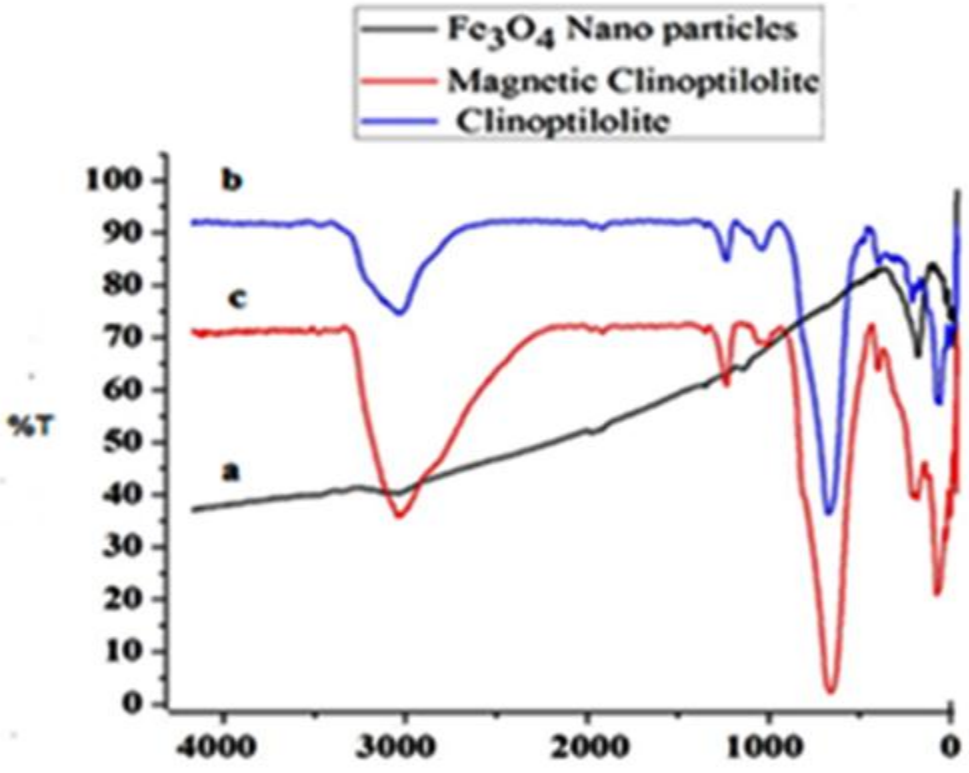

Fig-1. FTIR spectra of: (a) Fe_3O_4 nanoparticles, (b) clinoptilolite,(c)magneticclinoptilolite

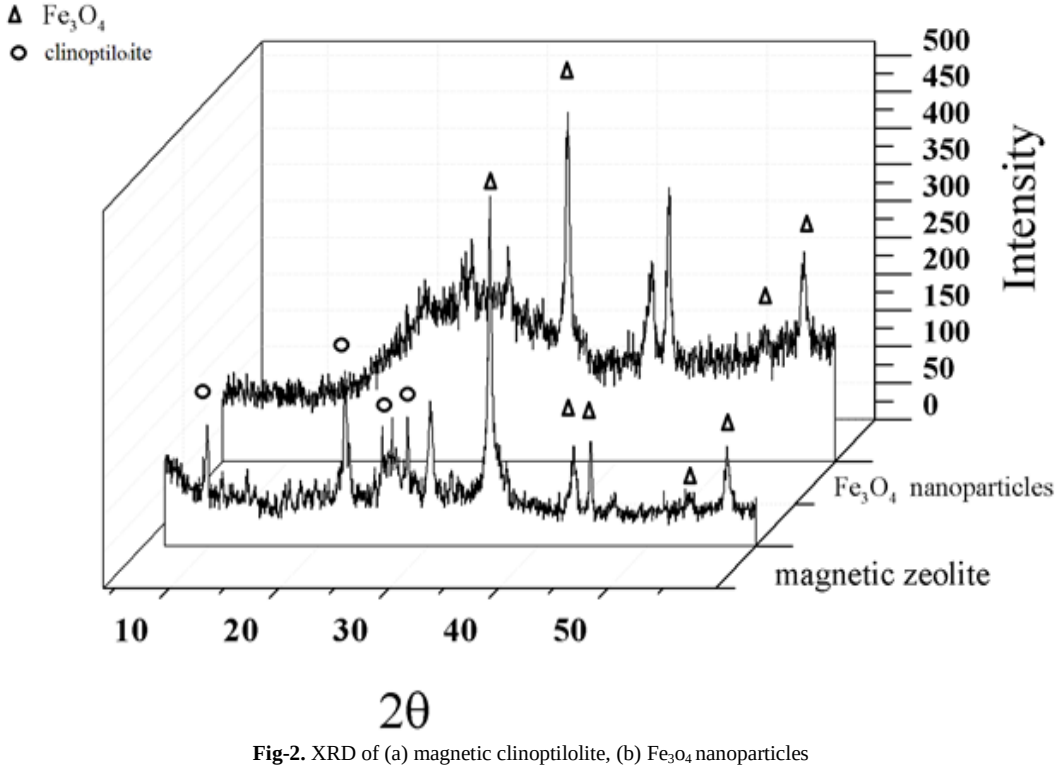

Fig-2. XRD of (a) magnetic clinoptilolite, (b) Fe_3O_4 nanoparticles

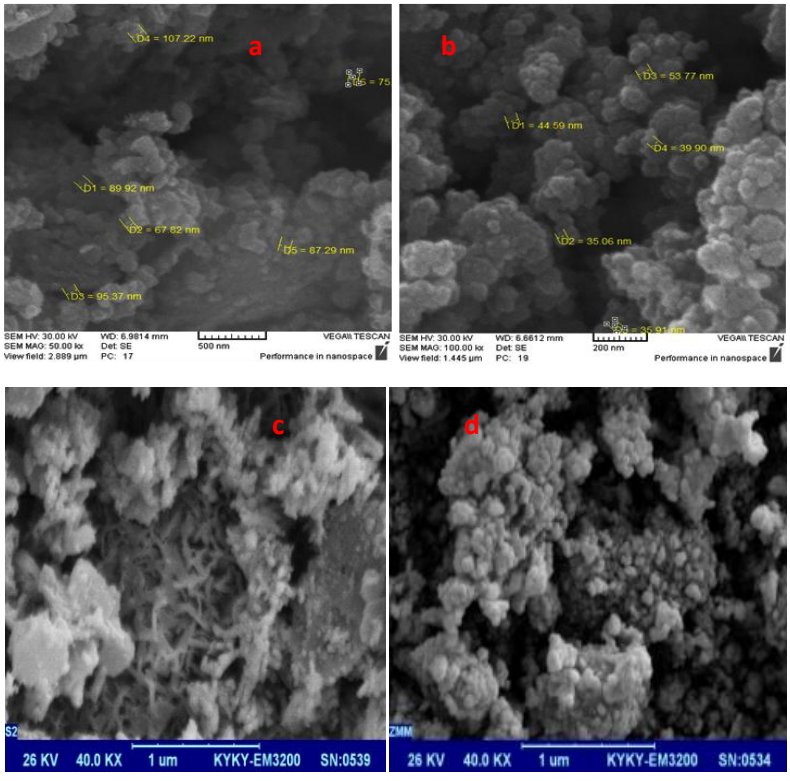

Fig-3. SEM images: Fe_3O_4 nanoparticles have been synthesizedat 45 ° and90 ° C(a-b), clinoptilolite (c) Fe_3O_4/clinoptilolite nanoparticles (d*)*