New magnetic zeolite-based nanocomposites for photocatalysis part 1: synthesis and characterisation.

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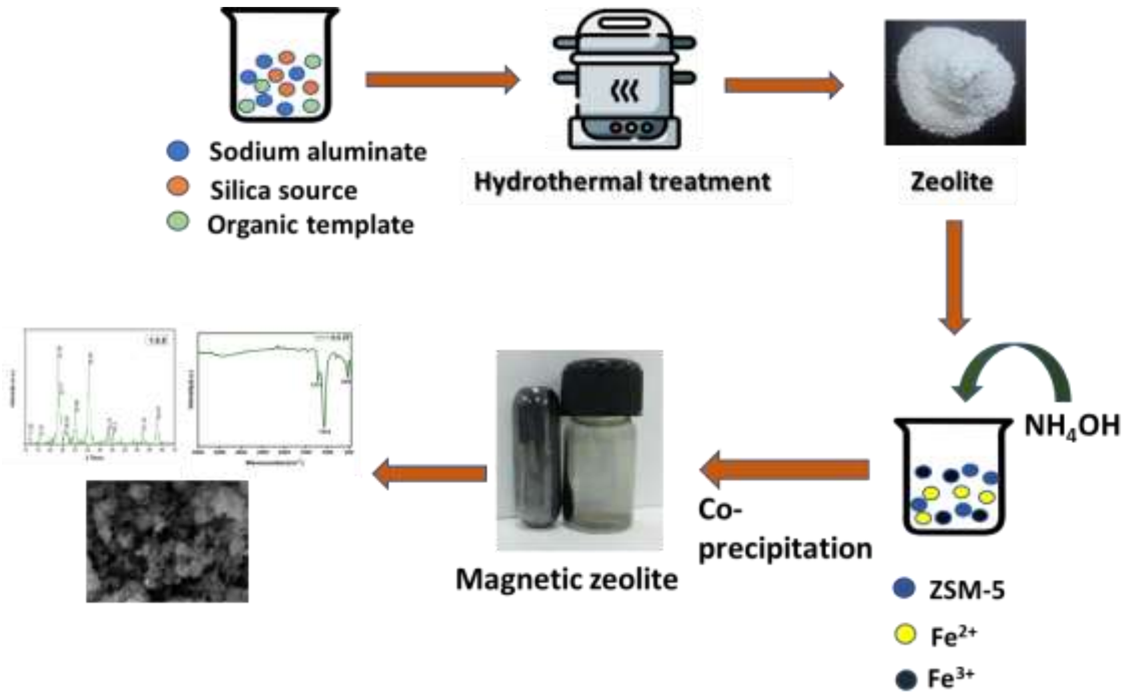
Abstract

Photocatalysis is considered to be the most efficient treatment as compared to the other methods and is suitable for highly cost-sensitivity and energy-restrictive applications. In this research, ZSM-5 and iron oxide magnetic nanoparticles were synthesised, followed by reporting their applications. We are going to publish it into related communications. In part 1, we synthesized ZSM-5 by hydrothermal method and magnetic nanoparticles of Fe_3O_4 using chemical co-precipitation. Then, the versatile ZSM-5/Fe_3O_4 magnetic nanocomposite was synthesised by in situ method and tested for its efficacy to degrade methylene blue using photocatalysis. This paper specifically reports the varying ratios of ZSM-5 and Fe_3O_4 in the nanocomposites that are 1:1, 1:2 and 1:0.5 and as the concentration of Fe_3O_4 varied, the properties of the nanocomposites changed as well. The physical and chemical properties of the three nanocomposites were studied thoroughly. Further, these nanocomposites were characterized by Field emission scanning electron microscope (FESEM), X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR).

In addition to this, in a second communication part 2, a comparison study was conducted between the three nanocomposites to study their photocatalytic efficiency and magnetic behaviour to treat wastewater. ZSM-5 is an excellent adsorbent but it is hard to separate it after application. Fe_3O_4 has less adsorption capacity but it is magnetic in nature so, it is easy to separate it after application. Hence, combining both will complement each other's properties and produce an enhanced magnetic zeolite-based nanocomposite. ZSM-5 alone has 77% and Fe3O4 has only 31% adsorption capacity. As the concentration of Fe_3O_4 increases, the photocatalytic degradation increases but adsorption decreases because of the blockage of the adsorption sites of the ZSM-5. Since the materials are magnetic in nature, therefore, after photocatalytic treatment, it can be easily recovered with the help of external magnets. Our approach provides an efficient and comparable synthesis process having photocatalytic applications in treating wastewater.



Keywords

Zeolite, Iron Oxide, Magnetic Nanoparticles MNPs, Methylene Blue MB dye, Adsorption, Photocatalysis

1. Introduction

Zeolites low-cost inorganic aluminosilicate adsorbent material. Zeolites have a high surface area, a negatively charged backbone and shape selectivity characteristics that makes them very demanding for the removal of heavy metals and other toxic chemicals.

Zeolites are three-dimensional porous aluminosilicate materials that consist of very fine intracrystalline cage structures. These cage structures have a negatively charged backbone that can be very useful for the adsorption and ion exchange processes. Synthesising zeolite is an active field because of its wider range of applications like adsorption, catalysis, separation etc. Various approaches are used for the synthesis of zeolite such as hydrothermal, sol-gel, Alkali-fusion, etc. The most common method for the synthesis of zeolite is a hydrothermal approach. The synthetic route consists of two steps, (i) batch preparation, and (ii) crystallization. The batch preparation is done based on the batch composition by stirring the mixture of silica, alumina and sodium at a fixed temperature to get a homogenous mixture. Followed by batch preparation, crystallization is done by a hydrothermal treatment which is done by heating the reaction mass in a Teflon-lined autoclave at a temperature higher than the boiling point of water. Different zeolites have different porosity that gives them the characteristics of size exclusion. However, the difficulties in the filtration of zeolites from an aqueous solution and the highpressure drop-in zeolite fix-bed column led the scientists to make various composites of zeolites due to their easy recyclability, high absorptivity and physiochemical stability [1].

Iron oxide magnetic nanoparticles have superparamagnetic properties and been used with zeolites due to easy separation and recovery of zeolite material by magnetic field after the environmental application. This magnetic nanoparticle consist of ferromagnetic materials exhibits superparamagnetic properties when the particle size is less than 20nm. Various mechanochemical methods such as laser ablation arc discharge, electrodeposition, pyrolysis and chemical methods such as sol-gel, reverse micelle, hydrothermal, co-precipitation [3]. Iron oxide MNPs are prone to oxidation and gets easily oxidized at ambient atmosphere. In this study, we have synthesized iron oxide MNPs (Fe_3O_4) via the co-precipitation method as it is an easy, facile, time-saving, high-yield method. To make magnetic zeolites, first, the dispersion of zeolite in water is made, followed by the common synthetic process of Fe_3O_4 on the surface of zeolite which introduces the magnetic behaviour in the zeolitic framework.

Magnetic zeolite- based nanocomposite will enhance the photocatalytic and separation properties and contributes in overcoming the limitations. Moreover, zeolites generally adsorb the contaminants and, in most cases, it is physisorption. While, in this work zeolite is doped with Fe3O4, which degrades the pollutants in presence of light.

2. Experimental Section

2.1 Materials

Colloidal silica (commercial grade, 30%), Tetra propyl ammonium hydroxide (TPAOH) (commercial grade, 40%), sodium aluminate (Sigma Aldrich, 56.15 %), Al203, 43.9% Na2O), Methanol (Finar, 99.8%), and acetone (Finar, 99.5%) Iron (III)chloride hexahydrate (reagent grade>98%, chunks, Sigma-Aldrich), Iron (II)chloride tetrahydrate (reagent plus 98%, Sigma-Aldrich), Ammonia solution 0.91 d (extra pure, Finar)

2.2 Preparation of ZSM-5

Traditional hydrothermal method was deployed with modification for the synthesis of ZSM-5. First sodium aluminate was dissolved in deionized water and then colloidal silica and tetra propyl ammonium hydroxide (TPAOH) were added dropwise to the solution as per the batch composition 30 SiO_2: Al_2O_3: 1.35 Na_2O: 6.54 TPAOH: 900 H_2O. The reaction mixture was stirred for 24 hours at 60^oC to produce a homogeneous mixture. The gel synthesized was then transferred to a Teflon-lined autoclave and treated at 160^oC for 48 hours hydrothermally. After 48 hours the obtained product was vacuum filtered, washed and oven dried at 120^oC.

2.3 Preparation of Fe_3O_4 MNPs

The magnetic nanoparticles were synthesised by using chemical co-precipitation method. According to this method, $FeCl_2.4H_2O$ (3.1736 gm) and $FeCl_3$.$6H_2O$ (7.5079gm) was dissolved in 320 ml distilled water and sonicated for 5 minutes. Then, the mixed solution was stirred under nitrogen atmosphere at 85 ºC for 1 hour. After an hour, 40 ml of ammonia was then added into the mixture rapidly with continuous stirring, maintaining the nitrogen atmosphere. Again, the mixture was stirred under nitrogen atmosphere for another hour. Then cooled down to room temperature. After cooling it down to room temperature, the precipitated particles were centrifuged and washed properly several times with distilled water. At last, the product was dried at 70 ºC for 4 hours.

2.4 Preparation of ZSM-5/Fe_3O_4 Composites

Three nanocomposites were prepared having different weight ratios of Fe_3O_4 (150, 300 and 600 mg with respect to 300 mg ZSM-5 zeolite). The varying ratios of ZSM-5 and Fe_3O_4 in these nanocomposites were 1:0.5,1:1 and 1:2. Calculated amount of $FeCl_2.4H_2O$ (130, 260 and 510mg) and $FeCl_3.6H_2O$ (350, 702 and 1400mg) were dissolved in distilled water. 300 mg of ZSM-5 is dispersed in 3 ml of distilled water in a separate beaker by sonication and was added into the above reaction mixture. The workup procedure was the same as described in the previous section. The obtained nanocomposites were labelled as 0.5ZF, 1ZF and 2ZF indicating constant concentration of ZSM-5 and varying 0.5,1 and 2 as the concentration of Fe3O4, respectively.

2.5 Characterization Techniques

All the synthesized materials were characterized via FESEM, XRD and FT-IR techniques. FESEM to see the morphology, FT-IR to find the molecular structure and XRD to know the crystallinity. FE-SEM was performed using Zeiss Ultra 55 instruments. Non-conductive samples were coated with gold layer using LEICA EM ACE200 to make samples conductive. XRD data was recorded using PANalytical X^+pert Pro diffractometer at 30 Ma and 40 kV utilising Cu Kα radiation (λ=1.53Å) in 5 to 50 degrees 2θ range with step size of 1ºper minute with goniometer speed. Perkin Elmer spectrum with two FT-IR spectrometer was used to record the FTIR spectra in the region of 4000-400 cm^{-1}. 10 scans per minute was performed to improve signal to noise ratio. UV/ VIS Spectrometer was used to obtain the absorption spectra of samples the 200-800 nm range using LABINDIA analytical model UV 3000+.

3. Result and Discussion

3.1 FT-IR Analysis

Fig 2 shows the FTIR spectra of ZSM-5, Fe_3O_4, 0.5 ZF, 1 ZF and 2 ZF zeolite-based magnetic nanocomposites. The characteristic peak of ZSM-5 at 1080cm-1 represents -Si-O asymmetric stretching. Peaks at 790 Cm^{-1} and 537 Cm^{-1} attributed to the vibrations of -Al-O. The characteristic peak of Fe_3O_4 is observed at 543 Cm^{-1} which represent the Fe-O asymmetric stretching. All the characteristic peaks of ZSM-5 and Iron oxide MNPs are present in all the composite materials.

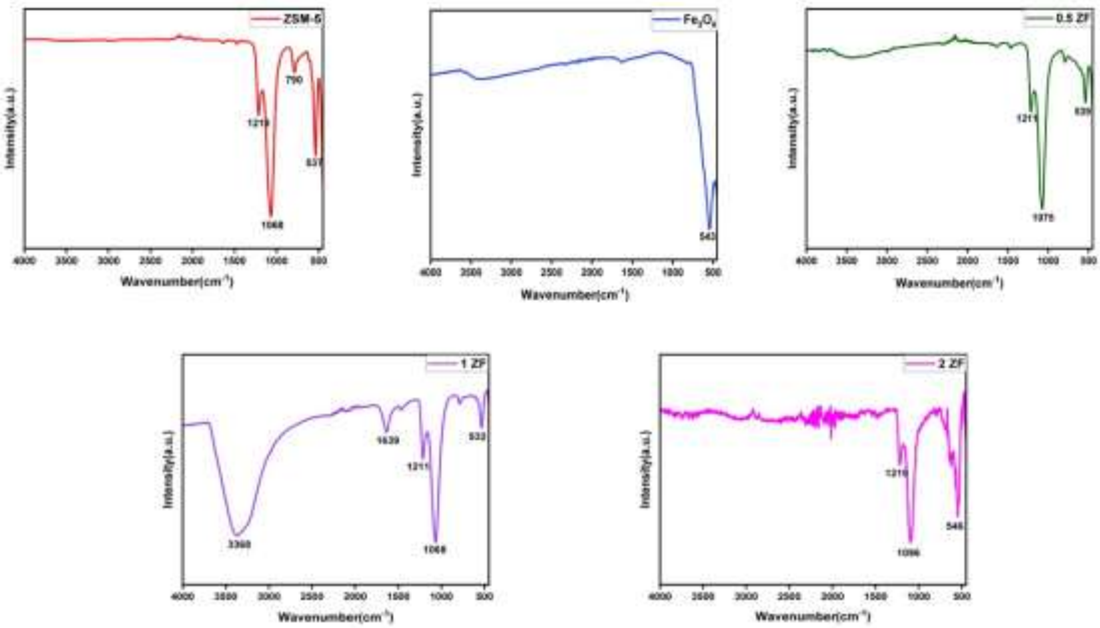


Figure 1: FT-IR Spectrum of (A) ZSM-5 (B) Fe_3O_4 (C) 0.5ZF (D) 1ZF (E) 2ZF

3.2 XRD Analysis

Fig 3 shows the X-Ray diffraction data of ZSM-5, Fe_3O_4 and 0.1 ZF nanocomposite. X-Ray diffraction data of ZSM-5 shown characteristic sharp peaks at 2Ɵ = 13.94^o (130 planes), 14.83^o (031 planes), 15.94^o (022 planes), 17.77^o (400 planes), 20.83^o (-113 planes), 23.11^o (051 planes), 23.88^0 (-303 planes), 24.44^o (-133 planes), 26.16^o (441 planes), 29.27^0 (352 planes), 29.74^o (360 planes), 36.11^o (470 planes), 45.38^o (941 planes).

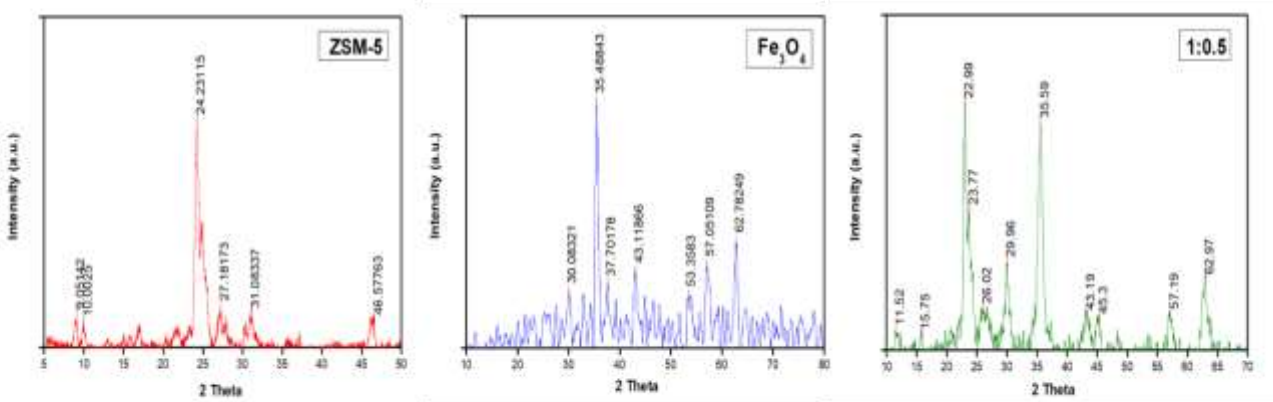


Figure 2: XRD patterns of ZSM-5, Fe_3O_4 and 0.5ZF nanocomposite

The XRD diffraction pattern of Fe_3O_4 has shown characteristic peaks at 30.08^o (220 planes), 35.48^o (311 planes), 43.11^o (400 planes), 53.35^o (422 planes), 57.05^o (511 planes) and 62.78^o (440 planes). The XRD data of composite materials consist all of the characteristic sharp peaks of ZSM-5 and iron oxide MNPs which indicates the formation of zeolite-based magnetic nanocomposites.

3.3 FE-SEM Analysis

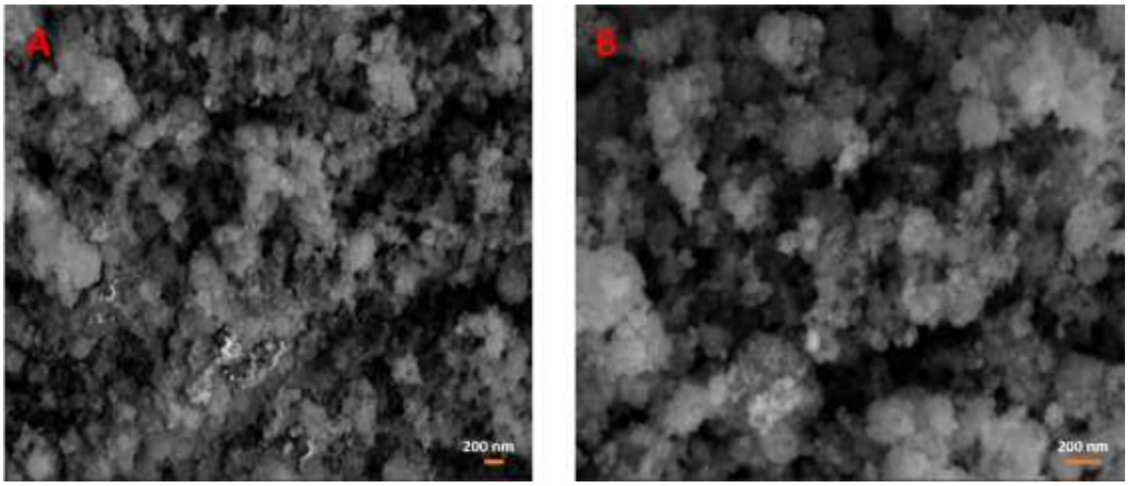


Figure 3: SEM images of 1:0.5 ZF nanocomposite (A) at 50K magnification (B) at 100K magnification.

Fig 4 shows the SEM images of 0.5ZF composite material. It suggests the uniform adhesion of Fe3O4 MNPs on the spherical surface of the zeolite. The MNPs got agglomerated on some of the ZSM-5 pore apertures that decreases its adsorption capabilities.

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