SYNTHESIS AND CHARACTERIZATION OF ZEOLITE-GOETHITE NANOCOMPOSITE

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ABSTRACT
In recent years, nanocomposite materials have received much interest in nanotechnology. This new trend in nanotechnology is aimed at producing materials of unique properties. In view of this, zeolite-goethite nanocomposite was synthesized to reinforce zeolite properties. Zeolite was synthesized hydrothermally from sodium aluminate, sodium silicate and sodium hydroxide at 100 ^oC for 24 h. The composite was synthesized using in-situ method by adding aqueous solution of the synthesized zeolite during the synthesis of goethite. The structure, morphology and surface area of the zeolite and the composite were investigated using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Brunnauer Emmet Teller (BET) surface area analyzer respectively. The FTIR spectra and SEM micrographs confirmed the formation of zeolite–goethite composite with the surface area increase from 163.491 m^2/g for zeolite to 304.839 m^2/g for zeolite-goethite nanocomposite. It is evident that properties of zeolite can be improved upon by compositing with other materials like goethite. It can also be employed as an adsorbent for different environmental applications as revealed by the surface area.

Keywords: *Zeolite; Zeolite-goethite; Nanocomposite; Characterization; Hydrothermal method*

INTRODUCTION

Nanocomposite is referred to as a multiphase solid material which one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material (Tyagi and Tyagi, 2014). This new nanotechnological product has attracted considerable attention recently because of their distinctive physical and chemical properties. Nanocomposites are high performance materials which exhibit unusual property combinations and unique design possibilities (Carmago *et al*., 2009).

The hybrid composites have characteristics such as flexibility, easy processabilty; lightness strength, dimensional stability, chemical inertness, and thermal stability are bestowed on them from their components. Application volume for composite materials have grown steadily and have a large appreciation in the removal of toxic ion from water (Montes-Hernandez et al., 2013; Li *et al*., 2011), preparation of electrochemical sensor, immunosensor for pesticides detection, membrane for alkaline fuel cells, catalyst, energy, sensors, medicine, construction, bio-applications, food and water treatments (Taher *et al*; 2011; Hossein *et.al*., 2013).

Zeolites are microporous crystalline hydrated aluminosilicate materials consisting of SiO_4 and AlO_4 tetrahedra which are connected by oxygen atom (Rocha *et al*., 1998). Their framework structure contains interconnection of channels that are filled with cations usually from group IA or IIA which can be exchanged with other cations (Olad *et al*., 2011). These physico-chemical properties along side with others like crystallinity, thermal stability, well-defined cage structure of molecular size give natural and synthesized zeolites various application possibilities in different technological processes (Doula, 2007, Shyaa *et. al*., 2015). Zeolites have been widely used in catalysis, adsorption and ion exchange, it is becoming increasingly important in several environmental applications such as water purification, particularly for the removal of ammonia, heavy metals, radioactive species and organic substances (Bogdanov *et. al*., 2009).

Iron, its compounds and iron oxide nanoparticles are of considerable interest because of their biological and chemical properties. Iron oxides are widespread in the earth crust and play an important role in nature. Recently they are widely utilized in nanocomposite for various applications such as magnetic storage, medicine, chemical industries and water purification (Mohapatra *et. al.,* 2010). Goethite is one of the most common iron oxy-hydroxides in natural systems, they are commonly found in all types of soils throughout the world. It is frequently formed during weathering of other iron bearing minerals and is often the cause of the yellowish-brown colour of many soils. Goethite can occur naturally and can be synthesized (Hua *et al*., 2012).

In order to improve the capacity of zeolite they are composited or modified with other substance. Modification of zeolites can be realized using several methods, such as acid or base treatment, ion exchange and surfactant functionalization (Kugbe *et al*., 2008; Mihajlovic *et al*., 2014, Doula, 2007). Recently, zeolites were modified by oxides or hydroxides of metals, such as Al, Fe and Mn (Barquist, 2009). In this work, we synthesized and characterized goethite nanoparticle on the surface of zeolite and produced zeolite/goethite nanocomposite directly using *in-situ* method under a very basic condition.

MATERIALS AND METHODS

All chemicals used for the work were of analytical grade. The sodium hydroxide, sodium metasilicate, sodium aluminate and ferric nitrate for the synthesis were purchase from Sigma-Aldrich.

Synthesis of Zeolite

Zeolite was prepared according to the procedure reported by Hashemian *et al* (2013) from sodium metasilicate and sodium aluminate in the presence of sodium hydroxide. 40 ml of 0.225 M sodium hydroxide was added to each of 8.25 g of sodium aluminate and 15.48 g of sodium metasilicate in two separate containers. These mixtures were stirred for 30 min for the solution to become homogenous after which they were simultaneously transferred into a Teflon container, resulting in the formation of a creamy gel. The Teflon container was sealed in an autoclave (hydrothermal bomb) and heated at 100 °C for 24 h. After cooling, the precipitate was dialyzed, filtered using a vaccum filter and dried in the oven at 100 °C.

Synthesis of Zeolite-Goethite Nanocomposite

The zeolite-goethite nanocomposite was prepared by the procedure reported by (Mihajlovic et al 2014, Kragovica *et al.,* 2012). A suspension was made by mixing 20.0 g of the synthesized zeolite in 100 cm^3 of freshly prepared 1M $Fe(NO_3)_3.9H_2O$ solution in a polyethylene flask. The KOH solution was added rapidly made up to 180 cm^3 under stirring. The suspension was diluted with deionized water to 2000 cm^3 and held in a closed polyethylene flask at 70 °C for 60 h. Finally, the obtained precipitate was dialyzed to remove the anions and then dried at 105 °C.

Characterization Methods and Instruments

Instrumental characterization techniques such as Fourier transform infrared (FT-IR) spectroscopy, Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) (CPI diffractometer model) and the Brunnauer Emmet Teller (BET). GX - FT-IR spectrophotometer (Model) were used for identification of surface functional groups, the SEM (SCOTech Mel-30000) was applied to observe morphology while the surface area was examined using BET. XRD pattern was used to observe the crystallinity of the sample. Other physicochemical properties like pH, colour, texture, bulk density and point of zero charge (pzc) were also observed. The point of zero charge (pzc) of the zeolite-goethite nanocomposite was determined by the batch equilibration technique (salt addition method) in which $NaNO_3$ solution of different ionic strengths: 0.1, 0.01, 0.001 mol/dm^3 were used as electrolyte solutions. The initial pH values (pH_i) of the electrolyte solution (25cm^3 of each in a series) of the predetermined concentration were adjusted by the addition of 0.1mol/dm^3 of HNO_3 or NaOH in the pH range of 3.5 to 10.5. Then 0.05 g of zeolite and the zeolite-goethite composite was added to each sample (At the ratio of solid: liquid=1:500). After 24 h of equilibration at room temperature under constant shaking, the suspension was filtered and then the pH of the filtrate was determined (pH_f). The initial pH versus the difference between the initial and finial pH values (ΔpH) was plotted. The pzc was taken as the point where $\Delta pH = 0$ (Mihajlovic *et al* 2014; Kragovica *et al.*, 2012).

RESULTS AND DISCUSSION

Physicochemical properties of zeolite and zeolite-goethite nanocomposite

The result of the physicochemical properties of zeolite and zeolite-goethite nanocomposite is presented in Table 1. The golden-brown colour of goethite imparts on the initial colour of the synthesized zeolite to make the colour of the composite brownish. The texture is however not affected by the introduction of goethite filler into the zeolite matrix. For the pH, the pH medium for the synthesis of both the zeolite and goethite is alkaline. This is likely to be based on the pH medium of the precursors.

Bulk density is a significant property which tends to correlate with other properties like porosity and cation exchange capacity. The bulk density of the zeolite-goethite nanocomposite gives higher value (0.6288g/cm^3) compared to zeolite alone (0.39778g/cm^3). This is an indication of the improvement shown on the nanocomposite material.

Point of zero charge (pzc) is the pH at which the surface of material has net neutral charge. From Figs. 1(a) and (b), the value obtained at the intersection of the pH_i with the $\Delta pH = 0$ gives the point of zero charge of the sample (Cardenas-Pena *et al*., 2012). As observed from Fig. 1(a), point of zero charge (pzc) of zeolite nanoparticle is 8.5 ± 1 while that of zeolite-goethite nanocomposite is found to be 9.5 ± 1. The higher pzc value obtained for zeolite-goethite nanocomposite is an indication of increase in alkalinity of its surface (Mihajlovic *et al.,* 2014) caused by introduction of goethite. Similar observation (i.e higher pzc value for Fe (III) modified zeolite, 7.5 ± 0.1 compared to natural zeolite, 6.8 ± 0.1) was also reported by Kragovic *et al* (2012).

Table1: Properties of zeolite and zeolite-goethite nanocomposite

Properties	Zeolite	Zeolite-goethite nanocomposite
Colour	Whitish	Brownish-red
Texture	Smooth	Coarse
pH	10.0	9.0
Bulk density	0.39778 g/cm^3	0.6288 g/cm^3
Point of zero charge	8.5 ± 1	9.5 ± 1

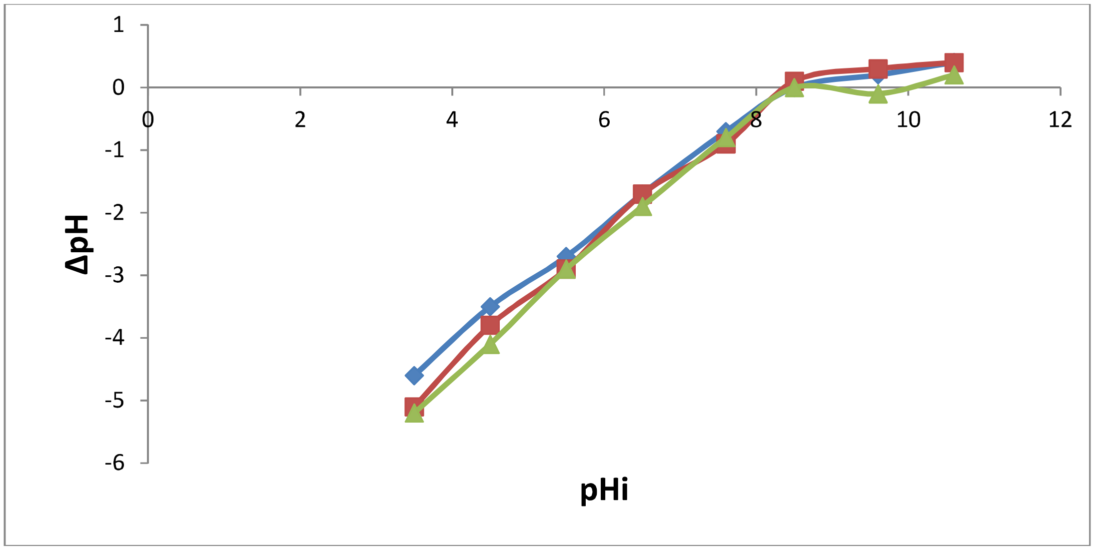

Fig.1a: Point of zero charge of zeolite-nanoparticles at 0.001, 0.01 and 0.1mol/dm^3

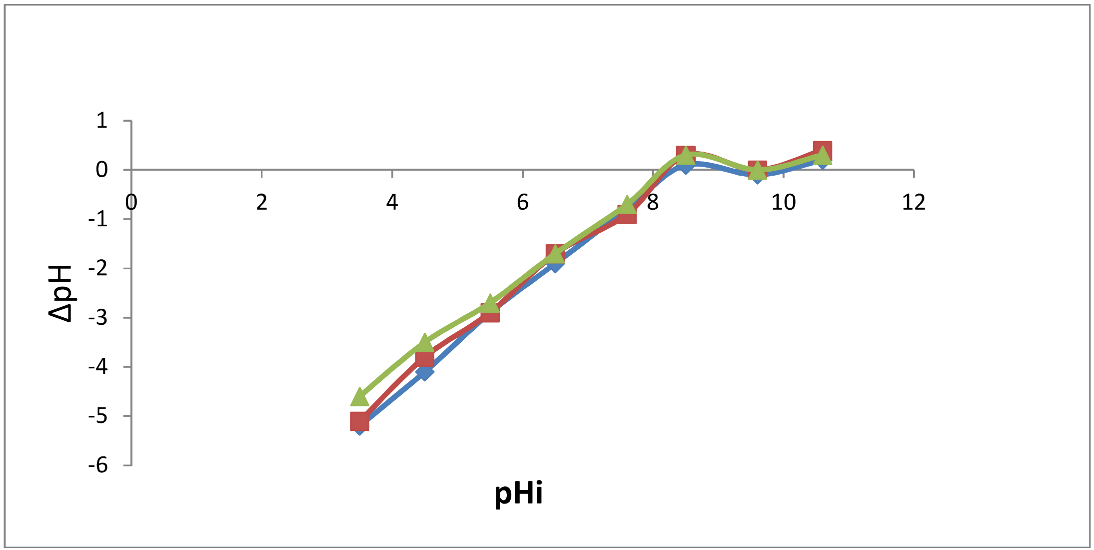

Fig.1b: Point of zero charge of zeolite-goethite nanocomposite at 0.001, 0.01 and 0.1mol/dm^3

Instrumental Characterization

Characterization of nanocomposite materials gives proper and better understanding of the materials towards its properties and applications.

FT-IR Spectroscopy

The FT-IR spectra of zeolite and zeolite-goethite nanocomposite are shown in Figures 2a and 2b respectively. The spectra show an absorption in the region of 1004 cm^{-1} in the zeolite and 997 cm^{-1} in the zeolite-goethite nanocomposite indicate terminal silanol groups [Si-O(Si) and Si-O(Al)] on the external surface of the samples (Huiping *et al*., 2014; Thuadaij and Nuntiya, 2012). Hossein *et al*., (2013) positioned that absorption in the regions of 900 to 1200 cm^{-1} resulted from stretching and bending modes of Si-O or Al-O in framework. The peak that is broad and strong at 3450 cm^{-1} in spectra (2a) for zeolite and 3423 cm^{-1} in spectral (2b) for the composite correspond to O-H stretching (Hossein *et al*., 2013; Ru´ız-Baltazar *et al*., 2015). The peak in the region of 1654 cm^{-1} and 1645 cm^{-1} corresponds to O-H bending vibration for zeolite and zeolite-goethite nanocomposite respectively. The three bands at 462, 559 and 694 cm^{-1} in 2(a) and 447, 555, and 640 cm^{-1} in 2(b) are associated with the asymmetric and symmetric stretching modes of internal tetrahedral (Kugbe *et al*., 2008, Khandanlou *et al*., 2015, Hossein *et al*., 2013; Thuadaij and Nutiya, 2012). Figure 2a and 2b also showed that zeolite and its composite spectra do not significantly differ from one another in the spectral regions 400 to 4000 cm^{-1}. This fact indicates that zeolite structure has not changed much in the reaction to form the composite.

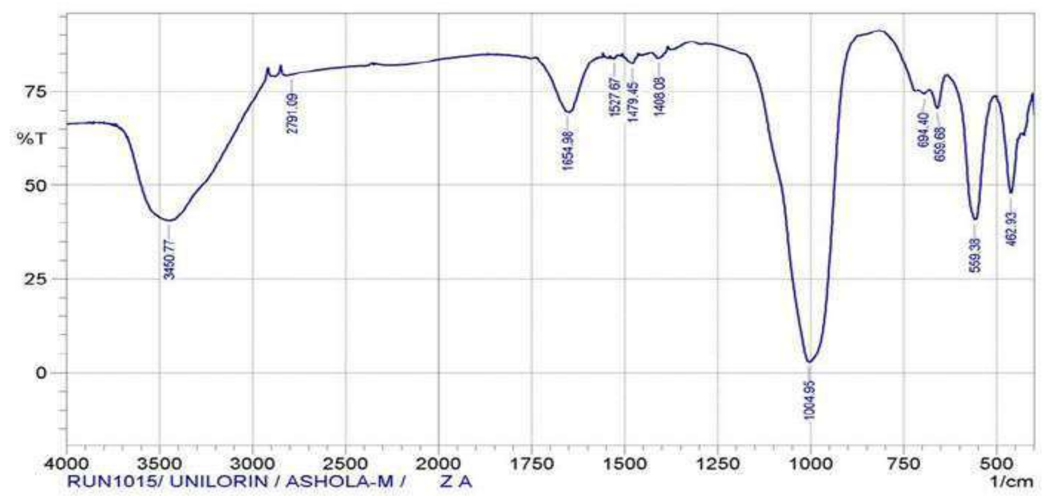

Fig 2a: The FTIR Spectrum of the zeolite nanoparticle

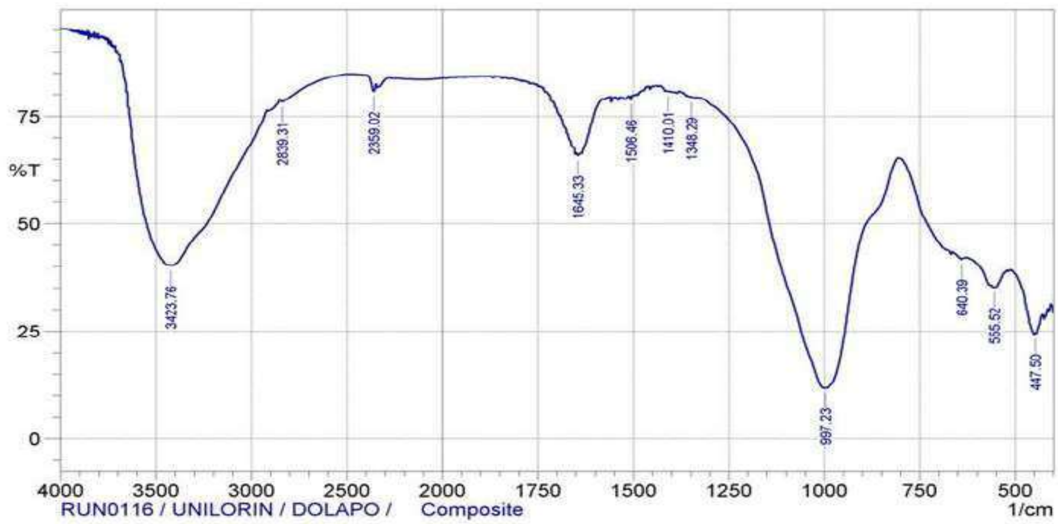

Fig 2b: The FTIR Spectrum of the zeolite-goethite nanocomposite

Scanning Electron Microscopy

The synthesized nanoparticle morphology was characterized by scanning electron microscope (SEM) using SCOTech Mel-30000 Scanning Electron Microscope. The SEM images for the surface morphology of both the zeolite and zeolite-goethite nanocomposites are shown in Figs. 3a and b. The surface morphology of zeolite, Fig. 3 (a) shows abundant small nearly spherical but scattered particles. While its goethite composite, Fig. 3 (b) indicates the deposition of goethite particles on the surface of zeolite and thereby forming an aggregate of particle with numerous pores. With this, it is evident that composite material of zeolite and goethite was successfully prepared (Kugbe *et al*., 2008)

Brunnauer Emmet Teller (BET)

The specific surface area (SSA_{BET}) of both materials, zeolite and zeolite-goethite nanocomposite was determined with low-temperature adsorption/desorption method based on the Brunnauer Emmet Teller theory multilayer adsorption. The result showed that zeolite-goethite nanocomposite has larger surface area, 304.838 m^2/g compared to that of zeolite, 163.491 m^2/g. Also from the t-plot micropore analysis, zeolite has smaller value of external surface area, micropore area and micropore volume as shown in Table 2. There is a significant increase in the external surface area and the micropore volume on the composite material. This observation can be assumed that the particles of iron oxide (goethite) were precipitated on the surface of zeolite forming aggregates (Mockovčiaková *et al*., 2006). The negative value of micropore volume in the zeoliote-goethite composite may however cause by noise and can be assumed to zero value.

X-ray Diffraction (XRD)

The XRD pattern of the zeolite sample is shown in Figure 4. XRD analysis shows the crystalline phases of the sample. There are pronounced peaks at 2Θ values of 15, 25, 32, 35 and 42°. The result is in good agreement with literature data of Ozdemir and Sabriye, (2013).

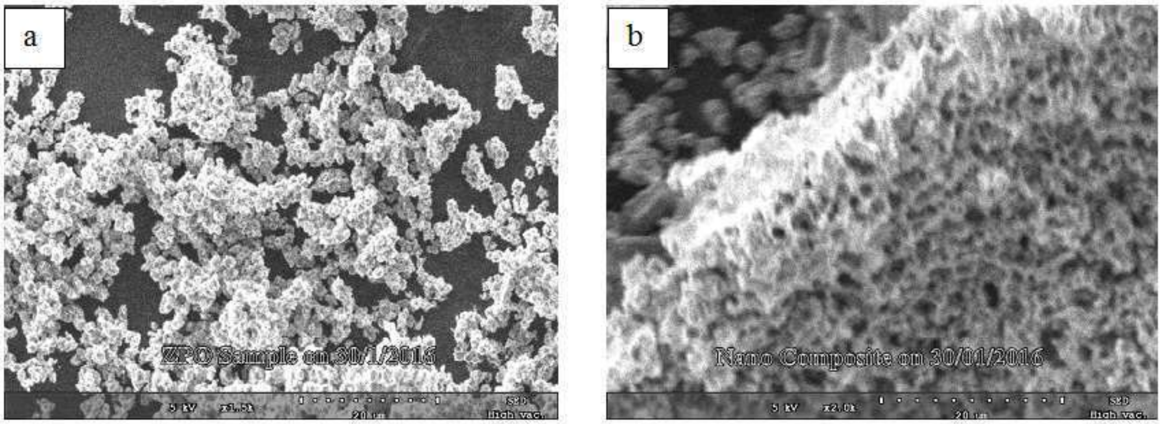

Fig. 3: SEM micrographs of (a) zeolite (b) zeolite-goethite nanocomposite

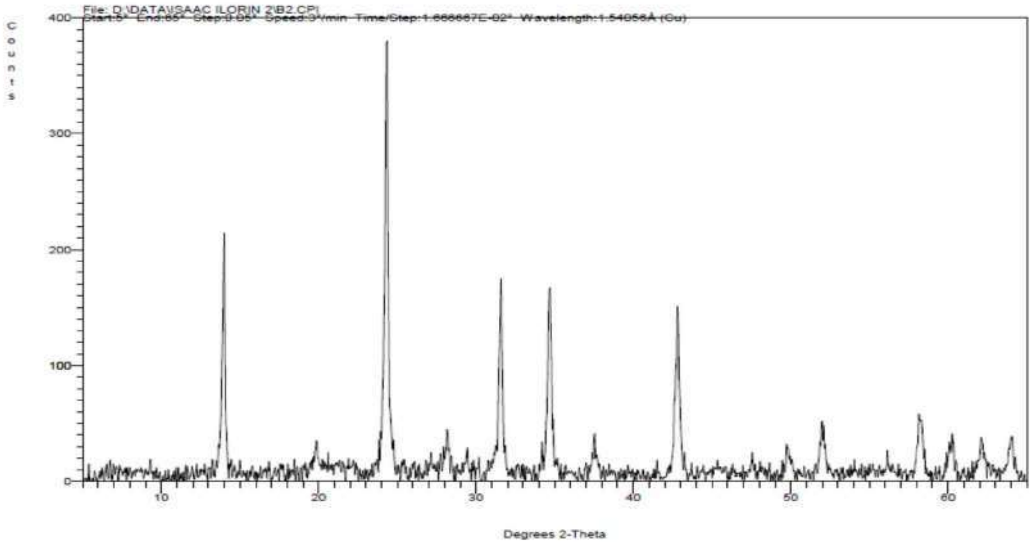

Fig 4: X-ray diffraction pattern of synthesized zeolite

Table 2: BET parameters of zeolite and zeolite-goethite composite

Materials	SSS(BET) (m^2/g)	External surface area (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)
Zeolite	163.491	163.491	0.00	0.00
Zeolite-goethite	304.838	261.154	42.684	-0.080

CONCLUSION

The zeolite and zeolite-goethite nanocomposite were synthesized and characterized towards its application as a possible adsorbent material for removal of pollutant from water. The zeolite-goethite nanocomposite was prepared from iron (III) trioxonitriate (V) and Potassium hydroxide aqueous solutions with aqueous solution of the synthetic zeolite by using *in-situ* method under basic condition. The obtained results of Fourier transform infrared spectroscopy (FT–IR), scanning electron microscopy (SEM), confirmed the formation of zeolite-goethite nanocomposite. This is a clear indication that properties of zeolite can be improved upon by compositing with other materials like goethite. Consequently, the synthesized zeolite materials can be employed as an adsorbent for different environmental applications as revealed by the surface area.

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