

Preparation and Characterization of Magnetite-Bentonite Nano Composites from Native Bentonite Mines of Kerman-Iran

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Bentonite is a kind of crystalline clay mineral with the major constituent of montmorillonite. Bentonite mines should be investigated in different areas with different climatic and environmental conditions. Kerman, is a province in the southeast of Iran famous for its rich resources of bentonite mines. In the present study, the physical and chemical characteristics of the supplied bentonites from three different mines of Kerman (Kheirabad, Tang-e Quchan and Horjand) were investigated. Kheirabad sodium bentonite sample was selected as a potent adsorbent of organic and inorganic pollutants due to high swelling index. Besides, magnetite nano composites were synthesized by stabilizing Fe₃O₄ nanoparticles on desired bentonite. The properties of nano-composites were studied using FTIR, XRD, VSM, BET and TEM analyses.

Keywords : Magnetite, Clay, Montmorillonite, Nano

1. Introduction

Clay minerals are hydrous silicates of aluminum or magnesium [1]. The main unit of all clay minerals is a tetrahedron in which one atom of silicon surrounded by four oxygen atoms. Tetrahedral sheets are created by consecutive connection of these units. In each structure, there are units in which cations such as aluminum or magnesium are bonded to six oxygen or hydroxyl groups. Consecutive connection of these units creates octahedral sheets. If two-thirds of the spaces intended for cations on the octahedral sheet is occupied by Al³⁺, it will be called dioctahedral sheet. Or else, if all of the space is filled with cations such as Mg²⁺ or Fe²⁺, the sheet will be called trioctahedral [1]. The combination of octahedral and tetrahedral sheets forms a layer. The clay minerals are formed from the stack of layers [1, 2].

Clay minerals are categorized into two kinds. Clay minerals like kaolinite and halloysite are consisted of one

octahedral and one tetrahedral sheet while in the second kind of clay minerals such as smectite, talc and mica; one octahedral sheet is placed between two tetrahedral sheets [1, 2].

Montmorillonite, a kind of dioctahedral mineral, is one of the most prominent minerals in smectite group. In structure of this mineral, a few aluminum ions on octahedral sheet are replaced by magnesium and iron ions. Therefore, montmorillonite will be negatively charged. In nature, some cations with different capacities such as sodium, calcium and magnesium are replaced by a number of cations on tetrahedral and octahedral sheets to neutralize this negative charge. Such displacements are called isomorphs substitutions [1-3].

Bentonite is a kind of crystalline clay mineral with the major constituent of montmorillonite or another members of other smectites with one octahedral and two silica sheets. bentonite has several applications in industry due to its physical and chemical properties such as swelling, huge surface area, adhesion and high adsorption capacity. [4-6].

Bentonites are classified into two types of sodium and calcium based on their interlayer cations. The sodium

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bentonite has higher swell index, ion adsorption rate, contraction strength and expansion in comparison to calcium bentonite. Adsorption and desorption capability of sodium bentonite is effective in wastewaters treatment [7, 8].

Organic pollutants of wastewaters have always been one of the major problems that severely threatens human health and aquatics due to their harmful effects [4, 9-11]. Removal of these pollutants by traditional methods like coagulation, chemical precipitation, chemical oxidation, membrane filtration, ion exchange and osmosis have not been very successful because of some significant disadvantages of these processes such as incomplete removal, high-energy requirements and high operational expenses [12-15]. Adsorption technique has been prioritized to the above traditional methods because of its considerable success in removing pollutants from effluents [11, 14, 16-19]. The use of adsorbents in nano range has been considered as an effective way in water treatment due to having a very small size and a huge surface area [10, 19-21]. Several studies have been conducted on the use of bentonite as an adsorbent.

Adsorption of cobalt (II) on the bentonite, Fe_3O_4 , and Fe_3O_4 /bentonite nanocomposite was studied by Hashemian *et al.* 2014. Fe_3O_4 /bentonite nanocomposite indicated the maximum adsorption capacity of cobalt (II) [9]. Zhichao Lou *et al.* 2014 reported the adsorption of methylene blue from aqueous solution by Fe_3O_4 magnetized bentonite [22]. The adsorption of 2,4,6-trichlorophenol (TCP) by activated carbon was investigated by Krishnaiah *et al.* 2013 [23].

The potential of bentonite for phenol adsorption from aqueous solutions was studied by Banat *et al.* 2000. The equilibrium time required for the adsorption of phenol on bentonite was almost 6 h [16].

In traditional adsorption methods by bentonite, separation has been conducted by difficult procedures such as centrifugation or self-precipitation, which are not suitable for large-scale applications. In contrast, magnetic nano materials such as Fe_3O_4 , which can be collected easily under an external magnetic field, have a unique superiority in separation and considered as one of the best choices for the removal of pollutants [10, 17, 24, 25].

Several studies have been conducted previously. Bentonite/iron oxide system was prepared by isothermal calcination of powder composed of bentonite clay and precursor containing ferric acetate by Petr Kristan *et al.*, 2013. In another report, Alekseeva *et al.*, 2016 studied Synthesis of a Bentonite-Magnetite Composite using prepared bentonite from Sigma-Aldrich. In contrast, in the present study synthesise of nano composites was operated

with three different ratios of bentonite/ Fe_3O_4 by co-precipitation method.

The original aspect which is distinct the present study from previous reports, is preparation of bentonite as a raw material for synthesise of bentonite/ Fe_3O_4 magnetic nano composites from three different mines of Kerman province after studying physical and chemical characterizations. Kerman province, located in the southeast of Iran, is one of the rich resources of bentonite mines. Natural clay is prepared from mines of Kerman abundantly and is easily purified in the laboratory. This kind of potent adsorbent can be produced in industrial scale for wastewater treatment.

2. Experimental

2.1. Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Merck Inc. Bentonite was supplied from Kheirabad (KhB), Tang-e Quchan (TQB) and Horjand bentonite (HB) mines of Kerman. Distilled water was used for preparing all aqueous solutions and 2 M NaOH was used to adjust the pH of the mixture.

2.2. Preparation of bentonite samples

Bentonite which is prepared from three different mines was finely grinded by a mill (Cross Beater Mill). Afterwards, samples were kept at 120 °C for 24 hours to dry.

2.3. Purification of bentonite samples

Sedimentation method was used for purification. For this purpose, 100 gr (gr = gram) of bentonite was dispersed in 5 L (L = liter) water and was stirred for 1 hour, Then the suspension was poured to a container with the height of 80 cm (cm = centimeter) and the volume of 5 L. According to Stokes' law for particles that are larger than 1 micron, it takes 5 days to precipitate at the bottom of the container. Finally, the material sediment in water was drained by a spout at the bottom of the container.

2.4. Chemical analysis of purified bentonite samples

Chemical analysis was carried out by wet chemistry method.

2.5. Swelling index of purified bentonite samples

The swell index was determined by ASTM5890 standard method. 2 gr of dry purified bentonite was dispersed gradually (0.1 gr every 10 minutes) in 100 ml (ml = milliliters) distilled water. After 24 hours the rate of swelling was determined.

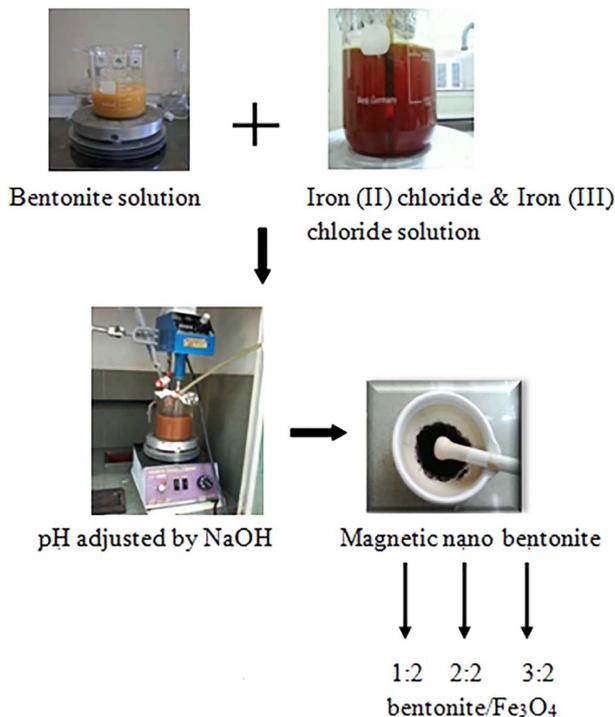


Fig. 1. (Color online) Preparation of magnetite-bentonite nanocomposites.

2.6. Preparation of magnetite-bentonite nano composites

A co-precipitation method was used to prepare the bentonite/Fe₃O₄ nano composites. Different amounts of KhB bentonite (1, 2 and 3 gram) were dispersed in 100 ml de-ionized water via adequate ultrasonic. The solution was then stirred overnight. The solution was added to 100 ml distilled water containing FeCl₂·4H₂O (2.2 g) and FeCl₃·6H₂O (4.7g) to obtain mass ratios of 2:1, 2:2 and 2:3 Fe₃O₄/bentonite. The mixture was stirred under the influence of N₂ (to avoid the presence of O₂) at room temperature (23-25 °C) for half an hour. The pH was slowly raised by adding 2 M NaOH solution up to 11, and stirring continued for 30 minutes. After sedimentation, the synthesized magnetic nano composite was frequently washed using distilled water. Through a simple magnetic procedure, the obtained materials were separated from water and then were dried in room temperature for 24 hours (Fig. 1).

2.7. Characterization of magnetite-bentonite nano composites

The zeta potentials were analyzed on a Malvern ZEN3600 Zetasizer Nano particle analyzer. Infrared spectrum was recorded applying FTIR instrument (Bruker, Tensor 27) in KBr medium between the 400 and 4000 cm⁻¹. The crystalline structure was determined via the X-ray powder diffraction (XRD) method applying a Philips PW1730 with Cu K α radiation employing a range from 0.8^o to 70^o. Magnetic measurements were carried out using a MDKFT VSM provided by Daneshpazhooch Inc. Iran. The specific surface area, BET (Brunauer, Emmett and Teller) method, was determined by using a BELSORP-mini II instrument. A transmission electron microscope (TEM) IEO912AB (LEO Inc.) was used to characterize the Fe₃O₄/bentonite composite regarding the particle size and shape.

3. Results and Discussion

3.1. Chemical analysis

Chemical analysis of purified bentonite samples is presented in Table 1. In clay minerals which consist of two silica and one octahedral sheets, the proportion of silicon to aluminum is 2:1. In nature isomorphs substitutions often occur in clays and this ratio changes slightly. Therefore, the SiO₂/Al₂O₃ proportion is considered to be about 4. The presence of ions such as sodium, calcium and magnesium in the interlayer space of montmorillonite changes the physical properties of bentonite. In sample (1) the Na₂O content is higher than CaO. Therefore, the major interlayer cations of montmorillonite, are sodium. The results of the swelling index test also confirm these results. In samples (2) and (3) the CaO content is higher than Na₂O which indicates that these two samples contain calcium montmorillonite.

3.2. Swelling index

The swelling index of samples from three different mines is presented in Table 2. The results indicated that sample 1 (KhB) had the most swelling index. It can be concluded that in this sample the major interlayer cations of montmorillonite are sodium. In the case of two other samples due to low level of swelling index the major

Table 1. Chemical analysis of samples from KhB, TQB and HB mines.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	L.O.I	SiO ₂ /Al ₂ O ₃
KhB	66.25	14.92	4.3	2.8	1.58	2.43	1.51	5.82	4.44
TQB	65.72	16.42	1.51	2.33	2.15	0.27	0.07	12.72	4.00
HB	66.41	14.75	2.23	1.9	2.17	0.76	0.35	8.62	4.50

Table 2. The swelling index of samples from KhB, TQB and HB mines.

Sample	KhB	TQB	HB
Swell index (ml/2gr)	22	9	6

interlayer cations are calcium or magnesium. These results are also consistent with the chemical analysis results.

The sodium bentonite sample 1 from KhB mine was selected for preparation of magnetite-bentonite nano composites due to higher swell index and adsorption capability.

3.3. Characterization

3.3.1. Particle size of magnetite-bentonite nano composites

Size distribution of 3 samples of nano composites (2:1, 2:2 and 2:3) are presented in Fig. 2 and Table 3, 4, 5. The main diameter of samples 1, 2 and 3 were 229.36, 1032 and 208.64 nm respectively.

3.3.2. Transmission electron microscopy (TEM)

The morphologies of Fe₃O₄ nano composites were studied by TEM. TEM micrographs of the prepared nano composites are shown in Fig. 3 illustrating Fe₃O₄ nano particles had a nearly uniform size of 10 nm and a spherical shape. In addition, these microspheres were scattered in a homogenous way on the surface of bentonite instead of agglomeration.

3.3.3. Crystal structure of magnetite-bentonite nano composites

The crystal structures of all 3 samples with different

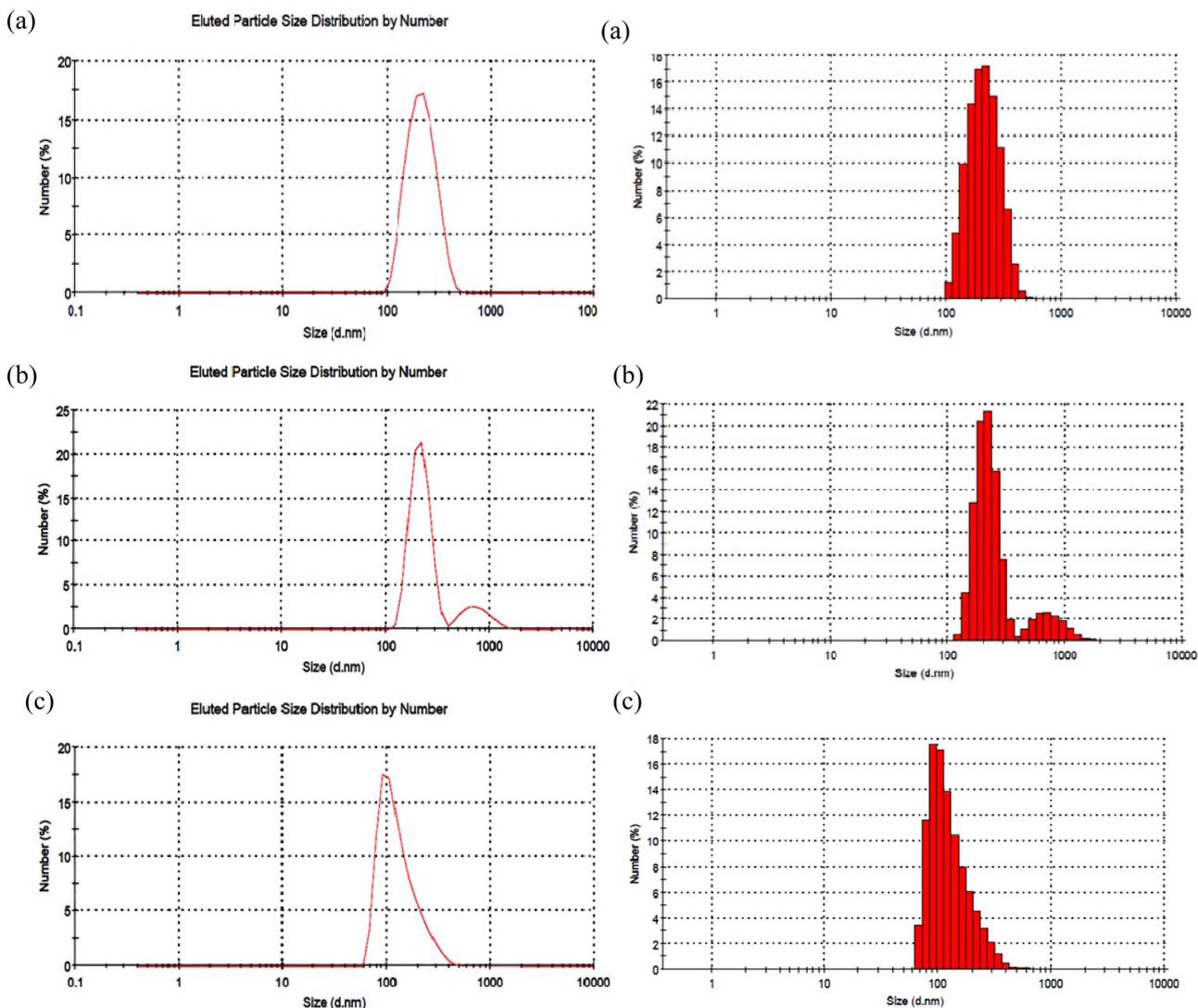


Fig. 2. (Color online) Particle size and size distribution of sample 2:1 (a), 2:2 (b) and 2:3 (c) magnetite bentonite nano composites.

Table 3. Size distribution of nano composite (2:1).

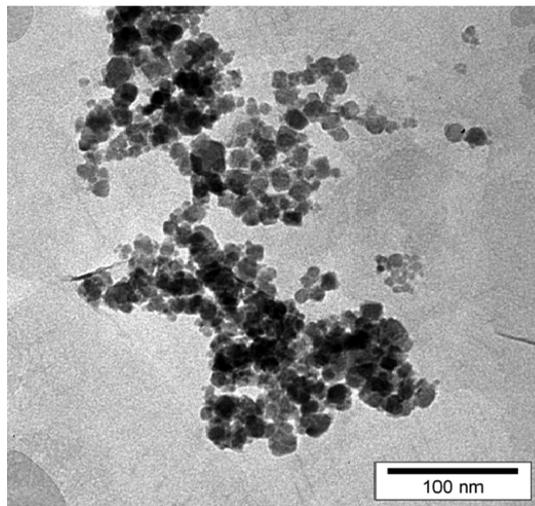
Rec #	Z-Avg d.nm	Pk 1 Avg (I) d.nm	Pk 2 Avg (I) d.nm	Pk 3 Avg (I) d.nm	DCR Kcps
145	229.4	248.6	0.000	0.000	344872.7

Table 4. Size distribution of nano composite (2:2).

Rec #	Z-Avg d.nm	Pk 1 Avg (I) d.nm	Pk 2 Avg (I) d.nm	Pk 3 Avg (I) d.nm	DCR Kcps
148	1032	896.2	223.4	5414	1430734.2

Table 5. Size distribution of nano composite (2:3).

Rec #	Z-Avg d.nm	Pk 1 Avg (I) d.nm	Pk 2 Avg (I) d.nm	Pk 3 Avg (I) d.nm	DCR Kcps
147	208.6	204.5	1321	0.000	2000559.0

**Fig. 3.** TEM images of magnetite bentonite nano composite (2:1 sample).

ratios of Fe_3O_4 /bentonite (2:1, 2:2 and 2:3) were characterized by XRD employing a range from 0.8° to 70° and the results which are presented in Fig. 4(2) indicated the characteristic peaks for Fe_3O_4 at 30.1, 35.5, 43.1, 53.4, 57.0 and 62.6, which are related to indices (220, 311, 400, 422, 511 and 440) according to database in JCPDS file PCPDFWIN v.2.02, PDF no. 85-1436. It is clear that Fe_3O_4 is the only detectable product. However XRD patterns still shows small peaks related to the impurities in nano composites that are inconsiderable. The main peak for montmorillonite, between 0.8° to 10° was observed at 6.9° Fig. 4(1). Based on XRD results, the average crystalline size of iron oxide nano particles was estimated about 15.95 nm using Scherrer's equation. This

value is almost consistent with the results of the TEM analysis.

$$D = (K\lambda)/(\beta\cos\theta)$$

D : The average crystallite size (nm)

K : The Scherrer constant

λ : The X-ray wavelength (nm)

β : FWHM (The peak width at half maximum-height) (degrees)

θ : Diffraction angle (degrees)

3.3.4. Magnetic results

Magnetic measurements of the nano composites were studied by a vibrating sample magnetometer (VSM). The magnetization curves (Fig. 5) showed that sample 1 (2:1 Fe_3O_4 /bentonite) had a magnetization saturation value of 47.09 emu g^{-1} , which is essentially super-paramagnetic and is sufficient to separate the magnetic adsorbent from aqueous solution [24]. Separating the synthesized magnetic adsorbent (0.1 gr) from aqueous solution of Trichlorophenol (TCP, 100 ml) as a model organic pollutant (100 mg L^{-1}) after adsorption process is also showed in Fig. 5.

3.3.5. Surface functional group of magnetite-bentonite nano composites

Figure 6 shows Fourier Transform Infrared spectroscopy (FTIR) spectra of KhB, Fe_3O_4 , Fe_3O_4 /bentonite -1, Fe_3O_4 /bentonite -2 and Fe_3O_4 /bentonite -3 composites. In FTIR spectrum of bentonite, the peaks at 3624 and 3443 cm^{-1} are O-H stretching and H-O-H hydrogen-binding water. The peaks of 1638 cm^{-1} and 1698 are H-O-H deformation. The peak of 1086 cm^{-1} is Si-O-Si, the sharp peak of 796 cm^{-1} is due to Si-O stretching of quartz and silica, peak of

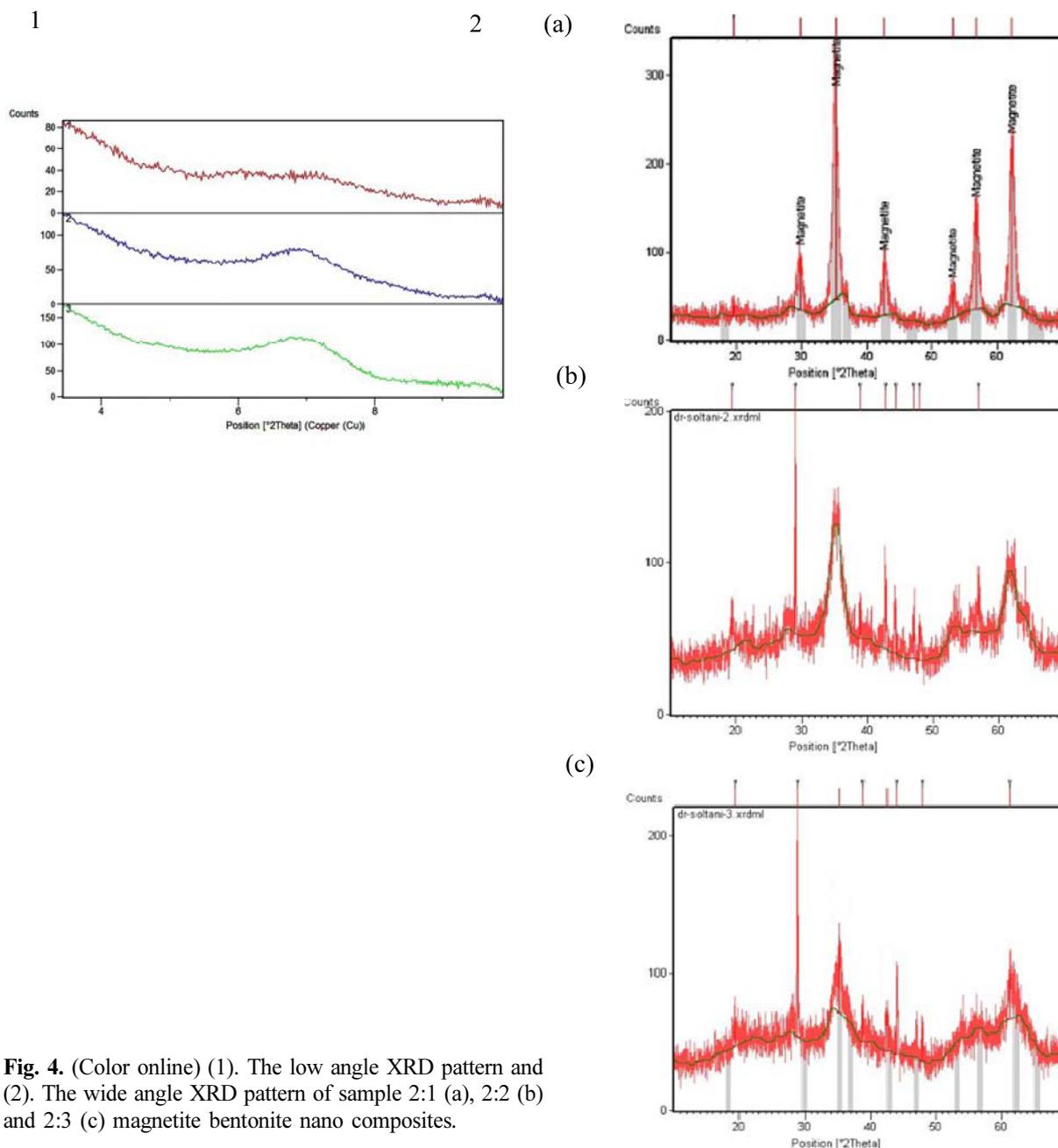


Fig. 4. (Color online) (1). The low angle XRD pattern and (2). The wide angle XRD pattern of sample 2:1 (a), 2:2 (b) and 2:3 (c) magnetite bentonite nano composites.

516 cm^{-1} is related to Al-O-Si deformation and the peak of 469 cm^{-1} corresponds to Si-O-Si deformation. In the FTIR of Fe_3O_4 , the peak at 592 cm^{-1} is related to Fe-O group and in Fe_3O_4 /bentonite composites the peak at 917 is related to Al-Fe-OH, which reveals Fe_3O_4 , is properly placed between the layers of bentonite [4] (Table 6).

3.3.6. Specific surface area (BET method)

The values for the specific surface area (BET method) and the average diameter of pores are given in Table 7. The BET analysis indicated that the specific surface area

of magnetized nano composite (2:1) and KhB were 108.73 $\text{m}^2 \text{g}^{-1}$ and 16.631 $\text{m}^2 \text{g}^{-1}$ respectively. These values represent a significant increase in the specific surface area of Fe_3O_4 nano composites.

3.2. Conclusions

A facile, efficient and economical method for successful synthesis of magnetite bentonite nano composite is described. Fe_3O_4 /bentonite nano composites with spinal structure were successfully synthesized by co-precipitation method. In order to determine the optimal rate of bentonite

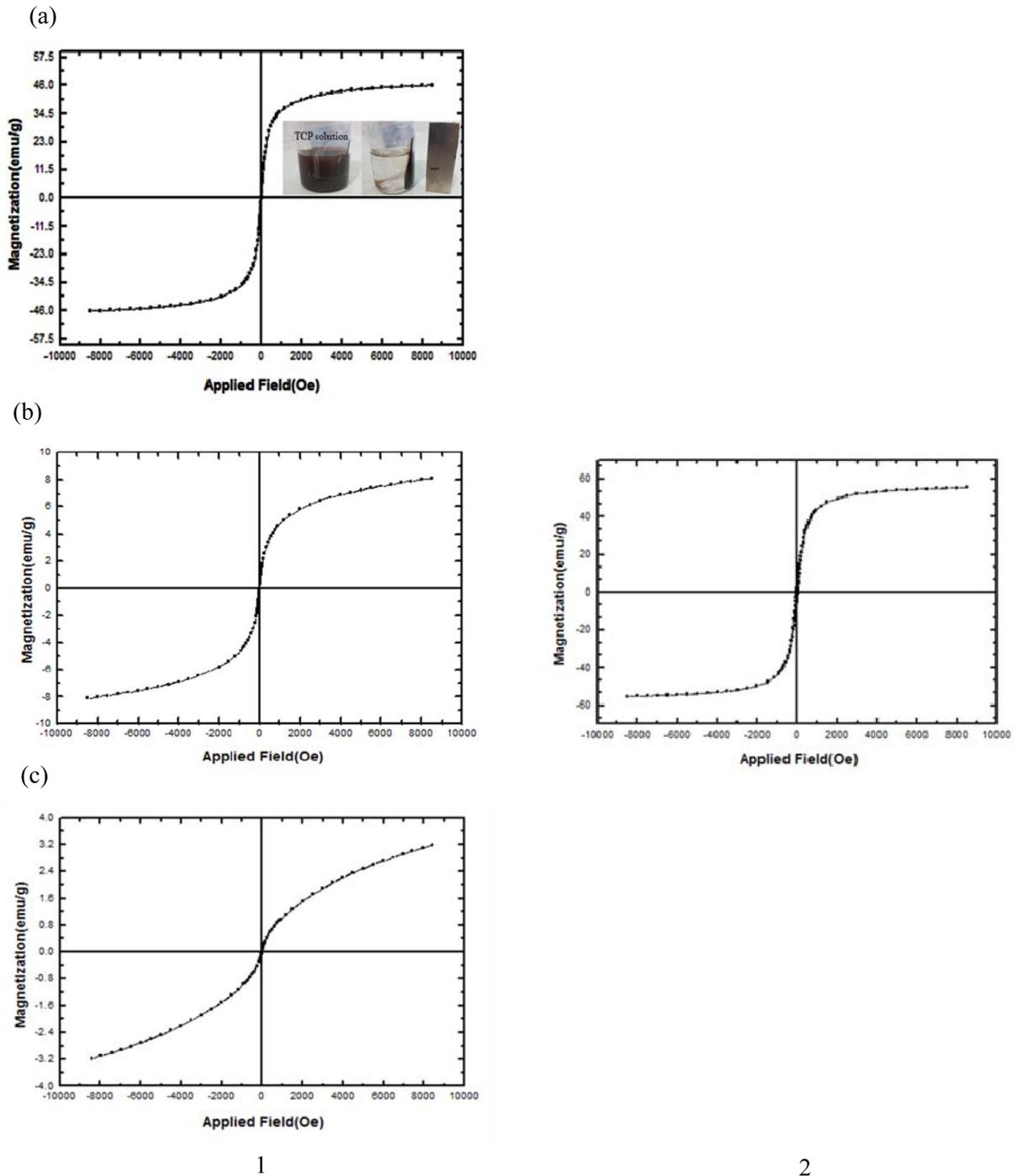


Fig. 5. (Color online) hysteresis loops of sample 2:1 (a), 2:2 (b) and 2:3 (c) magnetite bentonite nano composites (1) and Fe_3O_4 (2).

in composites, 3 different amounts (1, 2 and 3 gr) were compared in terms of characteristics. Sample 1 (2:1) and 3 (2:3) nano particles exhibited regular morphology with more homogeneous particle size distribution. The XRD and TEM results of sample 1 (2:1) indicated that Fe_3O_4 nano particles had optimal crystallinity with tiny cubic structure. The FTIR spectroscopy confirmed the structure

of obtained nano composites. The magnetization data of sample 1 (2:1) showed super-paramagnetic property which indicated that this adsorbent has a great potential in the treatment of wastewaters with organic pollution. This study indicated that Fe_3O_4 nano composite (2:1) due to the small particle size and huge surface area has the potential of high adsorption.

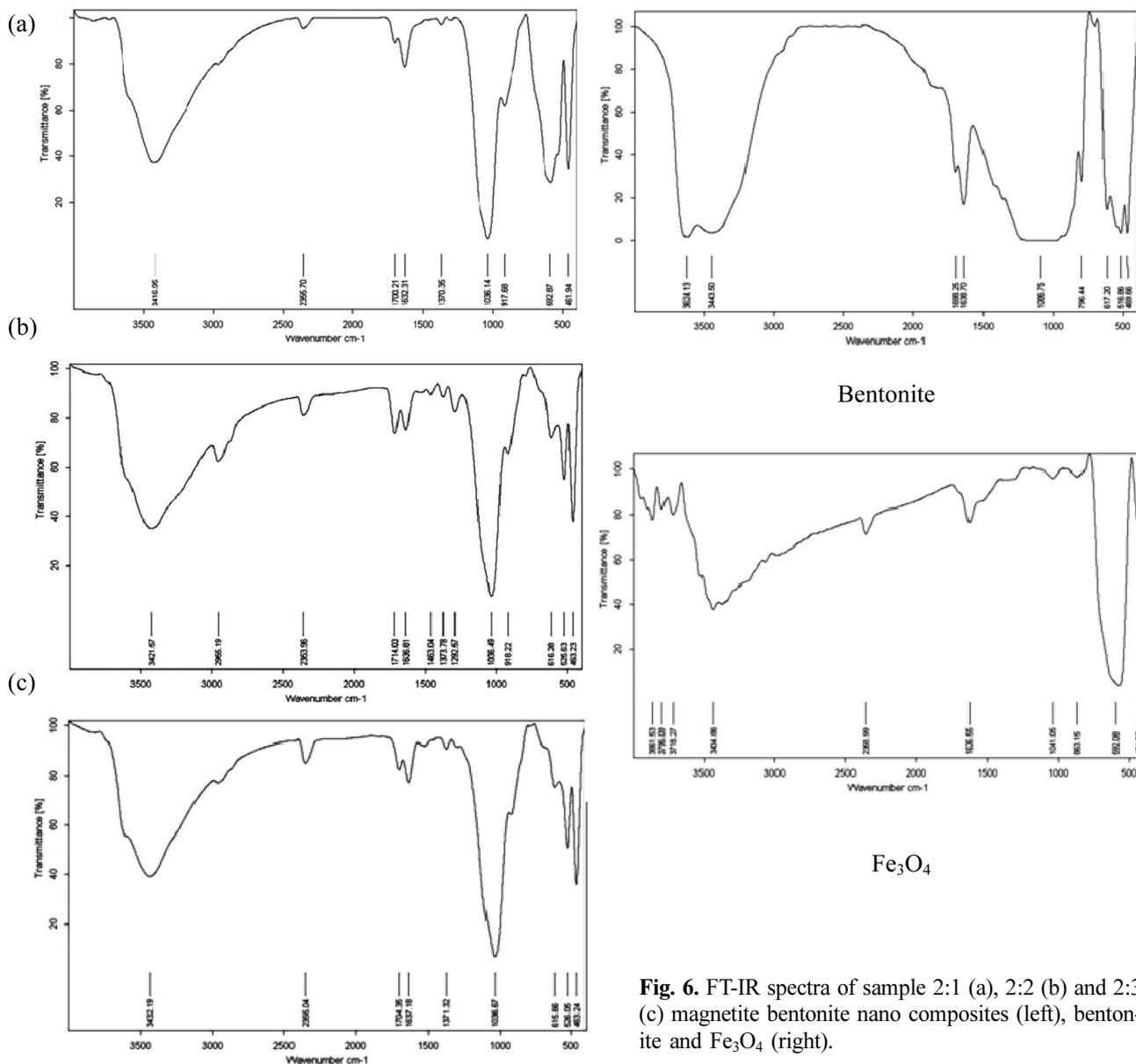


Table 6. Functional groups attributed to characteristic absorption peaks.

Wavenumber (cm ⁻¹)	Functional Group
Bentonite	
3624	-OH
3443	H-O-H hydrogen-binding water
1638-1698	H-O-H deformation
1086	Si-O-Si
796	Si-O stretching of quartz and silica
516	Al-O-Si deformation
469	Si-O-Si deformation
Fe₃O₄	
592	Fe-O group
Fe₃O₄/bentonite	
917	Al-Fe-OH

Table 7. BET parameters.

Sample	S _{BET} [m ² /g]	Mean pore diameter (nm)	Pore volume (cm ³ /g)
KhB	16.631	24.216	0.1007
Magnetized nano composite	108/73	10.69	0.2906

Although some techniques still need to be improved before our material can be widely applied in water treatment systems, the nano Fe₃O₄/bentonite with the optimal ratio of 2:1 is a potential candidate as a high efficient, inexpensive and renewable adsorbent for the removal of

organic contaminants from polluted water.

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