



Preparation And Characterization of Organo-Clay Composite Beads

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ABSTRACT

Chitosan/bentonite composite beads were prepared by addition of activated clay into chitosan solution. Bentonite clay was activated by Cetyl Trimethyl Ammonium Bromide (CTAB). The composite structure was confirmed by FTIR spectroscopy and X-Ray Diffraction. The morphology of beads was examined by scanning electron microscopy (SEM). Thermal Gravimetric Analysis (TGA) was used to investigate the thermal stability of composite beads. It was observed that the activation of bentonite is essential for composite preparation. The composite grade increased with decreasing particle size of bentonite clay and by using a higher concentration of chitosan solution.

Keywords: Chitosan, Bentonite, Organo-clay, Composite, Beads.

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1. INTRODUCTION

Chitosan is a high molecular weight polysaccharide composed mainly of β -(1,4)-linked 2-deoxy-2-aminod-glucopyranose units and partially of β -(1,4)-linked 2-deoxy- 2-acetamido-d-glucopyranose. Chitosan is inexpensive as well as nontoxic and exhibits high mechanical strength, hydrophilic character, good adhesion, etc. Thus chitosan are used as a food additive, a supporting material for chromatography and a chelating polymer for heavy metals removal (Guibal et al., 1999, Tianwei et al., 2001 and Han et al., 2010). Interest in the modification of chitosan through graft copolymerization has grown significantly. The combination of natural and synthetic polymers via grafting yields hybrid materials which may produce desirable properties (Yasemin et al., 2015).

Clay is a natural raw material that has been used for various purposes. Bentonite clays have a high content of montmorillonite mineral and contain fewer amounts of other clay minerals. Montmorillonite is a member of smectite group clay minerals. Bentonite clay (hydrated aluminum silicate) was shown to be efficient in the removal of many pollutants from aqueous solutions (Bailliez et al., 2004, Smicklas et al., 2006, Corami et al., 2007, Zhu et al., 2008 and Mobasherpour et al., 2011). On the other hand, it is not easy to separate the

suspended fine solids of bentonite from aqueous solution (Choi and Jeong 2008). Therefore, it is needed to bind bentonite with polymer to solve this problem. The polymer/clay composites have attracted extensive interests around the world because they combine the structure, physical, and chemical properties of both inorganic and organic materials. Compared to the pure polymers, these composite have excellent properties; such as higher storage modulus, low thermal expansion coefficients, low gas permeability, and high ionic conductivity because of the larger filler/matrix interfacial surface area (Vaia, 2000, Yao et al., 2002, Sun and Garces 2002, Ray and Okamoto 2003, Song et al., 2005, Seo et al., 2005 and Abdel Khalek et al., 2012).

In this study, Chitosan/bentonite composite beads were prepared using organophilic bentonite clay and chitosan as a natural polymer. The reason behind choosing chitosan as a binding material for bentonite is its high abundance in nature and special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc.

2. MATERIALS AND METHODS

2.1. Materials

Natural bentonite was collected from Kasr El-Sagha locality, El-Fayom, Egypt. It was ground using ball mill and purified using dispersion method. Chitosan was supplied by Merck, Germany and used without further purification. All other chemicals used were reagent grade and purchased from El-Nasr Co. for Chemical Industries (Egypt) and used as purchased without further purification.

2.2. Preparation of Organo-Clay Composite Beads

The air classifier was employed for size classification of dry bentonite sample. The products of different size were characterized chemically and physically. Chemical activation of bentonite was achieved by adding a 1% CTAB solution (Cetyl Trimethyl Ammonium Bromide) to 1% bentonite suspension and stirred for 24 h. The activated bentonite was filtered off, washed and dried. A chitosan solution (2 wt.%) was prepared by dissolving a 2 g of chitosan in 1% acetic acid solution and stirred for 24 hours. One gram of the activated bentonite was swelled by 50 ml of deionized water (1g bentonite in 50 ml water for 24 hrs.) added to 50 ml chitosan solution and stirred at 60°C overnight. The latter mixture was drops in 3M NaOH solution. Chitosan droplets formed a bead shape (precipitated).The chitosan/clay beads were washed and stored in the water (Pandey and Mishra 2011).

2.3. Characterization

FTIR study was carried out on Nicolet IS-10 FTIR, USA to analyze functional groups, using potassium bromide (KBr) disk method and the morphology was investigated by JEOLJSM-5400 scanning electron microscopy SEM, Japan. A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co K α operated at 30 kV/30 mA, to determine crystallinity of the material. A Laser particle size analyzer "FRITSCH" model "Analystte 22" was employed for size analysis of samples.

3. RESULTS AND DISCUSSION

3.1. Chemical Analysis and Surface Area of Bentonite Clay

The Egyptian bentonitic clay was dominated by Fe-montmorillonite, Table 1. The surface area of the bentonite sample and its size fraction products, Table 2, shows that increasing in surface area with decreasing particle size.

Table-1. Chemical analysis of Bentonite Clay

Item	%
Ignition loss	8.56
SiO ₂	52.49
Al ₂ O ₃	21.58
Fe ₂ O ₃	10.82
TiO ₂	1.56
CaO	0.42
MgO	3.21
Na ₂ O	0.84
K ₂ O	0.41
P ₂ O ₅	0.09
Total	99.98

source: (Chemical analysis)

Table-2. Surface area of Bentonite and its size fractions

Bentonite sample	Surface area, m ² /g	Size D ₅₀ , μm
Original	0.4355	7.24
Coarse	0.3963	8.17
Medium	0.5197	5.36
Fine	0.9433	2.81

source: (Size analysis)

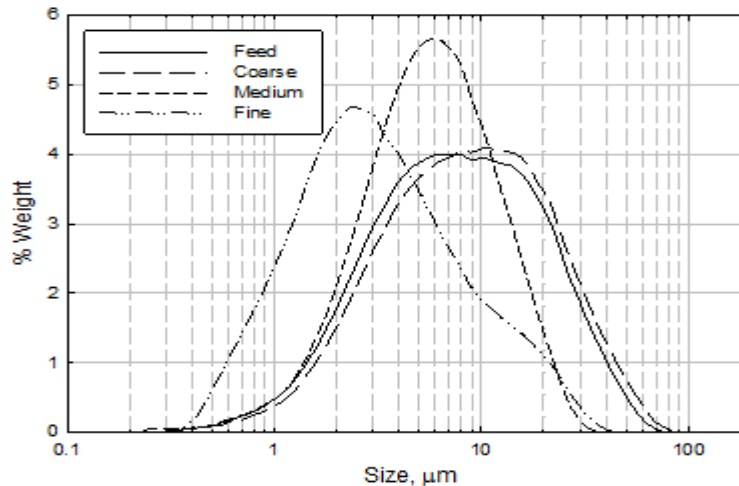


Fig-1. Size analysis of bentonite sample by air classifier

source: (Size analysis)

3.2. FTIR Analysis of Bentonite and Bentonite-Chitosan Composite

The spectrum of bentonite, Fig. 2, shows the characteristic bands at 3640 and 3449 cm^{-1} responsible for stretching vibrations of O–H, the band at 1112 and 1035 cm^{-1} due to Si–O stretching (Rayanaud et al., 2002). The spectrum of size fractions contains all characteristic bands of bentonite.

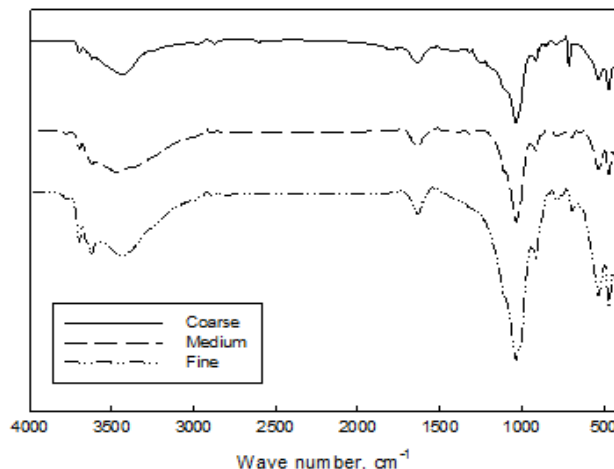


Fig-2. FTIR spectra of bentonite size fractions
source: (FTIR analysis)

Fig.3. shows the FTIR spectra of bentonite and chitosan-bentonite composite. It is clear that activation of bentonite by CTAB is essential for preparation of composite. The positively charged ammonium of CTAB can combine with the negatively charged montmorillonite, making part of chitosan intercalate into the interlayers of the montmorillonite. As a result, the montmorillonite interlayer spacing was increased and its adsorption efficiency was improved (Dalida et al., 2011 and Liu et al., 2012). Fig.4. shows the increasing of CTAB concentration, increased the characteristic peaks of composite with bentonite.

FTIR spectra of chitosan-bentonite composite of original and different size fractions bentonite were recorded in the region of 4000–400 cm^{-1} and are shown in Fig.5. The peaks present on the range 3400–3800 cm^{-1} were also corresponding to combination of characteristic peaks of O–H, NH_2 and intramolecular hydrogen bonding. The peaks at 2920 cm^{-1} are assigned to the symmetric $-\text{CH}_2$ vibrations of carbohydrate ring. The absorption peak at 1650 cm^{-1} (C=O in amide group, amide I vibration), 1545 cm^{-1} ($-\text{NH}_2$ bending of amide II) and 1390 cm^{-1} (N–H stretching or C–N bond stretching vibrations, amide III vibration). The peak at 1092 cm^{-1} corresponds to the symmetric stretching of C–O–C groups. The absorption peaks in the range 900–1200 cm^{-1} are due to the antisymmetric C–O stretching from the pyranose ring and wagging of saccharide structure of chitosan (Pawlak and Mucha 2003). The peak of bentonite shifted from 1112 to 1092 cm^{-1} due to interaction with chitosan. In general, decreasing of particle size of bentonite, improve the composite composition. This may be due to increasing surface area of bentonite particles.

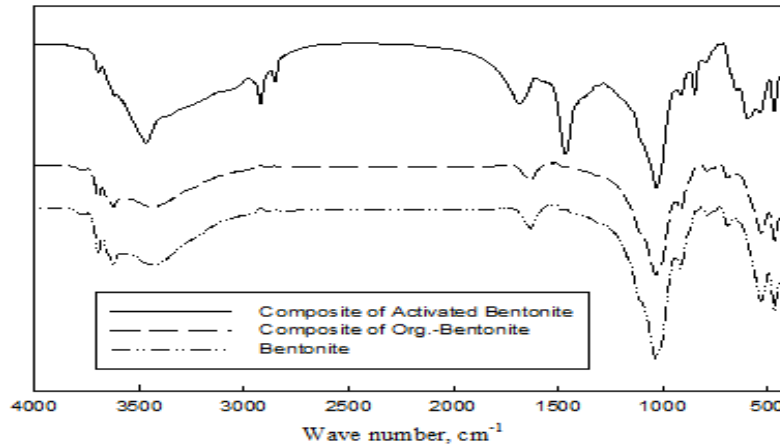


Fig-3. FTIR spectra of bentonite and composite of activated and non-activated bentonite.
source: (FTIR analysis)

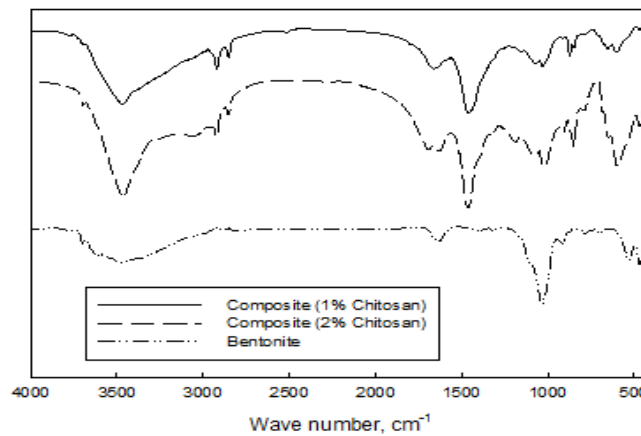


Fig-4. Effect of chitosan percent on composite composition.
source: (FTIR analysis)

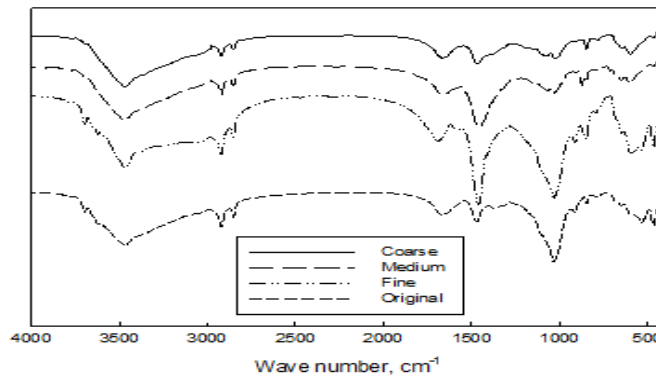


Fig-5. FTIR spectra of composite of different bentonite size fractions
source: (FTIR analysis)

3.3. XRD Analysis of Bentonite and Bentonite-Chitosan Composite

XRD spectra of bentonite and composite are presented in Fig.6. The crystalline peaks of bentonite at $2\theta=20, 35, 40$ and 62 are also found in bentonite–chitosan composite with very small shifting in 2θ . This may be due to binding of bentonite with chitosan. This indicated that there was no marked change in the peak

structure after the composite formation and confirmed that the crystal structure of bentonite is retained in composite (Sundaram et al., 2008). The peaks at 2θ about 27 and 30 are attributed to the traces of quartz and calcite minerals.

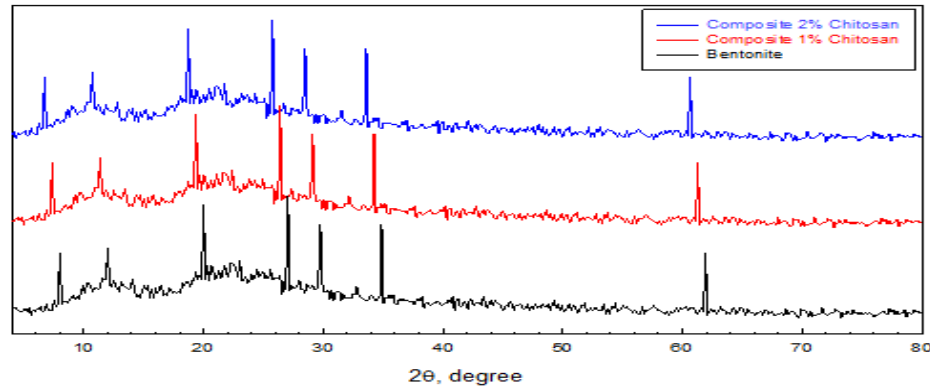


Fig-6. XRD spectra of Bentonite and Bentonite-Chitosan Composite.
source: (XRD analysis)

3.4. TGA Analysis of Bentonite and Bentonite-Chitosan Composite

TGA curves of bentonite and composites with different chitosan content are shown in Fig.7. As shown from the Figure, the thermal stability of bentonite is high, only 14% of bentonite is decomposed until 600°C. TGA data exhibited a lower thermal decomposition temperature of composite compared to bentonite. The remainder weight at 600°C is only 48% and 60% for composite with 1% and 2% chitosan, respectively. Because inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components into organic materials can improve their thermal stability. This increase in the thermal stability can be attributed to the high thermal stability of clay and to the interaction between the clay particles and the chitosan (Günister et al., 2007).

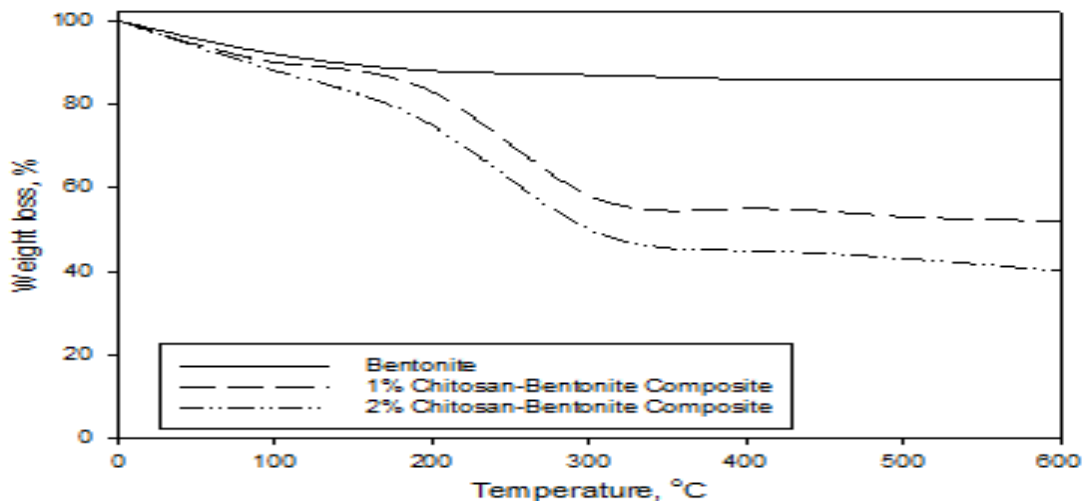


Fig-7. TGA analysis of Bentonite and Bentonite-Chitosan Composite.
source: (TGA analysis)

3.5. SEM of Bentonite and Bentonite-Chitosan Composite

The bentonite sample, Fig. 8, exhibited the typical morphology for this mineral, consisting of complex aggregates of grains of a few microns in size. The edges of these grains were sharp and rugged. The granular aggregates were, as a rule, not transparent to an electron beam. Clays have a large capacity for adsorbing organic compounds. Expanding silicate layers are especially reactive towards organic materials and uncharged polar molecules, because the organic species can enter the interlayer space forming intercalation complexes. Large surface area, particle size distribution and pore volume play important roles in adsorption capacity of clay minerals.

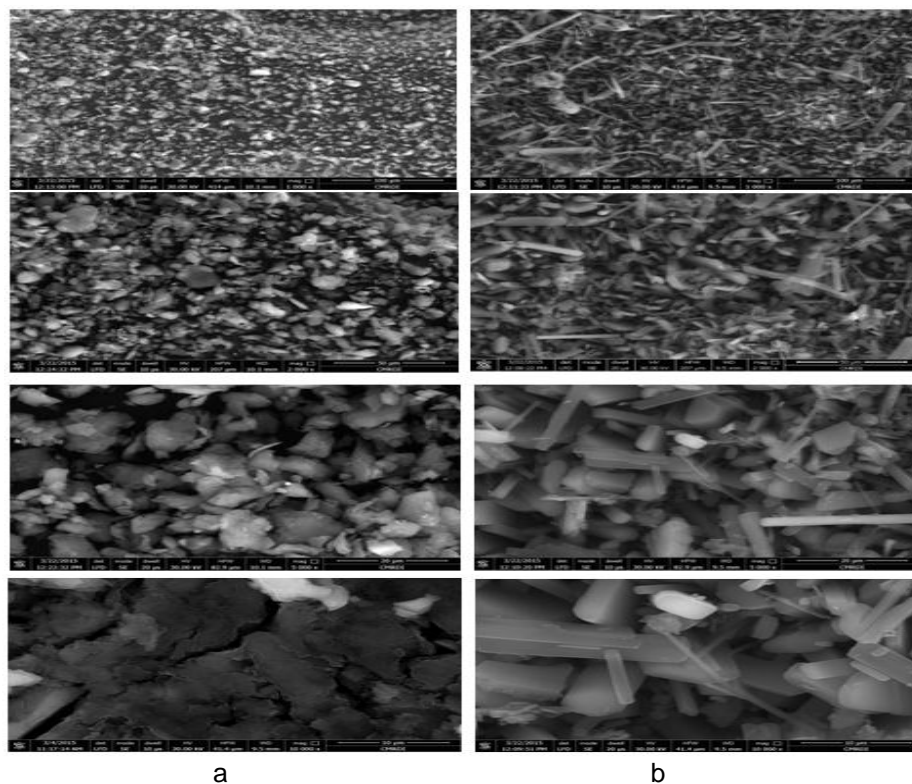


Fig-8. SEM of (a) Bentonite and (b) Composite with different magnifications.

source: (Scanning Electron Microscope (SEM) investigation)

The SEM pictures of composite verify that it has a porous structure. A SEM picture also shows that there is a crack on the surface which confirms the miscibility of the prepared composite. The increase in surface area and mesopores may be ascribed to the attacks on some layers edges. This decomposition, which crumbles several layers in the edge region, creates a considerable amount of mesopores. The surface of composite is abundant in folds.

4. CONCLUSIONS

The Egyptian bentonitic clay was dominated by Fe-montmorillonite. FTIR spectra showed that the activation of bentonite by CTAB is essential for preparation of composite. The positively charged ammonium of

CTAB can combine with the negatively charged montmorillonite, making part of chitosan intercalate into the interlayers of the montmorillonite. The increasing of CTAB concentration, improve the composite composition. The peak of bentonite slightly shifted due to interaction with chitosan. In addition, decreasing of particle size of bentonite, improve the composite composition.

XRD spectra of composite showed that very small shifting in 2θ compared to bentonite. There is no marked change in the peak structure after the composite formation and confirmed that the crystal structure of bentonite is retained in composite.

TGA data exhibited a lower thermal decomposition temperature of composite compared to bentonite. The introduction of inorganic components into organic materials can improve their thermal stability.

The morphology showed that the bentonite mineral consisting of complex aggregates of grains of a few microns in size. The edges of these grains were sharp and rugged. Expanding silicate layers are especially reactive towards organic materials and uncharged polar molecules, because the organic species can enter the interlayer space forming intercalation complexes. The composite has a porous structure and there is a crack on the surface which confirms the miscibility of the prepared composite. The surface of composite is abundant in folds.

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