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PREPARATION AND CHARACTERIZATION OF $CaFeO_3$ POWDER AND ITS COAGULATION ACTIVITY IN TERMS OF REDUCING TURBIDITY

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Abstract

In recent years, materials with porous structure and high surface area are being developed for several applications in nanotechnology. The present research deals with a study on the preparation and characterization of $CaFeO_3$ nanocrystalline powder and its coagulation performance in a bentonite clay sample solution and river water. $CaFeO_3$ nanocrystalline powder was synthesized by citric acid sol-gel combustion method using citric acid and ethylene glycol as a fuel and the corresponding metal nitrates as oxidizers. The resulting xerogel was thermally treated in the muffle furnace at different temperatures (300 °C, 400 °C and 500 °C) for a maximum of 4 h each. The thermal behavior of samples was determined by Thermal-Gravimetric and Differential Thermal Analysis (TG-DTA). The prepared powder samples were characterized by X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Fluorescence (EDXRF), and Fourier Transform Infrared Spectroscopy (FT IR). X-ray diffraction (XRD) was used to study the transformation from precursor powders to rhombohedral crystals by calcination. Scanning Electron Microscopy (SEM) analysis showed the porous nature of the prepared powders. Physicochemical properties of the prepared nanocrystalline powder such as pH, moisture contact, bulk density and surface area also studied. Bentonite clay sample solution and river water sample were used to investigate the coagulation activity of the prepared $CaFeO_3$ nanocrystalline powder in terms of reducing turbidity.

Keywords: Sol-gel method, $CaFeO_3$, nanocrystalline powder, turbidity, coagulation

Introduction

In recent years, materials with porous structure and high surface area are being developed for several applications in nanotechnology (Bharat, 2010). Particular areas of interest include catalysis and separation science. The development of such materials is important for solving economic problems, which include the shortage of natural resources. Since the discovery of the

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ordered mesoporous silica, a large number of porous materials have been made using surfactants as template. However, most of these materials are unstable on removal of the surfactant and the porous skeleton readily collapse when heated above 400 ºC. The collapse of mesostructure in mesoporous materials might be related to the structural rearrangement due to crystallization after removal of organic templates during calcination (Nagaraja *et al.*, 2012) Therefore, it is desirable to develop new methods of synthesis. Thermal stability, i.e., the ability of the material maintaining porous structure at high temperature is a key to both coagulation of ordered porous material and its practical applications (Emongor *et al.*, 2005, Tiwari *et al.*, 2008). This research deals with a study on preparation and characterization of calcium iron oxide ($CaFeO_3$) powder and its coagulation activity in terms of reducing turbidity (Jebun *et al.*, 2016).

In the present work, $CaFeO_3$ powder was prepared by sol-gel method. The thermal analysis on $CaFeO_3$ precursor powders were carried out at the temperature range of 30 to 600 ºC for 3 h by Thermogravimetry and Differential Thermal Analysis (TG-DTA). X-ray diffraction (XRD) was used to study the transformation from precursor powders into orthorhombic crystal structure. The Scherrer's formula was used to compute the average crystallite sizes of $CaFeO_3$ powders. The morphology of prepared powder was characterized by Scanning Electron Microscopic (SEM) analysis. Inorganic synthetic coagulants are commonly used in non-potable water and wastewater industries. The prepared $CaFeO_3$ nanocrystalline powder was first time used as coagulants and study the coagulation activity in terms of reducing turbidity from both collected river water and betonite clay sample suspension.

Materials and Methods

All the chemicals were analytical grade. Calcium nitrate $Ca(NO_3)_2.4H_2O$, iron nitrate $Fe(NO_3)_3.9H_2O$, citric acid $C_6H_8O_7$ were Merck product with a purity of 99.99 %. Ethylene glycol was product from Applichem, Germany. All solutions were prepared using distilled water during preparation procedures. Various conventional and modern instruments techniques were used throughout the experimental procedure. These include X-ray Diffractometry (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Scanning Electron Microscope (SEM), Thermogravimetry/

Differential Thermal Analysis (TG-DTA) and Fourier Transform Infrared Spectroscopy (FT IR). Physicochemical properties of prepared $CaFeO_3$ nanocrystalline powders such as free moisture contact, pH, bulk density and specific surface area were determined by conventional laboratory methods. Coagulation activity in terms of reducing turbidity from both collected river water and betonite clay suspension were carried out.

Preparation of $CaFeO_3$ Powders by Sol-Gel Method

Calcium nitrate, iron nitrate, citric acid and ethylene glycol were used as starting materials for synthesis of nanocrystalline $CaFeO_3$ powders. First calcium nitrates and iron nitrate were dissolved in deionized water and solution (I) was obtained. Citric acid was dissolved in distilled water and solution (II) was obtained. The solution (I) and (II) were mixed as the molar ratio of citric acid and metal ion in 1:2 and then 5 mL of ethylene glycol was added to the mixture solution. This mixture solution was stirred with magnetic stirrer and heated at 70 °C-80 °C for 7 h to get $CaFeO_3$ gels. The gels were dried oven at 110 °C for 4 h and ground with mortar and pestle to get dry as-prepared $CaFeO_3$ powder. A small part of the as-prepared powder was used for thermal analysis (TG-DTA). The prepared as-prepared $CaFeO_3$ powder was calcined at 300 °C, 400 °C and 500 °C for 4 h, and the samples were designated as CFO-300, CFO-400 and CFO-500 with their calcination temperatures. Finally, the samples were ground smoothly in an agate mortar and nanocrystalline $CaFeO_3$ powders were obtained (Mya Theingi 2013). Flowchart of the preparation procedure is shown in Figure 1.

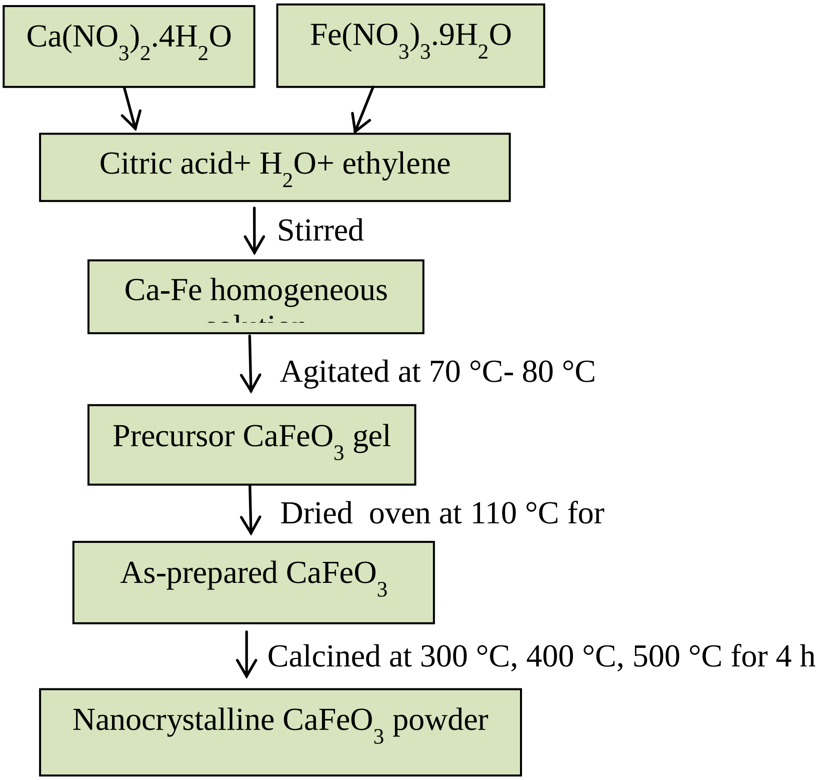


Figure 1: Flowchart of the preparation of $CaFeO_3$ by Sol-gel method

Characterizations of Prepared $CaFeO_3$

The thermal decomposition behaviours of the as-prepared and nanocrystalline $CaFeO_3$ powders were examined by means of thermal gravimetric and differential thermal analysis (TG-DTA) by using a Perkin Elmer in the range of 35–600 °C with heating rate 10 °C/min in static air and Al_2O_3 as a reference. Crystal structure and phase analyses were performed by X-ray diffraction (XRD) using Rigaku, D-Max 2200, Japan. Morphology of the powder and the elemental composition were recorded by scanning electron microscope, ZEISS Gemini SEM, Germany. Energy dispersive X-ray fluorescence (EDXRF) confirms the elemental compositions of the prepared sample by using Perkin Elmex 700, ED XRF spectrometer. FT IR transmission spectra in the region from 400-4000 cm^{-1} were measured using Shimadzu model IR 408, Japan. The physicochemical properties such as free moisture contact, pH, bulk density and specific surface area of the prepared nanocrystalline $CaFeO_3$ powders were determined by conventional laboratory methods. For examples, moisture contact was measure by oven dry test; pH was measure by a pH meter, bulk density was measured by tapped method and specific surface area was determined by methylene blue adsorption test.

Coagulation Activity of the Prepared Nanocrystalline $CaFeO_3$ powders

Bentonite Clay ample Suspension was prepared by 0.7 g of bentonite clay was dissolved in 1L of water and river water was collected from Yangon River (Kyee Myindaing Kanner Road, Kyee Myindaing Township, and Yangon, Myanmar). The coagulation activity in terms of reducing turbidity from both collected river water and betonite clay sample suspension were investigate by effect of contact times of coagulants.

Effect of Contact Time

About 0.1 g of the prepared $CaFeO_3$ samples (coagulants) was taken into the conical flasks and then 50 mL of bentonite clay sample suspension or 50 mL of collected river water were added to each conical flask. The conical flasks were shaken in orbital shaker with 150 rpm in 30, 60, 90 minutes. The conical flasks were kept for 1 day. The top layer of water was collected from each conical flask with pipette and the turbidities were measured by turbidimeter. Coagulation activity was calculated by using the following equation: coagulation activity = $\frac{\mathrm{TB}-\mathrm{TS}}{\mathrm{TB}} \times 100$, where TB is the turbidity of blank and TS is the turbidity of the sample, (Ebeling *et al.*,. 2003).

Results and Discussions

Thermo Gravimetric and Differential Thermal Analysis (TG-DTA) of $CaFeO_3$ Powders

Thermal analysis was carried out on the as-prepared $CaFeO_3$ powder by sol-gel method and TG-DTA thermogram are show in Figure 2 and the interpretation data are summarized in Table 1. There are four weight loss steps in the TG curve accompanied with one endothermic and three exothermic peaks which are observed in DTA curve. The first step was found a small endothermic peak which at the temperature range of 30-100 ºC with the 8.255

% weight loss and this may be due to the evaporation of absorbed water or bound water. In the second stage, an exothermic peak in the temperature range of 200 °C and 300 °C with the weight loss percent was 30.958 % could be attributed to the decomposition of organic matters in the as-prepared powder like C-N, C-H and C-O. In the third stage, an exothermic peak in the temperature range 300 °C and 400 °C with the weight loss percent was 21.67 % and this may be due to the decomposition of nitrates (NO_3^-) and crystallization of $CaFeO_3$. In the fourth stage, an exothermic peak in the temperature range 400 °C and 500 °C with the weight loss percent was 15.48 % due to due to the formation of the expected perovskite phase of $CaFeO_3$. With respect to above result calcination temperatures of the samples were taken at 300 °C, 400 °C and 500 °C and these samples were designated as CFO-300, CFO-400 and CFO-500, respectively. Thermal analysis was also carried out on the prepared CFO-500 powders by TG-DTA and their curves are shown in Figure 3. There was no prominent weight loss on TG curve indicating that the prepared powder was almost stable (Heshem, 2004)

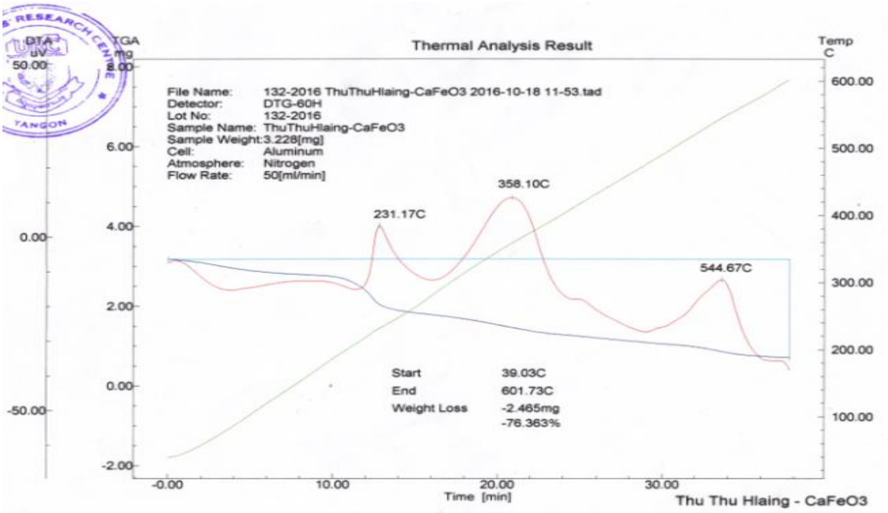


Figure 2: TG-DTA curves of the thermal decomposition of as-prepared $CaFeO_3$ powder

Table 1: Interpretation Data for the Thermal Decomposition of $CaFeO_3$ As-prepared Powder by TG-DTA Analysis

Temp. Range /°C	Weight loss (%)	Nature of peak	Peak's temp. /°C	Remark
80-100	8.255	endo	80	evaporation the absorbed water or bound water
200-300	30.958	exo	231	decomposition organic species
300-400	21.67	exo	358	decomposition of nitrate and crystallization
500-600	15.48	exo	544	formation of the expected perovskite phase of $CaFeO_3$

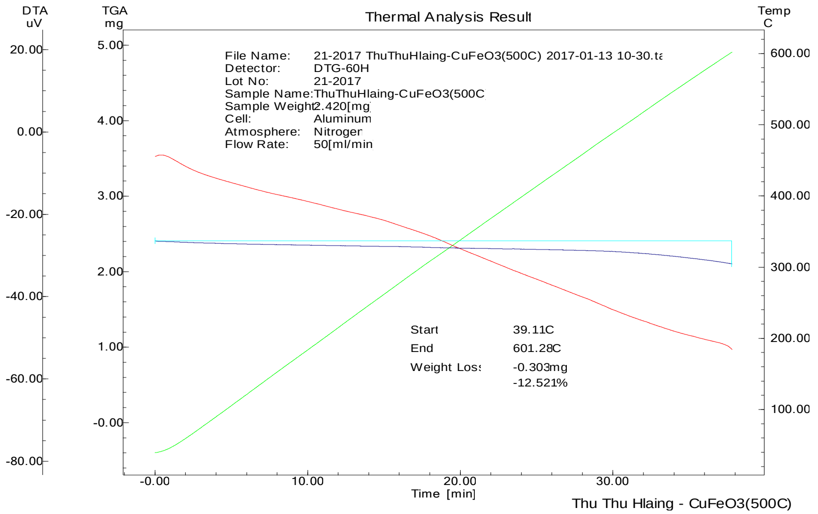
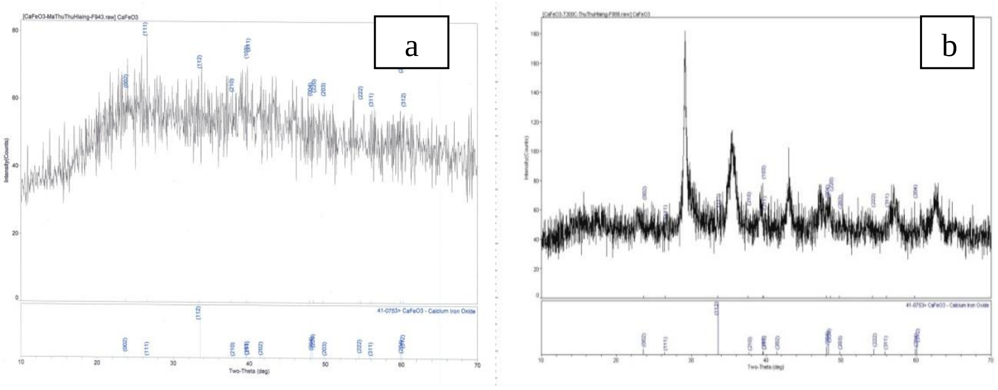


Figure 3: TG-DTA curves of the thermal decomposition of CFO-500

X-ray Diffraction Studies (XRD) of $CaFeO_3$ Powders

The formation of the crystalline structure and crystallite size of prepared samples were confirmed by XRD analysis. XRD diffractograms for as-prepared powder, CFO-300, CFO-400 and CFO-500 are shown in Figures 4 (a)-(d). From these analyses, the as-prepared powder is amorphous nature and X-ray powder diffraction patterns of CFO-300, CFO-400 and CFO-500 confirm the crystalline forms of the samples. XRD pattern of CFO-300 matched with PDF card No. 84-08847 of calcium iron oxide ($CaFeO_3$) but some of the peaks is disappeared due to impurities and crystal structure of CFO-300 is tetragonal. XRD pattern of CFO-400 also matched with PDF card No. 84-08847 of calcium iron oxide ($CaFeO_{2.5}$) and it has pure phase and other secondary phases are not observed. Crystal structure of CFO-400 is orthorhombic. XRD pattern of CFO-500 also matched with PDF card No. 84-08847 of calcium iron oxide ($Ca_4Fe_{14}O_{25}$). Crystal structure of CFO-500 is hexagonal. The average lattice constants, the average crystallite sizes of the prepared samples that were calculated by using the Debye-Scherrer equation: $D = k\lambda/B \cos \theta$, (Zafar *et al.*, 2015) where D is the average size of crystalline particle, assuming that particles are spherical, $k = 0.9$, λ is the wavelength of X-ray radiation, B is full width at half maximum of the diffracted peak, and θ is angle of diffraction, are shown in Table 2. Crystallite size of CFO-300 has 46.18 nm, CFO-400 has 29.81 nm and CFO-500 has 35.27 nm. It was found that the crystallite size of $CaFeO_3$ decrease with increasing calcination temperature and the crystal structure of the prepared sample is mainly depended on calcination temperatures.



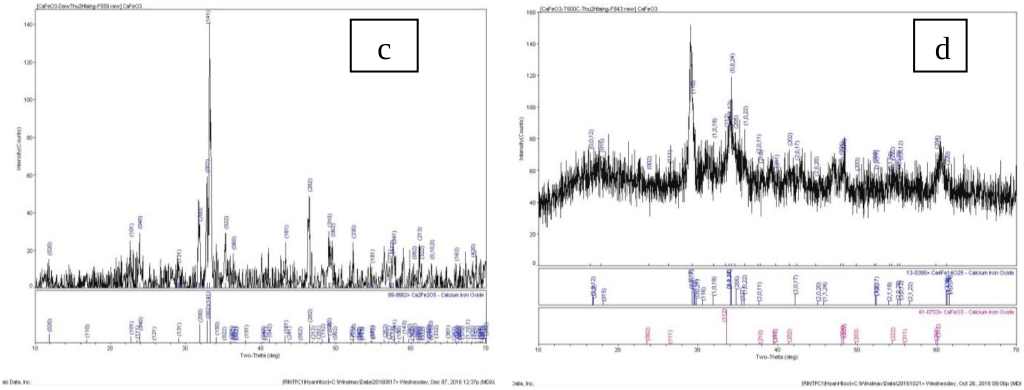


Figure 4: X-ray diffraction patterns of (a) as-prepared powder (b) CFO-300 (c) CFO-400 (d) CFO-500

Table 2: Average Lattice Constants, Crystal Structure and Average Crystallite size of CFO-300, CFO-400 and CFO-500

Samples	Average Lattice Constants /A°			Crystal structure	Crystallite Size/nm
	a	b	c		
CFO-300	5.3394	-	7.5511	Tetragonal	46.18
CFO-400	5.6224	14.9187	5.4532	Orthorhombic	29.81
CFO-500	6.0998	-	58.3881	Hexagonal	35.27

Scanning Electron Microscopy Studies (SEM) of $CaFeO_3$ Powders

The surface morphologies of the prepared CFO-300, CFO-400 and CFO-500 were studied by SEM and their micrographs are shown in Figures 5 (a)-(c). The SEM images reveal that all of the products look like low density, loose and porous materials that is favorable for filtration process. It was also found that agglomeration of the particles increased with increasing temperatures.

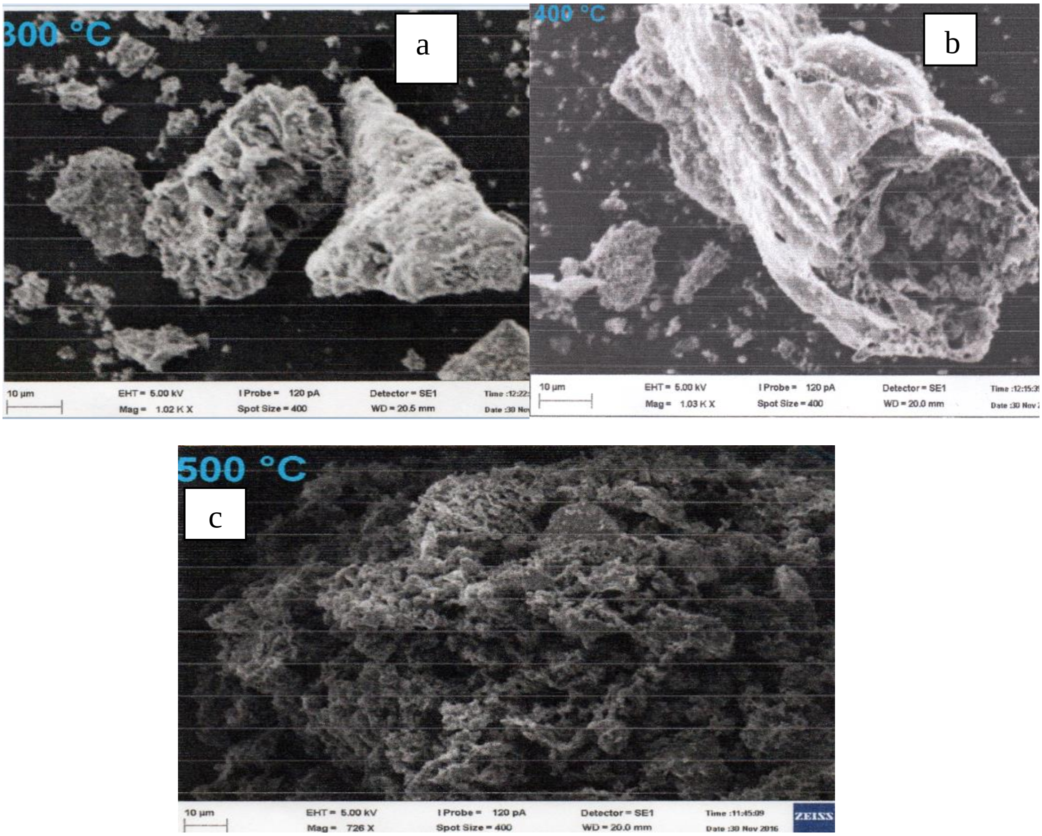


Figure 5:SEM micrographs of the prepared (a) CFO-300 at 1.0 kX magnification, (b) CFO-400 at 1.0 kX magnification and (c) CFO-500 at 0.75 kX magnification

Elemental Studies (ED XRF) **of $CaFeO_3$ Powders**

Figures 6 (a)-(c) show energy Dispersive X-ray Fluorescence (EDXRF) spectra of $CaFeO_3$ samples, which confirm the relative abundance of the elements in $CaFeO_3$ nanocrystalline powders. From the EDXRF spectra, it is further confirmed that no elements other than Ca and Fe were present hence it shows that the prepared samples were highly pure. The relative abundance of the elements (%) of the samples is listed in table 3.

Table 3: Relative Abundance of Elements of the prepared CFO-300, CFO-400 and CFO-500 by EDXRF Analysis

Elements	Relative Abundance of Elements in the Samples (%)			Molar mass (gmol^{-1})
	CFO-300	CFO-400	CFO-500	
Ca	37.205	39.222	39.413	40
Fe	62.456	60.426	60.255	56

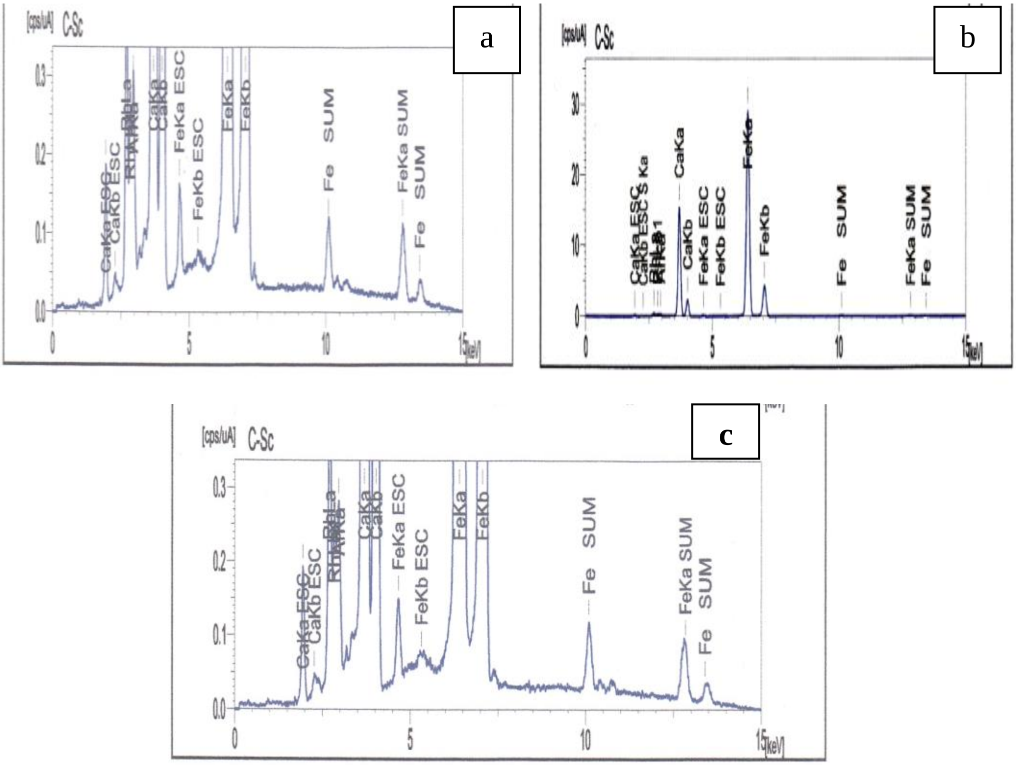
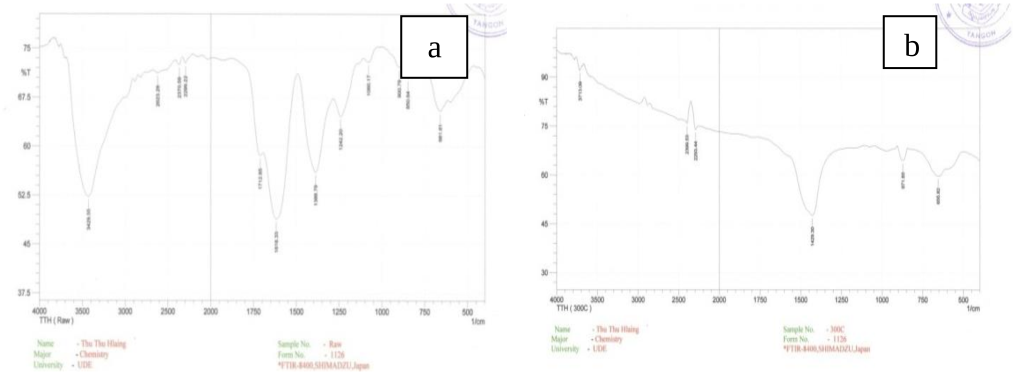


Figure 6: ED XRF spectra of the prepared CaFeO$_3$ nanocrystalline powders (a) CFO-300, (b) CFO-400 and (c) CFO-500

Fourier-transform Infrared Spectroscopy Studies (FT IR) of $CaFeO_3$ Powders

FT IR spectra of the prepared $CaFeO_3$ xerogel powder before calcination and after calcined (CFO-300, CFO-400 and CFO-500) are shown in Figures 7(a)-(d). In the FT IR spectrum of the prepared as-prepared $CaFeO_3$ powder, the band occurred at 3429 cm^{-1}, due to O-H stretching vibration and the band occurred at 1618 cm^{-1} due to N-O stretching vibration. The band at 1242 cm^{-1} shows C-O stretching vibration of chelating agent and the band at 661 cm^{-1} attribute the stretching of metal-oxygen vibration. The results suggested that the as-prepared gel consists of an intermediate/complex of citric acid, water, and metal ions. The FT IR spectra of the prepared CFO-300, CFO-400 and CFO-500 samples exhibit absorption bands between 3400-3000 cm^{-1} due to the O-H stretching vibration, a band between 1400-1500 cm^{-1} which represent the C-O stretching vibration from residual carbon, the band at 800-900 cm^{-1} shows C-H bending vibration from residual carbon and the bands between 400-750 cm^{-1} show stretching vibration of metal-oxygen bond. The observed FT IR data of the prepared $CaFeO_3$ powders were consistent with literature values, (Nakamoto1970).



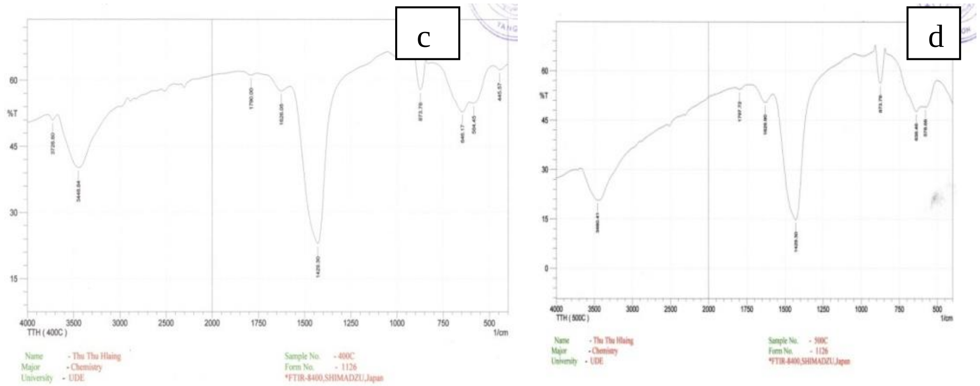


Figure 7: FT IR spectra of (a) as-prepared $CaFeO_3$ powder (b) CFO-300,(c) CFO-400 and (d) CFO-500

Physicochemical Properties of $CaFeO_3$ Powders

Physicochemical properties of prepared calcium iron oxide powders were determined by conventional laboratory methods. The physicochemical properties such as free moisture contact, pH, bulk density, specific surface area of prepared calcium iron oxide powder are presented in Table 4. It was found that pH of the prepared samples are almost neutral. Moisture contact decreases with increasing calcination temperature. Surface areas of the prepared CFO-300, CFO-400 and CFO-500 powders are 3.87 6 m^2/g, 5.612 m^2/g and 4.808 m^2/g, respectively. It was found that CFO-400 has the largest surface area among three prepared samples.

Table 4: Some Physicochemical Properties of the Prepared $CaFeO_3$ Nanocrystalline Powders

Sample	pH	Moisture Contact / %	Bulk Density/ gmL	Surface Area/ m^2/g
CFO-300	7.55	8	0.623	3.876
CFO-400	7.45	7	0.395	5.612
CFO-500	7.44	5	0.51	4.808

Coagulation Activity of $CaFeO_3$ Powders

The coagulation activity or removal percent of turbidity of $CaFeO_3$ powders were studied on river water as well as betonite clay suspension by varying contact time effect. The measurement of turbidity is a key test of water quality. WHO (2017) water quality standard is not exceeding 5 nephelometric turbidity units (NTU). Variation of reduced turbidity and removal percentages of turbidity from river water and betonite clay suspension with contact time are shown in Tables 5-8.

Table 5: Variation of Reduced Turbidity of Bentonite Clay Suspension by the Prepared Samples with Different Contact Time

Sample	Turbidity (NTU) at Different Shaking Time (minutes)			
	0	30	60	90
Bentonite Clay Suspension	77.20	26.60	23.60	23.80
CFO-300	-	7.83	10.00	13.30
CFO-400	-	1.25	2.42	1.42
CFO-500	-	1.62	1.45	0.91

Table 6: Variation of Coagulation Activity of the Prepared Samples on Bentonite Clay Suspension with Different Contact Time

Sample	Coagulation Activity (%) at Different Contact Time (minutes)		
	30	60	90
CFO-300	89.86	87.05	82.77
CFO-400	98.38	96.87	98.16
CFO-500	97.90	98.12	98.82

Table 7: Variation of Reduced Turbidity of River Water by the Prepared Samples with Different Contact Time

Sample	Turbidity (NTU) at Different Shaking Time (minutes)			
	0	**30**	**60**	**90**
River Water	83.5	26	23.4	21.9
CFO-300	-	9.23	8.42	9.96
CFO-400	-	1.44	1.46	1.24
CFO-500	-	1.41	1.43	1.43

Table 8: Variation of Coagulation Activity of the Prepared Samples on River Water with Different Contact Time

Sample	Coagulation Activity (%) at Different Contact Time (minutes)		
	30	**60**	**90**
CFO-300	88.95	89.92	88.07
CFO-400	98.28	98.25	98.51
CFO-500	98.31	98.29	98.29

Conclusion

$CaFeO_3$ nanocrystalline powders are of considerable interest due to their wide range of applications in fields such as magnetic storage, medicine, chemical industries and water purification. The present research deals with a study on preparation, characterization and coagulation activity of the prepared $CaFeO_3$ powders. By TG-DTA analysis the minimum crystalline temperature or required $CaFeO_3$ structure formation temperature was started from 400 °C. The XRD patterns of the three prepared powder samples, CFO-300, CFO-400 and CFO-500, $CaFeO_3$ described the tetragonal, orthorhombic and hexagonal phases with respect to their calcination temperatures. The average crystallite sizes of the CFO-300, CFO-400 and CFO-500 were found to be 46.18, 29.81, 35.27 nm, respectively. From SEM results, it was confirmed that the CFO-300 sample showed porous nature with less agglomerate, CFO-400 samples had porous and fibrous and porous nature and CFO-500 had porous and more uniformly agglomerate. From EDXRF results, the main constituent elements of all three samples are Fe and Ca and all are approximately 1:1 molar ratio. According to FT IR, C-O stretching vibration at 1408 and 1033 cm^{-1}, C-H stretching vibration at 874 cm^{-1} and metal oxygen stretching vibration at 712 cm^{-1} are observed in all three prepared sample. Surface area of CFO-400 (5.612 m^2/g) is greater than that of other two samples. The coagulation activities of $CaFeO_3$ powders were studied in term of turbidity of bentonite clay suspension and river water. The coagulation activities of prepared samples from river water are 87.05 % by CFO-300, 96.87 % by CFO-400 and 98.12 % by CFO-500 powder with contact time 1h. The coagulation activities of prepared samples on the bentonite clay suspension are 89.92 % by CFO-300, 98.25 % by CFO-400 and 98.29 % by CFO-500 powder with contact time 1h. According to these removal percentages, CFO-400 and CFO-500 powders were found to be more efficient than CFO-300 for the removal of turbidity from both river water and bentonite clay suspension. This research mainly concerns with the preparation and characterization of $CaFeO_3$ nanocrystalline powders but only study coagulation activity of the prepared samples in terms of reducing turbidly of water and further characteristic factors of water are still needed to study.

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