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CALCIUM FERRITE NANOPARTICLE PRODUCTION FROM MINING WASTES: MARBLE DUST AND PYRITE ASH

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ABSTRACT

Calcium ferrite nanoparticles were prepared by microwave-sonication assisted hydrothermal route obtained from mining wastes, marble dust and pyrite ash. The magnetism strength, XRD, and FT-IR were performed. Different thermal modifications as microwave and autoclave following sintering applications were investigated. Scanning Electron Microscope images show that microwave treated calcium ferrite nanoparticles have formed as cubic shape while others have irregular-noncrystallized shapes. The arsenic removal was searched by calcium ferrite nanoparticles, found that microwave treated samples have higher capacity.

Key words; calcium ferrite, nanoparticles, adsorption, arsenic, copper

1 INTRODUCTION

Nanomaterials are one of the most attractive and practical aspect of nanotechnology today. Nano scale adsorptive materials can be used in water treatment, such as heavy metal, organic pollutants and radionuclides removal. At nanoscale, materials can have unique character, such as large surface area, catalytic potential and high reactivity, which make them better adsorbing capability (Sharma et al., 2009). Among nano adsorbents, magnetic nano adsorbents are more interesting owing to their ease of application ranging from fundamental research to industrial use.

The preparation method of ferrites varied as sol-gel methods (Atif et al., 2006), the ball-milling technique (Jiang et al., 1999), coprecipitation (Shenoy et al., 2004), polymeric-assisted route (Zhang et al., 2005) the hydrothermal method (Li et al., 2010, Yenial et al., 2016), the reverse micelles process (Kale et al., 2004), and the microemulsion method (Hochepied et al., 2000). Most of these methods have achieved particles of the required sizes and shapes, but they are difficult to employ on a large scale because of their expensive and complicated procedures, high reaction temperatures, long reaction times, toxic reagents and by-products, and their potential harm to the environment (Naseri et al., 2011).

In comparison with other ferrites such as $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$ and $CuFe_2O_4$, calcium ferrite has a significant advantage; it is biocompatible and eco-friendly due to the presence of Ca^{2+} instead of heavy metals (Khanna and Verma, 2013). There are several reports on usage of $CaFe_2O_4$ as a pigment, an anode in lithium batteries, adsorbent of hydrogen sulfide, and solid catalyst but none on its use for the separation and pre-concentration of organic and inorganic materials. In the literature calcium ferrites are mostly produced by sol-gel method. There are a few applications about co-precipitation method of synthesizing calcium ferrites, such as Pirouz et al., (2015) synthesized calcium ferrite nano particles with ultrasonic assisted co precipitation method. They found that the calcium ferrite nanoparticles were sphere-like particles possessing superparamagnetic properties with an average diameter of 40 nm.

The aim of this study is the production of magnetic nano materials as adsorbents for toxic metal removal from aqueous solutions. The target is the production of magnetic nanoparticles from mining wastes, magnetic separation of loaded adsorbents from solution are the main steps of this research.

2 MATERIAL AND METHOD

2.1.Material

The material pyrite ash was recieved from sulfuric acid production plant which is located in Balıkesir, Turkey. The pyrite ash is a waste product of pyrite incineration to produce sulfuric acid and mainly contains iron oxides, silicates and some unburned pyrites. The chemical analysis of this sample is given in Table 1. The determination of particle size was accomplished with Malvern Mastersizer 2000. The particle size of pyrite cinder was originally found as 0.09 mm and ground to 0.032 mm. The marble dust was received from Muğla Yatağan Kavaklıdere marble production plant belongs to Tekmar Marble and Mining Industry. Around 20-30 tones of marble dust are generated while marble is cutting and generally these dusts do not put to good use. The sample is used after ground in agate mortar according to particle size analysis, the original sample has 0.85 mm d_{80} size and 0.4 mm d_{50} size whilst the ground sample has 0.03 mm d_{80} size and 0.01 mm d_{50} size. The marble dust contains 98.4% $CaCO_3$ and the chemical analysis is shown in Table 1.

Table 1. The chemical analysis of the materials

Pyrite Ash		Marble Dust	
Content	**Assay, %**	**Content**	**Assay, %**
Fe_2O_3	75.88	Fe_2O_3	0.29
CaO	0.62	CaO	98.4
Al_2O_3	0.37	Al_2O_3	0.12
MgO	0.13	MgO	0.64
SiO_2	1.70	SiO_2	0.27
FeS_2	20.61	K_2O	1.78

2.2.Methods

Calcium ferrite nanoparticles were synthesized upon the method of ultrasonic wave and surfactant assisted hydrothermal synthesis. The preparation flowsheet is shown in Figure 1. The Fe bearing solution was obtained after leaching pyrite ash in microwave digester assisting H2SO4 as leaching agent at 200°C for 2 h with 1/10 solid-liquid ratio. The calcium was obtained dissolution of marble waste in nitric acid. The Fe-bearing liquor and Ca-bearing liquor mixed in the molar ratio of Fe^{3+} and Ca^{2+} 2:1. Under vigorous stirring, organic solvent dodecyl trimethyl ammonium bromide (DTAB) was added to the solution in the same molar ratio of Fe^{3+}. The pH of the solution was constantly monitored as the 5M NaOH solution was added. The reactants were constantly stirred using a magnetic stirrer until a pH level of 12.5 was reached and orange-brownish precipitate was obtained. After 1 h mixing time at 60°C, 5 min sonication was applied and after 1 h another mixing time, the solution replaced in autoclave for 2 h at 120°C or microwave digester for 2h at 200°C for thermal treatment. The precipitate was washed three times with distilled water and once with ethanol to remove excessive amount of sodium hydroxide and organic from precipitate. To isolate the supernatant liquid, the solution was centrifuged for fifteen minutes at 3000 rpm. The precipitate was dried in oven for 24 h at 105°C. After drying, sintering was applied for some nanoparticle products in muffle furnace such as, 300 500 and 700°C. The experimental conditions are shown in Table 2. The resulted materials were classified as magnetic or nonmagnetic which was determined with hand magnet.

The metal releasing tests were done in falcon tubes with 0.01 g nanoparticle material and 2 different reagent solutions. The solutions were shaken for 24 h in ambient temperature. The reagent solutions were first one is distilled water with pH: 5.86 and second one is acidic water (1 drop of HCl) at pH 3.07. The solutions were analyzed for Ca, and Fe ions and pH change was recorded in the end of the experiment.

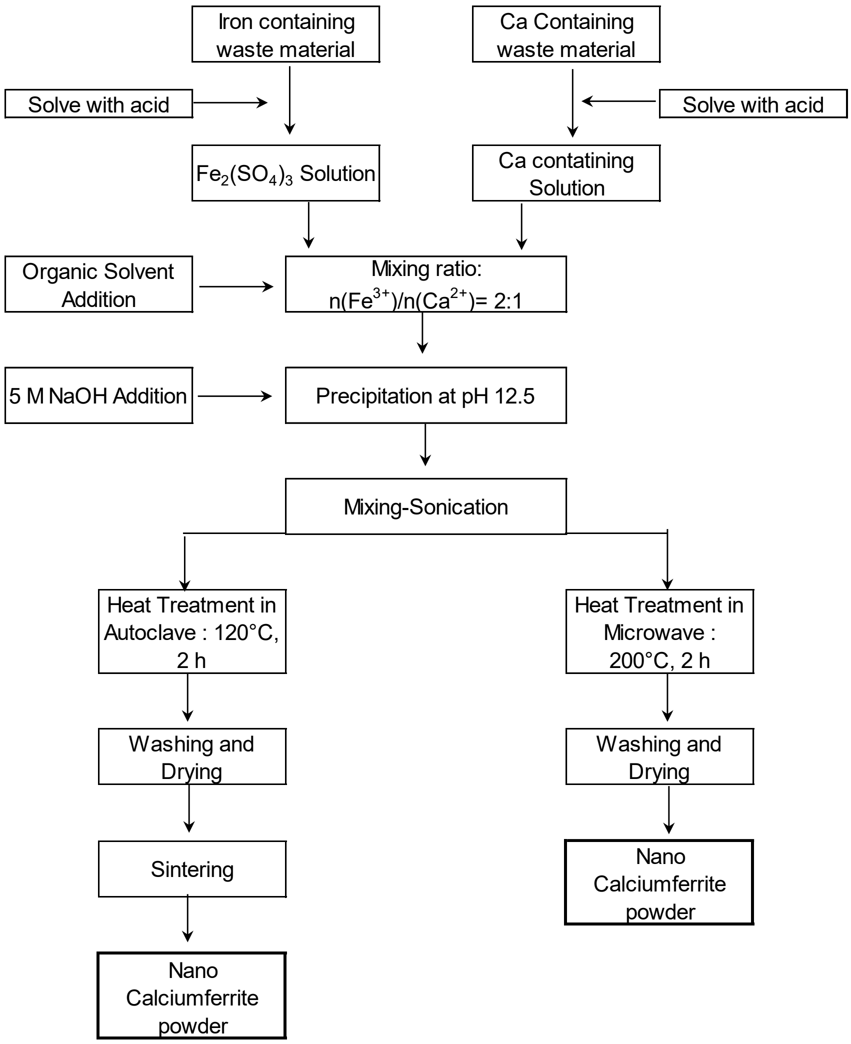


Figure 1. Flowsheet of $CaFe_2O_4$ nanoparticle production

In the adsorption experiments, 0.05 g calcium ferrite nanoparticles were mixed with 0.4 mM (30.9 ppm) As(V) containing solution. The adsorption experiments were carried out at ambient temperature to test the adsorbing capability of the produced nanoparticles. Adsorption experiments were conducted at pH 5, 2 h mixing time at ambient temperature.

Table 2. Experimental Conditions

Material	Thermal Treatment	Magnetic Result
C1	Microwave	Magnetic
C43	Autoclave + Sintering 300°C	Nonmagnetic
C45	Autoclave + Sintering 500°C	Nonmagnetic
C47	Autoclave + Sintering 700°C	Magnetic

2.3.Analyses

The chemical analysis of the samples was done with Atomic Absorption Spectrometry (Jena 300). The micro structure and surface morphology of the samples have been examined using HR FESEM Zeiss Auriga field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX). XRD patterns have been provided by Rigaku D-max and interpreted with Match! XRD calculation program. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a PerkinElmer spectrum FTIR using KBr pellets. The magnetic properties of the nanoparticles were measured with a Physical Properties Measurement System magnetometer at 298 K (Quantum Design, USA). The magnetization measurement was taken from the −70 kOe to 70 kOe field. The saturation magnetization, residual magnetization and coercive fields and were determined from the magnetization versus applied field curve.

3 RESULTS AND DISCUSSIONS

Two different thermal routes were applied to obtain $CaFe_2O_4$ nanoparticles. In this manner, autoclave following sintering treatment at 300, 500, 700°C was applied to nanoparticles, while other was treated with microwave. SEM was used to exhibit the morphology and particle sizes of the samples. SEM images of sintered $CaFe_2O_4$ samples are shown in Fig. 2a, b and c. It is clear that autoclave following sintering application results solid noncrystallized nanoparticles which is an unwanted result indicates bad crystallization therefore found to be ineffective for calcium ferrite synthesis. Only 700°C sintered sample shows magnetic behavior due to formation of iron hydroxides to iron oxides while others are nonmagnetic. Figure 3 shows the microwave treated $CaFe_2O_4$ nanoparticles had cubic identical shapes and the size of one cube was varied as 94.07 nm, 214.19 nm and 253.9 nm which were also found to be magnetic. In Figure 4, the EDX analyses of the sample was shown, the ratio of Fe to Ca by wt is found 2.54, and C is originated from marble dust ($CaCO_3$), therefore some of the Ca is bounded by carbonates, and Fe is found as oxidized form, which is confirmed by XRD analysis as shown in Figure 5. The observed sample shows 51.9% hematite, 32.4% calcite and 15.8% $CaFe_2O_4$ nanoparticles. Figure 6 shows the FT-IR spectrum of $CaFe_2O_4$ nanoparticles.

The FT-IR spectrum of $CaFe_2O_4$ nanoparticles were shown in Figure 6. The peaks 874, 712 564 and 479 cm^{-1} in the fingerprint region arises from lattice vibrations of oxide ions against relatively metal ions (Fe). The peaks between 3000 to 1300 cm^{-1} correspond to organic functional groups present on the surface of nanoparticles. Two intense peaks 2512 and 1798 and 1420 cm^{-1} were arise from the asymmetric and symmetric stretching modes of $–CH_3$ functional group of organic agent on the surface of nanoparticles, respectively.

Magnetic properties of $CaFe_2O_4$ nanoparticles were studied at room temperature in the applied magnetic field from -10 to 10 KOe, as shown in Figure 7. The sample is soft magnetic, the saturation magnetization of the powder sample was obtained as 9.65 emu/g and the coercivity of the composite was estimated to be 6.7 Oe and residual magnetization is 4.2 emu/g. The negligible coercivity and low remanence indicated that $CaFe_2O_4$ nanoparticles have a single magnetic domain.

The metal release of the two different thermal modified $CaFe_2O_4$ samples were investigated at pH 3 and pH 5, and the results are displayed at Table 3. The microwave treated sample found to more resistant to acidic conditions and Ca and Fe dissolutions were found lower than autoclave + sintering treated sample at both pH's. The pH change is also different in both sample, autoclave treated sample has more alkalinity to increase pH.

The adsorption capacities of different thermally treated $CaFe_2O_4$ nanoparticles were investigated for arsenic removal from aqueous solutions and results are shown in Table 4. The highest arsenic removal capacity was observed with microwave treated sample, the arsenic removal capacity was found as 85.85%. The sintering temperature increasing caused decrease in adsorption removal from 80.14% to 6.75%, due to increasing oxidation and crystallinity and decreasing amorphous structure thus active sites for arsenic bonding.

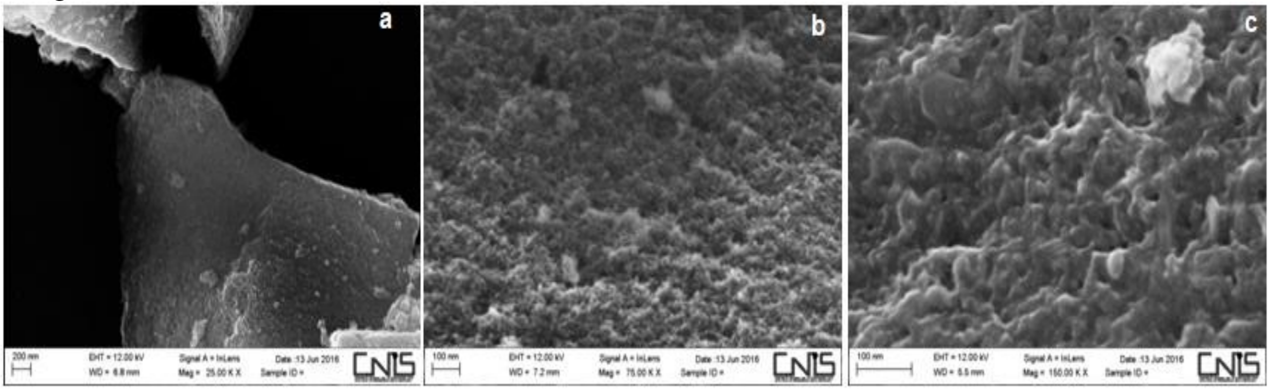


Figure 2. Autoclave treated following sintered at 300°C (a), 500°C (b), 700°C (c)

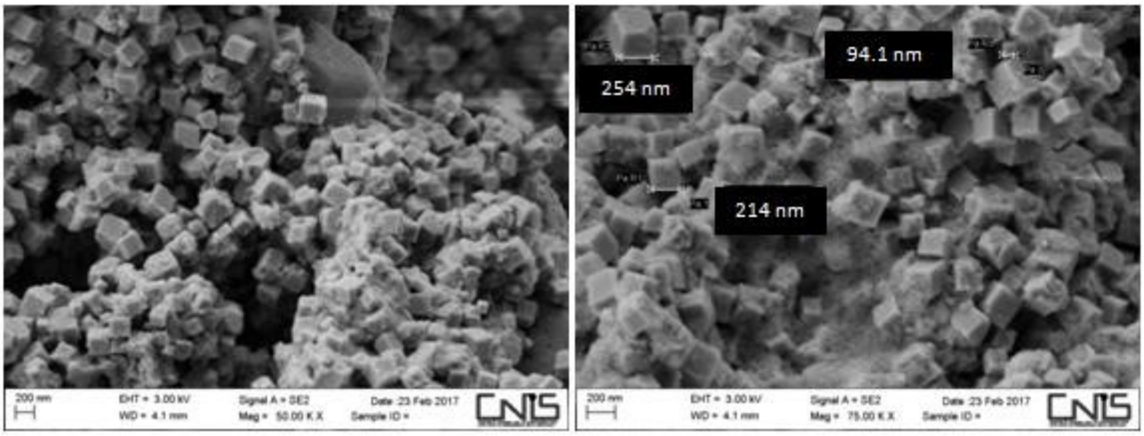
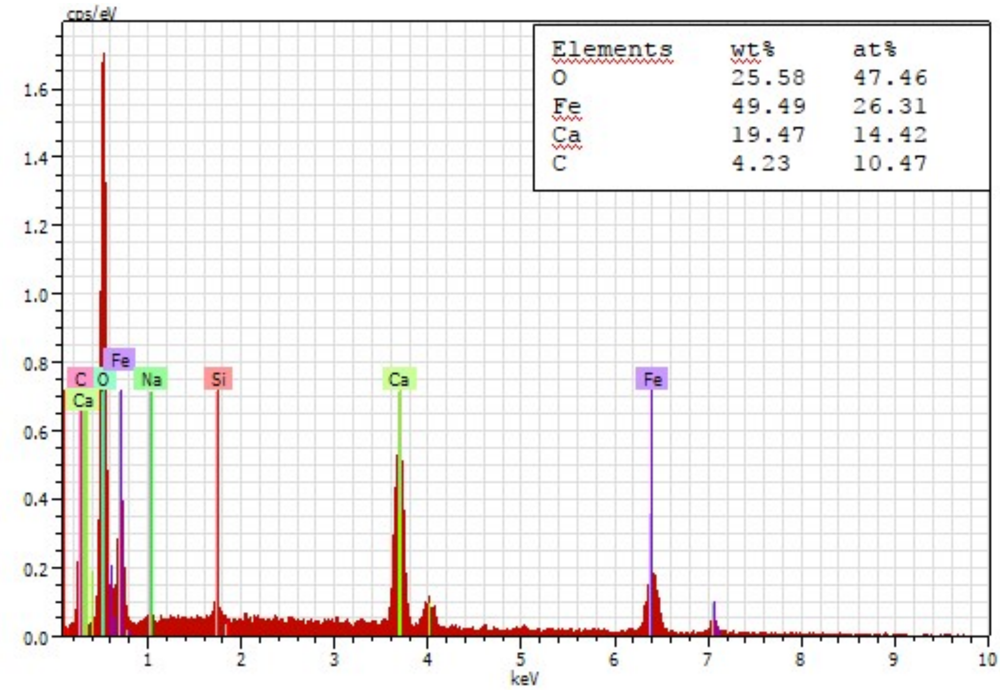


Figure 3. Microwave treated $CaFe_2O_4$ nanoparticles



Figures 4. The SEM and EDX measurement of $CaFe_2O_4$ nanoparticles

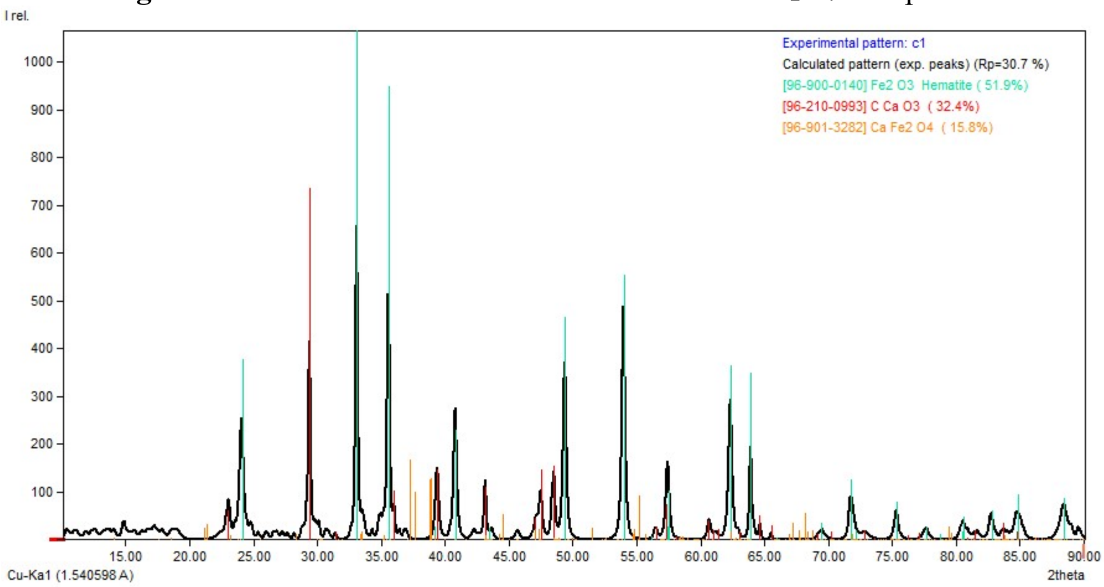


Figure 5. XRD analysis of $CaFe_2O_4$ nanoparticles

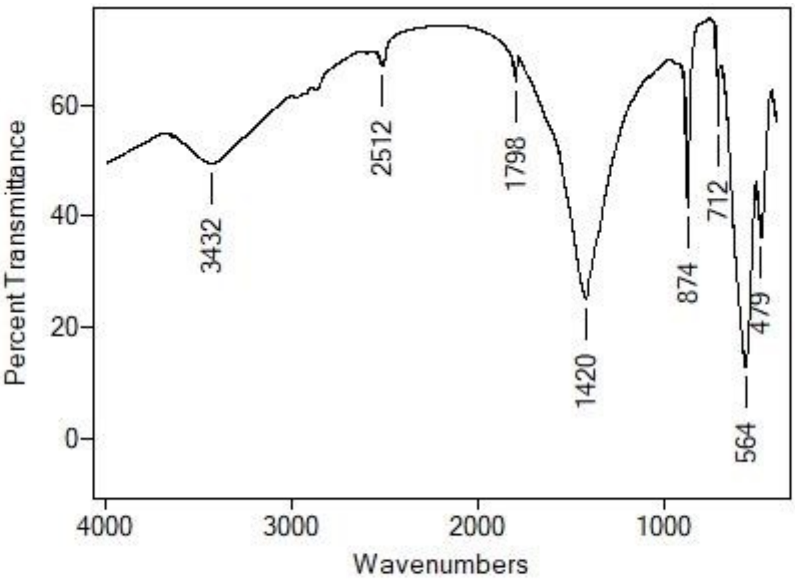


Figure 6. FT-IR spectra of $CaFe_2O_4$ nanoparticles

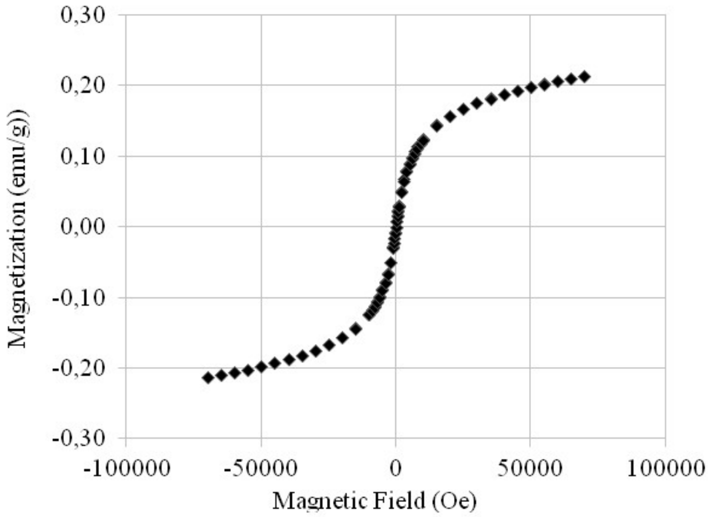


Figure 7. Magnetism measurement of $CaFe_2O_4$ nanoparticles (C1 sample)

Table 3. The metal releasing of $CaFe_2O_4$ nanoparticles

Material	pHi	pHf	Ca, mg/g	Fe, mg/g
C1	3.07	3.98	37.04	0.02
	5.86	8.85	6.50	u.d
C43	3.07	7.06	44.30	0.22
	5.86	9.76	8.50	0.05

u.d: under detection limit

Table 4. The results of arsenic adsorption on $CaFe_2O_4$ nanoparticles

Material	Cf, As, ppm	Qm, mg/g	% Removal
C1	0.438	2.66	85.85
C43	0.615	2.48	80.14

C45	1.323	1.77	57.27
C47	2.887	0.21	6.75

4 CONCLUSION

$CaFe_2O_4$ nanoparticles are produced from marble dusts and pyrite ash as abandoned mining wastes. The nanoparticles are synthesized by a facile method of ultrasonic wave and surfactant assisted hydrothermal synthesis. Different thermal applications autoclave treatment following sintering and microwave treatments were tested by means of magnetism, and it is found that microwave treated and 700°C sintered calcium ferrite nanoparticles have magnetic feature, and higher stability to acidic environmental conditions. The adsorption capacities of calcium nanoparticles were investigated to remove arsenic from solutions, it is found that increasing sintering temperature cause a decrease in adsorption capacities of nanoparticles, the highest arsenic removal capacity is found with microwave treated calcium ferrite nanoparticles.

5 ACKNOWLEDGEMENT

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