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Synthesis, Characterization, scaling up and use of Calcium Carbonate Nanoparticles to prepare nanoporous PVC film

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Abstract

$CaCO_3$ nanoparticles synthesized from $CaCl_2$ and Na_2CO_3using a new, simple and fast technique. Factors affecting on the particle size such as concentration of Ca^{2+} and CO_3^{2-}, PEG weight dissolved in Ca^{2+} solution, flow rate, temperature, media type, PEG weight dissolved in the used medium, concentration of CO_3^{2-}, *stirring* speed, medium volume and additive dissolved within Ca^{2+} solution investigated. The obtained particles were characterized by SEM, XRD, EDS, IR and TGA. The characterization clarified that the particles prepared were spherical with size range of 19-30 nm, ultra-pure and the crystal was calcite. Moreover, the preparation system was redesigned to be continuous preparation system. The histogram showed that the $CaCO_3$ nanoparticles obtained were homogenous in size (30 nm). Finally, the obtained nanoparticles were used in preparation of nanoporous PVC film with pores size range 80-120nm

Keywords:CaCO3 nanoparticles, calcite, precipitation, chemical control reaction, spherical, nanopores film

1. Introduction

In a precipitation process, two or more reactants form a solid product. In many cases, the solubility of this product is very low. So when the reactants are brought together, a high degree of super saturation occurs, which leads to the nucleation of new crystals and subsequent crystal growth and finely agglomeration.

Nanoparticles are ultrafine particles in the size in order of nanometer order. "Nano" is a prefix denoting the minus 9th power of ten (10^{-9}), namely one billionth. Here it means nanometer.nm, applied for the length. These nanoparticles can cause significantly change in the properties of materials, such as optical properties, hardness, shape and morphology.

$CaCO_3$ nanoparticles attract attention, due to their wide range application coating, plastic industry, paper, drug delivery, etc.$CaCO_3$ nanoparticles have been produced using several methods; carbonization [1-9], tubular reactor [10], microemlusion [11-15], mechanochemical reaction by mechanical milling of $CaCl_2$+ Na_2CO_3 powder mixture [16] and milling of calcite in presence of additive [17].

In the present paper we prepare a homogenous spherical nanoparticles of $CaCO_3$ by chemical control reactionusing a new laboratory scale designed apparatus. The synthesized method is simple and consumed shorter time than other methods. These nanoparticles were used to prepare a PVC film with nanopores size.

2. Experimental

2.1. Chemicals

Calcium Chloride(95%) from Park, U.K., Sodium Carbonate (99.5%) from Oxford, India, Poly ethylene glycol (A.R.) from Serva, Vegetable oil from Arma Oils, Dehydrated Ethanol (99.9%) from International Co. for Supp. &Med. Industries, Benzene (99.7%) from BDH, 1-propanol (99.7%) from Sigma-Aldrich,

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Cetyl trimethyl ammonium bromide (CTAB) (99%) Winlab, U.K., Poly vinyl chloride (PVC) (A.R.) Winlab, U.K., fromWinlab, U.K. and Tetrahydrofuran (99%) from Panreac, Spain.

2.2. Instruments:
GP 3202 analytical balance (Sartorius, USA.), SB 162 hot plate stirrer (Stuart, UK.), Pump drive S101 (Heidolph,Germany), Centrifuge,Rotofix32 (Hettich, UK.), Furnace model 107801(Boekel industries INC., USA.).

2.3. For characterization:
JSM-636 OLAScanning Electron Microscopy (SEM) (Jeol, Japan) with EDS analysis was used to measure the elemental analysis, XRD- 7000X-Ray Diffraction (Shimadzu, USA.), 8400s Thermogravimeteric-differential analysis (TGA) Shimadzu, Japanand8400s Fourier Transmission Infra-red spectroscopy (FTIR) Shimadzu, Japan.

2.4. Procedure*:*
2.4.1. Preparation of $CaCO_3$ nanoparticles

1M of $CaCl_2$ and Na_2CO_3 solutions were prepared by dissolving 11.2g and 10.4g respectively in 100 ml doubly distilled water and desiredconcentrations were obtained by further dilution.
The continuous removal of MB was carried out through a self-made equipment. A plastic pipe connected to a peristaltic pump. One end of the pipe (input) immersed in the dye solution. The other end of the pipe (output) packed with the sponge and the output solution collected in a glass beaker.
The preparation is based on formation of $CaCO_3$ from the reaction between $CaCl_2$ and Na_2CO_3 according to Eq. 1.

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl \quad (1)$$

The experimental set up for synthesizing nanoCaCO3 is seen in Fig. 1. CaCl2 and Na2CO3 solutions presented in 50 ml falcon tubes were pumped usingperistalticpump through two plastic tubes. Two steel ages of insulin syringe were cupped the ends of the plastics tubes (output). A certain volume of solution medium present in 250ml glass jar receive CaCl2 and Na2CO3 solutions.a magnetic stirrer was used tostir the solution in the glass jar.
The CaCl2 and Na2CO3 solutions were introduced in different media with continuous stirring using magnetic stirring. The precipitate produced was centrifuged at 6000 rpm for 15min and the solution was decanted. The precipitate was then dispersed in dehydrated alcohol, deposited on glass slide and air dried before characterized by SEM and dried powder used for TGA, XRD, IR and EDS analysis.

2.4.2. Preparation of PVC film with nanopores size

0.1g of $CaCO_3$powder was dispersed in 10ml ethanol and added to 1g PVC was dissolved in 25ml THF under stirring then this solution was casted in petridish and left to dry in air, the film placed in 1M HCl for 24hr, then the film was characterized by SEM to determine the pores size.

3. Results and discussion

3.A.1. Effect of Ca^{2+} and CO_3^2concentration on the $CaCO_3$ particle size

The relation between the Ca^{2+} and CO_3^{2-} ions concentration (M) and the average particle size (µm) is illustrated in Fig. 2. The particle obtained at using different concentration of Ca^{2+} and CO_3^{2-} (where $[Ca^{2+}] = [CO_3^{2-}]$) 0.10, 0.20, 0.50, 0.75 and 1M the particle size ranged between 25-37nm, 15-34nm, 22-48nm, 11-32nm and 1.04-3.12µm, respectively.

3.A.2. Effect of PEG weight dissolved in Ca^{2+} solution on the $CaCO_3$ particle size

The experimental results obtained were plotted as values of PEG weight, g, versus the average particle size (µm) as in the Fig. 3. The relation traced shows clearly that by increase PEG weight there is no large difference in the size of particles nor average particle size. The range $CaCO_3$ particle size 14-27nm, 11-32nm and 16-29nm at dissolving 0.0, 0.05 and 0.10gm PEG in Ca^{2+} solution, respectively.

3.A.3.Effect of flow rate on the $CaCO_3$ particle size

Fig. 4, shows the effect of flow rate on the $CaCO_3$ particle size. It was found that by increase the flow rate there is decrease in size of particles an average particle size. The range $CaCO_3$ particle size was 25-52nm at flow rate = 0.25 L/hr, 27-44nm at flow rate = 0.37 L/hr and 14-27nm at flow rate = 0.60 L/hr.

3.A.4. Effect of temperature on the $CaCO_3$ particle size

Dependence of $CaCO_3$ particle size on the oil temperature was indicated by Fig. 5, which showed that there is increase in the size of particles and average particle size with increase the temperature. When the temperature of oil 25°C, 50°C and 100°C the range particle size was 14-27nm, 22-47 nm and 18-42 nm, respectively.

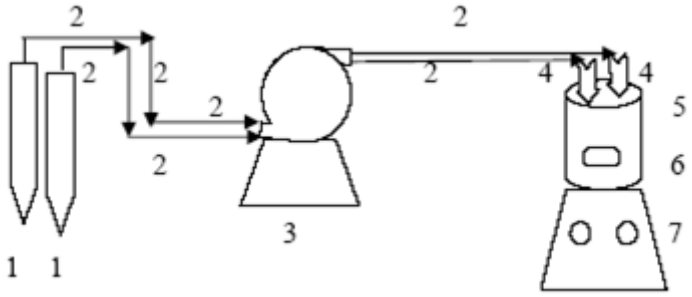


Fig. (1): The schematic diagram of synthesis apparatus**.**
1: Plastic tube 50ml 2: Plastic pipe 3: Pump 4: Age steel of Insulin Syringe 5: 250ml glass Jar
6: Magnet 7: Hot plate stirrer

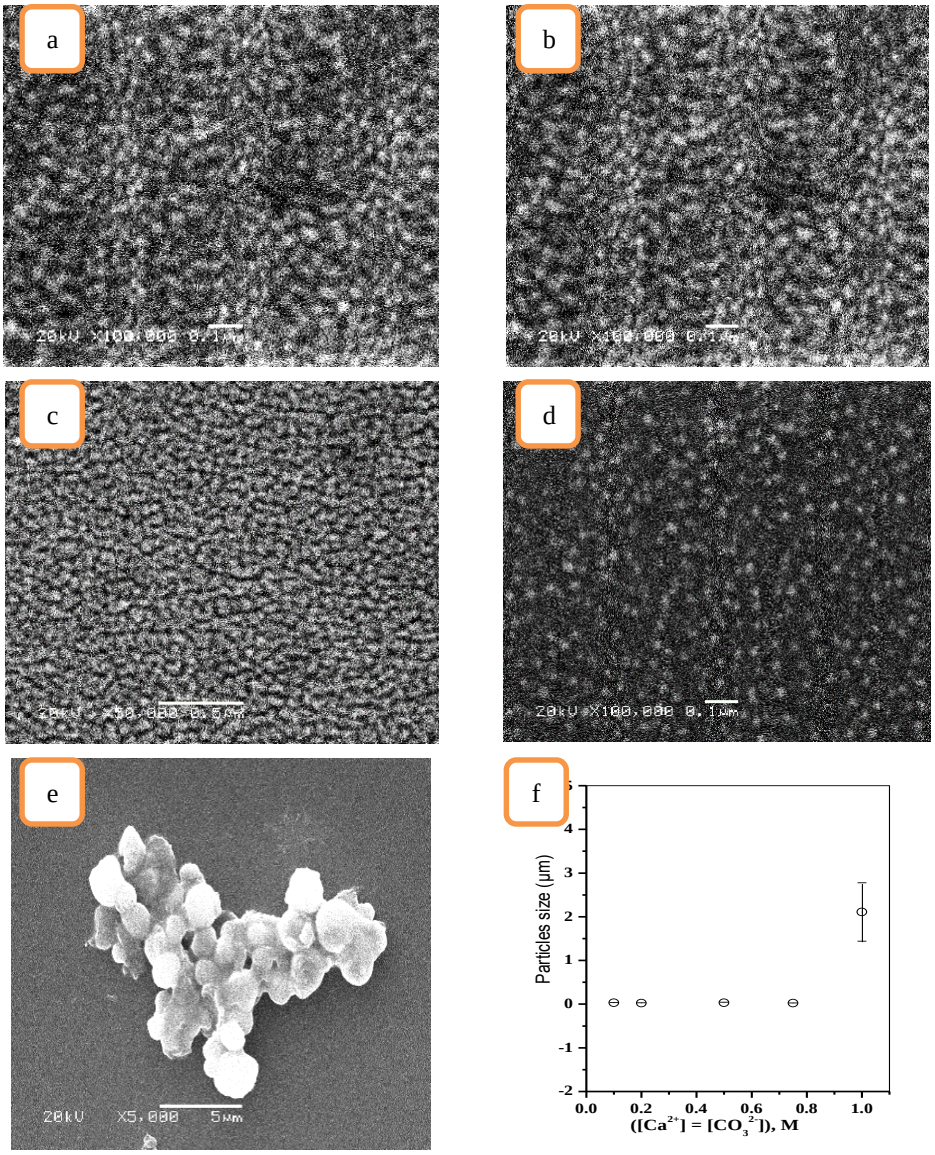


Fig. (2): Effect of Ca^{2+} and CO_3^{2-}concentration on the $CaCO_3$particle size
Flow rate: 0.6 L/h Stirrer speed: 1500rpm Oil volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml PEG weight: 0.05g
Oil temperature: 25°C.a)[Ca^{2+}] = [CO_3^{2-}] = 0.1M, b) 0.2M, c) 0.5M, d) 0.75M e) 1M and f) average particle size

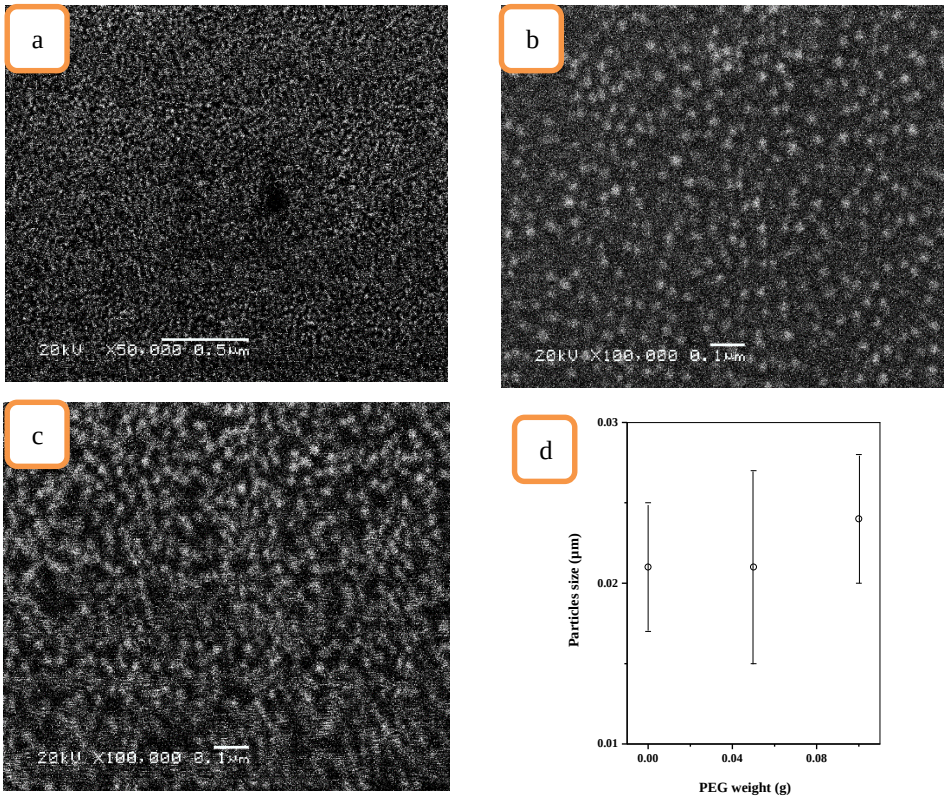


Fig. (3): Effect of PEG weight in Ca^{2+} solution on the $CaCO_3$ particle size

Flow rate: 0.6 L/h Stirrer speed: 1500rpm Oil volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$
Oil temperature: 25°C. a) PEG weight = 0.0g, b) 0.05g c) 0.1g and d) average particle size

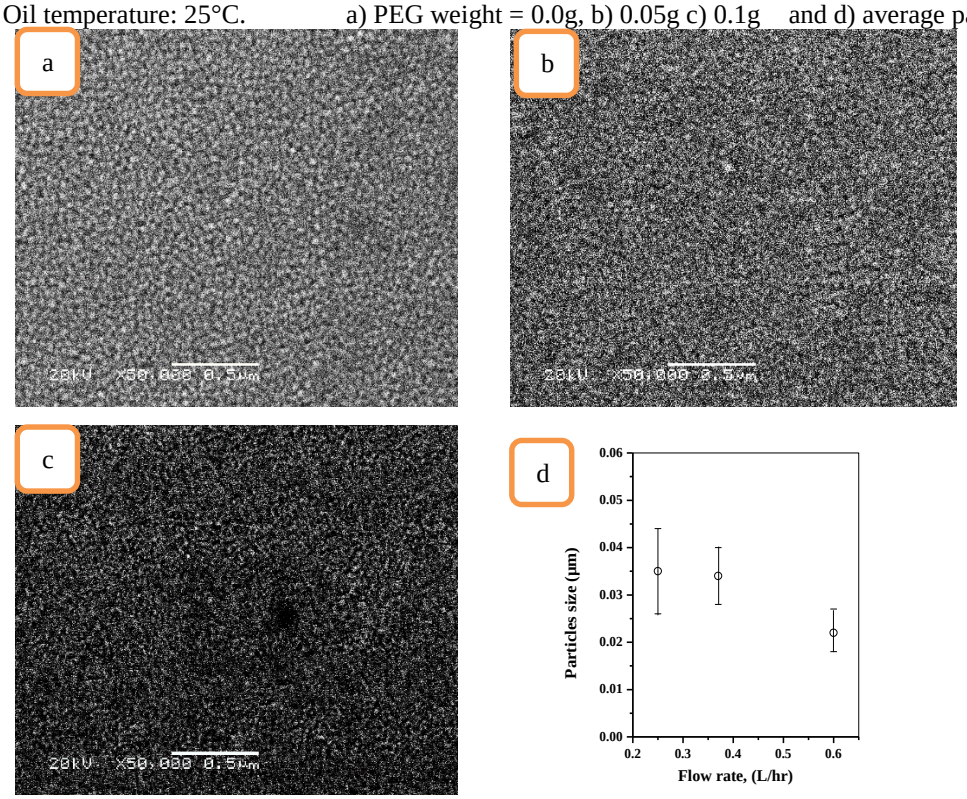


Fig. (4): Effect of flow rate (L/hr) on the $CaCO_3$ particle size

Stirrer speed: 1500rpm Oil volume: 50ml Ca^{2+} volume: 25ml
CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$
PEG weight: 0g Oil temperature: 25°C.
Flow rate = 0.25 L/hr, b) 0.37 L/hr c) 0.60 L/hr and d) average particle size

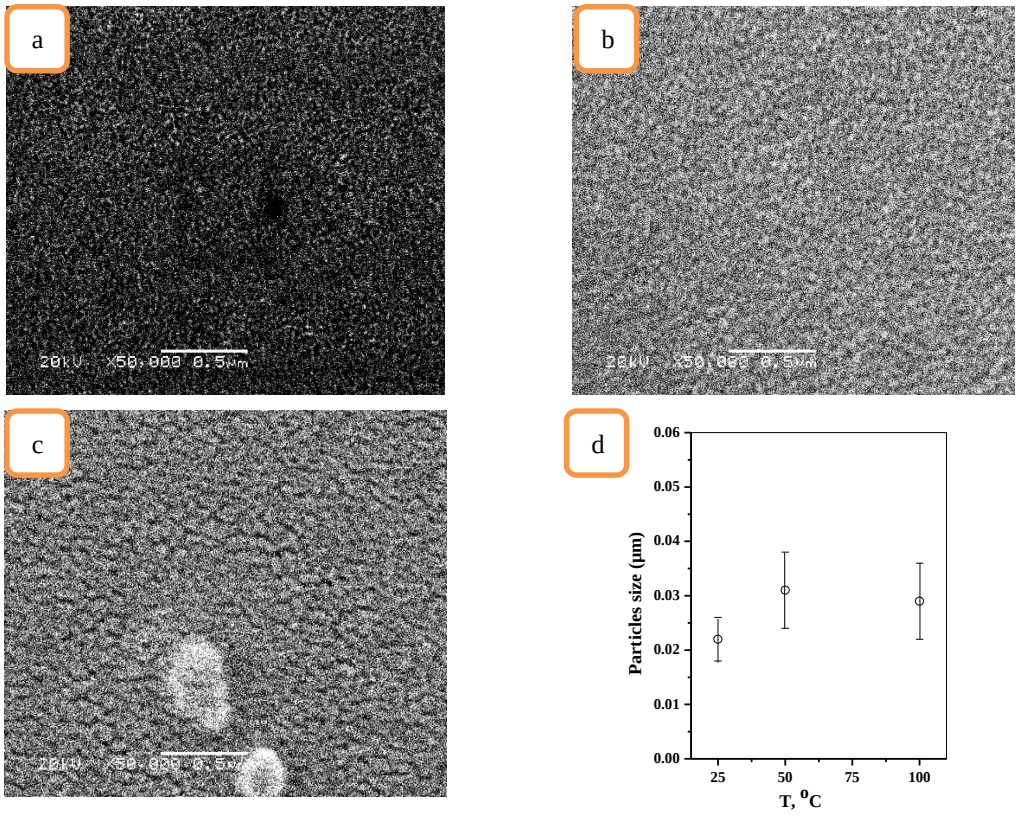


Fig. (5): Effect of temperature on the $CaCO_3$ particle size

Flow rate: 0.60 L/h Stirrer speed: 1500rpm Oil volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$
PEG weight: 0g.

a)T= 25°C, b) 50°C c) 100°C and d) average particle size

3.A.5. Effect of mediatypeon the $CaCO_3$ particle size

Fig. 6,indicates that at using vegetable oil, water and benzene the range size of particles small change to give 14-27nm at using vegetable oil, 19-44 nm at using water and 16-47 nm at using benzene.While at using 1-propanol and ethanol there is large increase in both the size of particles an range particle size 0.075-0.335 µm at using 1- propanol and 0.062-0.391 µm at using ethanol.

3.A.6. Effect of PEG weight on the media on the $CaCO_3$ particle size

The influence of PEG weight dissolved on the media on the $CaCO_3$ particle size was given in Fig. 7. It is clear that as the PEG weight increase the size of particles increase and the average particle size remain unchanged 19-44 nm, 25-60nm and 55-79 nm at using 0, 2 and 5gm PEG.

3.A.7. Effect of CO_3^{2-}concentration on the $CaCO_3$ particle size

Fig. 8, shows that the size of particles increase as CO_3^{2-}concentration increase while the average particle size is constant. The particles obtained with range particle size 14-30nm, 19-44nm and 48-75nm at using 0.3, 0.75 and 1.5M CO_3^{2-}.

3.A.8. Effect of stirrer speedon the $CaCO_3$ particle size

The results obtained showed that at low stirring speed the average particle size is very large while at high stirring speed the range particle is small where at 300 rpm the average particle size 0.022-0.328 µm, at 800 rpm 19-30 nm and at 1500 rpm 19-44nm as showed in Fig. 9.

3.A.9. Effect of media volume on the $CaCO_3$ particle size

It is clear that by increase the media volume the size of particles and average particle size decrease. Fig. 10, indicates that the particles with range size 41-82 nmand19-30 nm at using 25 and 50 ml of the media, respectively.

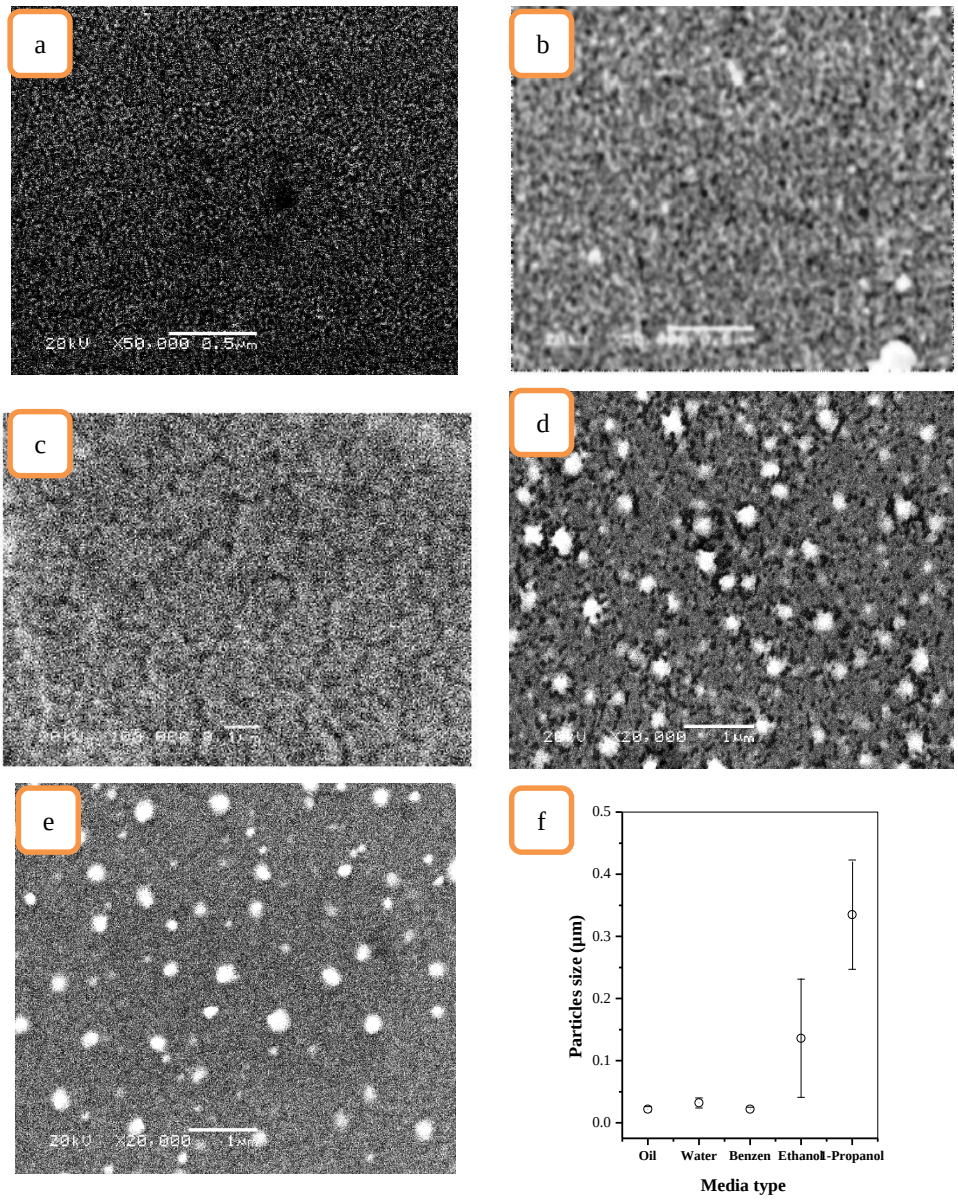


Fig. (6): Effect of media on the $CaCO_3$ particle size

Flow rate: 0.60 L/h Stirrer speed: 1500rpm Media volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$
Temperature: 25°C PEG weight: 0g.
a) Vegetable oil, b) Water, c) Benzene, d) 1-propanol e) Ethanol and f) average particle size

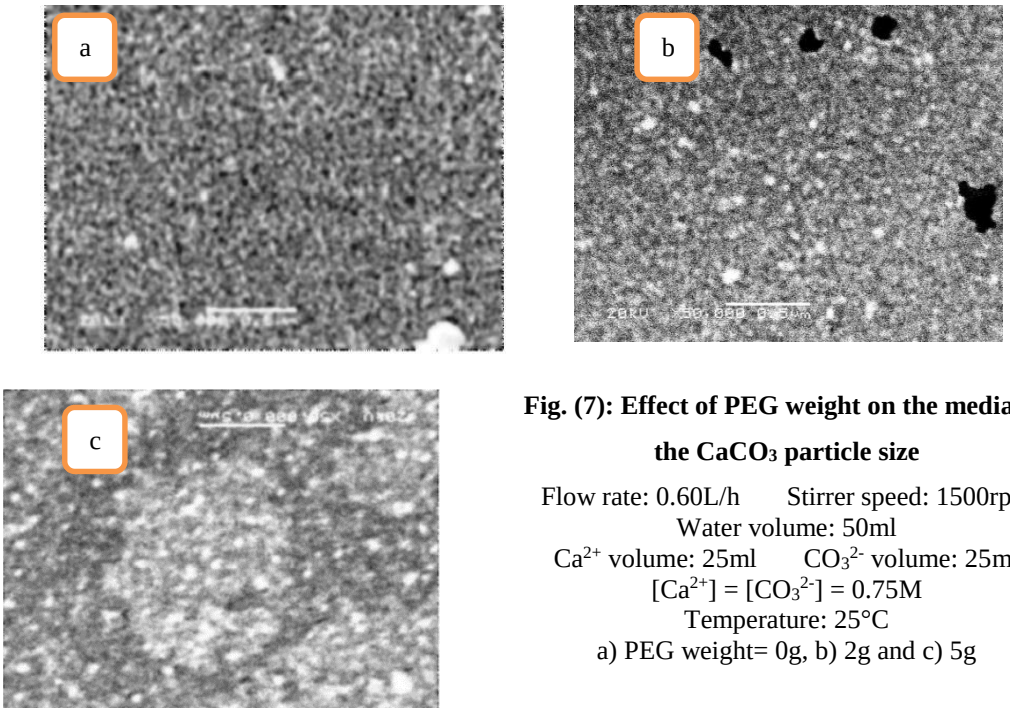


Fig. (7): Effect of PEG weight on the media on the $CaCO_3$ particle size

Flow rate: 0.60L/h Stirrer speed: 1500rpm
Water volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml
$[Ca^{2+}] = [CO_3^{2-}] = 0.75M$
Temperature: 25°C
a) PEG weight= 0g, b) 2g and c) 5g

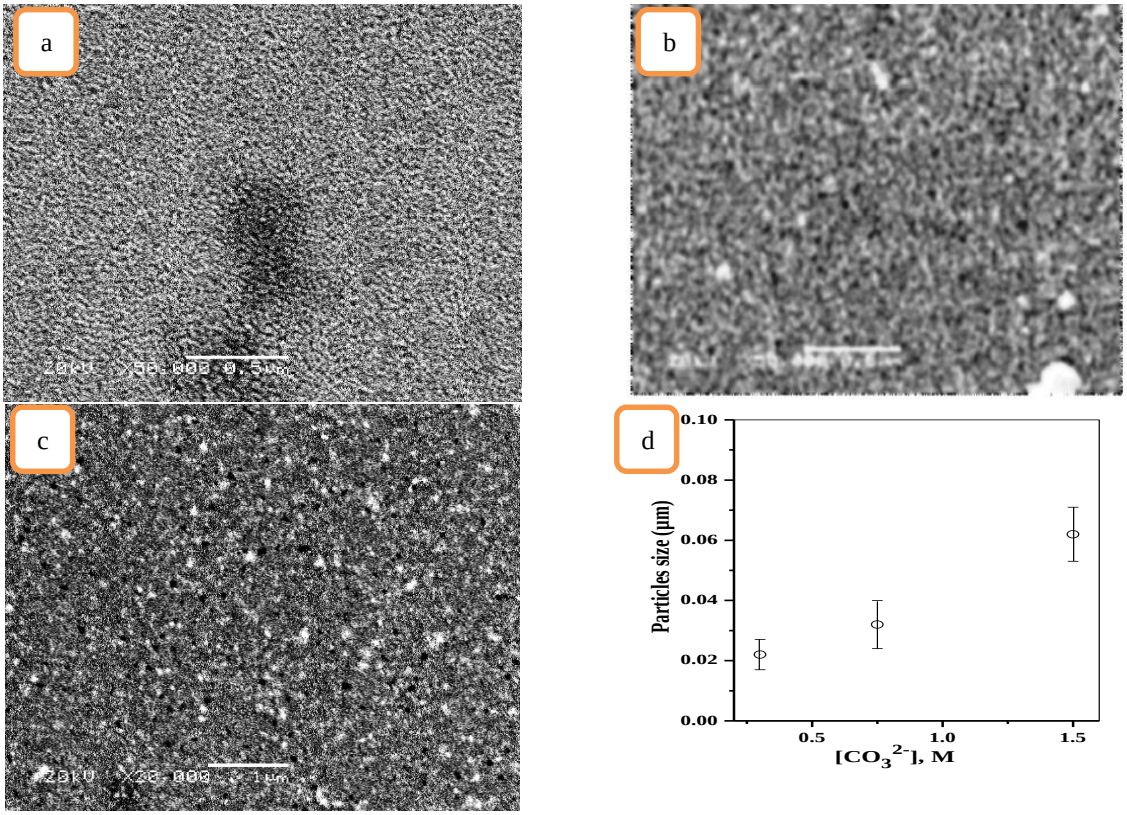


Fig. (8): Effect of CO_3^{2-}concentration on the $CaCO_3$ particle size

Flow rate: 0.6 L/h Stirrer speed: 1500rpm Water volume: 50ml
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = 0.75M$
PEG weight: 0g Temperature: 25°C
a)$[CO^{3-}] = 0.30M$, b) 0.75M c) 1.5M and d) average particle size

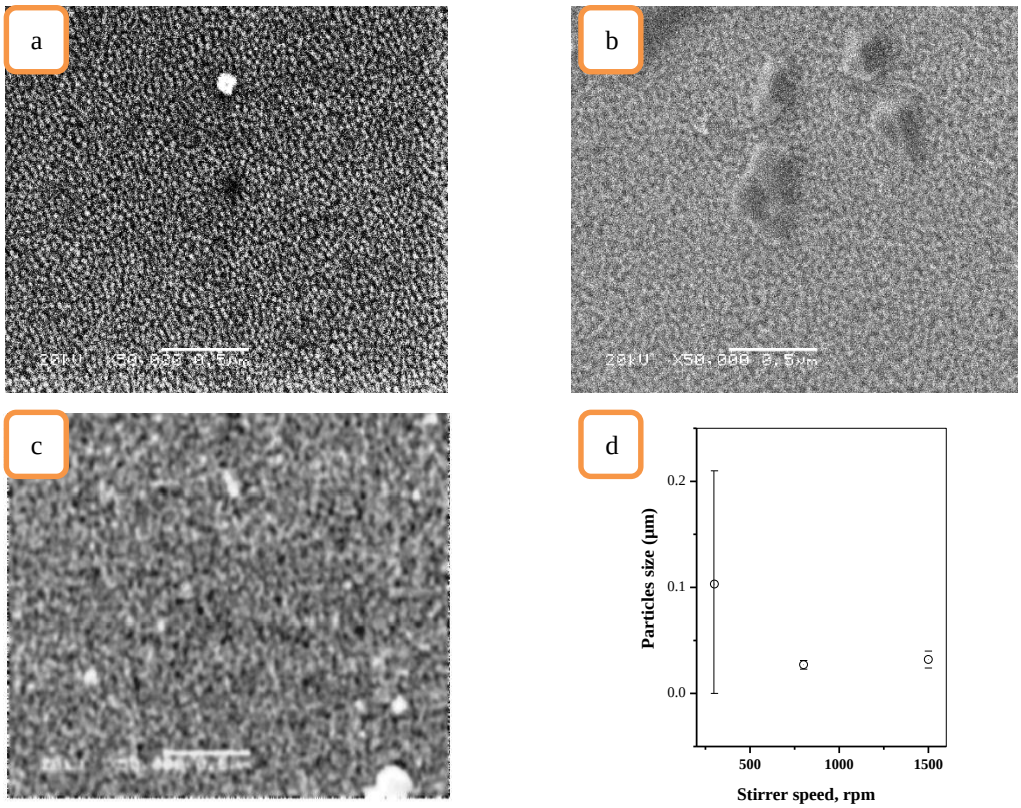


Fig. (9): Effect of stirrer speedon the $CaCO_3$ particle size
Flow rate: 0.60L/h Water volume: 50ml Ca^{2+} volume: 25ml
CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$ PEG weight: 0g
Temperature: 25°C, a) Stirrer speed = 300 rpm, b) 800rpm c) 1500rpm and d) average particle size

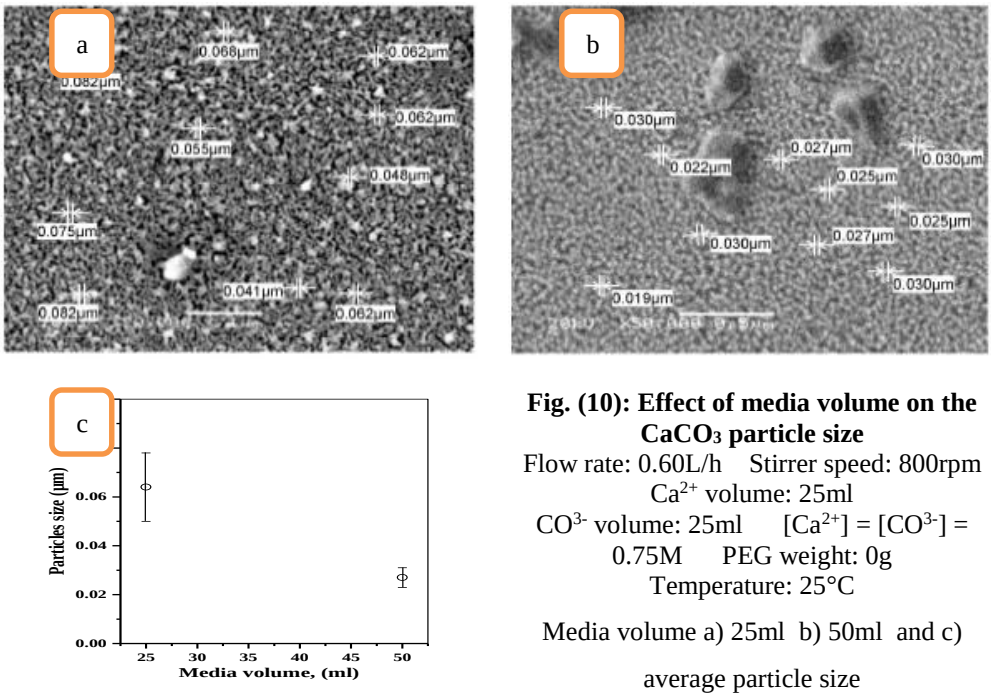


Fig. (10): Effect of media volume on the $CaCO_3$ particle size
Flow rate: 0.60L/h Stirrer speed: 800rpm
Ca^{2+} volume: 25ml
CO^{3-} volume: 25ml $[Ca^{2+}] = [CO^{3-}] = 0.75M$ PEG weight: 0g
Temperature: 25°C

Media volume a) 25ml b) 50ml and c) average particle size

3.A.10. Effect of additive with Ca^{2+} on $CaCO_3$ particle size

Three types of additives were tested surfactant, polymer and alcohol compared with the results with no additives added, we observed that the introducing of CTAB and ethanol increase the size of particles and average particle size than that no additives were used while at using PEG the particle size small increased as in Fig.11. The particles obtained with range particle size 19-30nm, 22-33nm, 30-49nm and 36-60nmat using no additive, PEG, ethanol and CTAB, respectively.

3.B. Characterization

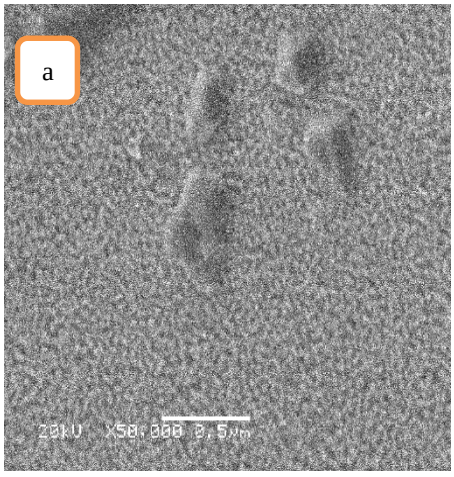
Fig. 12a, is SEM photograph of $CaCO_3$ nanoparticles, it can be obviously found that the grain of spherical type. The particles have fine dispersion and clear boarders between particles andthe average particle size between 19-30nm.Fig. 12b, of X-ray diffraction pattern of $CaCO_3$ nanoparticles which shows an intense sharp peak at $2\Theta = 29^{o}$ which indicate that $CaCO_3$ nanoparticles have crystal structure, this crystalline polymorph is calcite with crystal size D = 32.467nm.The EDS analysis show that the CaCO3 nanoparticles prepared was ultra-pure and with high oxygen content (% At Ca =17.28, C = 10.31 and O = 17.41) as shown in Fig. 12c. IR spectra of CaCO3 nanoparticles is shown in Fig. 12d, CaCO3 has three main peaks U3= 1425cm-1, U2= 874cm-1 and U4= 712cm-1. The U3 band is strong and broad while U2 and U4 bands are weak and narrow. The main peaks in our sample are estimated at U3 = 1415-1474cm-1, U2= 870.80cm-1 and U4= 728.8cm-1.the broadened absorption band at U3 due to the crystal field effect. The fact that the U2 and U4 bands are not split denotes that the crystalline structure CaCO3 nanoparticles was calcite [18]. TGA curve is shown in Fig. 12e, which show that the weight loss is complete within one step and a resultant weight loss 40.886% is found to be started at 643.23^{o}C and ended at 780.71 ^{o}C.

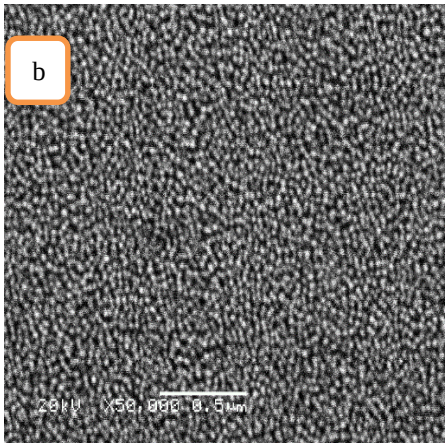
Scaling up of the $CaCO_3$ preparation

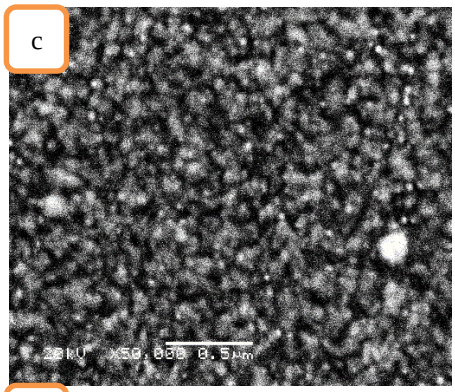
In order to scal up of our experiments, Part 5(250ml glass Jar) in Fig. 1, was modified by making inlet of water and outlet for suspension as seen in Fig. 13a. This modification allows to convert the process from batch to continuous process for production of CaCO3 nanoparticles. One drop of the suspension put to air dried on a glass slide for SEM analysis, Fig13 b and c, shows different images of CaCO3 nanoparticles obtained. To obtain good statistical measurements for particle size, the work of, the slide was scanned for at least 20 particles at different 25 areas of the slide to give a total of 500 particles. Fig. 13d, shows the particle size distribution for the three slides. The mean particle size of the sample was found to equal31 nm with standard deviation ±6 using the software Smile View.

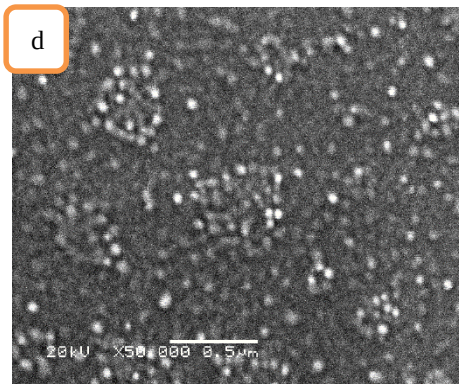
3.C. Preparation of nanopores PVC film

Fig. 14, shows SEM photographs of PVC film with nanopores at using different 0.1g of CaCO3 nanoparticles. Fig. 17, shows the PVC film has pores size range from0.08 to 0.12 µm.









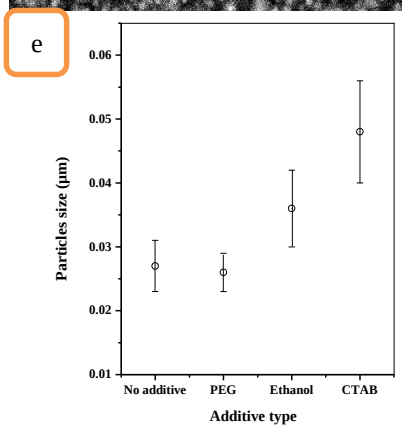


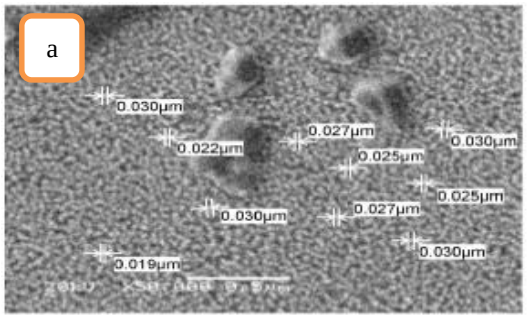
Fig. (11): Effect of additive with Ca^{2+} on $CaCO_3$ particle size

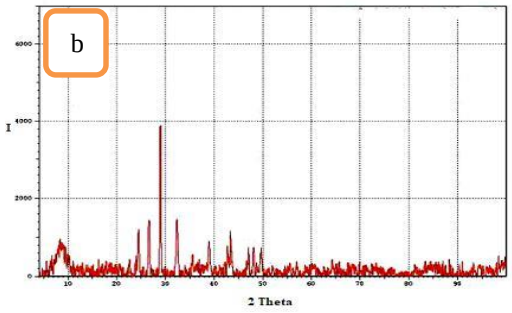
Flow rate: 0.60L/h Stirrer speed: 800rpm Water volume: 50ml

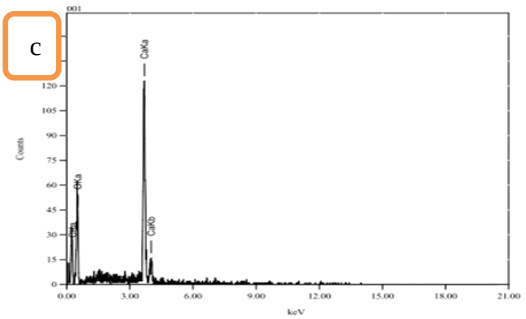
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$

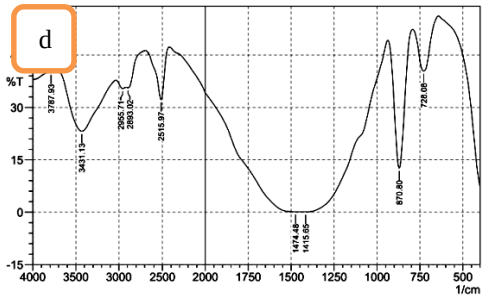
Water temperature: 25°C Additive weight = 0.10g.

a) No additive, b) PEG, c) ethanol d) CTAB and e) average particle size









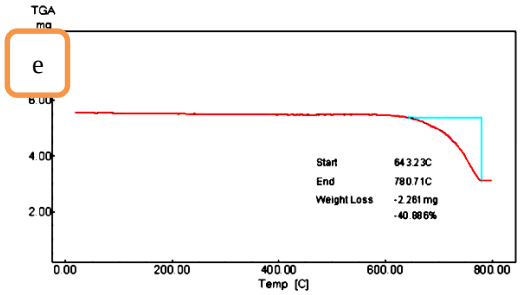


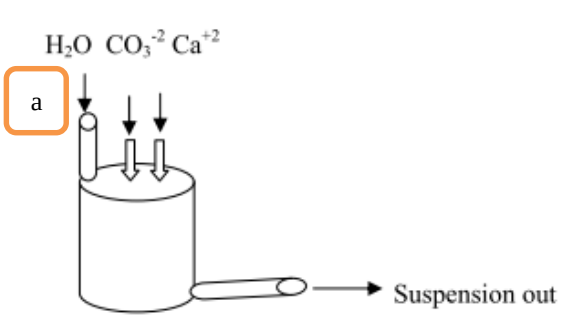
Fig. (12): The characterization figures of $CaCO_3$

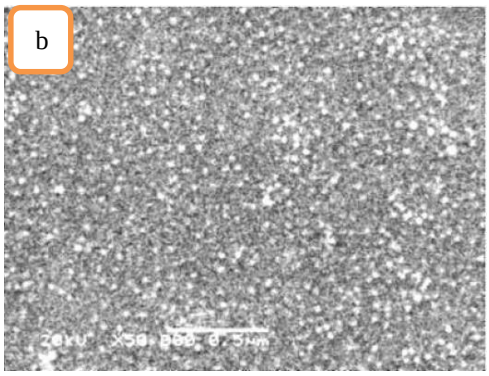
Flow rate: 0.60L/hStirrer speed: 800rpm Water volume: 50ml

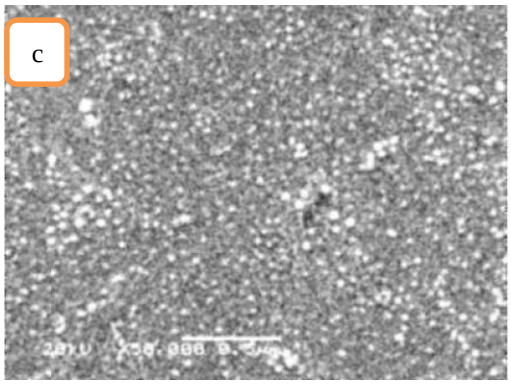
Ca^{2+} volume: 25ml CO_3^{2-} volume: 25ml $[Ca^{2+}] = [CO_3^{2-}] = 0.75M$

Water temperature: 25°No additive

a) **SEM, b) XRD, c) EDS, d) FTIR and e) TGA**







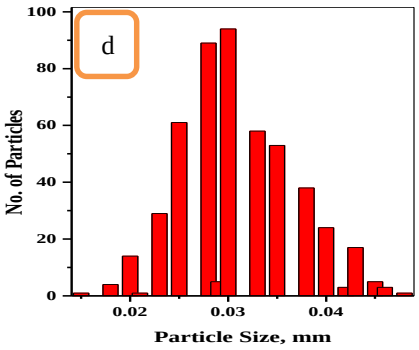


Fig. (13): a) the modified part, b and c) the SEM image of $CaCO_3$ obtained from continuous experiment and d) particle size distribution.

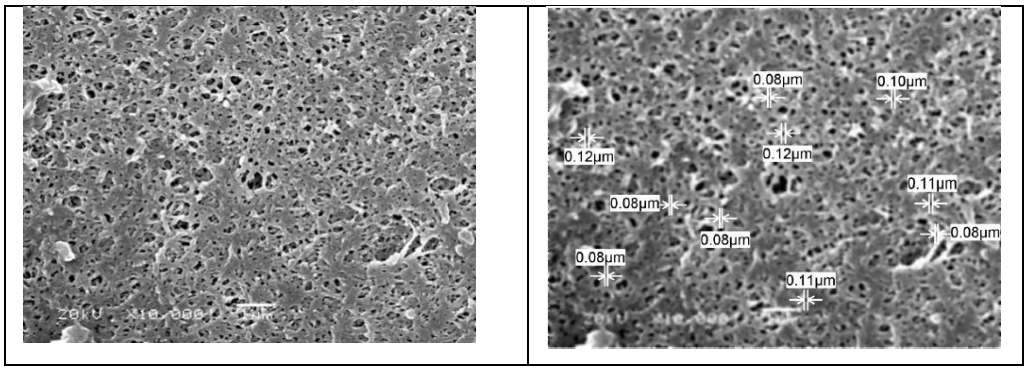


Fig (14) SEM photographs of PVC film with nanopores

.CONCLUSION

A new apparatus was designed to prepare $CaCO_3$ nanoparticles. The new apparatus could not only reduce the preparation time but only produce homogenous spherical $CaCO_3$ nanoparticles with range size19-30 nm. These synthesized nanoparticles could be used in preparation of PVC film with nanopores size.

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