# REMOVAL OF LEAD FROM POLLUTED WATER USING WASTE EGGSHELL

*A Dissertation submitted in partial fulfillment of
the requirements for the degree of*



Master of Science
In

PHYSICS
By

## DEBABRATA PANDA
ROLL NO-411PH2107

*Under the supervision of*

Dr. B.K. CHAUDHURI

National Institute of Technology, Rourkela

Rourkela-769008, Orissa, India

June-2013

# Department of Physics



*National Institute of Technology, Rourkela*

*Rourkela-769008, Orissa, India*

## CERTIFICATE

This is to certify that, the work in the report entitled **"Removal of Lead from polluted water using waste eggshell"** by **Mr. Debabrata Panda,** in partial fulfillment of Master of Science degree in **PHYSICS** at the National Institute of Technology, Rourkela (Deemed University); is an authentic work carried out by him under my supervision and guidance. The work is satisfactory to the best my knowledge.

Date- 21/06/13

Prof. B.K Chaudhuri

Department of Physics

National Institute Of Technology

Rourkela-769008

## ACKNOWLEDGEMENT

**Date: 21/06/13**                                                      **Debabrata Panda**

# CONTENTS                                                    PAGE NO.

# CHAPTER-4

## 4. RESULTS AND DISCUSSION

# CHAPTER-5

## CONCLUSION

**ABSTRACT**

In the present project work our plan was to make an attempt to remove heavy metal ions (Pb ions in our case) from polluted water using low cost materials. Eggshell composed of mostly calcium carbonate is a waste natural product available abundantly. Since Ca ions have large affinity towards heavy metal ions, eggshell could be used for said purpose. We prepared artificially Pb-polluted water by adding $Pb(NO_3)_2$ in pure water and processed eggshell was used successfully to absorb lead from the solution used as the precursor impurity . Our aim was also to use simple and easily available instruments to detect the absorption of Pb ions from the impure water. The eggshell used was calcined at three different temperatures $300^0C$, $500^0C$ and $950^0C$, respectively. The samples were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy and chemical test. We also used $950^0C$ annealed powder (which is CaO) to make hydroxyapatite or $Ca_{10}(PO_4)_6(OH)_2$ (HAp) by dissolving CaO in pure $K_2HPO_4$ solution which directly converted CaO to HAp. Results show that the calcinations temperature affected the absorbance of lead from water. Both $500^0C$ annealed sample and HAp are good lead absorber. However, HAp is found to absorb Pb more quickly but its processing temperature is higher and also needs another chemical for making HAp from eggshells. The XRD spectra of $500^0C$ and $950^0C$ processed samples after Pb absorption from water indicate the presence of lead in different compositional forms (mostly $PbCO_3$ and PbO). The UV-VIS and FTIR spectra were studied to characterize the samples. Finally chemical test was done for confirming the absence of Pb salt in the filtered solution (water). With increasing calcinations temperature the calcium carbonate slowly converts to CaO. HAP produced from CaO using $K_2HPO_4$ is found to absorb Pb ions very quick but as it is not a direct product from Eggshell, we conclude that it is better to use $500^0C$ annealed eggshell powder with is cost effective for the removal of Pb from lead-polluted water. Finally, this simple process can be extended for the removal of other heavy metal ions like Cd, As etc. Our future plan is to work in this project.

Keyword: lead nitrate, Eggshell, Calcium carbonate, hydroxyapatite, water pollution, Characterization.

Chapter 1

**INTRODUCTION**

**1.1Motivation and Background**

In recent years there has been an increasing concern over the discharge of industrial waste water containing dissolved species of heavy metal ions. Mainly automobile exhausts results lead pollution. Metallurgical operation, lead battery industries and industries manufacturing lead arsenate insecticides contribute a considerable amount of lead to environment. During the past, the use of utensils either made up of lead coated with lead glass was considered to be another source of lead. Lead is taken mainly from food even though the lead content in water is lesser than that in air. Lead adsorption is greater from the lungs compared to gut. After adsorption of lead food through the lungs, 97% of it enters the blood where it is taken up by the red blood cells. The half-life of lead in these cells is around three weeks. Due to some redistribution, lead is transferred to some other parts like kidney or liver. This leads to either excretion into the bile or deposition in bone or teeth. It is possible to estimate the past exposure of lead, because of this kind of deposition in bone or teeth. It is also possible to estimate the amount of lead from blood and urine analysis. Lead interferes with the synthesis of porphyrin. Myoglobin is also considered to be affected. The activity of enzyme is inhibited by lead and a correlation is available between the degrees of inhibition and blood lead level. Lead causes skeletal change. Chronic exposure causes interstitial nephritis whereas acute exposure causes kidney damage. Comparing inorganic lead with organic lead, the latter is found to be more toxic because it is lipid soluble. For example, Tetraethyl lead is readily taken up through skin to brain, causing encephalopathy. To remove heavy metals from aqueous solutions several procedures are available and also some metals removing techniques such as neutralization, precipitation, cementation, reverse osmosis, ion-exchange and adsorption can be performed. However the method to be chosen should be decided largely by economical factors as well as conditions of the effluent. In the present work, the removal of lead from waste water using egg shell is attempted. Though many conventional adsorbents are used for the effective removal of heavy metal ions, we have chosen egg shells as they are thrown in kitchen, and as waste materials from hotels, restaurants and hostels of schools and colleges, with an aim to use waste

pollutant (Example-Trichy is an industrial area, where a large number of small scale industries is located and these industries pollute the nearby soil and ground water with lead as a heavy metal).

Industrial wastewater contaminated with heavy metals is commonly produced from many kinds of industrial processes. Therefore, if this wastewater is not treated with a suitable process, it can cause a serious environmental problem in the natural eco-system. Accumulation of metal ions such as lead, cadmium and mercury in human body will be occurred through either direct intake or food chains, whenever toxic heavy metals are exposed to the natural eco-system. Therefore, heavy metal should be prevented before it reaches to the natural environments because of its toxicity. Although coagulation, chemical precipitation, ion exchange, solvent extraction, filtration, evaporation and membrane methods are applied in order to remove toxic heavy metals from water systems, most techniques have some limitations such as requirement of several pre-treatments as well as additional treatments. Also some of them are less effective and require high capital cost. Generally silica gel, activated carbon, activated alumina and ion exchange resin have higher capacity in the removal of toxic heavy metals. However, their utilization is not common and restricted to special treatment due to high installation and operating cost. Therefore, many researchers have applied regenerated natural wastes to treat heavy metals from aqueous solutions. We know Eggshell waste is widely produced from house, restaurant and bakery. Eggshell has a little developed porosity and pure $CaCO_3$ as an important constituent.

**1.2 Egg Shell-**

An eggshell is the outer covering of a hard-shelled egg and of some forms of eggs with soft outer coats. Bird eggshells contain mostly calcium carbonate ($CaCO_3$) and dissolve in various acids, including the vinegar used in cooking. During dissolving, the calcium carbonate in an egg shell reacts with the acid to form carbon dioxide.

Calcium carbonate ($CaCO_3$) is found in nature giving hardness and strength to things such as seashells, rocks, and eggshells. A good quality eggshell contains, on average, 2.2 grams of calcium in the form of calcium carbonate. Approximately 94% of a dry eggshell is calcium carbonate and has an approximate mass of 5.5 grams. The remaining mass is composed largely of magnesium, phosphorus and trace amounts of potassium, sodium, zinc, manganese, iron, and

copper. The different color of the eggs is a result of a different breed. The quality, taste and nutritional value are identical between white and brown eggs, except two notable differences as size and price.

**1.3 Objective of Study-**

Aim of this project work was focused on the following steps:

- Preparation of the powdered eggshell and also pallets for further study.
- Characterizing the crystals structure and pure phase by using XRD diffraction patterns.
- Characterizing the surface morphology of the powdered eggshell after heat treatment by Scanning Electron Microscopy.
- Detecting the various characteristic functional groups in molecules of solid and liquid phase eggshell by FTIR spectroscopy analysis.
- To study the absorption properties by UV-VIS spectroscopy.

# CHAPTER 2

# LITERATURE SURVEY

## 2.1 Toxic Elements In Waste Water-

The maximum concentrations of potentially toxic elements found in commercial wastewater are generally greater than those in domestic wastewater. Commercial and light industrial sectors contributed more potentially toxic elements to urban wastewater than household sources. However, stringent and more widespread limits applied to industrial users has resulted the reduced levels of potentially toxic elements emitted by industry into urban wastewater considerably. This continues to be a general decline of potentially toxic elements from industrial sources since the 1960s, due to factors such as cleaner industrial processes, trade effluent controls and heavy industry recession.

The following illustrates the principal potentially toxic elements that enter urban wastewater:

**Cadmium:** Predominantly found in rechargeable batteries for domestic use (Ni-Cd batteries) and in paints. The main sources of cadmium in urban wastewater are from diffuse sources such as food products, detergents and body care products etc.

**Copper:** Generates mainly from leaching of plumbing, corrosion and fungicides (cuprous Chloride), pigments, wood preservatives, and antifouling paints etc.

**Mercury:** Mercury is still used in thermometers and in dental amalgams. Also, it can be found as an additive in old paints for water proofing and marine antifouling (mercuric arsenate),in wood preservatives (mercuric chloride), in embalming fluids (mercuric chloride), in germicidal soaps and antibacterial products (mercuric chloride and mercuric cyanide) , in old pesticides (mercuric chloride in fungicides, insecticides) etc.

**Nickel:** It is found in alloys used in food processing and in rechargeable batteries (Ni-Cd), and protective coatings.

**Lead:** The main source of lead is from old lead piping in the water distribution system. It can be found in solder, pool cue chalk (as carbonate), in certain cosmetics, old paint pigments (as oxides, carbonates), glazes on ceramic dishes and porcelain also in "crystal glass". Lead is also found in wines, possibly from the lead-tin capsules used on bottles and from old wine processing installations.

**Zinc:** Generates from corrosion and leaching of plumbing, water-proofing products, wood preservatives (as zinc arsenate), deodorants and cosmetics (as zinc chloride and zinc oxide), medicines and ointments (zinc chloride and oxide as astringent and antiseptic, zinc formate as antiseptic),anti-pest products (zinc arsenate - in insecticides, zinc dithioamine as fungicide, rat poison, rabbit and deer repellents, zinc fluorosilicate as anti-moth agent), paints and pigments (zinc oxide, zinc carbonate, zinc sulphide),printing inks and artists paints (zinc oxide and carbonate), coloring agent in various formulations (zinc oxide), a UV absorbent agent in various formulations (zinc oxide), "health supplements" (zinc oxide).

**Silver:** Comes from household products such as polishes, domestic water treatment devices, etc.

**Arsenic and Selenium:** Arsenic inputs come from natural background sources and from household products such as washing products, garden products, wood preservatives, old paints and pigment medicines. Selenium comes from shampoos and other cosmetics, old paints and pigments, food products and food supplements.

## 2.2Presence of Toxic Elements Table-

| Product type | Ag | As | Cd | Co | Cr | Cu | Hg | Ni | Pb | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Amalgam fillings And thermometers | | | | | | | √ | | | | |
| Cleaning products | | | | | √ | √ | | | | | |
| Cosmetics, shampoos | | | √ | | | √ | √ | √ | √ | √ | √ |
| Disinfectants | | | | | | | √ | | | | |
| Fire extinguishers | | | | | √ | | | | | | |
| Fuels | | | | | | √ | √ | | √ | | √ |
| Inks | | | | | | √ | | | | √ | |
| Lubricants | | | | | √ | | | | √ | | √ |
| Medicines and Ointments | | √ | | √ | | √ | √ | | | | √ |
| Food products | | √ | | √ | | √ | | | √ | | √ |
| Oils and lubricants | | | | | √ | √ | | | √ | | √ |
| Paints and pigments | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Photographic | √ | | | | √ | | √ | | | | |
| Pesticides | | | √ | | √ | √ | √ | | √ | | |
| Washing powders | | | √ | | | | | | √ | | √ |
| Wood preservatives | | √ | | | | √ | | | √ | | |
| Tap Water | | | √ | | √ | √ | | √ | | | √ |
| Water treatment and heating systems | | | √ | | √ | √ | | | | | √ |
| Faeces and Urine | | √ | √ | | √ | √ | √ | √ | √ | √ | √ |

## 2.3 COMMERCIAL SOURCES

**Cadmium** originates from electroplating and coating shops, plastic manufacture and also from enamels, paints, photography, batteries, glazes, alloys, solders, pigments, artisanal shops, engraving, and car repair shops etc. It's estimated that worldwide, 16000 tones of cadmium were consumed each year; (50-60% of this in the manufacture of batteries and 20-25% in the production of colored pigments).

**Chromium** is found in alloys and is discharged from diffuse sources and products such as dying, preservatives and tanning activities. Chromium VI uses are now restricted and there are a little commercial sources.

**Copper** is usually used in electronics, paper, textile, rubber, printing, plastic, brass and other alloy industries. It used to be emitted from various small commercial activities.

**Lead** is used as a fuel additive, in batteries, pigments, solder, roofing, cable covering, ammunition, chimney cases, lead jointed waste PVC pipes (as an impurity), fishing weights ,yacht keels and other sources.

**Mercury** is used in the production of electrical equipment. The main sources in effluent are from clinical thermometers, glass mirrors, dental practices, electrical equipment and caustic soda solutions.

**Nickel** is used in the production of alloys, catalysts, electroplating, and nickel-cadmium batteries. The emissions of nickels are predominantly from corrosion of equipment from launderettes, small electroplating shops and jewelry shops, from old pigments and paints.

**Zinc** is used in brass and bronze alloy production, galvanization processes, in batteries, paints, paper, textiles, taxidermy (zinc chloride), embalming fluid (zinc chloride), plastics rubber, fungicides, building materials and special cements (zinc oxide, zinc fluorosilicate),dentistry (zinc oxide), and also in cosmetics and pharmaceuticals etc.

**Platinum**: Other sources of platinum metals in the environment related to commercial activities come from catalysts used in petroleum/ammonia processing and wastewaters, from the small electronic shops, laboratories and glass manufacturing etc.

## CHAPTER -3

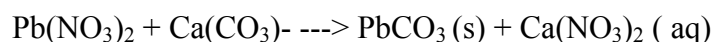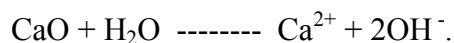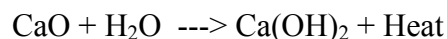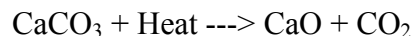## MATERIALS AND METHODS

### 3.1EXPERIMENTAL

Collected eggshell were cleaned and boiled for maximum of 15 minutes. The membrane was removed from the inner parts of the shell carefully. The eggshells were crushed into smaller parts and then were calcined for about two hour at an temperature of $300^0$ C. Likewise 20 gram each of the eggshell was taken and were calcined at $500^0C$ and $950^0C$ for two hour. The color of the eggshell after heating was distinct .The weight of all the eggshells found to be decreased.

Two gram of each of the eggshell was taken in powdered form. Approximately 0.0828 gram of lead nitrate was taken and dissolved in 50 ml of distilled water and stirred for about fifteen minutes. That indicates preparing an one molar solution of $Pb(NO_3)_2$ solution. The solution was divided into ten ml each. Two gram of each of the eggshell was dissolved in the corresponding beaker marked as 300,500,950 respectively. The 950 one showed heating while the eggshell was mixed with lead nitrate solution. The solution were left over night and then were filtered .Individual UV was taken for all the three filtered solution and also that of the only lead nitrate solution that is of 0.0828gm lead nitrate in 50 ml distilled water.

Simultaneously the FTIR of these filtered solution and the lead nitrate solution was also performed. The FTIR of the calcined eggshell at different temperature and of the hydroxyapatite was done by making them into pallets .The filtered eggshell were taken for XRD. One molar solution of lead nitrate was prepared and two gram of eggshell calcined at $950^0C$ was dissolved in the 10 ml of the lead nitrate solution. The solution was filtered after keeping it few hour and few drops of concentrated $H_2SO_4$ was mixed to see precipitation.

Preparation of Hydroxyapatite (HAp) from eggshell: HAp or $Ca_{10}(PO_4)_6(OH)_2$ was prepared by dissolving $900^0C$ annealed eggshell powder in 0.25M $K_2HPO_4$ solution for seven day and then filtering and washing the precipitate several times with distilled water until pH for the solution is around 7.

Essential Equations-

$$CaCO_3 + Heat ---> CaO + CO_2$$

$$CaO + H_2O ---> Ca(OH)_2 + Heat$$

$$CaO + H_2O -------- Ca^{2+} + 2OH^-.$$

$$Pb(NO_3)_2 + Ca(CO_3)- ---> PbCO_3 (s) + Ca(NO_3)_2 ( aq)$$

The calcinated powders are studied using different characterization techniques. Confirmation of the presence of lead is verified by XRD analysis. The shape and morphology of particles are studied by SEM pictures obtained. Finally UV absorption spectroscopy and Fourier transform infrared (FTIR) spectroscopy were performed and the results are studied to understand the optoelectronic properties of sample prepared.

## 3.2 CHARACTERISATION TECHNIQUES

In order to investigate various properties of the sample, it used to go through a number of characterization techniques. The result gives the information about the different properties of sample.

### 3.2.1 STRUCTURAL CHARACTERISATION

In order to get exact information about the crystal structure, surface morphology etc. the following characterization techniques are useful.

- XRD (X-ray Diffraction)

- SEM (Scanning electron microscope)

### 3.2.2 OPTICAL CHARACTERISATION

Following characterization techniques gives information related to optical properties.

- UV-Visible Spectroscopy

- Fourier Transform Infrared Spectroscopy (FTIR).

### 3.3XRD (X-ray Diffraction)

Till 1895 the study of matter at the atomic level was a difficult task but the discovery of electromagnetic radiation with 1 Å ($10^{-10}$ m) wavelength, appearing in the region between gamma-rays and ultraviolet, makes it possible. As the atomic distance in matter is comparable with the wavelength of X-ray, the phenomenon of diffraction find its nature and gives many significant results related to the crystalline structure. The unit cell and lattices that are distributed in a regular three-dimensional way in space forms the base for diffraction pattern to occur. These lattices form a series of parallel planes with its own specific d-spacing as well as with different orientations exist. The reflection of incident monochromatic X-ray from successive planes of crystal lattices occurs following famous Bragg's law:
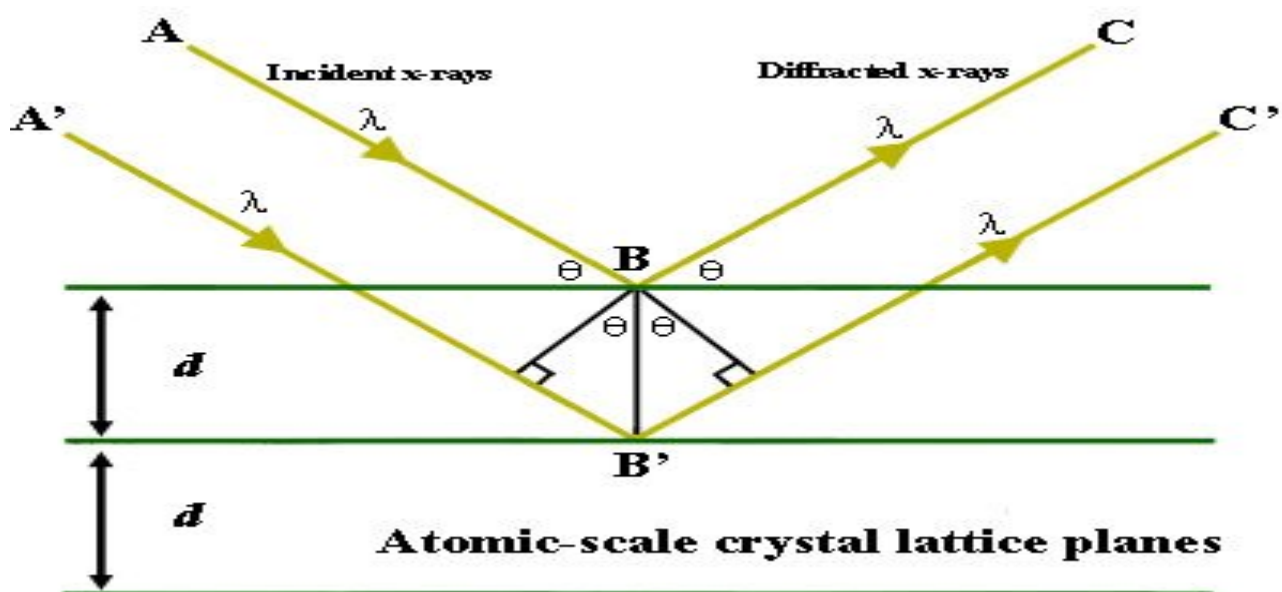


Figure.3.1 X-ray Diffraction in accordance with Bragg's Law

$$n\lambda = 2d\sin\theta$$

Where $n$ is an integer 1, 2, 3….. , d is inter atomic spacing in angstroms, $\lambda$ is the wavelength in angstroms and $\theta$ is the diffraction angle in degrees. By plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, showing characteristic of the sample. The determination of the structure of materials and the fingerprint characterization of crystalline materials are the two fields where XRD has been mostly used. Unique characteristic X-ray diffraction pattern of every crystalline solid gives the designation of "fingerprint technique" to XRD for its identification. XRD may be used to determine the structure, i.e. how the atoms pack together in the crystalline state and what the angle and inter atomic distance are etc. Hence we can conclude that X-ray diffraction has become a very important and powerful tool for the structural characterization in solid state physics and materials science.

### 3.4. SEM (Scanning electron microscope)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a different type of signals at the surface of solid specimens. The signal that originates from electron reveals the information about the sample including external morphology (texture), crystalline structure, orientations of materials and chemical composition of the sample. In usual practice, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated displaying spatial variations in these properties. Using conventional SEM techniques, areas ranging from approximately 1 cm to 5 microns in width can be imaged in the scanning mode (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analysis of selected point locations of the sample; this approach is especially useful qualitatively or semi-quantitatively for determining chemical compositions (using EDS), crystal orientations (using EBSD) and crystalline structure.
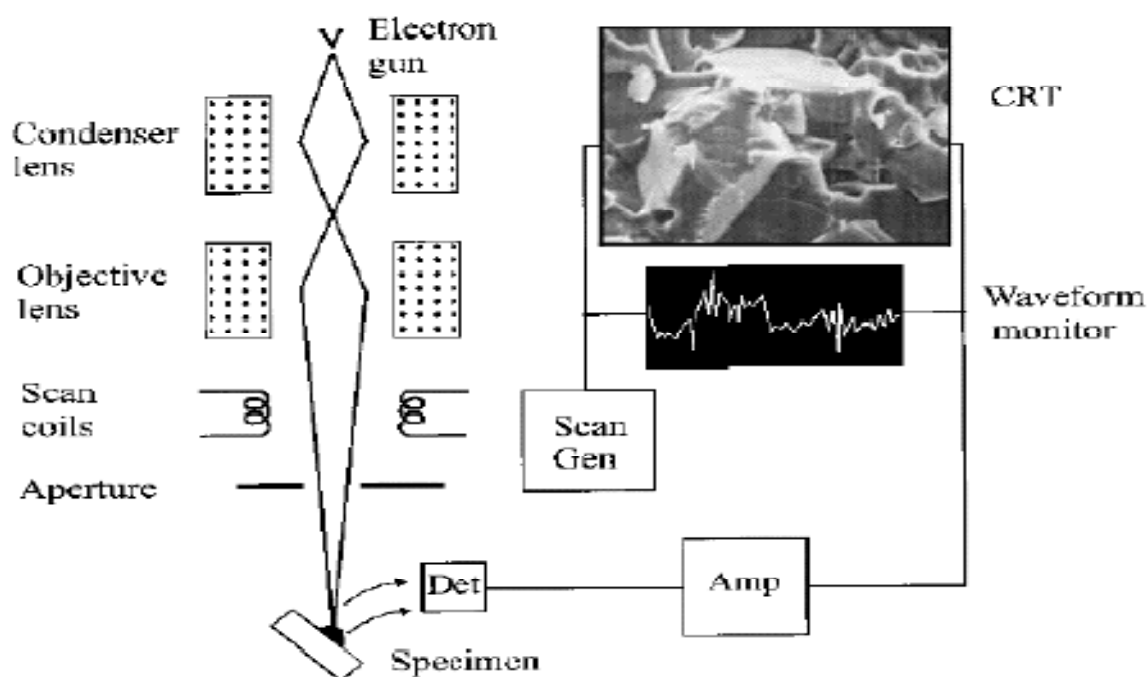
Figure 3.2.Diagram of SEM.

Accelerated electrons in an SEM carry significant amounts of energy and this energy is dissipated, as a variety of signals produced as a result of electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathode luminescence--CL), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals) and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for determining morphology and topography of samples and backscattered electrons are most valuable for deciding contrasts in composition in multiphase samples (i.e. SEM analysis is considered to be "non-destructive" that is, x-rays generated by electron interactions do not lead to any volume loss of the sample, as a result it is possible to analyze the same materials repeatedly). The SEM is regularly used to generate high-resolution images of objects and to show spatial variations in chemical compositions or to do chemical analysis using EDS. The SEM can be used to identify phases based on qualitative chemical analysis. Exact measurement of very small features and objects down to 50 nm in size is also accomplished using SEM.

### 3.5. UV-VISIBLE SPECTROSCOPY

The wavelength of UV is shorter than the visible light ranging from 100 to 400 nm. In UV-Vis spectrophotometer, a beam of light is used to split; one half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analyzed, and one half (the reference beam) is directed through an identical cell that does not contain the compound but contains the solvent. When the compound absorbs light at a particular wavelength, then the intensity of the sample beam will be less than that of the reference beam. Absorption of radiation by a sample is measured at various wavelengths and then plotted to give the spectrum. The band gap of the sample is easily obtained by plotting the graph between (αhν versus hν) and extrapolating it along x-axis. UV-Vis spectrometry is also used for quantitative analysis that is for determining the amount of a compound present in the sample.

### 3.6. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR).

In the region of longer wavelength or low frequency the identification of different types of chemicals is possible by using infrared spectroscopy .The instrument required for its execution is known as Fourier transform infrared (FTIR) spectrometer. The spectroscopy is broadly based on the fact that molecules absorb specific frequencies that are characteristics of their structure which is termed as resonant frequencies that is the frequency of the absorbed radiation matches with the frequency of the bond or group that vibrates. And the detection of energy is done on the basis of the masses of the atoms and the associated vibronic coupling. Occasionally the help of approximation techniques like harmonic approximations and Born–Oppenheimer are also taken. As every different material is a unique combination of atoms, no two compounds produce the same infrared spectrum. For this reason, infrared spectroscopy results in a positive identification (qualitative analysis) of every unique kind of material. The size of the peaks in the spectrum is a direct indication of the amount of materials present. FTIR is also used to analyze a wide range of materials in bulk or thin films, liquids, solids, pastes, powders, fibers etc. FTIR analysis gives not only qualitative (identification) analysis of materials, but with relevant standards, which can be used for quantitative (amount) analysis. FTIR is used to analyze samples up to ~11 millimeters in diameter. It either measure in bulk or the top ~1 micrometer layer. FTIR spectra of any pure compounds are so unique that they are like a molecular "fingerprint".

**CHAPTER 4**

**RESULTS AND ANALYSIS**

## 4.1. X-ray diffraction (XRD)

Figure.4.1 (a), (b) & (c) gives the X-ray diffraction pattern for samples S1, S2 & S3 calcined at $300^0$C, $500^0$C and $950^0$C, respectively. Comparing our data with standard data JCPDS 76-0704 confirmed that $CaCO_3$ bond breaks at $898^0$C hence the $300^0$C and $500^0$C XRD data shows calcium carbonate and calcite while the $950^0$C XRD indicates the presence of calcium oxide (CaO) ( actually , Eggshell $CaCO_3$ +$950^0$C = CaO +$CO_2$) .
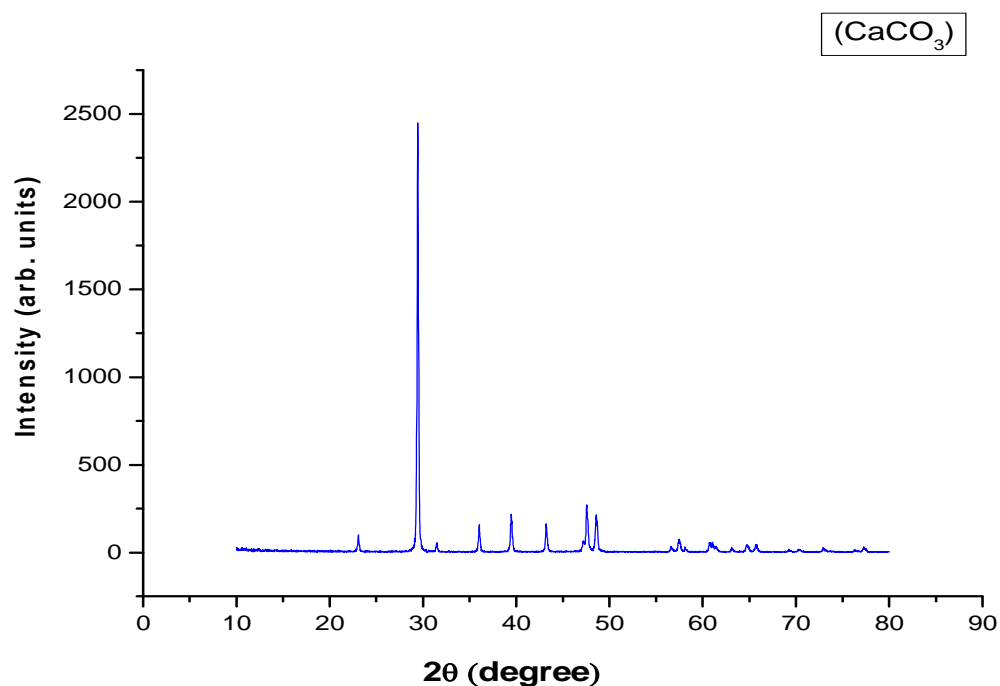


Fig4.1 (a)-Eggshell calcined at $300^0$C

Calcite-Ca(CO3)
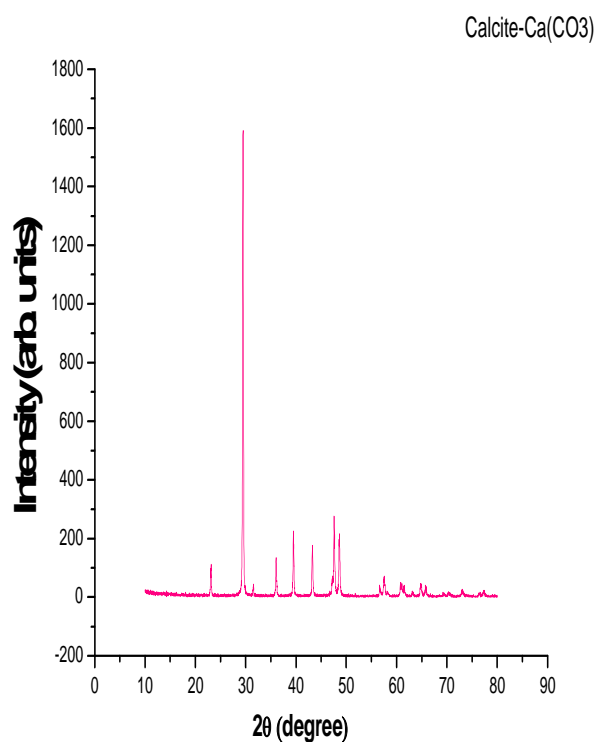


Fig4.1(b)-eggshell calcined at 500$^0$C

Calcium oxide-(CaO)
oxygen-O$_2$
carbon dioxide-CO$_2$
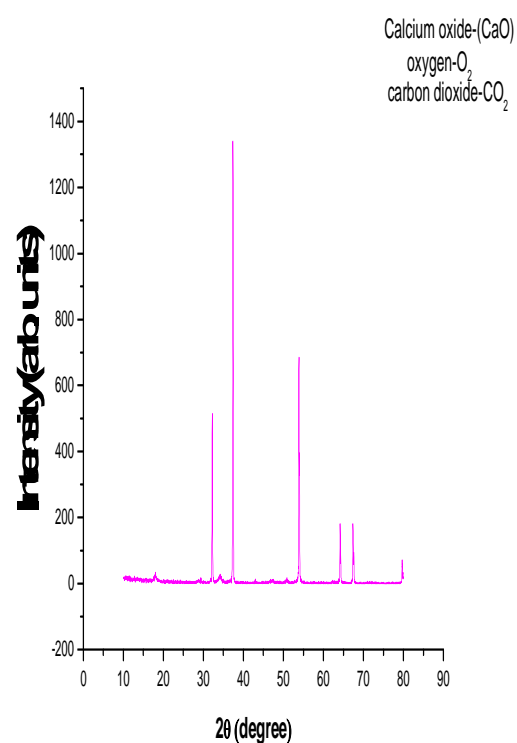


Fig4.1(c)-eggshell calcined at 950$^0$C

Figure 4.1(d),(e) illustrates the XRD pattern for samples calcined at 500$^0$C ,950$^0$C  after being  dissolved in lead nitrate solution and then filtered, respectively. After comparison with the JCPDS data it confirms that lead is present in both the samples, but in different compositional form. In filtered 500$^0$C sample the second peak as shown in the figure indicates the presence of lead in the form cerussite (PbCO$_3$) and in 950$^0$C lead is present as lead oxide (PbO).This clearly indicates that the calcium present in eggshell absorb the lead and lead forms compound with surroundings.

Calcite-Ca(CO3)
Cerussite,syn-PbCO3
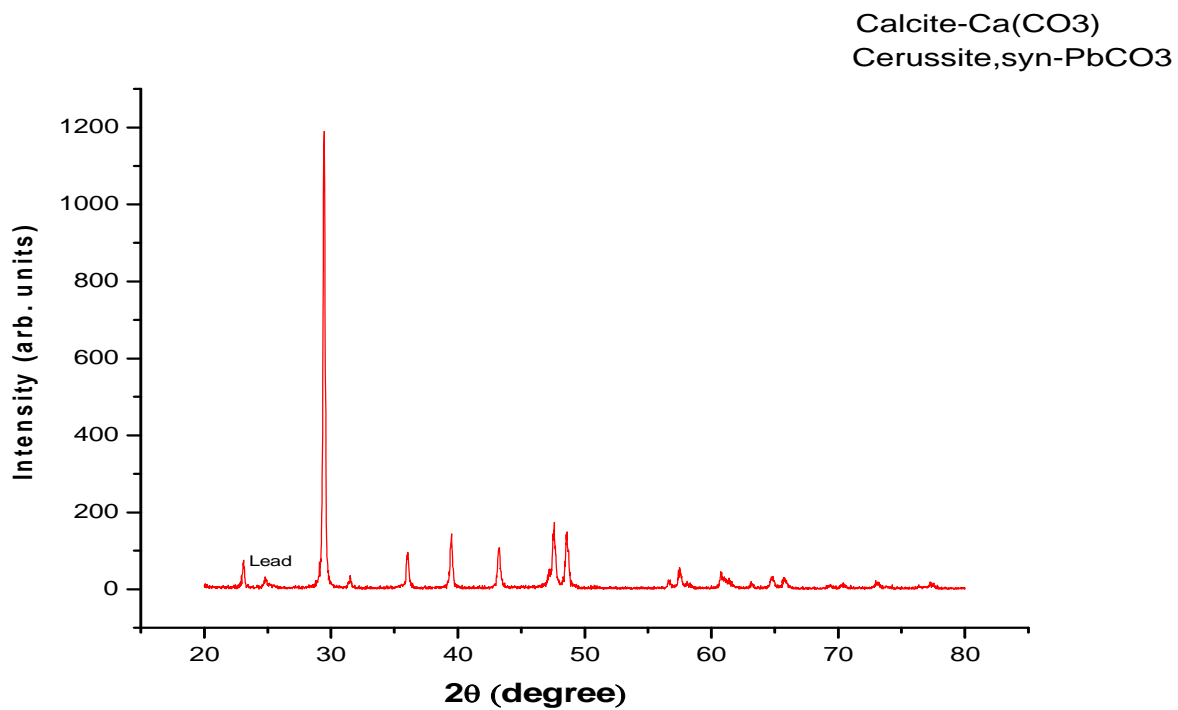


Fig4.1 (d)-Filtered eggshell of $500^0$C

Calcium Hydroxide-Ca(OH)2
Lead Oxide-PbO
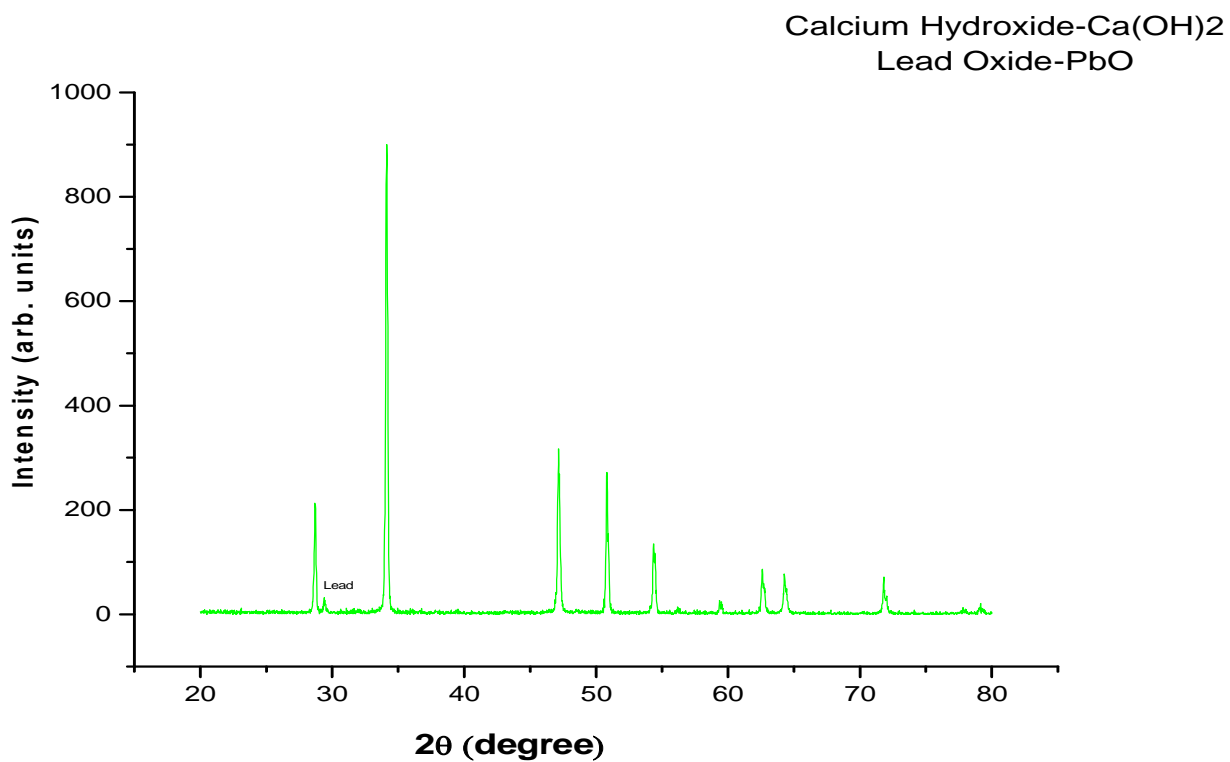


Fig 4.1(e)-Filtered eggshell of $950^0$C
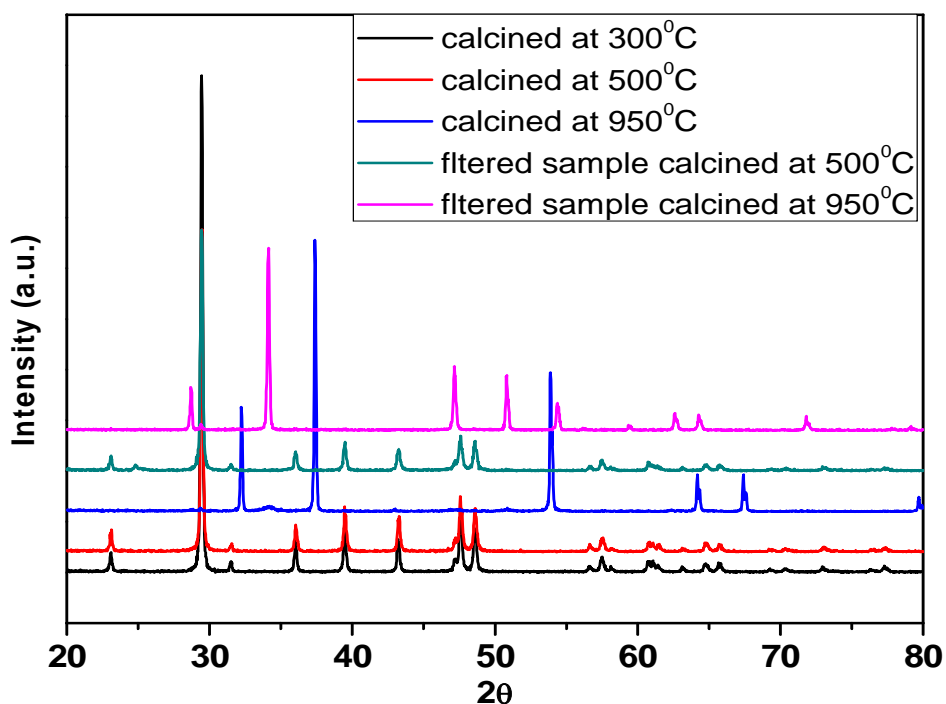
Figure 4.1(f) Mixed plot

Figure 4.1(f) gives the comparison of the XRD data. The figure clearly indicates the structural change corresponding to different temperature. Comparing all together the second peak in filtered $500^0C$ and $950^0C$ shows the presence of lead.

## 4.2 Fourier Transform Infrared Spectroscopy (FTIR)-

Figures 4.2 (a), (b), (c), (d) shows the FTIR spectrum of lead nitrate solution and the filtered lead nitrate solution dissolved in eggshell overnight ,which was acquired in the range of 400-4000 $cm^{-1}$. The table gives information about the bonds present and the functional groups.
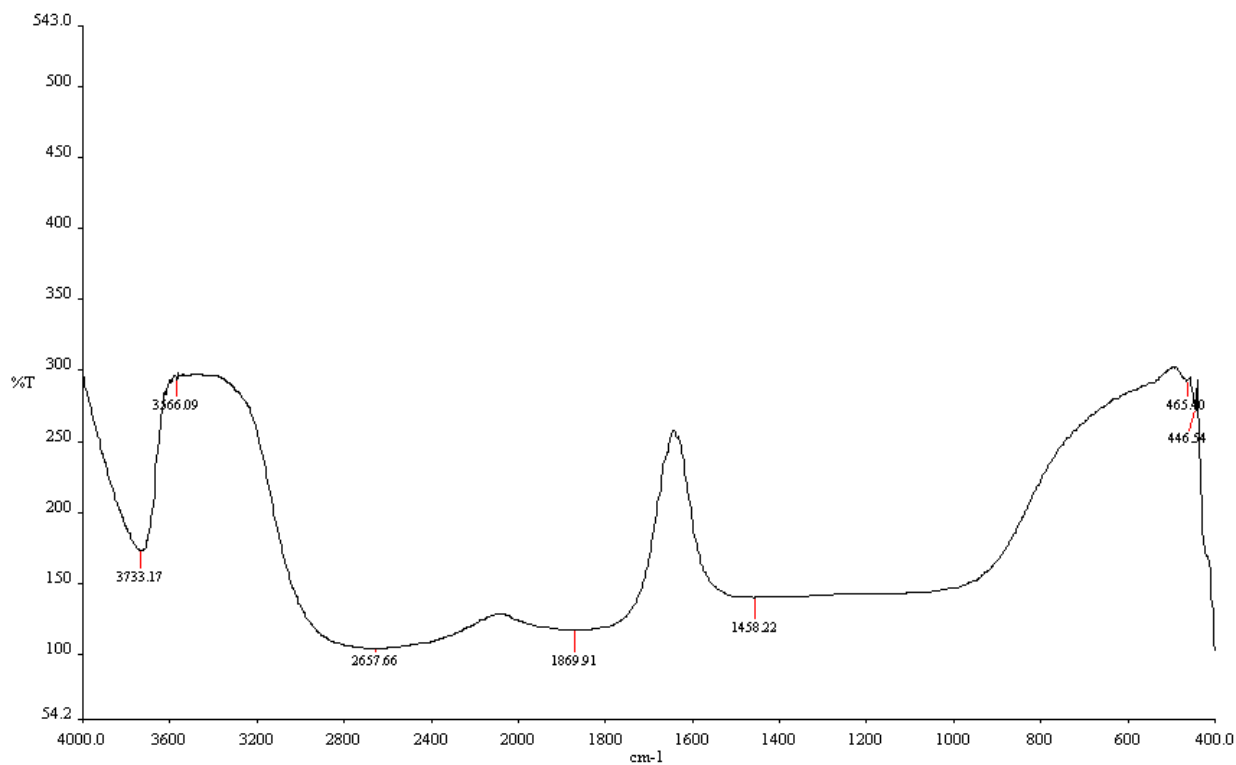
Figure 4.2 (a) FTIR of Lead nitrate solution

| Type | Wavelength(cm$^{-1}$) | Bond present | Functional groups |
|---|---|---|---|
| | 3733.17 | O-H stretch | Acid |
| | 3566.09 | N-H stretch | Amines |
| Lead nitrate sol. | 2657.66 | O-H stretch | Acid |
| | 1869.91 | Cyclic | Ketone |
| | 1458.22 | N-O asymmetric stretch | Nitro compounds |
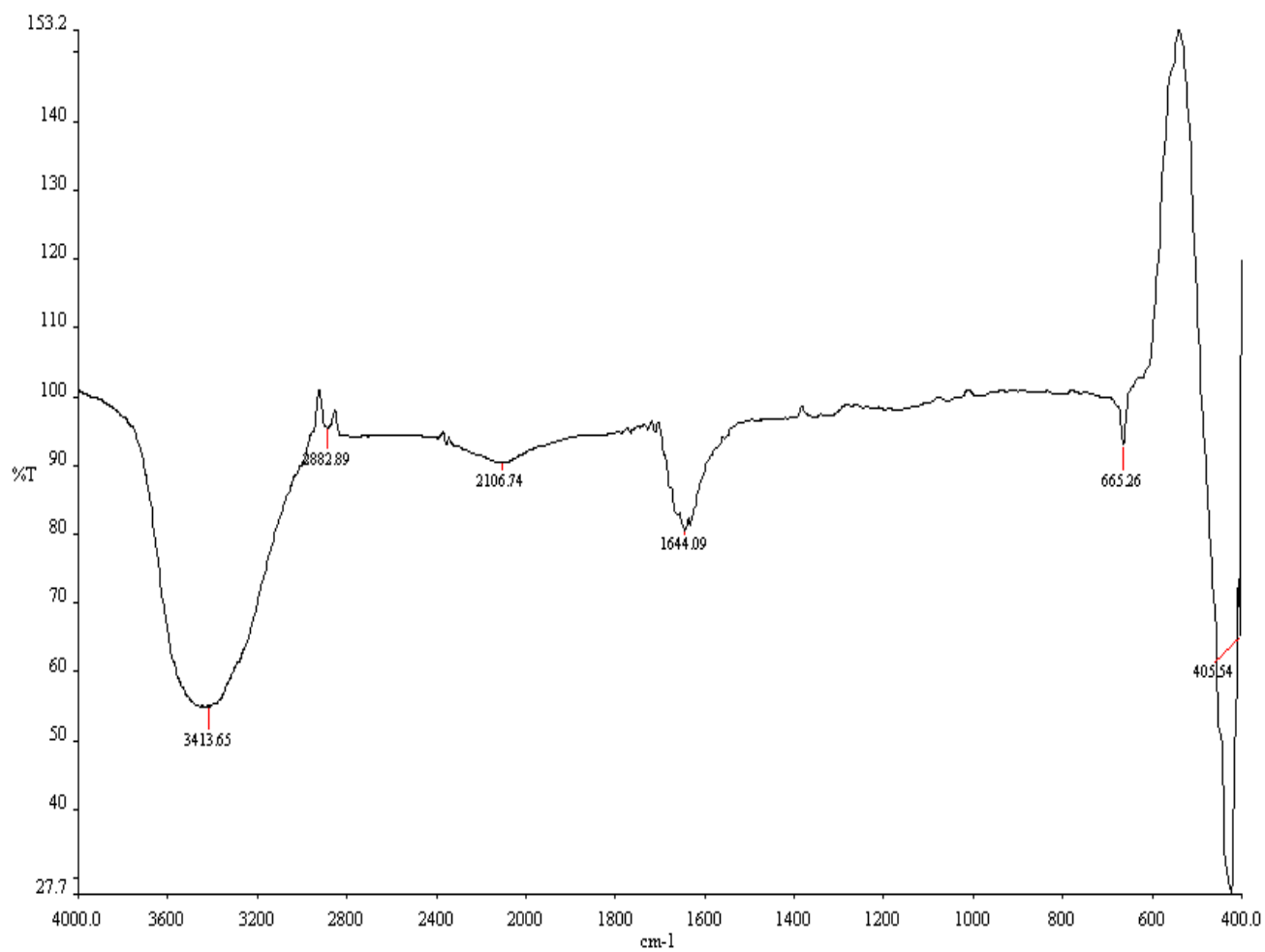
Fig 4.2(b)-FTIR of filtered 300
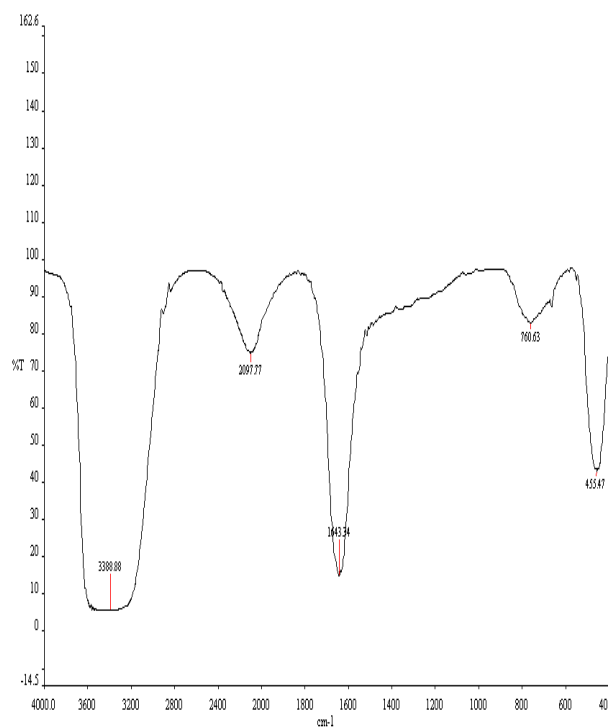
Fig4.2(c)-FTIR of filtered 500                    Fig4.2(d)-FTIR of  filtered 950
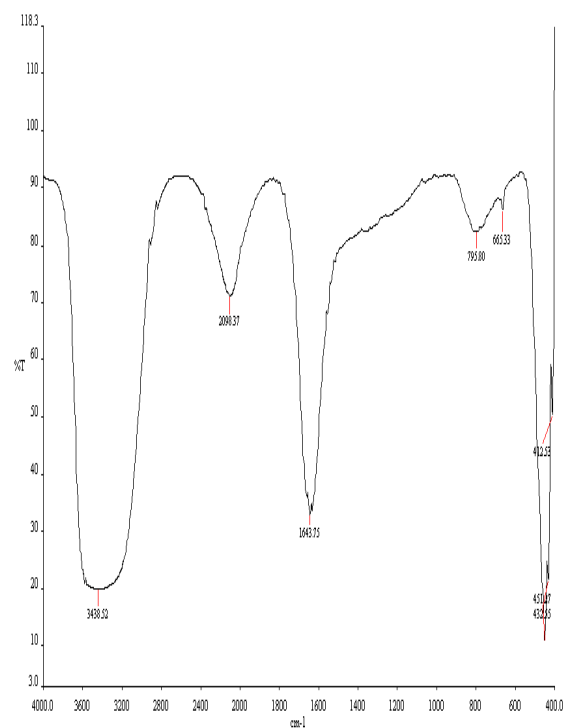
| Type | Wavelength(cm$^{-1}$) | Bond present | Functional groups |
|---|---|---|---|
| 300 filtered | 3413.65 | O-H stretch | Alcohol |
| | 2882.89 | C-H stretch | Alkane |
| | 2106.74 | C-H stretch | Alkyne |
| | 1644.09 | C=C stretch | Alkene |
| 500 filtered | 3388.88 | O-H stretch | Alcohol |
| | 2097.77 | C-H stretch | Alkyne |
| | 1643.34 | C=C stretch | Alkene |
| | 760.63 | =C-H bending | Alkene |
| 950 filtered | 3438.52 | O-H stretch | Alcohol |
| | 2098.37 | C-H stretch | Alkyne |
| | 1643.75 | C=C stretch | Alkene |
| | 795.80 | =C-H bending | Alkene |

As per figure and the table given, it's clearly indicates that the nitrogen hydrogen and nitrogen oxygen bonds are present in the lead nitrate solution as it contains lead nitrate and water. But the presence of bond varied in the three filtered liquid FTIR data. Hence we conclude that calcium carbonate reacts with lead nitrate and forms bond.

## 4.3. UV- Visible spectroscopy

The band-gap energy ($E_g$) was determined based on numerical derivative of the optical absorption coefficient. The fundamental absorption method refers to band to band transitions by using Mott and Davis relation of Equation .For photon energies just above fundamental edge, the absorption coefficient follows the standard relation.

$$\alpha=(h\nu - Eg)^n \, A/ \, h\nu$$

Where A is a constant related to the extent of the band tailing and n = 1/2 for allowed direct transition, n= 2 for allowed indirect transition. Eg is the energy gap between the valence band and the conduction band. A graph of (($\alpha h\nu$ )$^2$ versus h$\nu$) is as shown in Figure by extrapolating the graph to X axis in order to calculated the band gap of the samples.
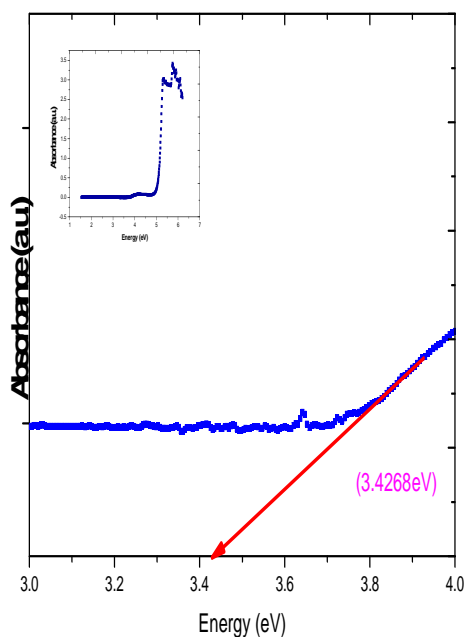


Figure 4.3(a)- UV of lead nitrate solution                    Figure 4.3(b)-UV of  300 filtered
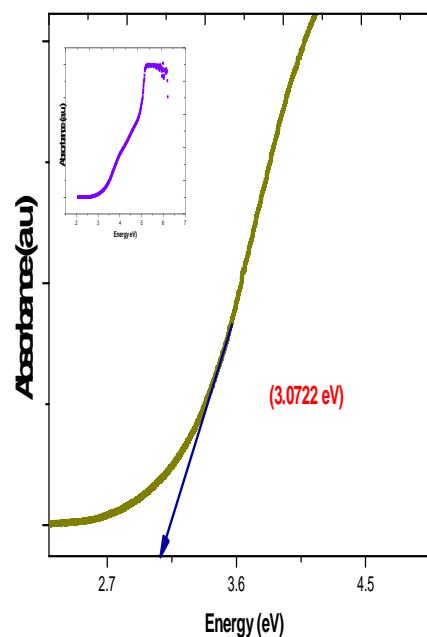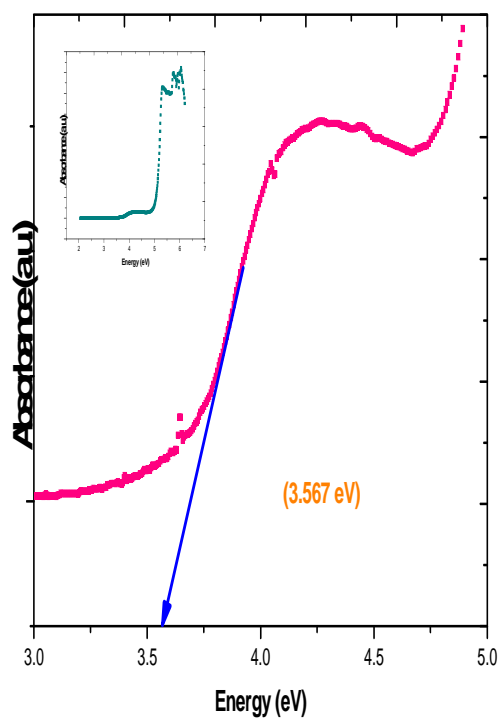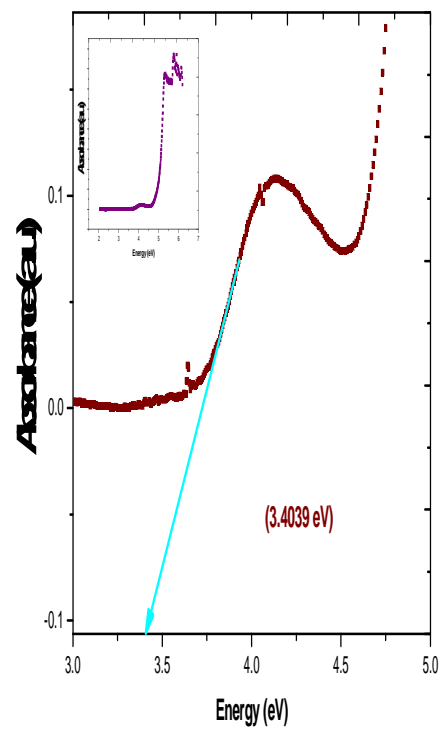
Figure4.3(c)-UV of 500 filtered



Figure 4.3(d)-UV of 950 filtered

Hence the band gap was found to be 3.4268 eV for lead nitrate solution and 3.0722 eV, 3.567 eV, 3.4039 eV for 300, 500, 950 calcined and dissolved samples respectively.
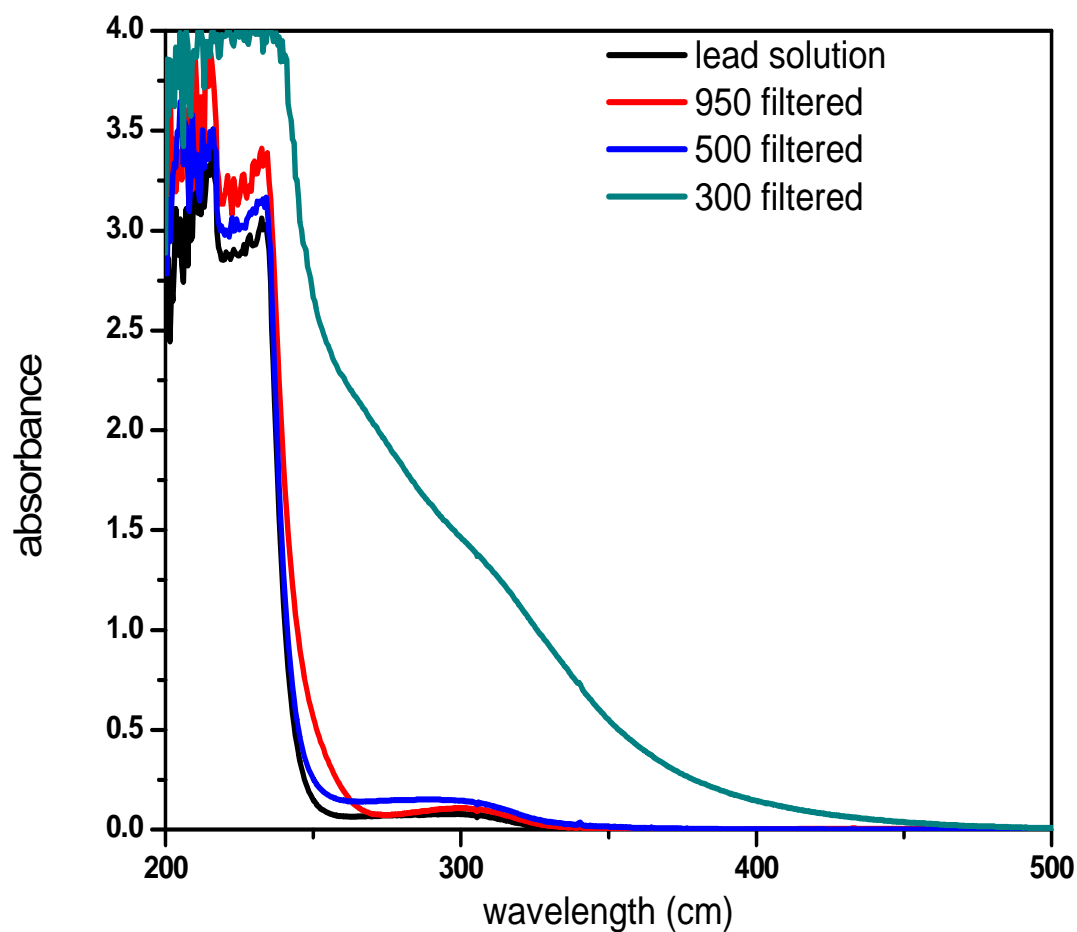
Figure 4.3(e) Comparison UV

Reason behind the variation of graph can be stated as-

At significantly high concentrations, the absorption bands saturate and show absorption flattening. The absorption peak appears to flatten as close to 100% of the light is already being absorbed. The concentration at which this occurs depends on the compound being measured. Hence as the concentration is more in 300 sample the peak flattens while in 500 and 950 it does not do that.

## 4.4. CHEMICAL TEST-

We have done a simple and effective chemical test to determine the presence of lead in water.

First I have taken 0.0828gm of lead nitrate and dissolved in the 50 ml distilled water, then I took 10 ml of it and dissolved two gram of the eggshell calcined at $950^0$C. After a few hours, I filtered it and put a little amount of concentrated $H_2SO_4$ in it. The aim is to see whether it forms any precipitate or not, because sulphuric acid to give white precipitate in presence of any Pb salt, but nothing happens. Again I put some lead nitrate in the solution and observed that the white precipitation occurred. This clearly indicates the absence of lead in the filtered water.

$$H_2SO_4+Pb(NO_3)_2----->2HNO_3+PbSO_4$$
...................................................(white)
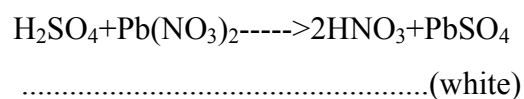
## 4.5. Scanning Electron Microscope (SEM)-

Figure 4.7(a),(b),(c),(d) shows the SEM morphology of the raw and calcined eggshell. The pictures will be considered useful for future work. We can study the change in morphology with the calcinations temperature. After soaking for overnight, we find the formation of clusters and agglomeration of the particles .This is because of the absorption of the lead ions in the surfaces of the calcium carbonates particles.
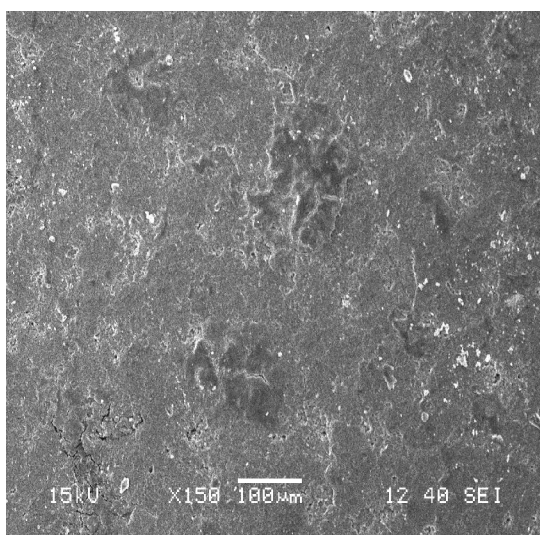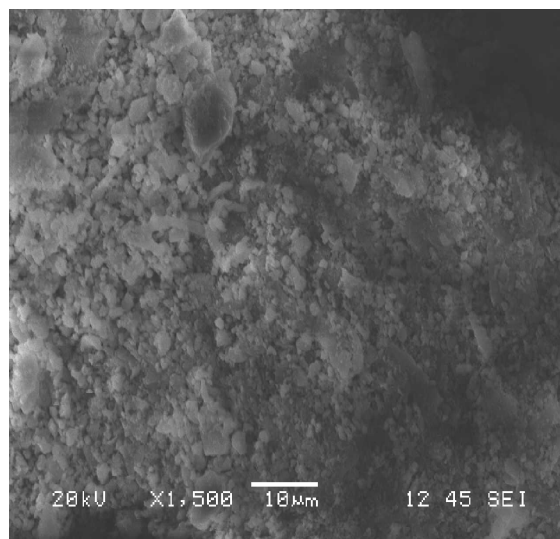


Figure 4.7(a)-SEM of outer part of eggshell



Figure4.7(b)-SEM of powdered eggshell
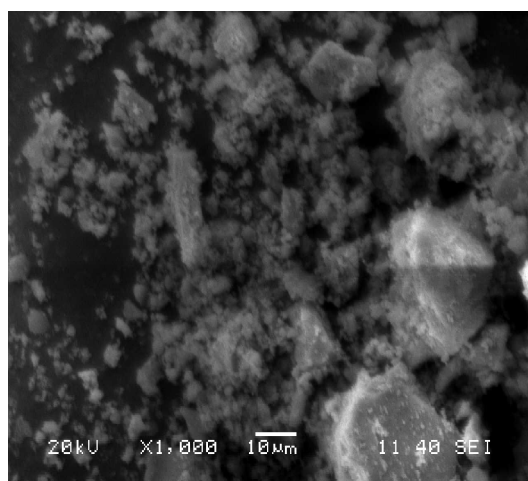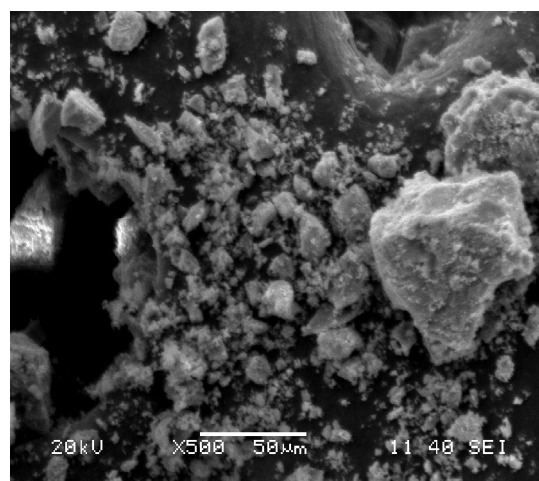


Figure4.7(c)-SEM of filtered $500^0$C eggshell



Figure4.7(d)- SEM of filtered $500^0$C eggshell

# CHAPTER-5

# CONCLUSION

Although natural eggshell powder also had some removal capacity of Pb but the Pb removal rate is extremely slow because of the small pore size. Rapid removal of Pb was observed with the calcined eggshell powder compared to the natural eggshell powder because of the larger pore size in the calcined eggshell powder. Before calcinations, natural eggshell had a generally irregular crystal structure. After calcination at 950°C for 2 h, the crystal structure has been changed with the formation of $CaO$ and with the emission of $CO_2$. But we noticed that the eggshells annealed around $500^0C$ are more efficient for absorption of foreign ions. $CaO$ treated with $K_2HPO_4$ solution becomes $Ca_{10}(PO_4)_6(OH)_2$ called hydroxyapatite which is more efficient than $500^0C$ annealed eggshell powder. But as $500^0C$ annealed eggshell powder is cost effective and no other chemical are required for its treatment, we conclude that $500^0C$ annealed egg shell powder could be used for the removal of Pb or other heavy metal ions. Further work in this direction will be interesting and important which would be undertaken.

**Important Reference-**

1. http://en.wikipedia.org/wiki/Band_gap

2. MatPaper1-s2.0-S0167577X13001146-main.pdf

3. http://en.wikipedia.org/wiki/Ultraviolet%E2%80%93visible_spectroscopy

4. http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/UV   Vis/spectrum.htm

5. http://en.wikipedia.org/wiki/Fourier_transform_spectroscopy

6. media.rsc.org/.../MCT4%20UV%20and%20**visible**%20spec.pdf

7. radchem.nevada.edu/classes/chem455/lectures/**uv-vis**(mar05)l9.ppt

8. www.perkinelmer.com/.../app_**uvvis**nirmeasure**bandgap**energyvalue.pdf

9. http://www.mri.psu.edu/facilities/MCL/techniques/UV-Vis/UV-VisTheory.asp

10. http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html

11. http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm

12. http://www.chem.ucla.edu/~webspectra/irtable.html

13. http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html

14. http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html

15. http://www.scribd.com/doc/21053651/Electronic-spectroscopy-UV-Visible

16. http://en.wikipedia.org/wiki/Scanning_electron_microscope

17. mmrc.caltech.edu/FTIR/FTIRintro.pdf

18. http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#Conceptual_introduction

19. http://en.wikipedia.org/wiki/Calcium_carbonate

20. wiki.answers.com › ... › Science › Chemistry › Elements and Compounds

21. http://www.cheneylime.com/chemist.htm

22. http://wiki.answers.com/Q/Reaction_of_lead_nitrate_and_calcium_carbonate

23. http://en.wikipedia.org/wiki/Eggshell

24. http://en.wikipedia.org/wiki/Lead%28II%29_nitrate

25. http://www.rsc.org/chemistryworld/News/2011/October/06101101.asp

26. Arunlertaree C, Kaewsomboon W, Kumsopa A *et al*., 2007.Removal of lead from battery manufacturing    wastewater by egg shell[J]. Songklanakarin J Sci Technol, 29: 857–868.

27. Borgwardt R H, 1985. Calcination kinetics and surface area of dispersed limestone particles[J]. AIChE, 31: 103 111.

28. sludge_pollutants_2.pdf

29. http://www.ncbi.nlm.nih.gov/pubmed/8010775

30. http://www.ncbi.nlm.nih.gov/pubmed/18277646

31. AASR-2012-3-3-1454-1458.pdf

32. 6_147_SRCC_2(4)2012_P.pdf

33. B K Chaudhuri et al , Mat. Letts. 92 (2013)140-150.