# Synthesis and Characterization of Hollow Silica Nano Particles on Calcium Carbonate for Possible Removal of Lead from Industrial Waste Water

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Abstract - This paper is intended to verify the applicability of Calcium Carbonate/Silica (CaCO<sub>3</sub>@SiO<sub>2</sub>) nano composites, in waste water treatment as an adsorbent for the removal of toxic heavy metals. Synthesis of CaCO<sub>3</sub>@SiO<sub>2</sub> composite was done using a precipitation method in which Calcium Carbonate particles were first prepared. This was followed by treatment of the formed carbonate particles with Sodium Silicate (NaSiO<sub>3</sub>). Characterization of the resultant nano particles was carried out to provide important information on morphology, surface structure, texture, particle shape, particle size and other characteristics. It was done using analytical techniques like XRD, DLS, SEM, and TG-DTA. The various analyses revealed that the nanoparticles are amorphous, porous and spherical in shape owing to the dominant presence of vaterite, with an average particle size of 85.5nm.The nano particles will be used as adsorbents for the removal of lead from industrial waste water.

*Key Words* - Calcium Carbonate, Silica, Nano Composites, Precipitation characterization, Morphology

# I. INTRODUCTION

Today, the availability of clean drinking water is a global cause of concern due to an increase in both surface and ground water pollution. A number of surface water contaminants in general, from their different sources, are increasingly finding their way into our main and strategic water bodies. The increase has been largely attributed to such factors as population growth, rapid industrialization and/or industrial growth as well as long term droughts [7, 16].

Heavy metals, along with other pollutants, are generated from quite a diverse matrix of chemical and process industries which include textiles, metallurgical, tanneries, battery manufacturing, mineral processing industries, and pharmaceutical industries, just to name a few, [15, 6, 5, 9, 30]. Owing to their toxicity, bio-accumulative nature, and the fact that they are generally non-biodegradable, heavy metals have been labeled

dangerous and hence a potential threat to both human and aquatic life. Chronic poisoning has been reported with metals such as Chromium and Arsenic which are carcinogenic, so that they cause cancer [15, 16, 17]. Badruddoza et al [15] further highlighted that Chromium is not only a carcinogen but also a mutagen as well as teratogen. Other heavy metals such as Lead have also been cited as highly toxic. Lead has been reported to cause brain damage apart from mental disturbances and retardation as well as serious reduction in hemoglobin production [9, 6, 4]. The metal has also been associated with the damage of various bodily systems which include the nervous and reproductive systems and the kidneys. Diseases like anemia and problems of high blood pressure have also been linked to the metal [16].

It is therefore clear from this background that an effective and efficient mitigation method is required. The method should be such that it is robust and capable of handling large volumes of effluent with even very low pollutant concentrations. The method should also be simple, friendly to the environment and above all cost effective.

From available literature, it is apparent that there are several conventional methods being used in pollution control particularly for the removal of heavy metals from industrial waste waters. Examples include: membrane separation, ion exchange, ultra-filtration, filtration, electrodialysis, sedimentation, chemical reduction, electrochemical treatments, biological treatment, reverse osmosis, flocculation/coagulation, and adsorption among others [15, 7, 17, 2, 13, 4, 11]. However, it should be noted that all of these methods, with the exception of adsorption, have been observed to have technical and/or economical shortcomings which include high capital and operational costs, unacceptable sensitivities to operational conditions, high energy consumption as well as high levels of sludge generation [6].

This being the case, several authors and/or researchers have revealed adsorption as a better option particularly in the removal of heavy metals. Zhu et al [12] for example noted that adsorption has proved to be superior over other technologies as far as operational costs are concerned. Generally, the method has been shown to be simple, efficient and effective, with zero sludge generation. The operation has been noted to be easy to handle with a potential and/or capacity for regeneration apart from of course being cost effective [14, 15, 6]. With these factors therefore, it follows that adsorption is a better alternative compared to the other available technologies.

In adsorption operations, several materials have been used as adsorbents and they include for example, synthetic resins, kaoline, zeolites, clays as well as activated carbon. From the list, activated carbon has been the most popular and most widely used [5, 10, 8]. The adsorbent however, has had one major impediment among others, the cost. The somewhat high cost of this adsorbent has limited its use especially in highly contaminated waste waters [5, 8]. Apart from activated carbon, all commercially available adsorbents in general, have also been labelled less efficient and costly. In view of these setbacks therefore, a low cost adsorbent should be sought, one that equally matches or better still outperforms activated carbon as well as other commercially available adsorbents. Todate, research is progressing in an effort to harness agricultural as well as industrial wastes in waste water treatment, as low cost adsorbents [8, 6, 5, 4]. Jin et al [5] has however pointed out that a decrease in material cost should be augmented by other material properties like for example adsorption capacity. Tan et al [6], further pointed out that the low cost adsorbents are in most cases characterized by low adsorption efficiencies. As a result, the issue of cost alone cannot define an ideal adsorbent. This implies, an adsorbent should not only satisfy the cost aspect, but should also provide high adsorption capacity and this is basically defined by the material's surface area. In other cases, the porosity of the material is also a considered property for an ideal adsorbent. Basically therefore, an ideal adsorbent should have strong affinity for the desired adsorbate and possess a large surface area, hence active or binding sites. The adsorbent should also be hydrothermally stable and be able to resist adverse environmental conditions. Lastly the aspect of regenerability and/or separatability from the treated water is also a feature and/or property to consider [2].

From this background therefore, considerable research effort has been directed towards harnessing nano particles as adsorbents. It should be commented that a lot of progress has been realized in this regard. The nano materials have responded very well to the call for low cost, high surface area and high adsorption capacity materials with the potential to efficiently and effectively handle metallic pollutants even in very low concentrations. They have also been widely commented for being environmentally friendly, that is, no secondary pollutants are produced with nanomaterials.

In this report, it has been highlighted that material porosity is one of the properties considered for an adsorbent. Guoliang et al, [2] confirmed this when they noted that a good number of researchers have focused on porous adsorbents which have shown remarkable improvement in heavy metal removal efficiency. This somewhat high efficiency is explained by the fact that porous materials exhibit both external and internal surface areas where both are available for adsorption.

Silica or silicon dioxide  $(SiO_2)$  is one good example of porous materials and a lot of research coverage has been given to this material. In all its forms, the material has received this considerable attention due to its uniquely large surface area, well defined pore size and shape [1]. Also according to Guoliang et al, [2] mesoporous materials with the already mentioned unique features have been extensively studied for their wide range of applications in adsorption, catalysis, sensors, semiconductor materials in electronics and separation. Silica nanoparticles in particular have attracted a lot of attention in view of their excellent optical, electrical and thermal properties [19]. The nanoparticles have also been applied in various fields such as cosmetics, catalysis, paints and drug delivery [20, 19].

The study of silica nanoparticles and their derivatives on the removal of heavy metals has also been carried out extensively. It should however be highlighted that the current studies on silica nanoparticles and their application as heavy metal adsorbents are mainly focusing on their modified forms, either functionalized or in composite form. For example, Bois et al, [1] studied the adsorption of heavy metal ions using silica functionalized with three different functional groups: Aminopropyl-, [Aminoethylamino]propyl- as well as [(2-amino-ethylamino)ethylamino]propyl-. Magnetic Silica, functionalized with a thiol- group was also investigated for the removal of Hg<sup>2+</sup> and  $Pb^{2+}$  ions [2]. Aguado et al, [10] and Heidari et al, [9] studied the removal of metal ions Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> using amino-functionalized mesoporous Silica. On nanocomposites, Cheng et al, [21] worked on the synthesis and characterization of Alumina particles coated with a uniform Silica shell. Li et al, [17] investigated the removal of Cr<sup>6+</sup> from waste water using Silica coated Iron nanocomposites. Lastly, Lim et al, [18] worked on the synthesis of Polypyrrole (PPy)/Silica nanocomposites for the removal of  $Hg^{2+}$ ,  $Pb^{2+}$  and  $Ag^+$ .

In this paper, work has been carried out to synthesize and characterize a core-shell nanocomposite of Silica on Calcium Carbonate (CaCO<sub>3</sub>) for adsorption and removal of heavy metals from waste water. It should be emphasized that very little work has been carried out on this composite

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and in cases where it was done, the application was not as an adsorbent. Nekhamanurak et al, [22] for instance studied the influence of the  $CaCO_3@SiO_2$  composite on the mechanical properties and fracture behavior of poly (lactic acid) nanocomposite. Li et al, [23] also worked on the preparation of hollow Silica on  $CaCO_3$  template for applications in drug release control. Lastly, Won et al, [3] investigated biological applications of  $CaCO_3@CdSe/ZnS/SiO_2$  microcomposites.

## II. EXPERIMENTAL WORK

This section describes the experiments that were carried out in the preparation of the core-shell nanocomposite  $CaCO_3@SiO_2$ . The materials together with the equipment that were used for the experiments are also presented in this section.

## A. Materials and Methods

## 1) Materials

Anhydrous Calcium Chloride (AR CaCl<sub>2</sub>, 99%), Potassium Carbonate (AR  $K_2CO_3$ , 99%), Sodium Hydroxide pellets (AR NaOH, 99%), Silica Gel (AR), Hydrochloric Acid (AR HCl, 36%) and Deionised Water (Millipore) were all used for the preparation of the nanocomposite.

## 2) Synthesis of $CaCO_3 @SiO_2$ Nanocomposite

*i.* Preparation of Calcium Carbonate Nanoparticles

The method by Won *et al*, [3] was adopted for the synthesis process. In the procedure, 11g of anhydrous Calcium Chloride was prepared in 200ml of deionised water. Also, 13.82g of Potassium Carbonate was separately prepared in 200ml to give equimolar solutions of the two salts. The prepared potassium carbonate solution was added to the Calcium Chloride solution to give a white precipitate. The mixture was then stirred for 20 minutes before separation by filtration. The solid product was washed several times with deionised water and was left to dry in air.

## *ii.* Preparation of Sodium Silicate

This reagent was prepared in the laboratory since it was not available in stock. In this procedure, 32g of Sodium Hydroxide were weighed and separately 24g of Silica Gel were also weighed. The Sodium Hydroxide was dissolved in 120ml of deionised water under heating at 230°C. To the dissolved Sodium Hydroxide, Silica Gel was then added in small portions so that it was dissolved in hot Sodium Hydroxide. The mixture was heated between additions until all the 24g of the gel were dissolved to give a Sodium Silicate solution.

*iii.* Preparation of the Nanocomposite

Work by Chen et al [31] was adopted for this synthesis procedure. То prepare CaCO<sub>3</sub>@SiO<sub>2</sub> nanoparticles, 2.0g of the prepared Calcium Carbonate nanoparticles were weighed into a conical flask. The material was dispersed in 100ml of deionised water with stirring at 700rpm. To the suspension, 100ml of 0.4M Sodium Silicate was added dropwise. The mixture was then heated to 80°C on a hot plate with stirring. The pH of the mixture was adjusted to 9.0 - 10.0 using 1.0M Hydrochloric Acid which was added dropwise with continuous stirring. On attaining the required pH, the suspension was further stirred for 40 minutes at 800 - 900rpm. The formed nanoparticles were then separated via filtration and then washed thoroughly with deionised water. They were then dried at 100°C for two hours in an air oven. The dried nanoparticles were pulverized in an agate mortar before calcination. The calcination process was done at 700°C for 4 hours after which the nanoparticles were now ready for characterization.

## B. Characterization

The crystal structure of the core-shell nanocomposite was determined using the X-Ray Diffraction (XRD) technique. Also from the XRD analysis, the average crystallite size was calculated using the Scherrer equation. The corresponding particle size as well as the particle size distribution were determined using the particle analyzer, Dynamic Light Scattering (DLS). Apart from particle size determinations, the general morphology of the nanoparticles was given by the electron microscopy method, the Scanning Electron Microscope (SEM). Thermal analyses for the determination of such properties as mass changes, thermal capacity, enthalpy and the coefficient of heat expansion was carried out using TG-DTA. This particular analysis was however mostly confined to mass and enthalpy changes.

## **III. RESULTS AND DISCUSSION**

In this section, the findings and observations from the experiments that were carried out are presented and discussed.

# A. X-Ray Diffraction (XRD)

# 1) Calcium Carbonate Nanoparticles

Fig 1 gives the XRD pattern for Calcium Carbonate nanoparticles. According to the work by Won *et al*, [3], the distinct peaks at around  $23^{\circ}$ ,  $29.5^{\circ}$ , and  $36^{\circ}$  correspond to calcite, the most thermodynamically stable variant of calcium carbonate. The other peaks at  $26.5^{\circ}$ ,  $31.5^{\circ}$ ,  $43^{\circ}$ ,  $48^{\circ}$ ,  $49^{\circ}$ ,  $56^{\circ}$  are consistent with vaterite, the other variant of Calcium Carbonate. This implies that some amount of vaterite is here coexisting with calcite to constitute the nanoparticles.

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It is also important to note from Fig 1 that the nanoparticles exhibited a crystalline structure and the corresponding crystallite size was estimated from the Scherrer equation given as:

$$d_{XRD} = \frac{K\lambda}{\beta Cos\theta} \tag{1}$$

Where  $d_{XRD}$  is the crystal size,  $\lambda$  is the diffraction wavelength,  $\beta$  is the corrected FWHM in radians,  $\Theta$  is the diffraction angle while K is the Scherrer constant close to unity. A value of 0.9 was adopted for K in this calculation [24]. The crystallite size was estimated from the first 7 peaks and the average value was found to be 38.4nm.

#### 2) CaCO<sub>3</sub>@SiO<sub>2</sub> Nanoparticles

The XRD pattern for the core-shell nanocomposite is given in Fig 2. From the image, the presence of Silica nanoparticles is evident and is shown by the broad peaks at  $26^{\circ}$  and  $53^{\circ}$ . According to Gorji *et al*, [25], peaks at  $24^{\circ}$ ,  $31^{\circ}$ ,  $43^{\circ}$ ,  $46^{\circ}$ ,  $54^{\circ}$ ,  $57^{\circ}$  are shown corresponding to Silica

nanoparticles. These agreed very well with those in the Calcium current work confirming that Carbonate were successfully coated with Silica nanoparticles amorphous nanoparticles to give an core-shell nanocomposite. The amorphous nature was also confirmed by Sadek et al, [19] and Singh et al, [26]. The average crystallite size was also estimated from equation (1) and the corresponding calculations gave an average size of 12.4nm.

#### B. Direct Light Scattering (DLS)

From Fig 3, it can be seen from the particle size distribution that the Calcium Carbonate nanoparticles are well within the nano size range of between 1 and 100nm and in this case, the synthesis method gave a reasonably narrow particle size range. The analysis gave a mean particle size of 44.6nm with a Z-average of 34.3nm. It should be highlighted that the DLS result directly matched that from the XRD method. From work by Stamm, [27], it was revealed that DLS as a particle size measurement technique, is mostly applicable to spherical nanoparticles, hence, these results serve to confirm that the synthesized Calcium Carbonate nanoparticles are spherical in shape.



Figure 3 Particle size distribution for Calcium Carbonate nanoparticles



Figure 4 Particle size distribution for CaCO<sub>3</sub>@SiO<sub>2</sub> nanocomposite

Fig 4 shows the particle size distribution for the core-shell nanocomposite. The result shows an increase in particle size

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with a mean particle size of 66.7nm and a corresponding Zaverage of 85.5nm. The graph (Fig 4) also shows that a small percentage of the particles fell in micro- size range. The increase in particle size is evidence enough that the Calcium Carbonate nanoparticles were coated with silica. Because of the amorphous structure of the nanocomposite, the average crystallite size could not quite match the DLS value as was the case with the crystalline Calcium Carbonate particles.

### C. Scanning Electron Spectroscopy (SEM)

The Scanning Electron Microscopy (SEM) was used to give important information on the morphology as well as the texture of the nanoparticles. It can be observed from Fig 5 that the particles were largely spherical in shape with the size averaging 94.7nm. The value however differed from both the DLS and XRD values.





Figure 5 SEM images for Calcium Carbonate nanoparticles in high and low magnification respectively.

From the images, Fig 5, there can be seen traces of rectangular shaped particles and these according to Won *et al*, [3] represent calcite, with the spherical ones which constitute the bulk of the material representing vaterite. Also according to the same authors, the evidently dominant

vaterite has a porous morphology and this makes the nanoparticles useful in various applications.





Figure 6 SEM images for CaCO3@SiO2 core-shell nanocomposite in low and high magnification respectively

The images for the core-shell nanocomposite (Fig 6) follow from the Calcium Carbonate nanoparticles (Fig 5) and from Fig 6, the presence and dominance of spherical particles is evident. The tendency to agglomerate is also observed in both nanomaterials. In both materials however the distinct particles were not clearly visible. As result, the particle morphology could not easily be ascertained so that the other electron microscopy method, Transmission Electron Microscopy (TEM) is recommended.

#### D. Thermogravimetric – Differential Thermal Analysis (TG-DTA)

The DTA curve in Fig 7 shows a single exothermic and endothermic effect. A weight loss of approximately 5% given by the TG curve in Fig 7 is possibly linked to moisture loss up to around 200°C followed by water of crystallization up to around  $620^{\circ}$ C. The endothermic effect between  $620^{\circ}$ C and  $775^{\circ}$ C is attributed to thermal decomposition of Calcium Carbonate to Calcium Oxide. This transition has also been observed by Aboutaleb and Mohammad, [28] and Deshmukh *et al*, [29] who noted thermal decomposition between  $600 - 620^{\circ}$ C and  $755^{\circ}$ C. The associated decomposition process is based on the following chemical equation:

 $CaCO_3$  \_\_\_\_  $CaO + CO_2$ 



From the corresponding TG curve (Fig 7), the weight loss associated with the decomposition process is approximately 43%, giving a total weight loss of approximately 48%.

For the core-shell nanocomposite, a 2% weight loss approximately, is observed up to around 200°C. This could be a result of loss of residual moisture. Apart from the moisture loss, notable is a further 14% material weight loss in the temperature range between 750°C and 810°C and this like in the calcium carbonate case (figure 7) is mostly a result of chemical decomposition as  $CO_2$  is formed from the carbonate. For this process, the DTA curve confirms an endothermic process. On the overall, approximately 25% material weight loss is observed, far less than the 48% recorded for the carbonate. A comparison with calcium carbonate nanoparticles in terms of thermal stability, shows that the latter are generally stable.

## **IV. CONCLUSIONS**

Synthesized Calcium Carbonate nanoparticles were successfully coated with silica to give a core-shell  $CaCO_3@SiO_2$  nanocomposite using the precipitation method. Performed analyses show that the composite particles are spherical with an average particle size of

85.5nm. Analyses also confirmed that the particles are largely amorphous and porous. The nanoparticles are also thermally stable and have the potential to extract heavy metal ions like lead from industrial waste water. However to fully ascertain the particle morphology, TEM analysis is recommended together with XPS.

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