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Synthesis of Zinc Oxide (ZNO) Nanoparticles From Zinc Sulphate, for Inclusion in Animal Feeds

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ABSTRACT

Stable zinc oxide (ZnO) nanoparticles were synthesized by sol gel method from Zinc sulphate and hydrazine hydrate. Zinc sulphate was selected for the process, as it was the cheapest and readily available source of zinc. The complex formed as a result was zinc hydrazine acetate. The percentage of zinc in the complex, as estimated by titration with EDTA was 25.14%, as against the theoretical 26.42%. Zinc hydrazine acetate complex formed as a result is subjected to pyrolysis in a muffle furnace and ZnO nano particles were obtained. The resultant material was a white, photostable and non-hygroscopic, fine free flowing powder. The XRD patterns of these samples revealed that the required phase is present with a little amount of impurities. The particle diameters were found to be 38.5nm, 28.6nm and 31.0 nm. The particle size measurement was done by particle analyzer and was supported by XRD Scherer's formula.

KEYWORDS : Zinc oxide nano particles, Zinc supplementation, x-ray diffraction (XRD)

Introduction

Nanoparticles are a special class of particles, designed to have structural features with at least one dimension less than 100nm (Oberdörster et al., 2005). Nano metals are usually impregnated in surface linings of other materials, where they exert the desired effect (Vermuelen et al., 2007; Jung et al., 2008). Nanotechnology is a field of convergence among life sciences, material science and IT sectors. The evolution of nanotechnology for medicinal and nutritional application have been found to exhibit useful properties, because they are different from those particles of micro and macro scale. Due to its varied properties, Nano- Zinc Oxide (ZnO) is the important of all the metal oxide nanoparticles manufactured until now.

Nano minerals are used for enhancing the bioavailability of minerals in livestock industry. In animals, zinc plays an important role in reproductive function due to its presence in FSH (follicle stimulating hormone) and LH (leutinizing hormone). It is a component of the enzymes alcohol dehydrogenase, lactic dehydrogenase carbonic anhydrase, ribonuclease, DNA Polymerase and the antioxidant copper zinc superoxide dismutase. Supplementation of nano zinc drastically reduced SCC in subclinical mastitis cow and improved milk production than macro zinc oxide (Garg et al., 2007, Rajendran, 2013). It also increased the weight of early weaned piglets (Cromwell, 2001).

Nano ZnO have high surface to volume ratio i.e. increased number of atoms per unit volume. It increases the proportion of atoms at the surface and hence increases its relative proportion inside the prescribed volume. They can be easily absorbed from the intestine and can go everywhere in the animal body and interferes with subcellular mechanisms (Nemmar et al., 2002).

A number of synthetic routes have been employed to synthesis of ZnO nanoparticles, such as sol-gel method, spray pyrolysis, physical vapour deposition, precipitation, solvothermal and hydrothermal method (Muller et al., 2003). This paper focuses on the simple method of sol-gel synthesis to manufacture ZnO nanoparticles, for its inclusion in mineral mixtures used to feed animals. The characterization of the particles is done by X-ray diffraction.

Materials and methods

Zinc sulphate was selected as the start material for the process because of its easy availability and cheaper price. Zinc carbonate was freshly prepared by adding a solution of A.R. Sodium carbonate (Merck) in double distilled water to an aqueous solution of A.R. Zinc sulphate and the precipitated Zinc carbonate was filtered off. This precipitate was then dissolved in glacial acetic acid in methanol to produce Zinc acetate, maintaining a ratio of 1:2 with a slight excess of zinc carbonate. The mixture was heated for a few minutes with continuous stirring. It was then filtered using Whatman no.1 filter paper. The clear filtrate was then used for the preparation of the complex. To the methanolic solution of zinc acetate, hydrazine hydrate solution was added slowly with constant stirring, keeping the zinc acetate to hydrazine in the ratio 1:2.

The reaction proceeded as follows.

$$ZnCO_3 + 2\,CH_3COOH + 2N_2H_4H_2O \rightarrow Zn\,(N_2H_4)2(CH_3C\,OO)_2 + CO_2 + 3H_2O$$

The zinc hydrazine acetate complex precipitated instantaneously and was filtered. It was then washed with methanol and then with petroleum ether and dried over anhydrous calcium chloride in a desiccator.

Preparation of ZnO nano particles

Nano ZnO was prepared from the precursor Zinc hydrazine acetate by pyrolysis (heating to 500°C in muffle furnace for half an hour). The synthesized samples were characterized for their structure and diameter by x-ray diffraction (Rigaku D max-C) with Cu Kα radiation.

In order to determine the percentage of Zn, about 0.1 mg of the complex was repeatedly evaporated with Con. HCl and the residue was dissolved in distilled water and the solution was made up to 100ml. The ZnCl2 solution thus obtained was titrated against standard EDTA by using Eiochrome Black T indicator. EDTA was standardized by standard ZnSO4 solution.

Results and Discussion

Zinc hydrazine acetate - $Zn\,(N_2H_4)2(CH_3COO)_2$ is a white fine powder, photo stable and non hygroscopic. It was insoluble in water, methanol, ethanol, carbon tetra chloride, chloroform, propanol and ether. Hence polymeric existence is suggested. Heating converts the complex to ZnO nanoparticles. Percentage of zinc present in the complex, as estimated by titration with EDTA was 25.14%, as against the theoretical 26.42%. This is suggestive of the composition of the zinc hydrazine acetate complex.

ZnO particles prepared by various techniques possess various particle size and properties. The ZnO sample was subjected to XRD studies and the particle size was calculated by Scherer equation from the value of Bragg angle (Θ) and FWHM (Full width at half maximum) obtained from the XRD data. Figure 1 shows the powder X-ray diffraction patterns of ZnO nanoparticles, prepared by pyrolysing zinc

hydrazine acetate complex. The diffraction patterns and interplane spacings can be well matched to the standard diffraction pattern of ZnO, demonstrating the formation of ZnO nanocrystals. The particle diameter was calculated using the Debye Scherer formula.

Calculation:
By Scherer equation,

Particle diameter, $L = k\lambda/\beta \cos \Theta$,
Where, k is the shape coefficient = 0.9, λ is the wave length of Cu- K_a = 1.54×10^{-10}

β is the FWHM.

Thus the particle diameter values of ZnO, as estimated from Θ values from the ZRD pattern are,

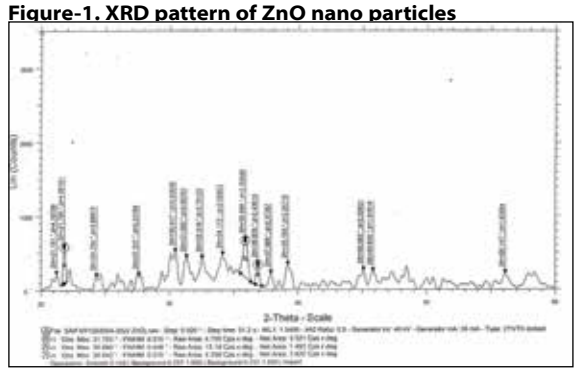
No. 1: $\frac{0.9 \times 1.54 \times 10^{-10}}{0.210 \times \pi/180) \times \cos(21.756/2)} = 38.5nm$

No. 2: $\frac{0.9 \times 1.54 \times 10^{-10}}{(0.448 \times \pi/180) \times \cos(35.886/2)} = 28.6nm$

No. 3: $\frac{0.9 \times 1.54 \times 10^{-10}}{(0.070 \times \pi/180) \times \cos(36.842/2)} = 31.0nm$

Conclusion
ZnO nano particles are biosafe, biocompatible and can be used for biomedical applications (Kathirvelu et al, 2009). With the promising role of nanotechnology, the potential of these novel materials as specific nutritional supplements for Zinc deficiency diseases in animals should be explored. Eventhough a number of synthetic routes have been employed to synthesis of ZnO nanoparticles, the product obtained should be free from harmful chemicals and the method used for its manufacture should be economical and user friendly. Taking that point into consideration, a modification of sol-gel method was considered for manufacturing process. Many other carriers like oxalates and ethylene diamine have been tried by various scientists with less degree of accuracy in complex formation, which hindered the final result. In this study, ZnO powder was obtained by the pyrolysis of the zinc hydrazine acetate, which yielded good result. The process described here is economical and can be simulated in any laboratories or mineral mixture manufacturing units in a large scale.

Figure-1. XRD pattern of ZnO nano particles



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