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BIOCHEMICAL SYNTHESIS AND CHARACTERISATION OF COBALT NANOPARTICLES

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Abstract

There is a need for competitive techniques for the synthesis of nanomaterials in the materials science research industry. Nanomaterials have significant relevance in the emerging technologies and cobalt nanoparticle being a modern nanomaterial is in high demand in this regard. In this research, cobalt nanoparticles have been synthesised through a simplified combined chemical-plant based technique which is non-toxic to the environment and most importantly less time consuming. The obtained cobalt nanoparticles were crystalline with uniformly distributed sizes, spherical in shape with little pores along the particles. The technique was simple and it can be replicated in the synthesis of other metal nanoparticles.

Keywords*:* *Biochemical Synthesis, Characterisation, Cobalt Nano-particles, Manihot esulanta, SEM-EDX Analyser.*

Introduction

There is a continual growth of interest in the field of nanotechnology due to the outstanding properties of nanoparticles which makes them highly priced at the material market. This is because of their intriguing shapes and sizes which have direct effects to their physio-chemical performance. The quantum effects and surface area characteristics play significant roles to the properties of nanoparticles, making them useful for optical, electronic, magnetic, catalytic as well as electrochemical applications [1]. This research is focused on the synthesis of nanomaterial particularly cobalt nanomaterial. Cobalt oxide nanoparticles particularly find versed applications for lithium batteries, electrochemical devices and corrosion control materials and solid-state sensors [2]. The continual demand for batteries to sustain clean energy calls for researches in the production of lithium battery having cobalt as a material to be used as one of its principal components hence a contribution to the present need for researches about cobalt and its synthesis. Several researches have proven that cobalt oxide has high potential of anode capacity used for lithium-ion batteries [11, 12, and 24]. Over some decades ago, it has as well been applied in the corrosion industry [7-10]. 70% of cobalt containing products has been employed as coating material in the last three decades [9, 28]. Consequently, it is evident that it contains features that might be advantageous in the coatings industry. Coatings which contain nano-crystalline cobalt have been shown to be an effective alternative to those which contains hard chromium films, which are known to cause severe environmental damage [4-6, 25-27].

Cobalt as a ferromagnetic metal is found in group 9 of the periodic table. It has an atomic number of 27 with a mass number 58.93. It’s melting and boiling points are 1495ºC and 2,870ºC respectively. It has a specific density of 8.9g/dm^3 and an electronic configuration of [Ar]3d^{7}4s^2. It is a lustrous silver-grey metal found in the earth’s crust in a chemically combined form in

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different ores. Processed and polished cobalt may be silvery or bluish grey [29-31]. Cobalt blue is medium blue, lighter than navy blue, but bluer than the light sky blue. Cobalt gotten as cobalt acetate is pink in colour. When cobalt salts and aluminium oxides are mixed, you get a good blue colour. This is why cobalt is used as colour pigment.

Cobalt has suitable electrical and magnetic properties and hence has been used for industrial applications in batteries and as core catalysts in chemical and petroleum processes. Cobalt exists in different forms in a combined state either as an ore or a compound. It is widely dispersed across the universe but makes up to 0.001% of the earth's crust [13]. It is very rare for an ore to exist principally as a cobalt ore hence majority of the cobalt mining comes as a by-product from the mining of other ores of iron, nickel, copper, manganese etc. This is why it requires series of skilled processing to win a good quantity of cobalt. This could be one of the reasons cobalt is classified to be costly. Cobalt can be found in small quantities in natural waters, in the sun, in ferromanganese crusts deep in the oceans and even in plants and animals. Some of the ores in which cobalt can be found include cobaltite (CoAsS), Safflorite ($(Co,Fe)As_2$) and skutterudite ($CoAs_3$) [32-34].

With the continuous rise in the demand for cobalt material in nanoparticle, various methods have been employed for the synthesis of the nanoparticle. This includes the general metal nanoparticle synthesis techniques ranging from reduction, thermal decomposition, mechano-chemical reaction, nano-casting methods and also high temperature solution phase [2, 12, and 14]. These methods are posed with their general challenge of prolonged thermal treatment, chemical pollution, and numerous uses of chemical additives. The physiochemical approaches used for the synthesis of cobalt nanoparticle are energy demanding, time consuming and unfriendly to the environment [41]. However today, an attempt to solve these issues are tried through bio - synthesis approach using plant extract and some renewable and sustainable routes. This approaches demand less thermal energy, less chemical additives, apparently low cost and most importantly, are non-toxic and hence eco-friendly to the environment [15, 16, 17, and 37]. The use of bio-synthesis for the fabrication of nanoparticles have been illustrated by several researches and it has been shown that plant derived materials eliminates the complex physio-chemical stages [18, 19, 35]. Basically, bio-synthesis of nanoparticles implies the use of plant extract which contains phytochemicals to catalyse the reduction of the precursor compound into nanoparticles. In 2017, cobalt oxide nanoparticle was fabricated from cobalt nitrate hexahydrate at low temperature using *punical granatum* leaf extract. The fabricated nanoparticles were apparently uniform ranging from the size of 40-80nm and they were used for photo-catalytic applications [1]. In 2017, cobalt nanoparticle was synthesised through a facile green synthesis using *Manihot esculenta* crantz as the plant extract. The nanoparticles when characterised showed pure crystallinity and also, was anti-ferromagnetic [23]. In 2019, a novel cobalt complex was synthesised to be used as an inhibitor in the corrosion of carbon steel in 1.0MHcl solutions. It was observed that the inhibition efficiency of the derivatives was good though depended on the concentration and structure of the derivatives and decreased with temperature [3, 36]. In 2020, cobalt oxide nanoparticles were synthesised from cobalt nitrate hexahydrate using *populus ciliata* for potential biological application and the synthesised cobalt particles were in the range of 40-50nm. The cobalt nanoparticles were used for anti-bacterial activity [22, 39, and 40]. In 2021, cobalt oxide nanoparticles were successfully synthesised via green method using *piper nigrum (p.nigrum)* leaves extract producing an efficient result with an environmentally friendly processes [42]. In 2022, Arun K Singh did a review on the synthesis of cobalt nanoparticles with plant extract and it was recommended that the process was less time consuming and environmentally friendly. It was also observed that a combination of plant extract from different plants in some few cases gave a better characteristics reduction feature [43]. In this research, a combination of chemical and bio-synthesis approach was adopted to synthesis cobalt nanoparticles. *Manihot esculenta* leaf extract was used for the plant reduction and sodium hydroxide being the chemical reagent while the precursor was cobalt II acetate tetrahydrate and the target product was cobalt oxide nanoparticle. The phytochemicals extracted from the plant which contains phenolic acids, tannins, flavonoids and saponin are bio-active and can donate hydrogen, quench singlet oxygen and also serve as chelation agents for the synthesis of the nanoparticles [20, 21].

Materials and Methods

The synthesis of cobalt nanoparticles was done using a bio-chemical production in the following techniques.

Preparation of the plant extract

The plant extract used in the experiment was *manihot esculanta leaf*. The fresh leaf was gotten from the Federal University of Petroleum Resources, Effurun Nigeria, cleaned thoroughly with water and left to dry at room temperature for approximately three weeks. Then it was taken to a grinding mill to be ground into powder particles. 10g of the powder particles was mixed with 2500ml of distilled water and boiled and stirred for 3 hours at 70ºC. The solution was allowed to cool at room temperature and then filtered. The filtrate was taken as the plant extract and the residue was discarded. The figs. 1 and 2 below show the *manihot esculanta* ground leaves for the preparation of plant extract and the prepared plant extract, respectively.

Fig. 1. Manihot esculanta ground leaves for the preparation of the plant extract.

Fig. 2. Sample of the prepared plant extract.

Synthesis of Cobalt nanoparticles

The cobalt nanoparticles were synthesised through reduction with plant extract. The cobalt acetate was gotten in particles, so the solution was prepared according to the following calculations.

$$\text{Molar concentration} = \frac{Mass\ concentration\ (\text{g/dm3})}{Molar\ mass(\frac{g}{mol})} \quad (1)$$

Molar mass = 249.10(g/mol) as prescribed by the manufacturer
0.02molar concentration was arbitrarily chosen to be prepared hence

$$0.02\text{mol/dm} = \frac{Mass\ concentration}{249.1},$$

Therefore: mass concentration = 249.1 x 0.02 = 4.982g/dm^3; 4.982g of the cobalt acetate was dissolved in 2000ml of distilled water.

The synthesis of the cobalt nanoparticles involved mixing 2000ml of cobalt II acetate tetrahydrate with 200ml of the freshly prepared plant extract and stirring with the aid of a magnetic stirrer at room temperature (25°C) for about 30 minutes. Then 60ml of sodium Hydroxide was added and the stirring continued, but then at 70ºC for a complete 3 hours. Upon addition of sodium hydroxide, the solution turned from orange to green and to deep blue and later purple after adding sodium hydroxide completely. All these colour changes occurred during the addition of the sodium hydroxide. The solution was further allowed to boil and stir for an additional 2 hours; it then turned completely black. The resultant solution was then centrifuged for 35 minutes and dried with the aid of a laboratory oven. After drying, the solution was allowed to cool at room temperature and the obtained nanoparticles were properly stored in a sample bottle. The synthesis stages are as shown in figs. 3-8 below.

Fig. 3. Cobalt acetate salt.

Fig. 4. Prepared Cobalt acetate solution.

Fig. 5. Solution of cobalt acetate with the plant extract during cobalt nanoparticles synthesis.

Fig. 6. Addition of Sodium hydroxide on the cobalt acetate and plant extract during synthesis of cobalt nanoparticles.

Fig. 7. The solution after boiling.

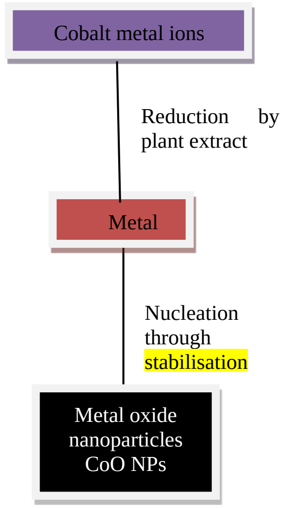


Fig. 8: Schematic representation of the synthesis of cobalt oxide

Characterisation

The research of the nanoparticles basic properties and compositions was made possible by characterisation. This was accomplished using energy dispersive x-ray analysis and a scanning electron microscope.

Morphological study

A scanning electron microscope was used in order to investigate both the microscopic and the nano-scale surface properties of the samples. A concentrated beam of electrons was then directed onto the surface of the sample after it has been hermetically sealed in a vacuum. After that, these electron beams were employed to scan over the surface of the sample, penetrate through it, and interact with it. This resulted in the production of x-ray emission, electron backscattering, and secondary electron emission, which revealed the topography of the sample. This process, in turn, produced micrographs, which are high-resolution, long-depth-of-field photographs of the sample surface. These micrographs could be used to describe things such as the composition of the material, any defects in the structure, the presence of impurities, and the presence of corrosion products. The JEOL-JSM-7600F was used throughout the course of the samples' examination. Micro-analysis was performed using energy-dispersive x-rays in conjunction with scanning electron microscopy. The scanning electron micrographs were captured at 8000x, 9000x, and 10000x system magnifications while the acceleration was set at 15 kV.

Characterisation with Energy dispersive X-ray Spectroscopy

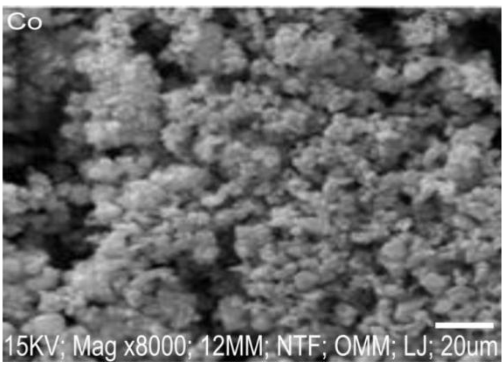
The energy dispersive x-ray spectroscopy was used to determine the chemical characteristics of the sample. It showed the elements present and their compositions. It was obtained by the interaction of the X-ray and the sample. The sample was clamped into the system of SEM-EDX analyser at an accelerating voltage of 15kv. The spectra were obtained using JEOL-JSM-7600F SEM-EDX analyser.

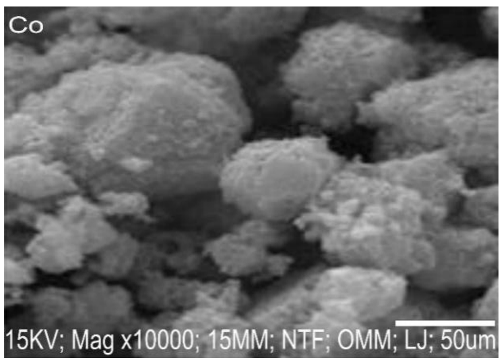
Results and Discussion

A physical examination of the synthesised nanoparticles indicates that they have smooth, dark and crystalline surface as presented in figure 9 below.

Fig. 9: Synthesised Nanoparticles cobalt oxide.

The nanoparticles of cobalt oxide were characterised as shown in figures 10(a) and 10(b). The scanning was done at 8,000 and 10,000 magnifications. The microgram showed that the cobalt particles are spherical in shape and dark ash in colour. The particles also have micro-pores which proved that it can be good for adsorption. The presence of pores therefore show that cobalt can be used as a nanocomposite to serve as a matrix house for nanofillers like carbon fibre and graphene to fit into, resulting to a mechanically stronger material. The particle sizes are smooth and are appear to be uniform, though there are few dense agglomerates. The smooth surface implies that the nanoparticles can have good contact with bacterial and can therefore be used for bacterial elimination.





a) b)

Fig. 10. (a) SEM analysis of cobalt-oxide nanoparticles 8kX and **(b)** SEM analysis of cobalt-oxide nanoparticles 10kX.

The Energy Dispersive X-ray (EDX) of the nanoparticles is shown in figure 11. The sample contained cobalt and oxygen as the key elements and traces of gold, carbon and silver. The EDX, further reveal strong peaks of Cobalt and Oxygen. The chemical composition in percentage indicates Cobalt and Oxygen having 67.02% and 15.9% respectively. The obtained cobalt nanoparticle is cobalt II oxide. The traces of gold, carbon and sulphur are due to the chemical compounds used during the reduction of the cobalt.

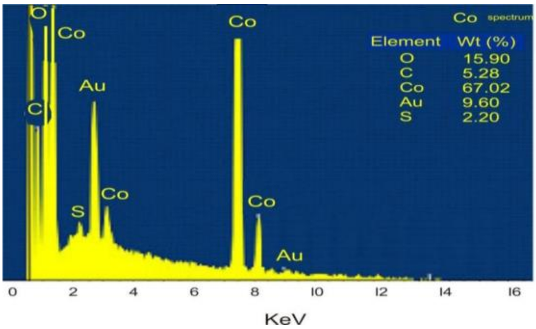


Fig. 11. Energy Dispersive X-ray of the cobalt oxide nanoparticles.

The EDX spectrum shows sharp peaks between 0Kev to 1.5Kev and between 7-8kev. These sharp peaks show that the nanoparticle is crystalline and this validates the physical examination of the nanoparticle being crystalline.

Conclusion

Cobalt nanoparticles have been prepared through a chemical-plant-based reduction technique where cobalt II oxide was prepared from cobalt II acetate tetrahydrate. *Manihot esulanta* leaf was used as the major reducing agent. It involved a combination of chemical and plant reduction. The chemical used was sodium hydroxide and the processes were simple and non-toxic to the environment. In general, the full techniques were simple and less time consuming. It does not require much time for growth. In addition, the cobalt nanoparticles produced were of high quality. The proposed synthesis technique is cheap, not time consuming and can be replicated. It can also be employed for the synthesis of other metal oxide nanoparticles, including zinc, copper, manganese, etc. The cobalt obtained from this technique can used for corrosion resistant materials, ferromagnetic applications, batteries and catalyst for chemical processes, etc. It can also be used as a matrix material to form a composite with graphene or any other active fibre, thereby producing an excellent modern-technology composite material.

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