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Baobab Leaves and its Potential in the Synthesis of Zinc Oxide Nanoparticles for the Removal of Lead and Copper from Aqueous Solution

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***Abstract*: Nanoparticles are materials with a size less than ~100 nm in diameter and they exhibit unique properties due to their nanoscale dimensions. This work aimed at determining the potentials of baobab leaves in the synthesis of ZnO nanoparticles for heavy metal removal in waste water. Phytochemicals were determined using standard laboratory methods. The green synthesis method was used to synthesise the ZnO nanoparticle. It was characterised using X-ray diffraction, Fourier transformed infrared spectroscopy, UV-visible spectroscopy, scanning electron microscopy and atomic adsorption spectroscopy. Taguchi method with L16 orthogonal array robust design was implemented to optimize experimental conditions of the purpose. Four key process parameters–temperatures, concentration, time and extract amount were considered for the optimization of ZnO nanoparticles. XRD patterns showed that ZnO nanoparticles have hexagonal unit cell structure, SEM picture reveal the morphology and particle size of prepared ZnO nanoparticle while Fourier transform infrared spectroscopy highlighted the functional groups. The UV-VIS absorption spectrum shows an absorption band at 364nm. The optimum conditions were obtained at a temperature of 70OC, concentration of 0.75M at time 2hr and an amount of 2ml. The synthesized nanoparticles have greater potential for absorption of heavy metal ions present in water sample. These nanoparticles can be effectively used as absorbents in the commercial scale to achieve the desired goal of a clean environment.**

***Keywords*: Absorption, Nanoparticles, Optimization, Spectroscopy, Synthesis.**

1. Introduction

In recent days nanotechnology has induced great scientific advancement in the field of research and technology. Nanoparticle is a core particle which performs as a whole unit in terms of transport and property [1]. As the name indicates nano means a billionth or 10-9 unit. Its size range usually from 1-100nm nanosize particles are quite unique in nature because nanosize increase the surface to volume ratio and also its physical, chemical and biological properties are different from bulk material [2]. Thus in recent years much research is going on metallic nanoparticle and its properties like catalyst, sensing to optics, antibacterial activity, data storage capacity [3]. Nanotechnology involves imaging, measuring, modeling, and manipulating matter at the nanoscale [4].The unique aspect of nanotechnology is the fact that materials and particles behave uniquely at nanoscale in a different manner from microscale [5]. There are several national and international funding programs that focus on nanotechnologies in areas of fundamental research aspects, applied research and commercialization. With this in mind, it is safe to say that there is no single scientific area that has not been touched by the nanoworld [6].

Nanoparticle of gold, silver, copper, silicon, zinc, titanium, magnetite, palladium formation by plants has been reported. Colloid silver nanoparticle had exhibited distinct properties such as catalytic, antibacterial [3], good conductivity, and chemical stability. Silver nanoparticles have its application in the field of bio labelling, sensor, antimicrobial, catalysis, electronic and other medical application such as drug delivery and disease diagnosis. Zinc Oxide (ZnO) nanoparticles are hydrophobic inorganic compound existing in white powder form. Three types of crystalline structures of ZnO nanoparticles include hexagonal wurtzite, cubic zincblende and cubic rocksalt [7]. Wurtzite is the most stable structure among all. It is hexagonal and symmetrical in shape with the absence of symmetrical center. This structure contributes to the high piezoelectricity property. Metal oxide nanoparticles such as zinc oxide have received an increasing attention as antibacterial materials in recent years because of their stability under harsh processing conditions, and also because they are generally regarded as safe materials for human beings and animals. Recently, many studies have proved that plant extracts act as a potential precursors for the synthesis of nanomaterial in non-hazardous ways [8]. Many studies have shown that ZnO nanoparticles have enhanced antibacterial activity. The use of plant materials for the synthesis of ZnO nanoparticles is relatively new and exciting research field.

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Table 1
Levels of different parameters

	Level			
Factor	1	2	3	4
A: Temperature (°C)	50	60	70	80
B: Concentration (M)	0.25	0.50	0.75	1.0
C: Time (Hrs)	1	1:30	21	2:30
D: Extract amount (ml)	2	4	6	8

Table 2
Experimental measured values for ZnO nanoparticles (Taguchi Orthogonal array Table L-16)

Run order	Temperature (^{O}C)	Concentration (M)	Time (Hrs)	Extract amount (ml)	Yield (absorbance)
1	50	0.25	1	2	3.612
2	50	0.50	1:30	4	3.436
3	50	0.75	2	6	3.913
4	50	1.0	2:30	8	3.436
5	60	0.25	1:30	6	3.612
6	60	0.50	1	8	3.436
7	60	0.75	2:30	2	3.913
8	60	1.0	2	4	3.436
9	70	0.25	2:30	8	3.436
10	70	0.50	2	6	3.913
11	70	0.75	1	4	3.436
12	70	1.0	1:30	2	3.913
13	80	0.25	2:30	4	3.436
14	80	0.50	2	2	3.913
15	80	0.75	1:30	8	3.612
16	80	1.0	1	6	3.362

Table 3
The ANOVA Table of ZnO Nanoparticles

Factors	ΔF	seaSS	AdjSS	AdjM	F-value	P-value
A	3	0.1138	0.1138	0.03792	0.46	0.732
B	3	0.6414	0.6414	0.21381	2.58	0.229
C	3	0.7072	0.7072	0.23573	2.84	0.207
D	3	2.4093	2.4093	0.80311	9.68	0.047
Residual Error	3	0.2489	0.2489	0.80298		
Total	15	4.1207				

ΔF- Degree of freedom, seaSS- sea sums of squares, AdjSS -Adj sums of squares, AdjM- mean sums of squares, F-value- functional value, P-value- probability value.

2. Material and Methods

A. Materials

The chemical reagents including zinc acetate dehydrate Zn $(CH3COO)_2$ 2H2O, sodium hydroxide NaOH, nickel nitrate $Ni(NO3)_2$, lead nitrate $Pb(NO3)_2$, copper nitrate $Cu(NO3)_2$ and chromic nitrate Cr (NO3)3 were applied in this study.

B. Methods

1) Green Synthesis of Zinc Oxide Nanoparticles

For the synthesis of ZnO nanoparticles, zinc acetate and sodium hydroxide were used as precursors. Both the solutions of Zn $(CH3COO)_2H_2O$ and NaOH were dissolved separately in deionized water to form the liquid media of the desired concentrations of 0.05M and 0.1M for sample A and B respectively the ratio of the concentrations was 1:1 (Zn $(CH3COO)_2$. $2H_2O$: NaOH). The solution of NaOH was solely added drop-wise to the zinc acetate solutions under vigorously stirring at room temperature, followed by 1cm3 aqueous leaf extract which was resulted in the formation of ZnO precipitate. Following the precipitation, the solution was washed over and over again with distilled water followed by ethanol to get rid of impurities. The pale white powder of ZnO NPs was obtained after drying at 60^{0}C in oven over night. This experiment was repeated 16 times under different conditions for each concentrations, temperature, time, and amount of leaf extract.

Mechanism of the zinc oxide nanoparticle

$$Zn(CH_3COO)_2.2H_2O + 2NaOH\ Zn(OH)_2 + 2CH_3COONa + 2H_20 \quad (1)$$

$$Zn(OH)_2(gel) + 2H2O = Zn_2^+ + 2OH^- + 2H_2O = [Zn(OH)_4]_2 \quad (2)$$

$$[Zn(OH)_4]_2^- ZnO22^- + 2H_2O \quad (3)$$

$$ZnO22^- + 2H_2O\ ZnO + 2OH^- \quad (4)$$

C. Characterization of Nanoparticles

Nanoparticles produced were characterised with a UV– Vis spectrometer (Analytic Jena, SPECORD 250, dual beam) in order to measure the absorption spectra of the colloidal nanoparticles. A Scanning electron micro- scope (SEM) was used to examine the morphology and size distribution of the nanoparticles. X-ray diffraction (XRD) (BrukerD8- Discover, step size [02θ] = 0.0200) was also be used during investigation of the crystalline structures of the nanoparticles [9].

D. Application of the Synthesized NPS in Waste Water Treatment

1) Preparation of Simulated Industrial Wastewater

1000ppm standard solution of copper and lead was prepared by dissolving appropriate quantities (1.0g) of their respective

salts in distilled water. The simulated waste water are prepared by using measured amount of standard solutions. The concentration of both Cu and Pb are 20ppm respectively [10].

2) Adsorption Studies

A series of batch experiments were carried to determine the adsorption isotherms of copper and lead on the adsorbents. Adsorption experiment was conducted by measuring 25mL of the wastewater sample and poured into a 100ml conical flask. 0.1g, 0.2g and 0.4g of the synthesized metal oxide nanoparticles are added to different conical flask containing 25ml of wastewater. The conical flask containing the adsorbent and the wastewater is placed on a rotary shaker and shook at 120 rpm at a room temperature for a period of 150min to ensure equilibrium. The suspension was filtered using 0.5 micron filter paper. The concentrations of the different metal ions present in the filtrate are to be analyzed using Atomic adsorption spectrophotometer (AAS).

3) Adsorption Isotherms

A series of batch experiments was carried out to determine the adsorption isotherms of copper and lead ions on the adsorbents [11]. The amount of metal ion adsorbed (Qe) was determined using a mass balance equation.

$$Q_e = \frac{(Ci - Cf) \times V}{M}$$

Where, Q is the metal uptake (mg g-1), Ci and Cf are the initial and final metal equilibrium concentration in the effluent sample (mg g-1), respectively, M is the mass of the adsorbent (g) and V is the volume of the effluent sample.

3. Results and Discussion

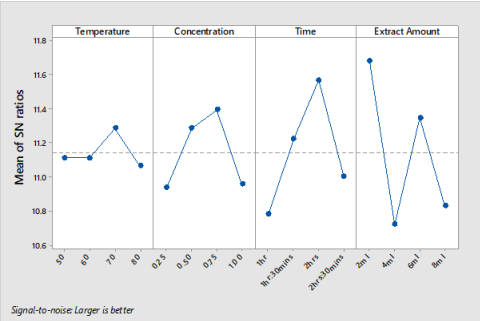

Fig. 1. Plot of mean effects for Signal to Noise Ratio

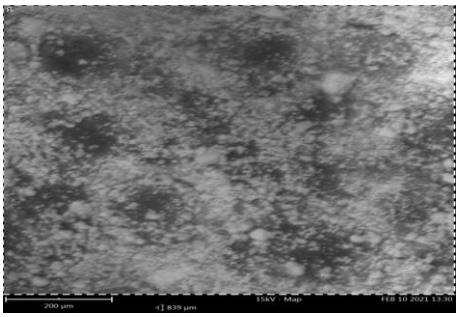

Fig. 2. SEM Image of the synthesised ZnO Nanoparticle before Optimisation at 50^{O}C, 2.5M, 1 hr and 2 ml

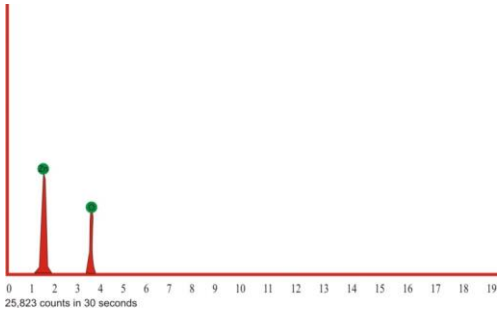

Fig. 3. EDX Patterns of ZnO Nanoparticle before Optimisation at 50 ^{O}C, 2.5M, 1 hr and 2 ml

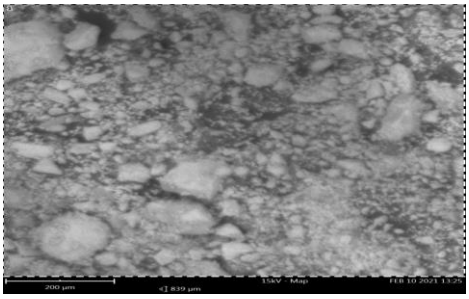

Fig. 4. SEM Image of the synthesised ZnO Nanoparticle after Optimisation 80 ^{O}C, 1.0M, 1 hr and 6 ml

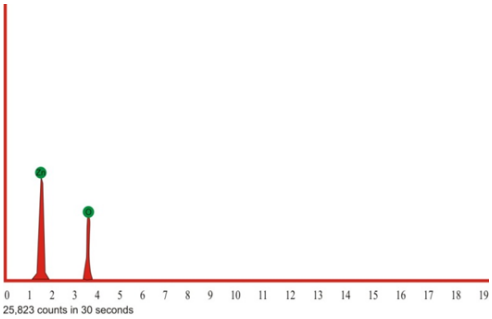

Fig. 5. EDX Patterns of ZnO Nanoparticle after Optimisation 80 ^{O}C, 1.0M, 1 hr and 6 ml

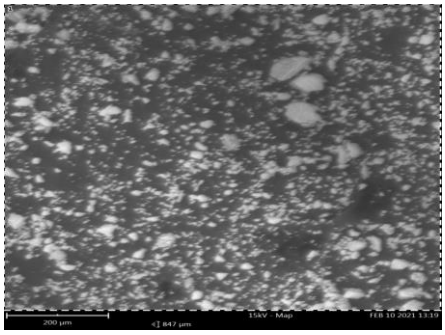

Fig. 6. SEM Image of the synthesised ZnO Nanoparticle at Optimal Parameters 70 ^{O}C, 0.75M, 2 hrs and 2 ml

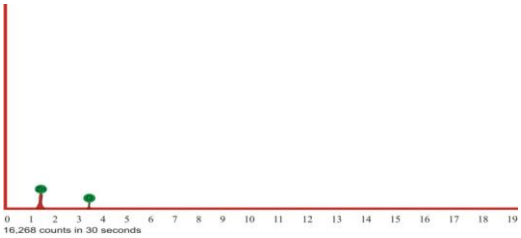

Fig. 7. EDX Patterns of ZnO Nanoparticle at Optimal Parameters 70 ^{O}C, 0.75M, 2 hrs and 2 ml.

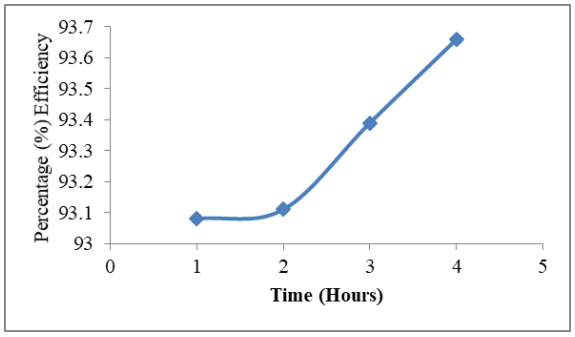

Fig. 8. Absorption Capacity of Copper against Time

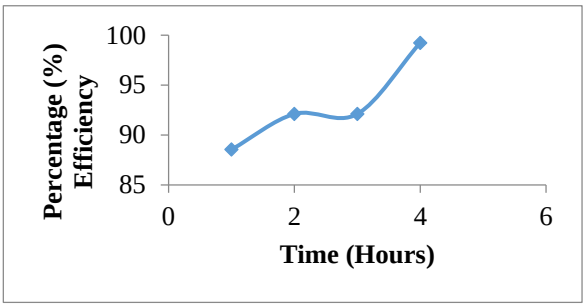

Fig. 9. Absorption Capacity of Lead against Time

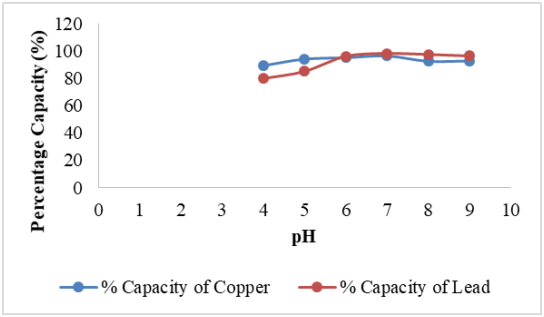

Fig. 10. Absorption Capacity of Copper and Lead against pH

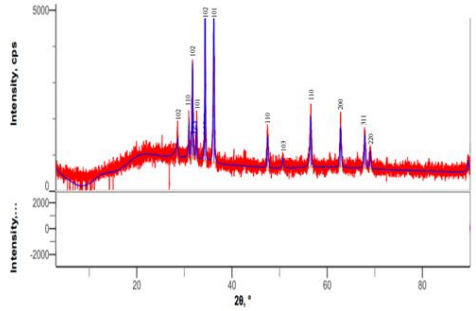

Fig. 11. XRD Spectrum of the Synthesised ZnO Nanoparticle

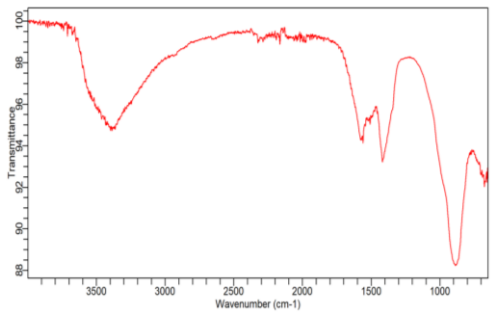

Fig. 12. FTIR Spectrum of the Synthesised ZnO Nanoparticle

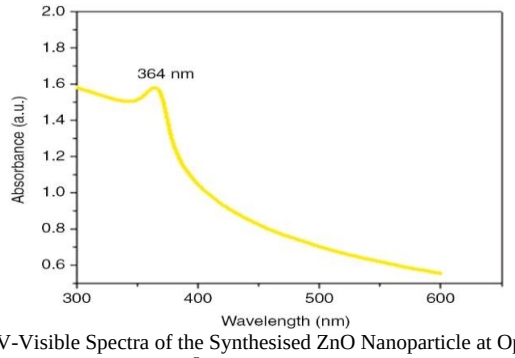

Fig. 13. UV-Visible Spectra of the Synthesised ZnO Nanoparticle at Optimum Conditions 70 ^{O}C, 0.75M, 2 hrs and 2 ml.

The optimization plot aimed at predicting the optimal processes conditions (temperature, concentration, time, and extract amount) at which the optimum conditions for the synthesis of zinc oxide nanoparticles can be attained. The optimal processes conditions as shown in figure 1 was discovered to be temperature at 700C, concentration at 0.75M, time at 2hr and extract amount at 2ml. For the temperature; it was observed that when the temperature is at 500C, few number of ZnO NPs were formed which is as a result of few number of effective collisions that occur between the reacting molecule. As the temperature is increased, the number of ZnO NPs also increased up to when the temperature is at 700C after which the ZnO NPs formed become aggloremated which is as a result of too much collision between the reacting molecules. Thus, 70oC is considered to be the best temperature for the synthesis of ZnO NPs. For the concentration; it was observed that when the concentration is at 0.25M, few number of ZnO NPs were formed which is as a result of few number of effective collisions that occur between the reacting molecule. As the concentration is increased, the number of ZnO NPs also increased up to when the concentration is at 0.75M. The formation of ZnO NPs become crowded which is as a result of too much collision between the reacting molecules. Thus, 0.75M is considered to be the best concentration for the synthesis of ZnO NPs. For the time; it was observed that when the time is at 1hr, few number of ZnO NPs were formed which is as a result of few number of effective collisions that occur between the reacting molecules. As the time increases from 1hr-2hr, the formation of ZnO NPs become aggloremated which is as a result of too much collision between the reacting molecules. Thus, 2hr is considered to be the best time for the synthesis of ZnO NPs. For the amount of extract; it was observed that when 2ml of the plant extract is used as a reducing agent, ZnO NPs of evenly distribution and size were formed which indicates that the plant extracts added is enough to reduce Zn+ to Zn atoms. But as the amount extract added increased above 2ml, the resulting ZnO NPs becomes aggloremated with poor distributions which is attributed to too much plant extract for the reduction of Zn+ to Zn atoms.

4. Discussion

1) Green Synthesis of Zinc Oxide Nanoparticles

In this research work, zinc oxide nanoparticles were prepared by a green synthesis method in which plan extracts of Baobab (Adansonia digitata) leaves are used as reducing agents and

stabilizing agents.

2) Characterization of Zinc Oxide Nanoparticles

The knowledge of the physic chemical properties of Zinc oxide nanoparticles is important as it greatly helps in evaluations their behavior, efficacy, safety, and potential applications. Therefore, characterization of Zinc oxide nanoparticles is conducted in order to assess the functional aspects of the synthesized particles. In this research work, the prepared ZnO NPs were characterized with UV-vis spectroscopy, X-ray diffraction, fourier transform infrared spectroscopy, and scanning electron microscopy.

3) Analysis of experimental data

Experimental data were analyzed using S/N ratio and ANOVA based on the results of the S/N ration and ANOVA, optimal parameter settings for better accuracy are obtained and verified experimentally. Regression models are developed to obtain the compensation factor for any set of process parameter.

4) Analysis using S/N ratio

In the Taguchi method, S/N ratio is a measure of quality characteristics and deviation from the desired value. The term 'signal' represents the desirable value (mean) and 'noise' represents the undesirable value (standard deviation from mean) for the output characteristics [12]. The S/N ratio (A) is defined at

$$N = - 10 \text{ Log } (MSD),$$

Where MSD is the mean-square deviation for the output characteristics. In the present study, Lio (4Λ4) orthogonal array [12] with 4 column and 16 rows was used which is presented in Table 2. In addition, S/N ratio was calculated for each experiment. The data generated are analyzed for identifying the optimum level of parameters. The average S/N ratio of each control factor at each level and the range of S/N ratio of each level (Δ = Delta = S/N min) are determined. Table 2 shows the main effects of the factors on the ZnO nanoparticle. The model F-value of 9.68 shows that the model is significant. Values of Prob > F less than 0.0500 indicate that the model term are significant. Therefore, Δ (Extract amount) is the only significant model terms and R.

5) Scanning Electron Microscope

The SEM images show agglomerations of individual zinc oxide nanoparticle. In Figure 2 which is before optimization; there is agglomerations of several nanoparticles which aggregates but the distribution is not evenly distributed because of the amount of ZnO nanoparticles needed to form a complete reaction is not sufficient along with the plant extract but as the increases, the concentration of the distribution increases. For the Figure 6 which is at the optimal as the increase in the concentration, the distribution increases i.e. the amount of the plant extract and the amount of the precursor are equal. Therefore, there is a formation of complete reactions that gives the ZnO nanoparticles of evenly distribution. Finally for Figure 4 which is after optimization; with the increase in the concentration of the precursor which is higher enough than the concentration of the plant extract i.e. causes the agglomeration of the formed nanoparticles leading it not to have an evenly distribution because the concentration is too much for the reaction which is not conformity to form a reaction. The morphologies of ZnO nanoparticles changes with different form of optimization. The size and morphology are compared to previously reported ZnO nanoparticles synthesized by Aloe Vera extract which is 40nm [13].

6) EDX of Zinc Oxide Nanoparticles

From Figure 3, 5 and7 the EDX data was composed of two element which are Zinc (Zn) and Oxygen (O) from both results of EDX it has confirmed that the ZnO nanoparticles has high purity similar finding was also found in previous studies by Brintha and Ajitha [14] that obtained the mass percentage of Zn and O were 73.9% and 26.1% respectively [15] has stated that the theoretical expected mass percent of Zn and O were 80.3% and 19.7%. Thus, the EDX result revealed that the synthesized ZnO nanoparticles were of high purity, which contain high Zn and O element composition. The % of Zn and O in this research were; for the before optimization, the % of Zn and O were 98.89% and 2.11%. For the optimal conditions, the % were 79.91% and 21.9% and finally for after optimization the % were found at 97.49% and 3.51%.

7) FTIR Spectrum of Zinc Oxide Nanoparticles

The FTIR spectra of ZnO nanoparticles observed a peak at the frequency of 1600cm-1 which indicates the NH bending and weal peaks were found at 1508 cm-1. A peak at 1641 cm-1 assigned to symmetric and asymmetric vibration of C=O and a broad peak around 3400 cm-1 showed the OH stretching bond vibration which was due to the water absorption on the surface of zinc oxide nanoparticles while the peak at 440cm-1 was attributed to the Zn-O stretch. And finally the band width of 1500-650 cm-1 exhibited the finger spring region of Zinc oxide nanoparticles. The metal oxygen frequencies observed for the respective metal oxide is in accordance with literature values. In a study by [16] on the synthesis of zinc oxide nanoparticles using plant leaf extract, they found out that broad peak obtained at 3321.42 corresponded to OH stretching vibrations, peak in the range of 1541.12 and 1429.25 corresponded to C=C stretch. These frequencies were higher than those obtained in this research.

8) X-Ray Diffraction of Zinc Oxide Nanoparticles

Figure 11 shows XRD diffraction pattern of ZnO nanoparticles. It is found that there exist strong diffraction peak with 20 values of 27.00, 32.500, 34.600, 38.550, 47.700, 50.800, 56.00, 62.500, 66.650, and 68.00 corresponding to the crystal planes of 102, 110, 102, 101, 102, 101, 110, 103, 110, 200, 311 and 320 respectively. All diffraction peaks of sample correspond to the characteristics hexagonal wurtzite structure of ZnO nanoparticles. All these characteristics peaks are of higher in intensity and indicated that the products obtained are pure and in good crystalline nature. No peaks corresponding to impurities were detected.

9) UV-VIS Spectroscopy

The absorption spectrum for synthesized ZnO NPs was shown in Figure 12. The absorption peak was observed at 364nm, which attribute to the intrinsic band gap of ZnO absorption, similar results of absorption band that represent ZnO NPs was also obtained from previous research in which the range of absorption band were from 355 to 380mm [17, 18, and 19]. These supporting data confirm the presence of ZnO

NPs as the absorption band obtained are similar [15] also obtained similar findings which deduced that the obtained peak showed a better UV absorption for ZnO NPs. Furthermore, the absorption peak of ZnO NPs also confirmed the properties of ZnO, NPs, which is known for UV protections in sunscreens products [20].

10) Absorption Studies

B. Influence of Contact Time

Contact time is one of the important parameters for successful bio sorption application. The effect of contact time for copper (Cu) is presented in Fig. 8. This is the removal of Cu from water sample as a function of time. The adsorption rate was rapid within the first hour and sharply increased from the second hour to the fourth hour. From the results, the absorption increases with increase in time. The effect of contact time for Lead (Pb) is presented in Fig. 9. This is the removal of Pb from water sample as a function of time. The adsorption rate was rapid within the first hour and gradually increased in the second hour and sharply increased in the third hour. The result showed that the absorption rate increases with increase in time, and sharply increases at 4hours. The findings of this study is similar to that of [21], which showed that the amount adsorbed increases with increase in the contact time till equilibrium was attained.

C. Influence of Adsorbent Dose

The amount of the adsorbent is an important parameter because it determines the adsorption capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dose has been studied with various amounts of sorbent (0.1 to 0.6), while keeping all the other parameters constant at their optimum values (pH and contact time). From the results, the removal percentage for both the Cu and Pb increases with increasing higher dosages. This attributed to the increased adsorbent surface area and more available adsorption sites or functional groups because of the increase in the increase in adsorbent quantity. The results of this study is in line with findings by [21], which showed that the removal efficiency increased with increasing adsorbent dose, after which it became almost constant.

D. Influence of pH

The pH values plays a very important role in the adsorption of copper and lead ions on ZnO NPs. It is a commonly known fact that anions are favorably adsorbed by the adsorbent at lower pH values due to presence of H+ ions and cations are adsorbed at high pH values due to negatively charged ions. The effect of pH on the adsorption of Cu and Pb ions was studied in the pH range 2-7 (higher pH could not be studied as precipitation of metal ions occur) and the results are shown in Fig. 10. It was observed that the adsorption of metal ions increased with increase in the solution of pH. The result of this study is also in line with findings by [21], which showed that the adsorption of metal ions increased with increase of pH of the solution due to increasing electrostatic force of attraction between positively charged sorbate and negatively charged sorbent.

5. Conclusion

EDX showed that the synthesized ZnO NPs contained Zn and O while SEM showed the morphology. FTIR showed the presence of functional groups. It is evident that the absorption of Cu and Pb ions are time dependent. The absorption peak of ZnO NPs confirmed the properties of ZnO, NPs, which is known for UV protections in sunscreens products. The synthesized nanoparticles have greater potential for absorption of heavy metal ions present in water sample. These nanoparticles can be effectively used as absorbents in the commercial scale to achieve the desired goal of a clean environment.

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