

SYNTHESIS AND CHARACTERIZATION OF ZnO NANOPARTICLES AND THEIR USE AS AN ADSORBENT FOR THE ARSENIC REMOVAL FROM DRINKING WATER

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ZnO nanoparticles were synthesized by using precipitation method. The crystalline phase of the material was characterized by using FTIR, thermo gravimetric analyzer (TGA), scanning electron microscopy (SEM) and x-ray diffraction (XRD) techniques. Samples containing trace amount of arsenic were collected from different localities of Lahore city. Arsenic concentration was determined in samples through HG-AAS method. The arsenic removal capacity of ZnO nanoparticles were tested by varying different parameters like adsorbent dose, pH of the solution, contact time and temperature. It was concluded that the synthesized ZnO NPs (nanoparticles) can be suitably used for removal of arsenic from drinking water.

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1. Introduction

In this modern era synthesis of metal nanoparticles with varying properties attracted the attention of researchers. These materials are synthesized by various methods, namely chemical vapor condensation method, laser pyrolysis in the vapor phase, microemulsion, hydrothermal, sol-gel, precipitation method, and microbial processes taking place in the liquid phase, and ball milling carried out in the solid phase[1-3]. Properties of synthesized materials are mainly dependent on their synthetic procedure. Zinc oxide is a unique semiconducting material and lot of other interesting applications. It plays an important in designing ceramic tires. Its broad band width and vitality linkage at room temperature leads to zinc oxide being used as part of electronic photography[4] and electronic gear[5], in gadgets producing a surface acoustic wave[6], production range[7], sensors[8], as well as UV laser[9], and sunlight based cells[10]. Water pollution caused by release of heavy metals through both industrial and urban sources is now a global problem[11-16]. Arsenic is widely distributed in the earth crust with an approximate abundance of 2 mg per kg. Arsenic may present in drinking water due to contact with arsenic rich sediment. If drinking water contains arsenic even at low concentration and used for a long period can cause adverse effects on human health. Recommended level of arsenic in drinking water is less than 10-50 $\mu\text{g}/\text{dm}^3$ (10-50 ppb)[17]. Arsenic exposure in drinking water may cause abdominal pain, diarrhoea, heart disease, skin disease and cancer[18]. There are many commercially available arsenic remover methods, which are used for the treatment of drinking water. These methods include activated charcoal (AC) and zirconium coated activated carbon, ion exchange resins, iron

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oxide (III), activated alumina, sand and zero valent iron are used for expulsion of arsenic from drinking water to make consumable for other domestic utilities[19].

Lahore city is the capital of Punjab and many patients were reported last year who badly affected by arsenic concentration in drinking water. Adsorption is widely popular technique to remove heavy metals due to its low cost, efficiency, and simplicity[20]. In this research project, synthesized ZnO nanoparticles were utilized to evacuate metallic arsenic from drinking water by adsorption methodology.

2. Materials and methods

Reagents and solvents used in this study were of analytical grade and used without any purification. Scientific Electro thermal melting point apparatus (1401Q) was used to determine the melting point. Synthesized material was calcined by using Nabertherm Muffle furnace LT 5/12 (Germany). In order to study Zn-O stretching frequency, Nicolet 6700P Infrared Spectrometer (USA) was used. The structural parameters of nanoparticles were calculated by using PANalytical (X'Pert PRO) diffractometer (using Cu-K α radiation). Thermal analysis was done on TGA/DSC (Q600) purging nitrogen gas using alumina crucible. Surface morphology of the sample was studied by using S3700N (HITACHI), Japan scanning electron microscope. Atomic absorption measurements were done on AAS-vario 6, Germany.

2.1. Synthesis of Zinc Oxide nanoparticles

ZnO nanoparticles were synthesized by following precipitation method which was reported by Hamid Reza Ghorbani et.al[21]. In this work 0.2 M zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution was prepared by dissolving 2.94 g of compound in 50 mL distilled water. A 0.4 M solution of KOH was prepared in a separate beaker by dissolving 1.12 g of KOH in 50 ml distilled water. KOH solution was slowly added to zinc nitrate solution with continuous stirring at room temperature. The solution stirred for 30 min on hot plate, which brought about the development of white suspension. The product was centrifuged at 5000 rpm for 20 min and washed three times with distilled water. At the end product was washed with absolute alcohol. Finally, the product was calcined in a muffle furnace for 3 hrs at 500°C in the limited supply of air.

2.2. Preparation of arsenic oxide standards

In order to make arsenic standard, dissolve 0.33 g As_2O_3 in 5 mL of 2 M NaOH solution and dilute it upto 250 mL with distilled water. In order to prepare 10-ppm solution, dilute 1 mL volume of this solution to 100 mL volume with distilled water. Similarly, to make 1-ppm solution, 1 volume of this arsenic solution (10 ppm) was further diluted up to 10 volumes. In this way arsenic standards of different concentrations were prepared through dilution method.

2.3. Hydride generation method to determine arsenic concentration in different samples

In order to determine arsenic concentration in water samples, AAS-vario 6, Germany, equipped with hydride generation and hollow cathode lamp was operated at 10 mA current. The optimum conditions used to determine arsenic by HG-AAS are given in Table 1.

Table 1. Operating conditions for HG-AAS to determine arsenic in water samples.

Sr.No	Parameters	Description
1	Resonance wavelength	193.7
2	Current (nm)	10
3	Current (mA)	5
4	Sample volume (mL)	20
5	Analysis time (s)	Peak area
6	Measurement mode (%)	3
7	HCl carrier solution (%)	1
8	NaBH ₄ reducing solution	
	Argon Flow rate (ml/min)	200

3. Results and discussions

3.1. FTIR analysis

The IR spectrum of ZnO nanoparticles is shown in Figure 1. Since water is absorbed on metal surface in nanoparticles that's why two characteristic absorption peaks which were recorded at 3406.30 and 1045.595 cm^{-1} might be due to $-\text{OH}$ stretching and twisting frequencies respectively. Literature proved that M-O stretching and twisting vibrations were seen beneath 1000 cm^{-1} so IR spectrum bellows this range of our interest. The crest at 691.48 cm^{-1} is attributed to the Zn-O twisting frequency [22, 23] which is a decent proof of development of Zn-O linkage. It is reported that IR stretching frequency of Zn-O are laying in the range of 453-430 cm^{-1} [24] which is out of the range of this IR spectrum.

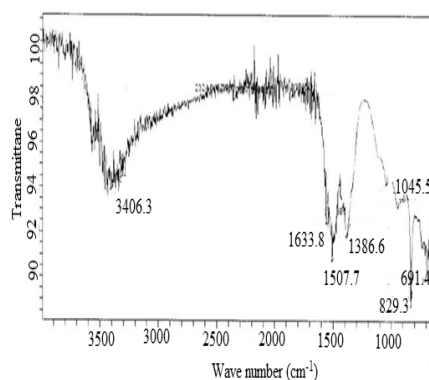


Fig. 1. FTIR scan for ZnO nanoparticles.

3.2. Powder XRD Analysis

Powdered XRD diffractogram of ZnO nanoparticles was obtained on X-ray powder diffractometer and studied through X'Pert High Score Plus software to search phases of nanoparticles, d-spacing and grain size. The various scan parameters and conditions included; 45 kV/40 mA X-ray, $2\theta^{\circ}$ scanning mode, fixed monochromator and with a range from $2\theta^{\circ} = 10$ to 90 with a step of 0.03 degree for a period of 30 min is shown in Fig.2. The seven major peaks were selected in diffractogram to calculate their miller indices as shown in Table 1.

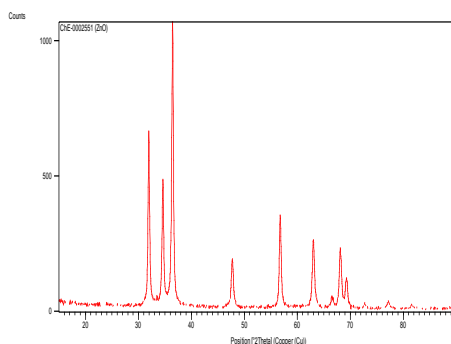


Fig. 2. XRD pattern of ZnO nanoparticles.

Table 2. Calculation of miller indices.

$2\theta/\theta$	θ/θ	$\text{Sin}^2\theta$	$1 \times \frac{\text{Sin}^2 \theta}{\text{Sin}^2 \theta_{\min}}$	$2 \times \frac{\text{Sin}^2 \theta}{\text{Sin}^2 \theta_{\min}}$	$3 \times \frac{\text{Sin}^2 \theta}{\text{Sin}^2 \theta_{\min}}$	Whole integers	hkl
31.9571	15.9786	0.0758	1	2	3	3	111
36.4501	18.2251	0.0978	1.2902	2.5804	3.8706	4	200
56.7233	28.3617	0.2257	2.9776	5.9552	8.9328	9	221
62.9795	31.4898	0.2728	3.5989	7.1978	10.7967	11	311
71.5990	35.7995	0.3422	4.5141	9.0282	13.5422	14	321
81.0012	40.5006	0.4218	5.565	11.13	16.69	17	322

The miller indices have been calculated from selected peaks as shown in the above table. The calculated pattern of ZnO nanoparticles was compared with reported patterns (present in the library) by peak search method and showed great resemblance. All the major peaks at positions $2\theta/\theta$ 31.9571, 36.4501, 56.7233, 62.9795, 71.5990, 81.0012 have miller indices 111, 200, 221, 311, 321, 322 respectively which are the characteristics of ZnO scan pattern.

Table 3. Calculation of material parameters with the help of $2\theta/\theta$ value.

$2\theta/\theta$	FWHM [$^{\circ}2\theta$.]	Intensity counts	d-spacing [\AA]	Grain size (D) (nm)
31.9571	0.2303	63.77	2.80058	6.2623
36.4501	0.2558	100.00	2.46503	5.7069
56.7233	0.1791	32.48	1.62290	8.7978
62.9795	0.1279	24.93	1.45791	12.7089
71.599	0.1791	22.00	1.37697	9.3433
81.0012	0.4605	10.40	1.35693	3.6594

It is obvious from above table that the grain size of nanoparticles was found to be in the range of 12.7089 nm at $2\theta/\theta = 62.9795$ to 3.6594 nm at $2\theta/\theta = 81.0012$

3.3. Thermogravimetric analyses (TTGA)

The decomposition pattern obtained after TGA/DSC analysis is given bellow in Fig. 3.

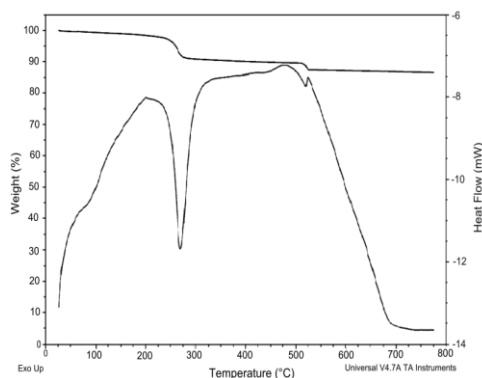


Fig. 3. TGA/DSC decomposition pattern of ZnO nanoparticles.

TGA curve showed 1st weight loss from 50°C to around 230°C which may be due to dehydration of surface adsorbed water. The 2nd weight loss was noticed from 300°C to 540°C which may be due to deterioration of Zn(OH)₂ and Zn(CO₃)₂ [25]. After 600°C onwards, there is no further weight loss by increasing temperature which indicates the complete conversion of precursor into ZnO NPs.

3.4. SEM analysis

Surface morphology of ZnO NPs was examined by SEM and the micrographs recorded at various magnifications are given below.

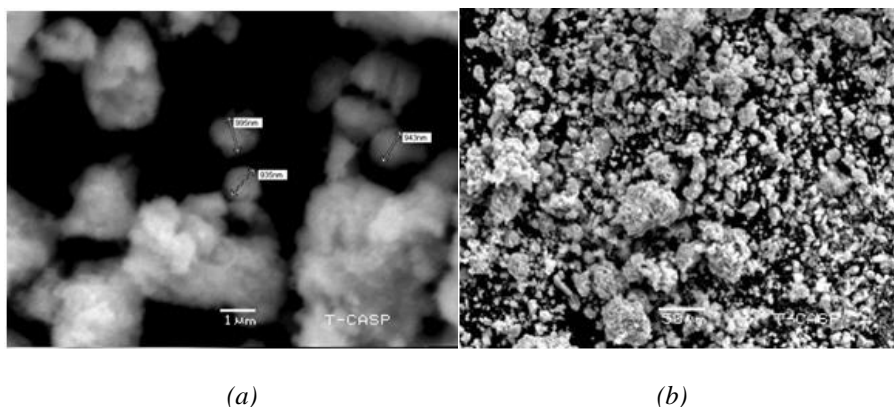


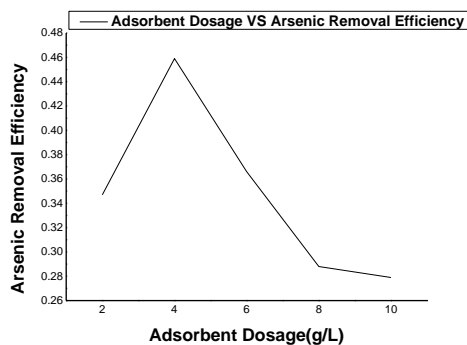
Fig. 4. (a) and (b) showed flower like morphology of ZnO NPs which showed great agreement with SEM data available in the literature. Since this morphology was observed throughout the sample so it is a good evidence of homogeneous nature of ZnO NPs.

3.5. Removal of arsenic ions through ZnO NPs

ZnO NPs were employed to remove arsenic ions from different water samples. In order to find out the optimum conditions for arsenic removal, ZnO NPs were tested by varying parameters. Arsenic removal from water samples was studied by varying adsorbent dose, pH of the solution, contact time and temperature.

3.5.1. Effect of adsorbent dosage

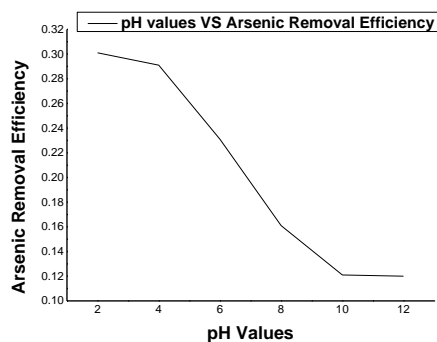
The effect of adsorbent dose on removal of arsenic ions was studied by varying its concentration in g/l at room temperature for 60 min contact time. As expected, the removal of arsenic were increased by increasing adsorbent dosage from 2 g/l to 4 g/l but then decreases onward as shown in graph 1. It can be seen that by providing dosage 6 g/l to onward, there is a continuous decrease in adsorption ratio of Arsenic ions. This decrease may be due to the saturation of available binding sites on synthesized NPs.



Graph 1. Adsorbent dosage vs arsenic removal efficiency.

3.5.2. Effect of pH

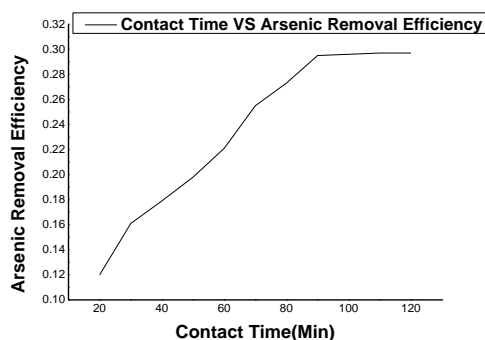
The effect of pH on removal of arsenic ions at different pH (1-12) was studied at room temperature for 60 min contact time. In this study sample solution must be neutral i.e pH=7. Greatest evacuation of arsenic ions was noticed at pH<5 as shown in graph 2. Essentially in aqueous media arsenic oxide produce oxy anions at high pH value. Moreover hydroxyl ions are in abundance on surface of synthesized NPs, that's why arsenic removal efficiency was found to be good in acidic media than in basic media.



Graph 2. pH values vs arsenic removal efficiency.

3.5.3. Effect of contact time

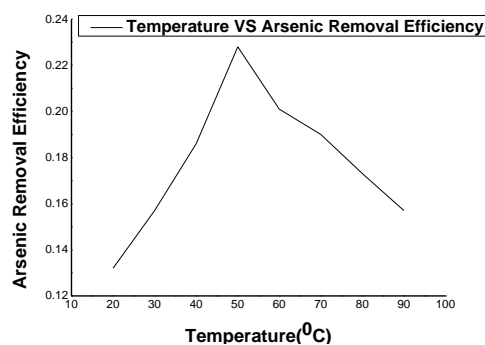
The effect of contact time on arsenic removal was examined in the range of 10 min to 120 min at room temperature while adsorbent concentration was kept constant. This whole process was studied in acidic media. A constant increase in arsenic removal was achieved from 10-90 min but after 90 min there was no considerable arsenic removal as shown in graph 3. Initially arsenic rate of removal was higher, which may be due to the availability of vacant sites on adsorbent and later on the decrease in arsenic removal may be due to the saturation of available sites on synthesized NPs.



Graph 3. Contact time vs arsenic removal efficiency.

3.5.4. Effect of temperature

The effect of temperature on arsenic removal was investigated from 20^oC to 90^oC by keeping adsorbent at constant concentration in acidic media. In experimental observations, the percentage uptake of arsenic by adsorbing material increases from 20^oC to 50^oC and then decreases upto 90^oC as shown in graph 4. At higher temperature desorption of arsenic from adsorbing material may take place which caused the decrease in arsenic removal efficiency.



Graph 4. Temperature vs arsenic removal efficiency.

4. Conclusion

In this study a ZnO NPs were synthesized and tested to remove arsenic ions from drinking water as an adsorbent. Different techniques including FTIR, powder XRD, TGA and SEM were utilized to study the properties of NPs and confirmed their preparation. Synthesized NPs were utilized to remove arsenic ions from drinking water by changing different parameters i.e. adsorbent dose, pH of the solution, contact time and temperature. Best arsenic removal from drinking water was found by using adsorbent dose at 4g/l, pH of the solution <5, contact time of 90 min and at temperature of 50^oC. From above study it is concluded that the synthesized ZnO NPs material can be suitably used for removal of arsenic from drinking water.

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