

## Adsorption of arsenic (III) by a novel adsorbent prepared from *Ocimum sanctum*

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**Abstract**— An economic novel alternative choice for chemical and physical methods for nanoparticles synthesis is green method. Green nano zinc adsorbent (ZnO-NPs-AS-*O*s) embedded with activated silica is synthesized from the aqueous leaf extract of *Ocimum sanctum* using Zinc acetate dihydrate and sodium hydroxide. The phytoconstituents present in the leaf extract is responsible for the formation, capping and stabilization of adsorbent (ZnO-NPs-AS-*O*s). The adsorbent is characterized by SEM for its morphology, XRD for its crystallinity, EDAX for its elemental constitution and FT- IR for phytocostituents present. The results confirmed the formed nano needle shaped adsorbent of 200nm is effective in removing As(III) ions from aqueous solution.

**Keywords**- Nanoparticles; Phytoconstituents; Adsorbent; Green Chemistry; Active site

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### I. INTRODUCTION

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. It is present in the wastewater of several industries, such as metal cleaning, plating baths, refineries, paper, pulp, fertilizer and wood preservatives [1]. The excessive intake of heavy metals by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney Effective methods for heavy metal removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery and adsorption. The application of such processes is often limited because of technical or economic constraints. Biosorption is a proven technology for the removal of heavy metal ions from synthetic and real industrial effluents. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption means. In recent years, considerable attention has been focused on the removal of heavy metals from water using adsorbents derived from low-cost materials. Several adsorbents, such as chitosan, polymeric adsorbent, apricot stones and granular ferric hydroxide have been used for the treatment of Arsenic (III) are represented in Table 1. Green nanotechnology has goals to produce nanomaterials and products without harming the environment or human health and producing nano-products that provide solutions to environmental problems. It uses existing principles of green chemistry and green engineering to make nanomaterials and nano-products without toxic ingredients at low temperatures using less energy and renewable inputs. In the present investigation Zinc Oxide nanoparticle (ZnO-NPs) synthesized from *Ocimum sanctum* (*O*s) entrenched on Activated Silica (AS) have been used as adsorbents for the removal of Arsenic (III) ions. The aim of the present work is to explore the possibility of utilizing ZnO-NPs-AS-*O*s for the

adsorptive removal of Arsenic (III) ions from aqueous solution. The effect of factors such as Concentration, Adsorbent dose, Contact time, pH and Agitation speed was investigated. The kinetics of Arsenic (III) adsorption on adsorbent was analysed by two kinetic models. Experimental equilibrium data were fitted to the Langmuir, Freundlich and Tempkin isotherm equations to determine the best-fit isotherm equation.

TABLE I. VARIOUS HYBRID MATERIALS/COMPOSITES AND THEIR ARSENIC REMOVAL

Different hybrid materials	Adsorption capacity /density /percentage	Ions removed	Methods used	Isotherm supported	Ref
Fe(III)/La(III)-chitosan	109 mg/g	As(III) and As(V)	Adsorption	----	[2]
Hybrid (polymeric /inorganic), fibrous sorbent, (FIBAN-As)	75.67 mg/g 81.66 mg/g	As(III) and As(V)	Adsorption	Langmuir	[3]
Fe(II) loaded and Fe(III) loaded apricot, stone-based ACs	2.023 mg/g, 3.009 mg/g	As(III) and As(V)	Adsorption	Freundlich and Dubinin–Radushkevich	[4]
GFH(granular ferric hydroxide)	68 mg/g	As(III)	Adsorption	Freundlich	[5]
Zinc Oxide nanoparticle entrenched on activated silica (ZnO-NPs-AS- <i>O</i> s)	98.31 %	As(III)	Adsorption	Langmuir Freundlich Tempkin BET	Current material

II. MATERIALS AND METHODS

A. Plant collection and extraction

Leaves of *Ocimum sanctum* from its natural habitat were collected in the month of May 2013 in Dindigul district, Tamil Nadu. Dr. D. Sarala Thambavani authenticated the taxonomic identification of the plants. Collected leaves free from disease are washed with double distilled water is ground fine and filtered. The filtered supernatant is used for analysis.

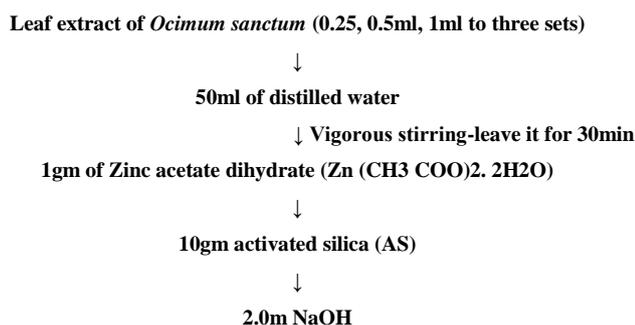
B. Phytochemical Screening

Qualitative phytochemical examination of the aqueous leaf extract of *Ocimum sanctum* was carried out using standard methods of [6], [7]. The presence (+) and absence (-) of phytochemical constituents are listed in Table. 2.

TABLE II. QUALITATIVE PHYTOCHEMICAL ANALYSIS OF AQUEOUS LEAF EXTRACT OF *OCIMUM SANCTUM*

Phytoconstituents in aqueous solutions	Reagents	<i>Ocimum sanctum</i>	Morphology of <i>Ocimum Sanctum</i> leaves
Alkaloid	Mayer's	+	
	Wagner's	+	
Carbohydrate	Molisch's	+	
	Benedict's	+	
Glycoside	Legal's	+	
	Borntrager's	+	
Steroid	Liebermann Burchard	+	
Fixed oil	Spot test	-	
Saponin	Gelatin	-	
	Lead acetate	-	
Tannin	Ferric chloride	+	
	Wagner's	+	
Protein	Xanthoprotein	+	
	Biuret	+	
Flavonoid	Alkaline Reagent	+	
	Shinoda's	+	

C. Schematic representation of green adsorbent synthesis (*ZnO-NPS-AS-Os*)



Stirr – 2hrs ↓ white aq soln at pH12  
 Washed with distilled water followed by ethanol  
 ↓ Δ 60°C  
**ZnO-NPs-AS-Os**

D. Batch Sorption Experiment

TABLE III. EXPERIMENTAL DETAILS OF ADSORBENT

Effect of the System	Concentration (N)	Adsorption dosage (g)	Contact time (min)	pH	Agitation speed (rpm)
Concentration (N)	0.005, 0.0075, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.0, 0.10	1 to 8	10 to 120	1 to 8	50 to 500
Adsorbent dosage (g)	0.005 to 0.10	1, 2, 3, 4, 5, 6, 7, 8	10 to 120	1 to 8	50 to 500
Contact time (min)	0.005 to 0.10	1 to 8	10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120	1 to 8	50 to 500
pH	0.005 to 0.10	1 to 8	10 to 120	1, 2, 3, 4, 5, 6, 7, 8	50 to 500
Agitation speed (rpm)	0.005 to 0.10	1 to 8	10 to 120	1 to 8	50, 100, 150, 200, 250, 300, 350, 400, 450, 500

The experiments were carried out as shown in Table. 3. The effect of parameters such as As(III) metal concentration, adsorbent dosage, contact time, pH and agitation speed was studied by changing one parameter progressively, keeping the others constant as shown in Table. 3. The quantity of As (III) adsorbed by *ZnO-NPs-AS-Os* was calculated using the following equation (1) and (2)

$$\% \text{ Removal} = (C_0 - C_e) \times 100 / C_0 \text{ ----- (1)}$$

$$q_e = (C_0 - C_e) \times V / W \text{ ----- (2)}$$

Where  $C_0$  and  $C_e$  are initial and equilibrium concentration of As (III) respectively (mg/L),  $q_e$  the amount of arsenic adsorbed at equilibrium (mg/g),  $V$  the volume of the solution (mL) and  $W$  the weight of the adsorbent used (g) [8], [9].

E. Adsorption isotherm

It is imperative to optimize the design of adsorption system. Equilibrium data commonly known as adsorption isotherm portrays the interaction of adsorbate with adsorbent and gives an inclusive understanding of the nature of interaction. The parameter obtained from different models provides important information on the surface properties of the adsorbent and its affinity. The four types of isotherms used are Freundlich, Langmuir, Temkin and Brunauer Emmet Teller (BET). The Freundlich linear expression is an empirical equation based on multilayer adsorption to a heterogeneous surface and is expressed as follows:

$$\log q_e = \log KF + 1/n \log C_e \text{ ----- (3)}$$

Langmuir isotherm applies to localized adsorption of monolayer surface coverage, assuming that each adsorbed molecule occupies one adsorption site. The Langmuir isotherm is expressed in the following formula:

$$C_e/q_e = (1/KL) + (aL/KL) C_e \text{ ----- (4)}$$

Temkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces. Temkin isotherm is expressed as follows:

$$q_e = B \ln A + B \ln C_e \text{ ----- (5)}$$

Specific surface area, pore volume and pore size of the sample were determined by means of N<sub>2</sub> adsorption-desorption at -195.629 C° using BET analysis. The physisorption and chemisorption is determined using Lagergren pseudo first order kinetics and Pseudo second order model equation as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{ ----- (6)}$$

$$t/q_t = (1/k_2 q_e^2) + (1/q_e) t \text{ ----- (7)}$$

### III. RESULTS AND DISCUSSION

#### A. Characterization of adsorbent (ZnO-NPs-AS-Os)

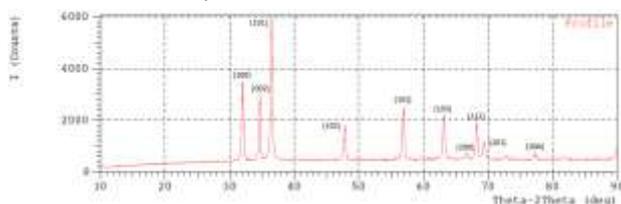


Figure 1. XRD spectra of ZnO-NPs-AS-Os

Fig. 1 shows predominant distinctive XRD peaks at about 32°, 34° and 36° which were in good accord with JCPDS CARD NO: 36-1451. The equivalent characteristic peak at (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) confirms that the synthesized adsorbent material is nanocrystalline nature of ZnO phase [10].

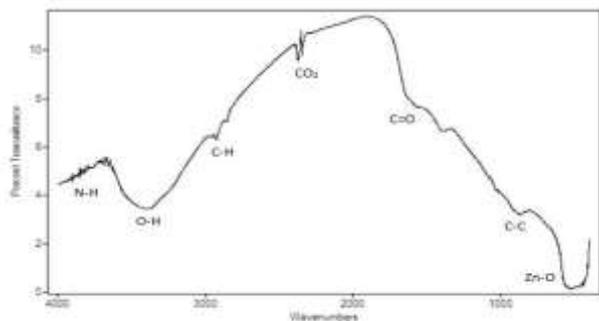


Figure 2. FT-IR Spectrum of Zinc ZnO-NPs-AS-Os

The broad absorption band at 3400-3300 cm<sup>-1</sup> is assigned to O-H stretching of H-bonded aliphatic alcohol. The absorption band at 2925 cm<sup>-1</sup> indicated the presence of C-H aliphatic asymmetric stretching of -CH<sub>3</sub>-CH<sub>2</sub>- and >CH<sub>2</sub> groups. The absorption band at 1720cm<sup>-1</sup> specify the presence of >C=O stretching of normal aliphatic ester. Medium absorption at 3534 cm<sup>-1</sup> corresponds to N-H bending of primary amine. The bands at 1444 and 1521 cm<sup>-1</sup> are related to C-C stretching of aromatic ring stretching. The band at 417-540 cm<sup>-1</sup> matches up Zn-O vibrational mode. The presence of functional groups of alcohols, esters and amines acts as a promoter, stabilizer and capping agent to form ZnO-NPs-AS-Os is further supported by FT-IR spectra as shown in Fig. 2.

The SEM (Fig. 3) observations denote that the particle size of the adsorbent (ZnO-NPs-AS-Os) is in the array of 200 nm at magnification X 55,000. The aggregation of the nanoparticle is

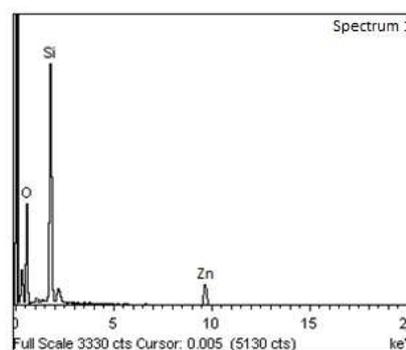
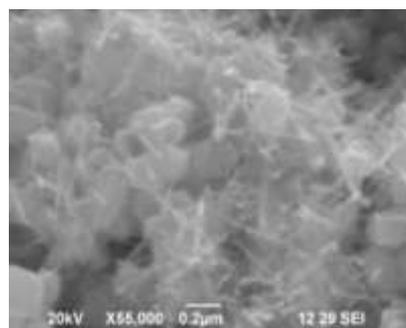


Figure 3. SEM and EDAX image of ZnO-NPs-AS-Os before adsorption of As(III)

visible, which confirms the surface of the adsorbent (ZnO-NPs-AS-Os) is jagged and not uniform which will give support to adsorption of As(III). The composition of elements is in reliable with EDAX with zinc, oxygen and silica elements before adsorption. The strong, intense and narrow peaks indicate that the resulted nanoparticles are highly free from impurity.

#### B. Batch adsorption studies for ZnO-NPs-AS-Os

##### 1) Effect of concentration

The trend in the adsorption of As (III) ions adsorbed over the surface of zinc oxide nanoparticle entrenched on activated silica using *Ocimum sanctum* (ZnO-NPs-AS-Os) shows the gradual decrease in adsorption from 92.38% to 59.28% with an increase in concentration from 0.005N to 0.01N and then it is constant at 0.07N (Fig. 4). It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active adsorbent sites (or) vacant sites on the surface of the adsorbent (ZnO-NPs-AS-Os). As the concentration of As (III) ion increases, more and more surface active sites of the adsorbent is covered. Hence at high concentrations of As (III) ions, the capacity of the adsorbent (ZnO-NPs-AS-Os) get exhausted due to non availability of the surface vacant sites and leads to saturation of monolayer adsorption.

##### 2) Effect of adsorbent dosage

The graph (Fig. 5) shows an increase in the adsorption percentage of As (III) from 57.11% to 93.3% as the dosage of adsorbent (ZnO-NPs-AS-Os) increases from 0.5g to 3g. This is because nano adsorbent has a higher surface area to volume ratio. Hence satisfactory results have been achieved with the fewer amount of adsorbent. By increasing ZnO-NPs-AS-Os amount of 0.5g to 5.5g, extraction of As (III) recovery slowly

increased to 95.31% from 57.11% and remained constant then after 3g. Any further addition of the ZnO-NPs-AS-Os beyond 5gm did not cause any significant change in the adsorption and the percentage removal decreases to 83.02% from 95.3%. This is due to overlapping of adsorption sites as a result of overcrowding of ZnO-NPs-AS-Os particle. The maximum removal of As (III) was obtained in the adsorbent dosage of 3g.

3) Effect of pH

The percentage of adsorption increases from 54.58% to 98.08% with increase in PH 1 to 6 at an agitation speed of 300rpm with a ZnO-NPs-AS-Os as 3g adsorbent dosage. When pH increases to 7 the percentage of adsorption decreases to 74.27% as shown in Fig. 6. The decrease in adsorption at pH 7 is mainly due to the competition between hydrogen ions and As (III) ions on the sorption site and leads to precipitation. Hence, higher pH > 6 was not selected for the present study.

4) Effect of contact time

The purpose of studying the effect of time on adsorption is to establish the equilibrium reaction time between ZnO-NPs-AS-Os and As (III) solution. The adsorption efficiency of As (III) increased gradually from 72.6% to 97.29% when the contact time is varied from 10 - 50 mins as shown in Fig. 7. A plateau reached at 50 min afterwards there was no change in adsorption. Hence the equilibration time is 50 min. Beyond 70 minutes the removal efficiency decreases to 88.58% from 97.4%.

5) Effect of agitation speed

It was found that the rate of removal of As (III) ions increases from 55.85% to 96.02% with an increase in agitation speed from 50 rpm to 300 rpm while keeping other experimental parameters constant. This indicates that the diffusion of As (III) ions from the solution to the surface of ZnO-NPs-AS-Os and into the pores occurs easily and quickly. Increase in agitation makes the particle to collide with each other with the greater speed, resulting in detachment of loosely bound ions. As shown in Fig. 8 by increasing the speed beyond 300 rpm there was no further increase in adsorption but adsorption decreases to 74.27%. This is because all the binding sites have been utilized and no binding sites were available for further adsorption.

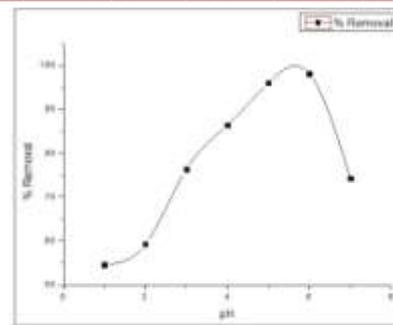


Figure 6. Effect of pH for ZnO-NPs-AS-Os

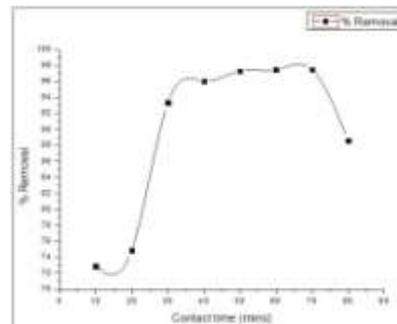


Figure 7. Effect of contact time for ZnO-NPs-AS-Os

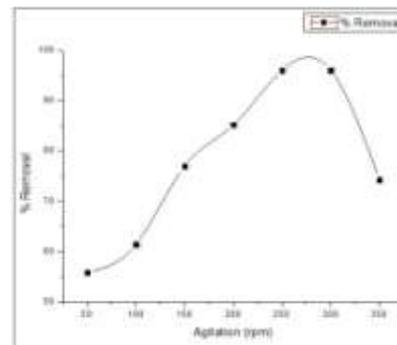


Figure 8. Effect of agitation speed for ZnO-NPs-AS-Os

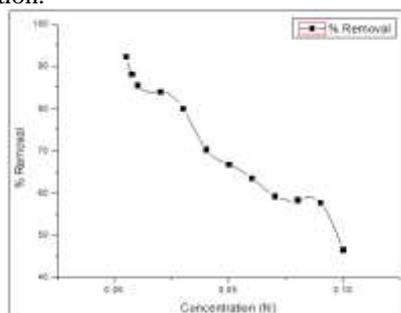


Figure 4. Effect of concentration for ZnO-NPs-AS-Os

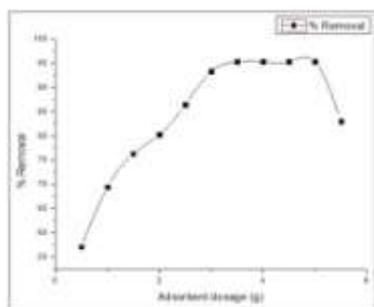


Figure 5. Effect of adsorbent dosage for ZnO-NPs-AS-Os

Maximum percentage removal for varying concentration (N), dosage (g), pH, contact time (min) and agitation speed (rpm) with equilibrium parameters are summarised for adsorbent (ZnO-NPs-AS-Os) in the Table. 4.

TABLE IV. EXPERIMENTAL STATISTICS FOR ADSORPTION OF AS(III) USING ZNO-NPS-AS-OS

Variables	Range	Maximum Percentage Removal (%)	Equilibrium Parameters
Initial arsenic concentration (N)	0.005-0.1	92.38	0.07 N
Adsorbent dosage (g)	0.5-6	95.30	3.5g
Initial pH	1-8	98.08	5
Contact time (min)	10-90	97.45	50 mins
Agitation speed (rpm)	50-400	96.02	250 rpm

In order to know As (III) adsorption behavior, the experimental data were applied to Freundlich, Langmuir, Tempkin Isotherm and BET. Fig. 9 to Fig. 13 shows the parameters obtained from different models which afford

important information on the surface properties of the adsorbent and its affinity for adsorbate.

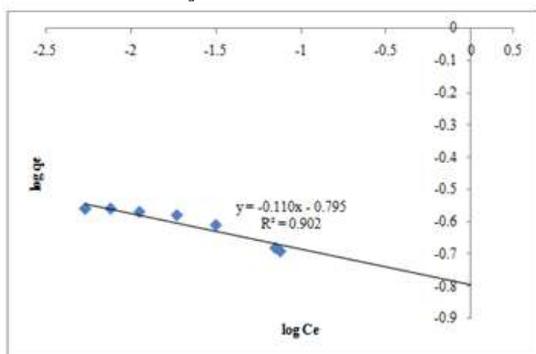


Figure 9. Freundlich adsorption isotherm for ZnO-NPs-AS-Os

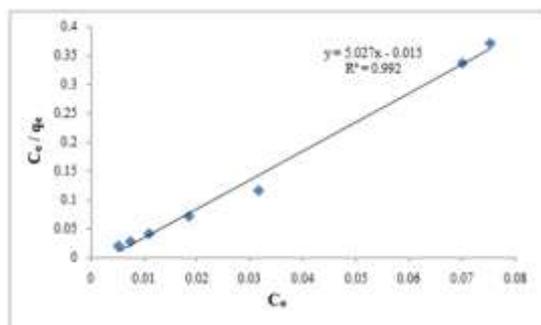


Figure 10. Langmuir adsorption isotherm for ZnO-NPs-AS-Os

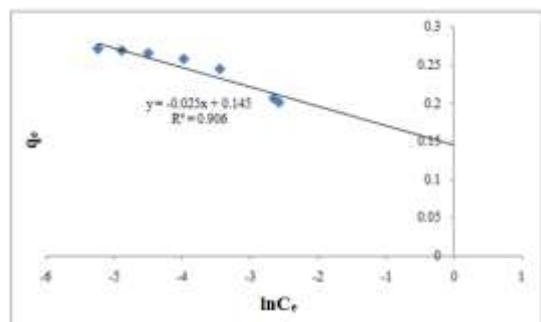


Figure 11. Effect of adsorbent dosage for ZnO-NPs-AS-Os

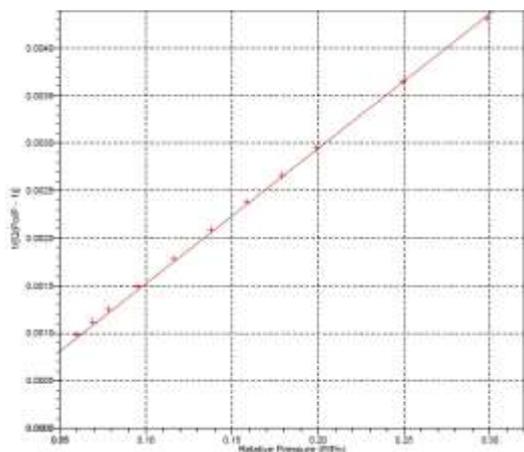


Figure 12. BET surface area plot

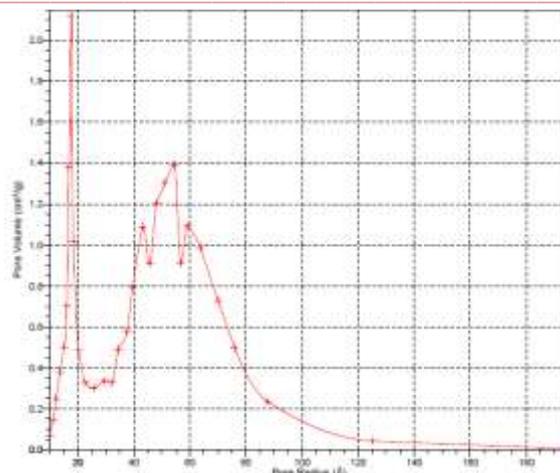


Figure 13. Pore volume plot

TABLE V. EXPERIMENTAL STATISTICS FOR ADSORPTION OF AS(III) USING ZNO-NPS-AS-OS

Equilibrium Isotherm	Equilibrium Parameters	Adsorbent ZnO-NPs-AS-Os
Freundlich	N	9.09
	$K_F$ (L/g)	6.237
	$R^2$	0.902
Langmuir	$K_L$ (L/mg)	66.66
	$R_L$	0.176
	$R^2$	0.992
Tempkin	A	1.396
	B	0.025
	$R^2$	0.906
BET	$R^2$	0.990
	Surface Area (m <sup>2</sup> /g)	300. m <sup>2</sup> /g
	Pore size (nm)	29.048 Å

Linear correlation coefficients for these equations determined by linear regression for Freundlich, Langmuir, Tempkin isotherm and BET showing that data correctly fits Langmuir isotherm than Freundlich isotherm, Tempkin isotherm and BET proving monolayer and homogeneous surface of adsorbent with  $R^2$  nearly 0.992, 0.902, 0.906 and 0.990 respectively. Table.5 shows the high fit of the Langmuir model among the four. The choice of Langmuir model is confirmed by high  $R^2$  value (0.992) and low  $R_L$  value (0.176) found to be less than 1 and greater than zero, indicating the favorable adsorption of As (III) onto the surface of the adsorbent ZnO-NPs-As-Os. Hence it confirms the adsorption is favorable. Hence ZnO-NPs-AS-Os can be used as an adsorbent because of its high adsorption capacity [11].

6) Adsorption kinetics for adsorbent ZnO-NPs-AS-Os

Adsorption Kinetics	Adsorbent ZnO-NPs-AS-Os
Pseudo first order equation	0.188
Pseudo second order equation	0.982

Correlation coefficients for these equations determined by linear regression for all kinetic models, pseudo-first and pseudo-second order was worked out. It can be inferred from Table.5 and Fig. 14 and Fig. 15 that adsorption did not obey well with the pseudo first order model because of the absence of linearity between  $\ln(q_e - q_t)$  and  $t$  ( $R^2=0.188$ ). In this study pseudo second model fitted better ( $R^2=0.982$ ) when compared with the first order kinetic model. Therefore the adsorption data in the present study supported chemisorptions. The linearity of

the plots also showed the validity of the model. The adsorption rate (t) decreased with increasing solute concentration.

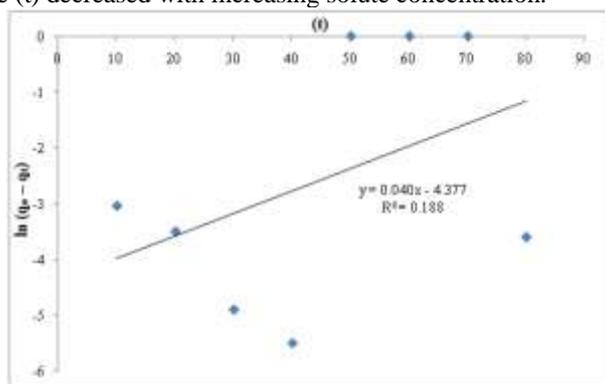


Figure 14. Pseudo first order Plot for ZnO-NPs-AS-Os

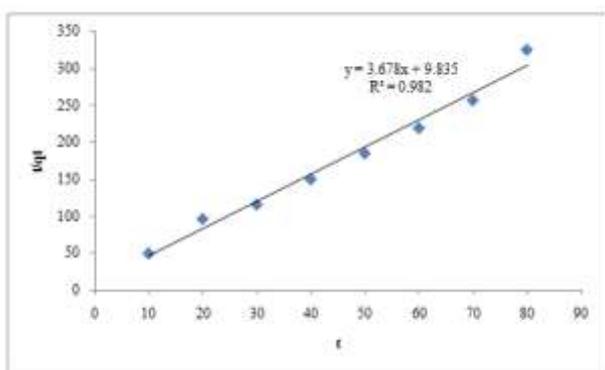


Figure 15. Pseudo second order plot for ZnO-NPs-AS-Os

### C. Characterization of adsorbent (ZnO-NPs-AS-Os)

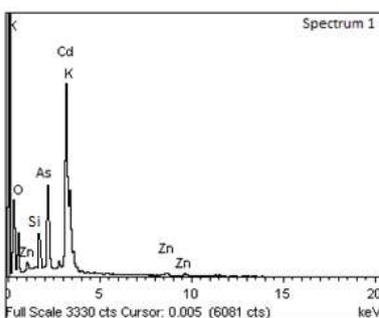
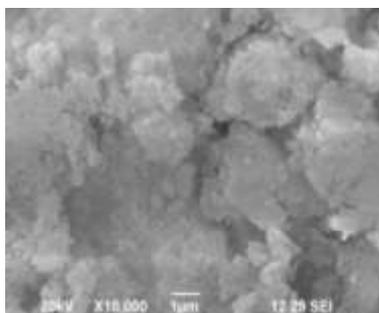


Figure 16. SEM and EDAX image of ZnO-NPs-AS-Os after adsorption of As(III)

Fig. 16 shows SEM and EDAX image of Zinc oxide nanoparticle from the aqueous leaf extract of *Ocimum sanctum* entrenched on activated silica (ZnO-NPs-AS-Os) from Zinc acetate and sodium hydroxide with water as a benign solvent

after adsorption of As (III). The observations indicated that the particle size of the adsorbent (ZnO-NPs-AS-Os) is in the range of 1µm at magnification X10000. The aggregation of the nanoparticle is visible, which confirms the surface of the adsorbent (ZnO-NPs-AS-Os) is not smooth and uniform which enhanced more adsorption of As (III). The composition of elements is consistent with EDAX with zinc (Zn), oxygen (O), silica (Si) and arsenic (As(III)) elements after adsorption. And no other peaks for impurity are present. Adsorption of As(III) by ZnO-NPs-AS-Os is authenticated.

### IV. CONCLUSION

In this study a novel biological approach for the formation of Zinc Oxide nanoparticle (ZnO-NPs) entrenched on activated silica (AS) using an aqueous leaf extract of *Ocimum sanctum* (Os) at room temperature is invented (ZnO-NPs-AS-Os). The experimental results showed that significant needle shaped adsorbent (ZnO-NPs-AS-Os) produced with distilled water as the reference environment is used to remove As (III) from aqueous solution with respect to change in Initial concentration, Dosage, Contact time, pH and Agitation. In order to understand the adsorption mechanism in detail, porosity, morphology, surface area, elemental analysis and particle size were determined. It was found that the pseudo second order mechanism is predominant following chemisorptions. The realistic and cost effective biological approach for the formation of (ZnO-NPs-AS-Os) has a promising application in water remediation. So the exploration of the plant systems as the potential nanofactories has heightened interest in the biological synthesis of nanoparticles as an adsorbent.

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