



Green Synthesis of Zinc Oxide Nanoparticles for Water Remediation

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Abstract : A novel green method for water remediation to remove arsenic (III) ions using Zinc oxide nanoparticle embedded in activated silica (ZnO-NPs-AS-*Eo*) is synthesized from leaf extract of *Emblica officinalis*. SEM, XRD EDAX and FT-IR analysis shows that the adsorbent is in rod shape with an average size of 16 nm with elemental composition of zinc, oxygen and silica elements with primary amine at about 3550-3300 cm^{-1} . The same acts as a stabilizer, promoter, reducing and capping agent to form (ZnO-NPs-AS-*Eo*) and prevents from agglomeration. The percentage of As (III) removal was very significantly from 85% to 96.7% at a concentration of .02N with 2.5g adsorbent dosage at a pH of 5 with a contact time of 60 min at an agitation speed of 300rpm. Results showed that the adsorption process by ZnO-NPs-AS-*Eo* was better represented by the Langmuir equation compared to the Freundlich isotherm, Tempkin equations and BET isotherm. Pseudo-second-order kinetics model provides a good correlation for the adsorption of As (III) on ZnO-NPs-AS-*Eo* and it also suggests that the adsorption is chemisorptions.

KeyWords: Zinc oxide Nanoparticles; Activated Silica; Isotherm and Kinetics.

Introduction

Green synthesis of nanoparticle for water remediation using plants is in the exploitation by researchers. Nanotechnology applications are highly suitable for biological molecules, because of their exclusive properties. Although chemical method of synthesis requires short period of time for synthesis of large quantity of nanoparticles, this method requires capping agents for size stabilization of the nanoparticles. Chemicals used for nanoparticles synthesis and stabilization are toxic and lead to non-ecofriendly byproducts. Green nanotechnology has goals to produce nanomaterials and products without harming the environment or human health and producing nanoproducts that provide solutions to environmental problems. To pursue a healthy life and space it is imperative to develop a green synthetic approach to obtain nano materials targeted on different applications. Many such experiments have already been started such as the synthesis of various metal nanoparticles using plants like *Oryza sativa*, *Helianthus annuus*, *Saccharum officinarum*, *Sorghum bicolor*, *Zea mays*, *Basella alba*, *Aloe vera* *Capsicum annum*, *Magnolia kobus*, *Medicago sativa* (Alfalfa), *Cinamomum camphora* and *Geranium sp*¹⁻³. In the recent days nanoparticles have been synthesized from the naturally occurring sources and their products like green tea (*Camellia sinensis*), Neem (*Azadirachta indica*), leguminous shrub (*Sesbania drummondii*), various leaf broth, natural rubber, starch, *Aloe vera* plant extract and lemongrass leaves extract⁴⁻⁵. This research 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.

Materials and Methods

Characterisation

Synthesis of the adsorbent(ZnO-NPs-AS-*Eo*) is schematically presented in figure 1.

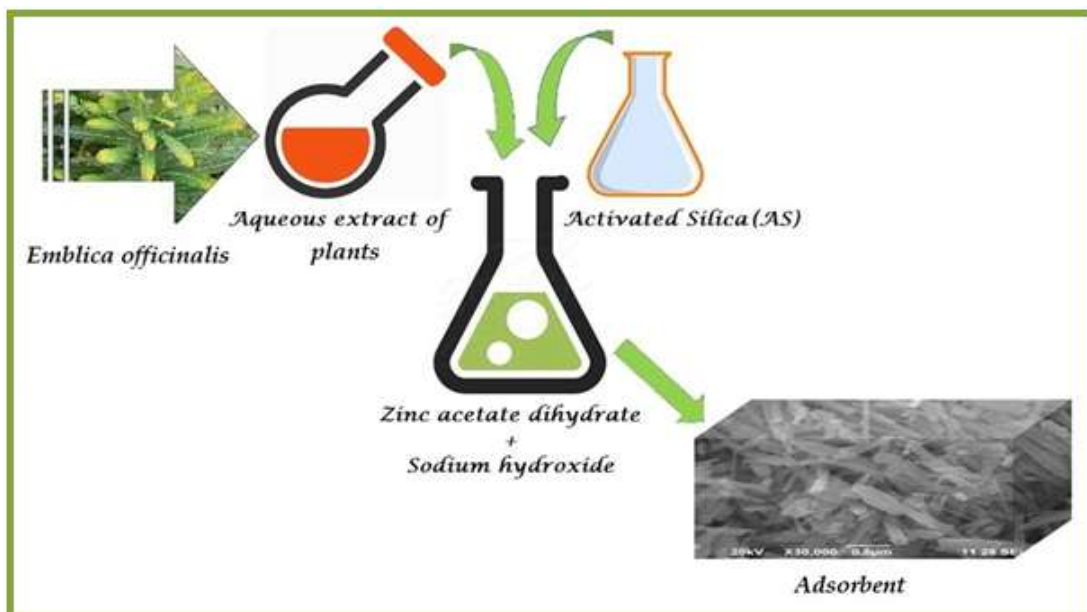



Figure 1: Schematic Representation of Green Adsorbent Synthesis (ZnO-NPs-AS-*Eo*)

The external morphology of ZnO-NPs-AS-*Eo* were characterized by scanning electron microscope (SEM) (JEOL JSM 6390). The X-Ray powder diffraction pattern of ZnO-NPs-AS-*Eo* was recorded on X-ray diffractometer (XRD, SHIMADZU, 6000) using Cu ($K\alpha$) radiation ($\lambda=1.5416 \text{ \AA}$) operating at 40 kv and 30 mA with 2θ ranging from 10 to 90°. The average particle size of ZnO-NPs-AS-*Eo* was determined from XRD patterns using Scherrer's equation. A Fourier transform infrared (FT-IR) spectrum was recorded on Jasco FT-IR5300 model spectro photometer in KBr pellets in the range of 4000-400 cm^{-1} . The surface characteristic and particle size distribution of ZnO-NPs-AS were investigated using Particle Size analyser (Malvern Model Micro-P, range 0.05-550 micron) and were summarized in table 1.

Table 1: Phytoconstituent Responsible for Crystallinity, Size, Morphology and Elemental Composition of ZnO-NPs-AS-*Eo*

Plant Species and Plant parts	Botanical & Common Name	Stabilizing Phytoconstituents	Crystal size & Morphology	Elemental Composition	Isotherm & Adsorption	Kinetics & Adsorption	Maximum removal of As (III)
 leaves	Emblicao fficinallis & Amla	Aromatic skeletal vibration, Primary amine 3550-3300 cm^{-1} , Aromatic stretching 930 cm^{-1} , Aromatic C-H 665 cm^{-1} , C=C stretching 1617 cm^{-1} , Alkane 1325-1213 cm^{-1} , ZnO NPs 557-417 cm^{-1} .	16nm & Nanorods	Zinc and Oxygen	Langmuir isotherm & Monolayer homogeneous adsorption	Pseudo second order & Chemisorption	96.7%

Results and Discussion

Batch experiments were conducted to study the effect of concentration, adsorbent dosage, pH, contact time and agitation speed on ZnO-NPs-AS-*Eo* for percentage removal of As(III) ions.

Effect of Concentration

As the initial As (III) concentration increases from 0.0075 to 0.07, the removal of As(III) decreases from 85.96 to 47.42%. This is due to the fact that at lower concentration almost all As(III) were adsorbed very quickly on the outer surface of the adsorbent, but further increase in As(III) concentrations led to fast saturation of ZnO-NPs-AS-*Eo* and thus most of the As(III) adsorption took place slowly inside the pores(Figure 2). It was observed that As(III) uptake is rapid upto 0.005N with 85.96% removal and there after it proceeds at a slower rate and finally attains saturation suddenly at low concentration of 0.02N .

Effect of Adsorbent Dosage

It can easily be inferred that the percent removal of As(III) ions increases from 47.46% to 80.43% with increasing the weight of adsorbent (ZnO-NPs-AS-*Eo*) from 1 to 3.5g(Figure 3). This is due to greater availability of exchangeable sites or surface area at higher dosage of the adsorbent. In the case of low dosage, the ratio of the initial number of moles of metal ions (As(III)) to the available surface area is larger and subsequently the fractional adsorption becomes independent of initial concentrations of adsorbent. The optimum amount of adsorbent 2.5g was found to be sufficient to reach the equilibrium for 0.02 N at this the maximum removal of As(III) is 80.43%.

Effect of pH

As(III) ions uptake was sensitive to pH variation over the examined range from 1 to 4 with removal of As(III) ions from 40% to 84.37%. At low pH values the surface of sorbent is surrounded by H⁺ ions which decrease the As(III) ion interaction with binding sites of the ZnO-NPs-AS-*Eo* by greater repulsive forces. At pH 5 maximum As(III) removal efficiency was only 89% whereas at pH 8 the removal efficiency decreased to 35.21%(Figure 4) further increase in pH was not attempted because of the possibility of precipitation of As(III) ions at pH > 7

Effect of Contact Time

The uptake of As(III) ions was 55% at 10 minutes and 89% at 50 minutes. According to the results, the equilibrium reached at 60 minutes with 88% removal and was taken as the optimal contact time for the subsequent experiments(Figure 5). The data showed that time is a significant factor contributing largely to the adsorption under different sets of condition as time is required for As(III) to diffuse in to the ZnO-NPs-AS-*Eo*.

Effect of Agitation Speed

The rate of As(III) removal was very significant from 50rpm to 250 rpm with percentage removal from 56.58% to 92.98%. Increase in agitation makes As(III) ion to collide with each other with the greater speed resulting in detachment of loosely bound ions. As shown in figure 6 by increasing the speed there was no further increase in adsorption. Beyond 300 rpm there is no change in As(III) removal from 96.7% till 400 rpm. This is because all the binding sites have been utilized and no binding sites were available for further adsorption. An increasing agitation rate may reduce the film boundary layer surrounding the ZnO-NPs-AS-*Eo* beyond 400 rpm and hence there in decrease in removal of As(III) of 71.95% .

Equilibrium Study

In this study equilibrium isotherms like Langmuir, Freundlich, Tempkin and BET were used to determine the adsorption mechanism of ZnO-NPs-AS-*Eo* for As(III) ions. According to the results, Freundlich and Tempkin model were not found to describe adsorption successfully than Langmuir isotherm model in respect to linearity coefficients obtained for four model ($R^2 = 0.970$). The Langmuir isotherm assumes that each adsorbate molecule is located at a single site, equivalent sorption energies, no interaction between sorbed

species and it predicts the formation of a monolayer of the adsorbate on the adsorbent surface. In mathematical form, it is written as.

$$C_e/q_e = (1/K_L) + (a_L/K_L) C_e \text{ ----- (1)}$$

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 homogenous surface of adsorbent with R^2 nearly 0.970, 0.949, 0.960 & 0.909 respectively. Table 2 shows the high fit of the Langmuir model among the four. The choice of Langmuir model is confirmed by high R^2 value (0.970) and low R_L value (0.885) 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-Eo. Hence it confirms the adsorption is favorable chemisorptions. The phenomenon of chemisorptions and physisorption were represented in Figure 7. The linear form of equations for the pseudo-first-order and pseudo-second-order kinetic models can be represented by (1) and (2), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{ ----- (1)}$$

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

where, k_1 is the first-order reaction rate constant (L/min) and k_2 represents the second-order reaction rate constant (g/mg.min). The plots of pseudo-first-order and pseudo-second-order are listed in table 2. The R^2 value for the pseudo-second-order model was higher (0.732) than the pseudo-first-order model (0.208). It can be concluded that the pseudo-second-order kinetics model provides a good correlation for the adsorption of As(III) on ZnO-NPs-AS-Eo and it also suggests that the chemisorption process could be the rate-limiting step in the adsorption process (Table 3). Similar conclusion was also reported for the adsorption of heavy metal ions by other adsorbents such as modified groundnut husks, oil palm fibers, waste tea leaves and tree leaves waste⁶⁻⁷.

Figure 2: Effect of Concentration for ZnO-NPs-AS-Eo

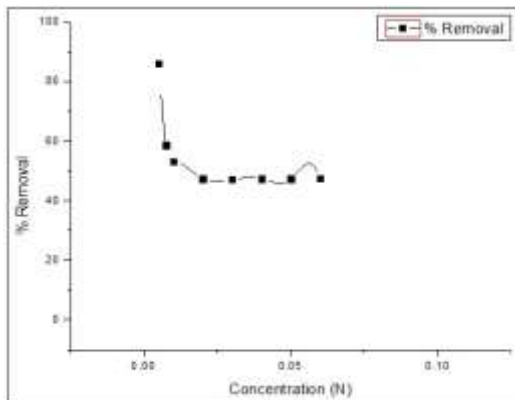


Figure 3: Effect of Adsorbent Dosage for ZnO-NPs-AS-Eo

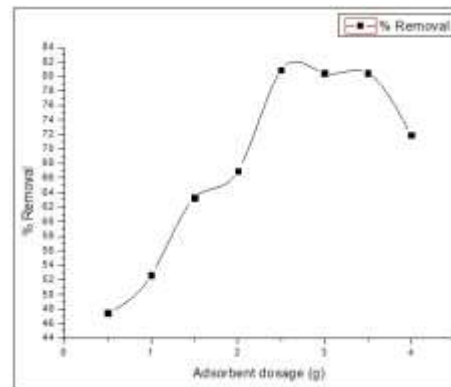


Figure 4: Effect of pH for ZnO-NPs-AS-Eo

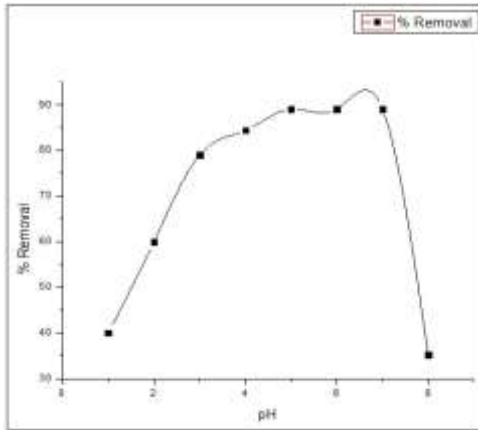


Figure 5: Effect of Contact Time for ZnO-NPs-AS-Eo

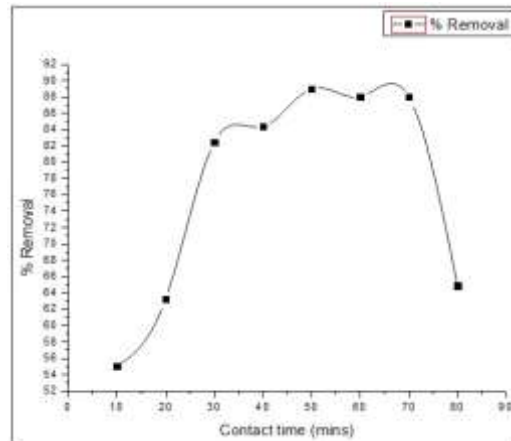


Figure 6: Effect of Agitation Speed for ZnO-NPs-AS-Eo

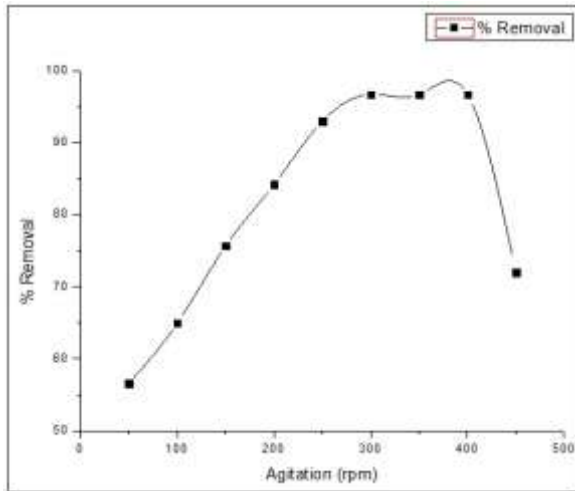
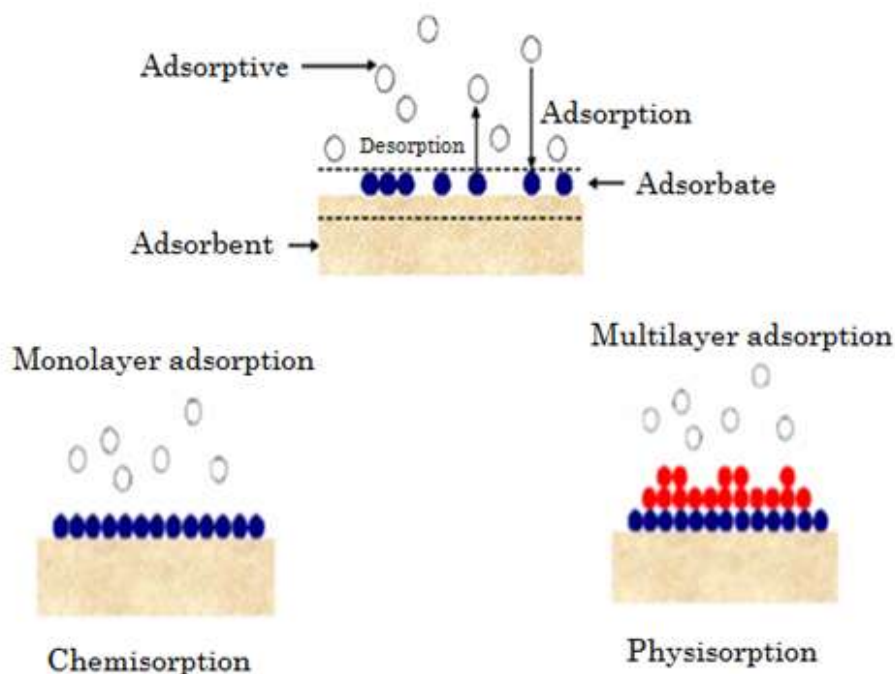


Table 2: Adsorption Isotherm Parameters for ZnO-NPs-AS-Eo

S.No.	Adsorption Isotherm	Equilibrium Parameters	Adsorbent ZnO-NPs-AS-Eo
1	Freundlich	n	2.67
		K_F (L/g)	45.39
		R^2	0.949
2	Langmuir	K_L (L/mg)	6.45
		R_L	0.885
		R^2	0.970
3	Tempkin	A	1.056
		B	0.030
		R^2	0.960
4	BET	R^2	0.909
		Surface Area (m^2/g)	302.73 m^2/g
		Pore size (nm)	28.048 Å

Table 3: Adsorption Kinetics for Adsorbent ZnO-NPs-AS-Eo

S.No.	Adsorption Kinetics	Adsorbent ZnO-NPs-AS-Eo
1.	Pseudo first order equation	0.208
2.	Pseudo second order equation	0.732

**Figure 7: Simple Principle to Illustrate Monolayer and Multilayer Adsorption**

Conclusion

The present piece of work demonstrates the successful removal of As (III) ions from the aqueous solutions using ZnO-NPs-As-Eo with maximum removal efficiency (96.7%). Adsorption equilibrium data were best described by Langmuir isotherm accomplished that the maximum adsorption corresponds to a saturated monolayer of As (III) molecules on the adsorbent surface with constant energy. The findings presented in this study suggested following pseudo-second-order equation for the adsorption of As (III) on to (ZnO-NPs-As-Eo). The maximum removal As (III) ions of 96.7% is obtained at concentration of 0.002 mg/L, adsorbent dosage to 2.5 g, contact time 60 min and agitation speed of 300 rpm at pH5 with particle size of 16 nm with rod like morphology.

References

- Chandran S.P., Chaudhary M., Pasricha R., Ahmad A. and Sastry M., "Synthesis of gold nanotriangles and silver nanoparticles using Aloe vera plant extract", *Biotechnology Progress.*, (2006), 22, 577-583.
- Raveendran P., Fu J. and Wallen S.L., "Completely green synthesis and stabilization of metal nanoparticles", *Journal of the American Chemical Society*, (2003), 125, 13940–13941.
- GardeaTorresdey J.L., Gomez E., Peralta Videa J.R., Parsons J.G., Troiani H. and Jose Yacaman M., "Alfalfa sprouts: A natural source for the synthesis of silver nanoparticles", *Langmuir*, (2003), 19, 1357–1361.
- Yang S.J. and Park Ch.R., "Microwave-assisted additive free synthesis of nanocrystalline zinc oxide", *Nanotechnology*, (2008), 19, 035609.
- Krishnakumar T., Jayaprakash R., Pinna N., Singh V.N., Mehta B.R. and Phani A.R., "Triangular CdSnanocrystals: Structural and optical studies", *Materials Letters*, (2008), 63 (2), 242.
- Gulnaz O., Saygideger S. and Kusvuran C., *Journal of Hazardous material B*, (2005), 120, 193.

7. Loys, Johnwase D.A. and Froster C.F., "Batch nickel removal from aqueous solution by sorghum-maes peat", *Water Research*, (1995), 29, 1327-1332.
