Benign ZnO nanoparticle as a practical adsorbent for removal of As\(^{3+}\) embedded on activated silica using Ocimum Sanctum

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ABSTRACT
This new-fangled green synthesis progress shows that the environmentally benign ZnO-NPs-AS is potent adsorbent for the removal of As\(^{3+}\) primed from leaf extract of Ocimum Sanctum. Competently wrecked Zinc oxide nanoparticle ingrained on activated silica (ZnO-NPs-AS) using Zinc acetate, sodium hydroxide and activated silica synthesised had assorted roles. The Adsorption parameters for the Langmuir, Freundlich, Temkin and BET isotherms were dogged and the constancy data were best described by Langmuir isotherm and BET model and fits pretty well with the experimental records with good correlation coefficient of 0.9929 and 0.999. The dispute of intra particle diffusion model suggested that intra particle diffusion was not the rate controlling process. The data were analyzed using kinetics models analogous to Pseudo first and second order. All the findings accessible in this study suggested following Pseudo second order equation for the adsorption of As\(^{3+}\) on to ZnO-NPs embedded on activated silica. From the standards it is consummate that the utmost adsorption corresponds to a saturated monolayer of As\(^{3+}\) molecules on the adsorbent.
surface persistently. The as synthesized particle was characterized for BET surface pore, pore size and specific pore volume. The morphology of ZnO-NPs embedded on activated silica was confirmed by scanning electron microscopy (SEM). Particle Size Analyzer (PSA) shows the fashioned ZnO-NPs embedded on activated silica ranged in dimension of about 100nm. The sharp peaks by X-ray Diffraction Analysis (XRD) pattern show the crystallinity and purity of the sample. Energy Dispersive X-Ray Analysis (EDAX) confirms the presence of Zn, O and Si elements. Green methods are being good competent for the chemical procedures, which are environment friendly and convenient. The results confirmed that aqueous leaf extract of Ocimum Sanctum is a suitable green stencil to prepare ZNO-NPs embedded on activated silica.

**Key Words:** Ocimum Sanctum; Adsorbent; Isotherm; Kinetics; ZnO-NPs-AS

### 1. INTRODUCTION

The amputation of heavy elements from drinking water is of great connotation due to their high toxicity. Metal pollutants are predictable contaminants that are not with ease recyclable chemically or biologically. Contagion of water by heavy metals through the expulsion of industrial waste is a worldwide environmental problem. Heavy metals are toxic and have the tendency to bio accumulate. They are therefore long-term chemical overload in the environment. The tribulations of our bionetwork are increasing with the encroachment in technology. Techniques used for deduction of heavy metals like lime coagulation, reverse osmosis, chemical precipitation, ion exchange and solvent extraction are expensive and non-environmental friendly as compared to adsorption. Adsorption is one of the easiest, safest and most expenditure effective methods for the removal of metals. The foremost advantage of an adsorption system of silica embedded zinc oxide nanoparticle are less investment in terms of both initial cost and simple designed easy operation and has no effect of toxic substance compared to conventional chemical treatment process. There is a vital requirement for development of innovative but low cost processes by which heavy metals can be removed. Adsorption technique is quite trendy due its simplicity and high efficiency, as well as the ease of use of a range of adsorbents. Various adsorbents have been tested and used for the removal of heavy metals from polluted water. Among the kinds of adsorbents, nano Zinc oxide NPs have been attracted interesting recently because it exhibit high surface area to volume ratio. Arsenic is a heavy metal with high toxicity when in excess in children. The dominant basis of Arsenic poisoning is from ground water that naturally contains high concentration of Arsenic. The study report received during the year 2000 showed that over 137 million people in more than 70 countries are probably affected by arsenic poisoning from drinking water (Gnanasangeetha et al., 2013). Symptoms of arsenic poisoning begin with headaches, confusion, severe nausea and drowsiness. The poisoning develops convulsions and changes in fingernail pigmentation called leukonychia. When the poisoning becomes acute symptoms may include vomiting, blood in the urine, cramping muscles, hair loss, stomach pain and more convulsions. The organs of the body that are usually affected by arsenic poisoning are the lungs, skin, kidneys and liver (Mayo Clinic et al., 2012). The final result of arsenic poisoning is coma and death. It is therefore essential to search benevolent product and to transform such materials to adsorbents (Muthusamy et al., 2012, Markovska et al., 2006). Increasing awareness towards green chemistry and biological processes has led to the efficacy and feasibility of an eco-friendly approach for the synthesis of ZnO nanoparticle entrenched on activated silica as proficient adsorbent for removal of As$^{3+}$.

### 2. MATERIALS AND METHODS

#### 2.1. Preparation of ZnO-NPs-AS

The preparatory material Zinc acetate dihydrate (99% purity) and sodium hydroxide (pellet 99%) used was supplied by Sigma-Aldrich chemicals, India. Green synthesis method was used to prime down ZnO-NPs-AS structure. Aqueous leaf extract of Ocimum Sanctum was stirred for 30 min to that 1g of Zinc acetate dihydrate was added under vigorous stirring. After 1hr stirring 10 g of activated silica was introduced into the above solution. Addition of drops of aqueous NaOH resulted in a white aqueous solution at pH 10-12. This was then positioned in a magnetic stirrer for 2Hrs. The activated silica surrounded ZnO nanoparticle were then filtered and washed with double distilled water. The synthesized ZnO-NPs-AS was maintained at 60ºC for 12 hrs. A mortar was used to homogeneously ground the ZnO-NPs entrenched on activated Silica. The proposed sorbent were stored in air at room temperature. The external morphology of the sample were characterized by scanning electron microscope (SEM) (LEO 1530FEGSEM). The surface characteristic and particle size distribution of ZnO-NPs-AS was investigated using Particle Size analyser (PSA, Zetasizer Ver.6.32). The X-Ray powder diffraction pattern of the as synthesized sample was recorded on an X-ray diffractometer (XRD, PW 3040/60 Philips X’Pert, Holland) using Cu (Kα) radiation (λ =1.5416 Å) operating at 40 kv and 30 mA with 2θ ranging from 10- 90°. Pore size, surface area and pore volume were determined from the quantity of gas adsorbed to form a monolayer over the surface of the adsorbent using Brunauer-Emmet-Teller (BET) isotherm.
3. EXPERIMENTAL DETAILS

The experiments were carried out as shown in Table 1. The effect of parameters such as As\(^{3+}\) Metal Concentration, Adsorbent dosage, Contact time, pH and Agitation speed were studied. The effect of each parameter is studied by changing it progressively keeping the others constant.

The quantity of As\(^{3+}\) adsorbed by ZnO-NPs-AS was calculated using the following formula:

\[
\text{% Removal} = \frac{(C_0 - C_e) \times 100}{C_0} \quad q_e = \frac{(C_0 - C_e) \times V}{W}
\]

Where \(C_0\) and \(C_e\) are initial and equilibrium concentration of As\(^{3+}\) respectively, \(q_e\) the amount of arsenic adsorbed, \(V\) the volume of the solution and \(W\) the weight of the adsorbent used.

Table 1
Experimental details of ZnO-NPs-AS for adsorption of As\(^{3+}\)

<table>
<thead>
<tr>
<th>Effect of the System</th>
<th>Concentration (N)</th>
<th>Adsorption dosage (g)</th>
<th>Contact time (min)</th>
<th>pH</th>
<th>Agitation (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (N)</td>
<td>0.005, 0.0075, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10</td>
<td>0.05</td>
<td>30</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Adsorption dosage (g)</td>
<td>0.05</td>
<td>0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5</td>
<td>30</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>Contact time (min)</td>
<td>0.05</td>
<td>3</td>
<td>10, 20, 30, 40, 50, 60, 70, 80</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>pH</td>
<td>0.05</td>
<td>3</td>
<td>30</td>
<td>1, 2, 3, 4, 5, 6, 7</td>
<td>250, 300, 350</td>
</tr>
<tr>
<td>Agitation (rpm)</td>
<td>0.05</td>
<td>3</td>
<td>30</td>
<td></td>
<td>50, 100, 150, 200, 250</td>
</tr>
</tbody>
</table>

3.1. Adsorption Isotherm
It is fundamentally 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. Quite a lot of conventional isotherm equations are fitted to such as Langmuir, Freundlich, Tempkin and BET. The parameter obtained from different models provides important information on the surface properties of the adsorbent and its affinity.

3.2. Freundlich Isotherm
The Freundlich linear expression is an empirical equation based on multilayer sorption to a heterogeneous surface and is expressed by the following equation:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where \(q_e\) and \(C_e\) are the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively. \(K_F\) and \(1/n\) are Freundlich constant characteristics of the system, which are determined from the log \(q_e\) vs. log \(C_e\).

3.3. Langmuir adsorption
Langmuir monolayer adsorption isotherm is very useful for predicting adsorption capacities and also interpreting into mass transfer relationship. The isotherm can be written as follows:
C\textsubscript{e}/q\textsubscript{e} = (1/K\textsubscript{L}) + (a\textsubscript{L}/K\textsubscript{L}) C\textsubscript{e}

The constant K\textsubscript{L} (L/g) is the Langmuir equilibrium constant, and the a\textsubscript{L}/K\textsubscript{L} gives the theoretical monolayer saturation capacity. These Langmuir parameters were obtained from the linear correlations between the values of C\textsubscript{e}/q\textsubscript{e} and C\textsubscript{e}. Generally the Langmuir equation applies to the cases of adsorption on completely homogeneous surfaces.

### 3.4. Tempkin Isotherm

Tempkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces and it has generally been applied in the following form:

q\textsubscript{e} = B \ln A + B \ln C\textsubscript{e}

A plot of q\textsubscript{e} versus \ln C\textsubscript{e} enables to determine the constants A and B.

### 3.5. BET Method

Specific surface area, pore volume and pore size of the sample were determined by means of N\textsubscript{2} adsorption-desorption at -195.629 °C applying the BET method.

### 3.6. Kinetic Studies

The adsorption kinetics is important as it can forecast the rate at which a As\textsuperscript{3+} is removed and provide important insights into the mechanism of sorption reactions. To study the rate constant for the adsorption of As\textsuperscript{3+} on ZnO-NPs-AS the following kinetic models were tested to fit experimental data obtained. As\textsuperscript{3+} of initial concentration of 0.005 to 0.10 was treated at different contact durations of 10 to 80 min at pH 1 to 7 and adsorbent dosage of 0.5 to 5.5g at an agitation of 50 to 350 rpm.

### 3.7. Pseudo first-order equation

The pseudo first-order equation is given as follows:

\[ \ln (q\textsubscript{e} - q\textsubscript{t}) = \ln q\textsubscript{e} - k\textsubscript{1}t \]

Where q\textsubscript{t} and q\textsubscript{e} are the amounts of As\textsuperscript{3+} adsorbed at time t and equilibrium respectively and k\textsubscript{1} is the pseudo first-order rate constant for the adsorption process. The linear graph of \ln(q\textsubscript{e} - q\textsubscript{t}) vs t shows the applicability of first order kinetic.
3.8. Pseudo second-order equation

This chemisorption kinetic rate equation is expressed as follows:

\[
\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t
\]

Where \(k_2\) is the equilibrium rate constant of pseudo second order equation. The linearity of \(\frac{t}{q_t}\) vs \(t\) suggests the best fitted with pseudo-second order kinetic.

3.9. Intra-particle equation

Kinetic data can also be analyzed by an intra-particle diffusion kinetic model formulated as follows:

\[
q_t = k_p t^{1/2} + C
\]

Where \(k_p\) is the intra-particle diffusion rate constant and \(C\) is the intercept of the plot of \(q_t\) versus \(t^{1/2}\). If this linear plot passes through the origin then intraparticle diffusion is the rate-controlling step.

4. RESULTS AND DISCUSSION

Figure 1 shows the unique XRD outline of ZnO-NPs-AS prepared by the green synthesis method at 60°C for 12 hours for aqueous leaf extract of Ocimum Sanctum. Corresponding emblematic peak primarily at about 12°, 20° for silica and 32°, 34°, 36° for ZnO NPs are indicative of nano-crystalline nature of ZnO-NPs-AS in combination. It can be seen that all of these peaks are well matched (Pingle Zhou, et al., 2007) with that of Zincite phase (JCPDS CARD NO: 36- 1451). The crystalline sizes of the ZnO-NPs-AS prepared at 60°C for 12 hours were observed to be 100nm which was determined by Debye Scherer’s formula according to the equation \((d=k\lambda/\beta \cos\theta)\), where \(\lambda\) is the wavelength of incident X-ray which is the Full Width Half Maximum (FWHM) of diffracted peak and \(\theta\) is diffracted angle. Figure 2 A, B, C, D shows the SEM micrograph of homogeneous shape and size for ZnO-NPs-AS at X10,000 and X20,000 which is the image of ZnO-NPs-AS obtained using aqueous leaf extract of Ocimum Sanctum. The size and morphology of the obtained ZnO-NPs-AS have been changed by increasing the magnification. The SEM image and Particle size distribution (Figure 3) of ZnO-NPs-AS is found to have the size ranging 100 nm. The EDX spectrum (Figure 4) shows the peak only for the presence of Zinc, Oxygen silicon elements in the as-prepared ZnO-NPs-AS. The percentage of zinc, silica and oxygen is found to be 100% which proves that it is completely free from impurities.

The effect of concentration on the sorptive removal of As\(^{3+}\) is presented in Figure 5. The results show gradual decrease in adsorption from 92.38% to 59.28% with increase in concentration from 0.005M to 0.07M and then constant. The decrease in percentage of adsorption may be caused by the lack of sufficient surface area to accommodate much more As\(^{3+}\) ions available in the solution. Hence at higher concentration lower adsorption yields were observed because of the saturation of the adsorption sites.
Similar trend is also noted by other researchers (Abdel-ghani et al., 2007, Resmi et al., 2010). Effect of adsorbent dosage on the adsorption of As$^{3+}$ is studied by changing the ZnO-NPs-AS dosage from 0.5gm to 5.5gm and the initial concentration of As$^{3+}$ was fixed as 0.07N. Figure 6 shows an increase in adsorption from 0.5gm to 3gm due to greater availability of the surface area at higher concentration of the adsorbent. Any further addition of the adsorbent beyond 5gm did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particle. The maximum removal of As$^{3+}$ was obtained in the adsorbent dose of 3gm which is in accordance with other researchers (Yang et al., 2006, Namasivayam et al., 1998).

The studies involving different contact times help in determining the uptake capacities of the As$^{3+}$ at varying time intervals keeping the amount of the adsorbents fixed at room temperature. The purpose of studying the effect of time on adsorption is to establish the equilibrium reaction time between adsorbent and As$^{3+}$. The adsorption experiment was carried out using contact time ranging from 10mins to 80mins and the results are depicted in the Figure 7. It was observed that metal adsorption occurred rapidly. The adsorption efficiency of As$^{3+}$ increased gradually with increasing contact time up to 30mins and reached a plateau afterwards and there was no change in adsorption and the equilibration time is 30mins. 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$^{3+}$ to diffuse in to the ZnO-NPs-AS similar results were observed by other reporters (Ben Hamissa et al., 2008, Kannan et al., 2009) for As$^{3+}$ on to different adsorbents. The pH is one of the important parameter controlling the removal of metal. It is clear from the Figure 8 that pH has a significant role on adsorption of metal using the synthesized ZnO-NPs-AS. It was found that increasing the pH of the solution from 1 to 6 increases...
the percentage removal of metal. This is due to the decline in the competition between proton and metals species for surface sites. Basic pH was also attempted but it could not be investigated due to precipitation (Stephan et al., 2004, Ratoi et al., 2008).

The effect of agitation speed on the adsorption rate was investigated by changing the speed in the range 50 to 400 rpm. The rate of As\(^{3+}\) removal was very significant from 50rpm to 250 rpm. Increase in agitation makes the particle to collide with each other with the greater speed resulting in detachment of loosely bound ions also they did not get appropriate time to interact with each other as shown in Figure 9. By increasing the speed there was no further increase in adsorption. This is because all the binding sides have been utilized and no binding sides were available for further adsorption. An increasing agitation rate may reduce the film boundary layer surrounding the ZnO-NPs-AS (Orhan et al., 1993, Cenciz et al., 2010). Figures 10, 11, 12, 13 and 14 shows the parameters obtained from different models provide important information on the surface properties of the adsorbent and its affinity of adsorbent. Several conventional isotherm equation fitted to Langmuir, Freundlich, BET and Tempkin. Linear correlation coefficients for these equations determined by linear regression for Langmuir isotherm, Freundlich isotherm, BET and Tempkin isotherm showing that data correctly fits Langmuir isotherm and BET than Freundlich isotherm, and Tempkin isotherm, proving monolayer and homogenous surface of adsorbent with R\(^2\) nearly 0.9929, 0.9024, 0.956 and 0.9064 respectively.

Correlation coefficients for these equations determined by linear regression for all kinetic models, pseudo-first pseudo-second order and intra-particle equation were worked out. High R\(^2\) (>0.9929) implies that the correlations fit well with the experimental data. It can be observed that correlation coefficient value i.e. 0.9827 of pseudo-second order equation for ZnO-NPs-AS were higher than other kinetic equations (Figures 15 and 16). So pseudo-second order equation is the most fitted with respect to other equations. Similar views have been expressed (Senthilkumar et al., 2009).
This new paradigm is rapidly opening possibilities in research to combine biological principles with chemical procedure to spawn ZnO-NPs-AS particle with precise function as adsorbent. This imperative branch of biosynthesis of ZnO-NPs-AS as adsorbent enable research to correct chemical defects in unhealthy environment.

5. CONCLUSION
This green approach confirmed the prediction of percentage adsorption efficiency for the removal of As (III) ions from aqueous solution by zinc oxide nanoparticle entrenched on activated silica (ZnO-NPs-AS) prepared from aqueous leaf extract of Ocimum sanctum. The off operational parameters such as initial concentration, pH, adsorbent dosage, contact time and agitation time are studied to optimize the conditions for maximum removal of As (III) ions. The maximum As$^{3+}$ removal of 98% is obtained at concentration of 0.07N, absorbent dosage to 3g, contact time 30 min and agitation speed of 250 rpm at pH 6. The equilibrium data have been analyzed using correlation coefficients of Langmuir, Freundlich, BET and Tempkin isotherms ($R^2$ = 0.9929, 0.9024, 0.956 and 0.9064) in which Langmuir isotherm and BET is more fitted than Freundlich and Tempkin isotherm. From the results it is accomplished that the maximum adsorption corresponds to a saturated monolayer of As$^{3+}$ molecules on the adsorbent surface with constant energy. The data were analyzed using pseudo-first order, pseudo-second order and intra-particle equation in which pseudo-second order ($R^2$ =0.9827) is more applicable than pseudo-first order ($R^2$ =0.7117) and intra particle diffusion was not the
rate controlling step. The present outcome recommend that ZnO-NPs-AS synthesized in a inventive green method may be used as an economical and effectual adsorbent for the confiscation of As\(^{3+}\) ions from aqueous solutions primed from leaf extract of Ocimum Sanctum.

**REFERENCE**