

## Research Article

Bio sorption of Arsenic from Aqueous Solution using *CLERODENDRUM INERME*: Characterization, Kinetics and Modeling

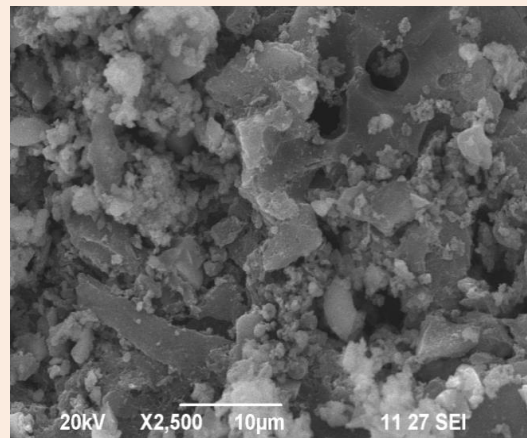
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**Abstract**

New low cost adsorbents activated *Clerodendrum inerme* has been developed for aqueous arsenic removal. Batch experiments were revealed that As removal was up to 86% using *C.inerme*. Kinetics studies revealed that Langmuir isotherm was followed with a better correlation than the Freundlich isotherm and adsorption was pseudo second-order model. The intra particle diffusion model described that the intra particle diffusion was not the only rate-limiting step. Thermodynamic study indicates an endothermic nature of adsorption and a spontaneous and favorable process. The optimum pH for As(III) removal was neutral. EDX analysis indicated the presence of Arsenic on the *C.inerme* surface. Thus, this recently developed cost-effective, novel activated *Clerodendrum inerme* can be used as household level to mitigate the arsenic problem.

**Keywords:** adsorption, As(III), Kinetic, Thermodynamic, *C. inerme*

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**1. Introduction**

Arsenic is ubiquitous in the environment and of worldwide serious concern due to its high drinking water exposure causes cancer of the liver, lung, kidney, bladder, and skin as well as skin thickening (hyperkeratosis), neurological disorders, muscular weakness, and loss of appetite and nausea [1-3]. To minimize these health risks, a strict guideline limit of 10 ppb (10µg/L) provided by the World Health Organization(WHO) [4]. In natural waters, arsenic occurs predominantly in inorganic form as arsenate and arsenite, referred to as As(V) and As(III).As(III) is much more toxic [5], soluble, and mobile than As(V). Adsorption methods are considered to be the most promising technologies because the system can be simple to operate and cost-effective[6].

*Clerodendrum inerme* (Verbenaceae) commonly known as “Vanajai” or “Garden quinine”. *C. inerme* is an evergreen mangrove plant. A hardy, straggling shrub, it reaches a height of 3-4 meters with closely arranged, almost round, shiny, deep green leaves. It has well known reputation of anti malarial plant. Juice of leaves is used for the treatment of skin diseases such as itches, leprosy, scabies, scrofulous[7-9]. It was also reported that tribals use *C. inerme* as an antidote of poisoning from fish, crabs and toads.

This study investigates the feasibility of the *C. inerme* for As(III) removal from aqueous solution. The main objectives are (i) to understand the As(III) adsorption kinetics, (ii) to evaluate the impact of temperature and, pH on the As(III) removal kinetics and/or capacities; and (iii) to describe and explain some important thermodynamic parameters.

**2. Materials and methods**

Fresh and healthy leaves of *C. inerme* were Chosen. Prior to analysis, the samples were air dried (away from sunlight) and ground into fine powder using a stainless steel mortar and pestle. All results are expressed on a dry weight basis.

Later the dried adsorbent was thermally activated in Muffle furnace at 450°C (here we avoid acid treatment for charring). The resulting product was cooled to room temperature. The powder was sieved to achieve uniform size. Finally, the product was stored in vacuum desiccator until required.

All chemicals were analytical grade (>99%) and were purchased from Sigma-Aldrich. The As (III) stock solution (1000 mg/L) was prepared by dissolving NaAsO<sub>2</sub> (>99%) in deionized water. Arsenic working solutions were freshly prepared by diluting arsenic stock solutions (1000 mg/L) with deionized water. The concentrations of arsenic species were always given as elemental arsenic concentration in this study.

## 2. 1. Arsenic analysis and equipment

The Arsenic concentrations in the water samples were determined using a ICP spectrometer apparatus of model ICAP 6000 series, Thermoscientific. The X-ray diffraction pattern of the activated carbon was obtained using a Bruker AXS D8 Advance, Inst ID: OCPL/ARD/26-002 X-ray diffractometer. Examination of adsorption with Scanning Electron Microscope (SEM) with HITACHI-S-3400N model fitted with an energy dispersive X-ray analyzer (EDAX) allows a qualitative detection and localization of elements in the adsorption.

## 2. 2. Sorption experiments

Batch adsorption experiments were carried out at the desired temperature (303, 313 and 323K) on a thermostatic shaker at 120rpm using capped 250mL conical flasks. The studies were conducted for the optimization of various experimental conditions like contact time, initial concentration adsorbent dose and pH. The arsenic concentration retained in the adsorbent phase,  $q_e$  (mg/g), was calculated, using the following equation,

$$q_e = (C_i - C_e) \times V/W \quad (1)$$

here  $q_e$  is the amount of arsenic adsorbed (mg/g);  $C_i$  and  $C_e$  are the initial and residual concentration at equilibrium (mg/L), respectively, of arsenic in solution; and  $W$  is the weight (g) of the adsorbent. The adsorption process was studied with Langmuir and empirical Freundlich, models.

## 2.3. Statistical analysis

The results are the average of three independent measurements along with standard deviation (SD), showing 95% confidence level with the precision in most cases being  $\pm 3.0\%$ . Computer software Microsoft excel program was employed for mathematical calculations of the data. Linear regression analysis was carried out to determine slope and intercept of the linear plots obtained and for statistical analysis of the data.

## 3. Results and Discussion

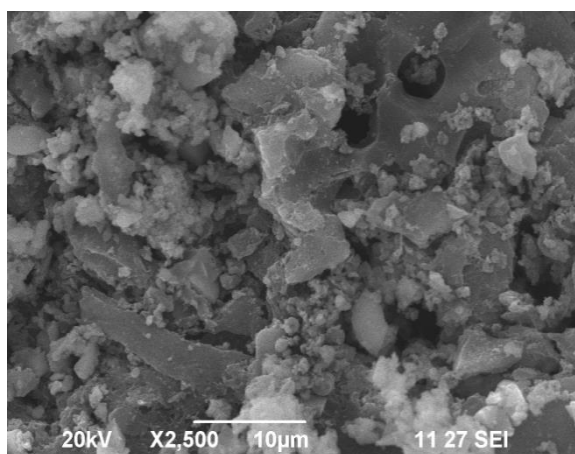
The adsorption of metal ions is influenced by various factors including pH, contact time, initial concentration, amount of adsorbent, and temperature.

### 3.1. Characterization of *C. inermis*

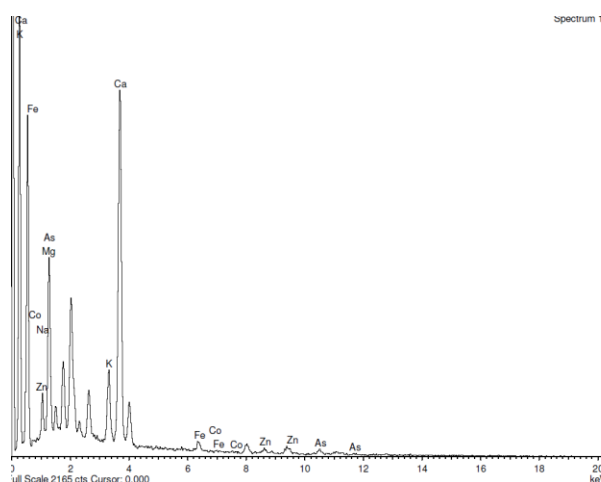
#### 3.1.1. SEM-EDX analysis

Adsorbent (i.e., *C. inermis*) shape and size impact the adsorption capacity of the adsorbent. The SEM micrographs of adsorbent treated Arsenic are presented in fig.1. A clear difference in the surface morphology was observed for Arsenic treated *C. inermis* from adsorbent. SEM image of adsorbent indicating the porous structure and an irregular surface of adsorbent. Arsenic treated *C. inermis* shows many aggregated small particles. The presence of voids on the surface of adsorbent revealed that the possibility of As(III) ion accumulation.

Energy dispersive X-ray(EDX)analysis was conducted to evaluate the adsorption of Arsenic on *C. inerme* . The EDX spectrum for fresh *C. inerme* indicated the presence of Fe, Ca, K, Mg and Co in the structure. but did not show the characteristic signal of As on the surface of freshly synthesized *C.inerme*.



**Figure 1** SEM image of Arsenic treated *C.inerme*



**Figure 2** EDAX pattern of Arsenic treated *C.inerme*

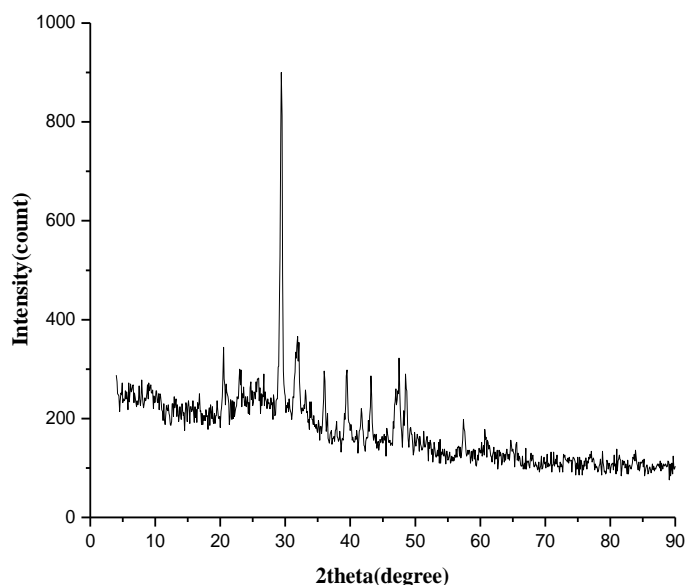
### 3.1.2. XRD analysis

The XRD data of arsenic treated adsorbent(Fig.3) provided evidence of considerable modification over the crystal cleavages by indicating some peak appearance at  $2\theta$  values 29.3616, 31.7883 and 47.4000° and intensity counts at 417,98 and 90. This shows the strong adsorption of arsenic on the surface of the adsorbent.

### 3. 2. Effect of pH

pH is the key factor for the control of the adsorption of metal ions on the adsorbent. The pH of the solution was adjusted using 0.1 N HCl and 0.1N NaOH solutions. The study was done in the pH range of 3 to 12. It was found that the adsorption of arsenic ion gradually increases as the initial pH of the solution is raised from 3 to 7. The maximum removal of arsenic was found to be 86 %, at pH 7. Hence, pH of the arsenic solution was maintained at 7 for further study. This agrees with the other results obtained on iron oxide coated on cement (IOCC)[10], carbon based

adsorbents[11], zero valent iron[12], magnetite-reduced graphene oxide composites[13] and on cellulose loaded with iron oxy hydroxide[14]. At pH more than 7 the removal process is very low. This is due to high OH<sup>-</sup> ion concentration, which reverses the process of removal, and hence the process of conversion of adsorbent into its OH<sup>-</sup> form plays an important role leaving behind arsenic (III) in the aqueous solution. At higher pH, (i.e. greater than 10) almost no removal occurs. This is due to effect of precipitation of Arsenic (III).



**Figure 3** XRD pattern of Arsenic treated *C.inerme*

### 3. 3. Adsorption kinetic modeling

Kinetic models can be helpful to understand the mechanism and the reaction rate of the adsorbate –bio sorbent, operating condition and examined their suitability for practical remediation of metals from natural water. In order to estimate the kinetic arrangement that controls the bio sorption phenomenon, the pseudo-first-order, pseudo-second-order model Weber and Morris model (Intra particle diffusion), and film diffusion model were tested to understand the experimental data.

Kinetic data analysis for arsenic sorption onto *C. inerme* was studied with a pseudo-first-order model [15] and a pseudo-second-order model [16]. The mathematical representations of the models are given in

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (2)$$

$$t / q_t = 1/k_2 q_e^2 + t / q_e \quad (3)$$

where,  $q_e$  and  $q_t$  are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at any time  $t$  (h), respectively; and  $k_1$  ( $h^{-1}$ ) and  $k_2$  (g mg/h) are the related adsorption rate constants. The poor  $r^2$  (0.82) values of the Lagergren pseudo-first-order model indicated that this model does not fitted well with bio sorption of Arsenic on bio sorbent material. For pseudo-second order high correlation coefficients (0.99) were observed for all fits, which indicates that the adsorption reaction could be approximated with a pseudo-second order kinetics model. The rate constant of the pseudo-second-order equation decreases with increasing initial arsenic concentration, indicating that arsenic adsorption may be more favorable at low solute concentration(17).

The initial adsorption rate,  $h$  (mg/(g min)), as  $t \rightarrow 0$ , can be defined as:

$$h = k_2 q_e^2 \quad (4)$$

The initial adsorption rate ( $h$ ) can be calculated based on the pseudo-second-order constants. It can be seen that the  $h$  value of As(III) adsorption at 50 °C was higher than that at 30 °C.

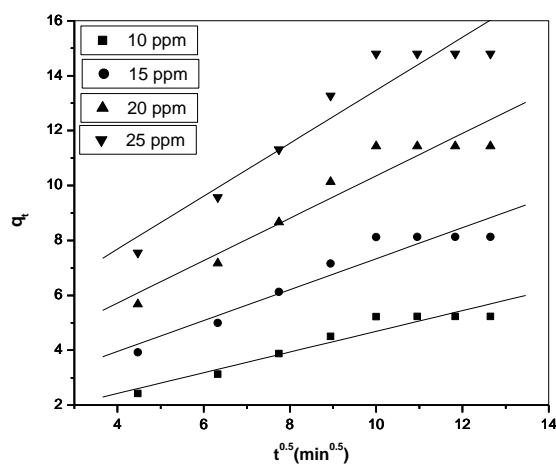
### 3.3.1. Intra particle diffusion

#### 3.3.1.1. Webber and Morris model

The use of the intra particle diffusion model has been greatly explored to analyze nature of the 'rate-controlling step', which is represented by Eq. (5) [18].

$$q = K_{id} t^{0.5} + C \quad (5)$$

where,  $K_{id}$  is intra particle diffusion rate constant (mg/(g min<sup>0.5</sup>)). The Weber and Morris plots of As(III) adsorption on *C. inermis* are shown in Fig.4. It indicates that the intra particle diffusion was not the only rate-limiting step for the whole reaction. Straight lines with a great correlation coefficient ( $r^2 = 0.96$ ) were obtained in very beginning period (20-80min), indicating that initial phase may be controlled by the intra particle diffusion. The greater diffuse rate in the early stage attributed to surface adsorption and gradual adsorption. Afterwards, the intra particle diffusion began to slow due to the low As concentration in solution [19]. The As was initially adsorbed by the exterior surface of the adsorbent. After the adsorption at the exterior surface reached the saturation, As entered the pores within the particles and was adsorbed by the interior surfaces.



**Figure 4** Plot for constant intra particle diffusion (Weber and Morris model) at different concentration

#### 3.3.1.2. Film Diffusion model

The adsorption process being controlled by film diffusion can be explained from the theory of fractional attainment of equilibrium [20]. The equation for fractional attainment of equilibrium is given as follows

$$\ln(1 - \alpha) = K_a t \quad (6)$$

where,  $\alpha$  the fractional attainment of the equilibrium,  $K_a$  - the overall rate constant and  $t$  - time observed that the fractional attainment of equilibrium ( $\alpha$ ) which can be calculated from the equation is an important parameter usually obtained from kinetic studies.

The rate of attainment of equilibrium may either be film diffusion or particle diffusion controlled, however, these two different mechanism cannot be sharply demarcated. A plot of  $\ln(1-\alpha)$  versus  $t$  showing a non-linear plot indicates that film diffusion did not control the arsenic uptake.

### 3.4. Adsorption isotherms

Adsorption of As(III) by *C. inerme* was modeled using the Freundlich and Langmuir isotherm with the quality of the fit assessed using the correlation coefficient. Langmuir isotherm parameter fits for As(III) adsorption on *C. inerme* yielded isotherms that were in good agreement with observed behavior ( $r^2 \geq 0.98$ ). The Arsenic adsorption capacity on *C. inerme* at room temperature (303K) was 2.78 mg/g. Freundlich isotherm constants  $K_F$  and  $n$  are determined from the intercept and slope of a plot of  $\log q_e$  versus  $\log C_e$ . In this study  $n$  values are greater than unity indicating chemisorption [21]. Isotherms with  $n > 1$  are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption [22]. The Freundlich constant,  $K_F$ , which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic.

### 3.5. Thermodynamic studies

An increase in temperature resulted in an increased rate of Arsenic adsorption onto *C. inerme* indicating that the process is endothermic. The Thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K \quad (7)$$

$$\ln K = \Delta S^\circ/R - \Delta H^\circ/RT \quad (8)$$

Based on some literatures, equilibrium constant can be derived from the point  $q_e = 0$  of plot between  $(\ln q_e / c_e)$  and  $q_e$  at different temperatures [23,24]. The plot of  $\ln K$  vs  $1/T$  was found to be linear (Figure not shown),  $\Delta H^\circ$  and  $\Delta S^\circ$  values were calculated from the slope and intercept of the plot by linear regression method. The change in the free energy ( $\Delta G^\circ$ ) is calculated to be  $-1.466$  KJ/mol at  $30^\circ\text{C}$ . The negative value of  $\Delta G^\circ$  means the sorption of Arsenic on the adsorbent is spontaneous, perhaps due to columbic attraction. The decrease in free energy ( $\Delta G^\circ$ ) with the rise in temperature shows an increase in feasibility of adsorption with increasing solution interface. It also indicates the affinity of temperatures [25].

The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $458.94$  KJ/mol and  $1.4612$  J/mol/K. The positive value of  $\Delta H^\circ$  confirms that the sorption process is endothermic in nature. The positive values of  $\Delta S^\circ$  reflect increases the randomness in the system.

### 3.6. Desorption and regeneration studies

Desorption of adsorbed Arsenic onto bio sorbent material was carried out by using different concentrations of HCl and  $\text{HNO}_3$ . It was observed that 1 mol/L HCl desorbed  $>95\%$  of Arsenic, whereas 90% Arsenic was recovered on using 1 mol/L  $\text{HNO}_3$ . For subsequent experiments 10 mL of 1 mol/L HCl was used for dissolution of adsorbed Arsenic on *C. inerme*. The capacity of the bio sorbent material was found to be nearly constant (deviation of 1–3%) after 10 experiments; thus manifold use of the bio sorbent material was seen to be adequate.

## 4. Conclusion

The present work was carried out using activated *Clerodendrum inerme* leaves powder as bio sorbents which were found to be quite effective for the adsorption of arsenic from aqueous solutions.

The effects of process parameters like pH, bio sorbent dosage, Arsenic concentration, contact time, temperature, various isotherm models and kinetic models were studied. *C. inerme* leaves is a high capacitance, economically viable and low cost adsorbent for Arsenic removal. Arsenic adsorption onto *C. inerme* leaves follows a pseudo second order kinetics. Weber and Morris model indicated that the adsorption rate of Arsenic onto the adsorbent is not solely controlled by pore diffusion. The order of isotherm equations obeyed by the present data is Langmuir  $>$  Freundlich isotherm. The bio sorption of Arsenic on the adsorbent is spontaneous and endothermic in nature. Characterization of bio sorbent surface by SEM and EDX revealed that highly accumulation of Arsenic resulting in loss of surface

porosity and roughness. The XRD data of arsenic treated adsorbent shows the strong adsorption of arsenic on the surface of the adsorbent. The sorption of Arsenic was found to be highly pH dependent. It was observed that maximum percentage removal of Arsenic was observed as 86% at pH of 7 and an elevated temperature. This study can conclude that *Clerodendrum inerme* leaves are the favorable alternative of Arsenic removal from water.

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