



## Kinetic Study of Arsenite Adsorption onto Dried Hyacinth Root Powder

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### Abstract

The potential use of dried hyacinth root (DHR) as biosorbent for mitigating arsenic from aqueous solution is studied combining kinetic model and elovich model, using scanning electron microscope coupled with energy dispersive X-ray (SEM-EDX). This analysis suggested the suitability of pseudo-second order type II and type IV kinetic model followed by elovich model for describing the adsorption process of Arsenic-DHR system. The validity of model was further justified based on normalized standard deviation percentage. Also, the applicability of the kinetics models was analyzed with the closeness of the experimental and modeled values of equilibrium adsorption capacity ( $q_e$ ). The SEM images of dried hyacinth roots before and after exposure indicates the adsorption of arsenic onto DHR. EDX spectrum analysis initially did not show any characteristic signal of arsenic but after exposing to an initial concentration of 2 ppm arsenic gives the characteristic peak for arsenic at 1.12, 1.15, 1.28, 10.54, and 11.72 KeV. This confirms the binding of the arsenite ion onto dried hyacinth root. This research concludes that chemisorptions is the rate-limiting step on the basis of highest coefficient of determination,  $R^2$ , and also on the lowest normalized standard deviation percentage,  $\Delta q_i$  (%).

**Keywords:** Adsorption, arsenic, biosorbent, kinetic, dried hyacinth root.

### Introduction

Arsenic is a metalloid. It is present in drinking water as a major global contaminant. The maximum contaminant level for arsenic in drinking water as per World Health Organization (WHO) and United State Environmental Protection Agency (USEPA) is 0.01 ppm. Arsenic contamination was first reported from West Bengal, India in 1983. Gradually it spread to other parts and soon Bangladesh, Pakistan, Chile, Thailand, Sri Lanka, Nepal, Myanmar, USA, United Kingdom, Mongolia, China were also found to be contaminated with arsenic in various concentrations reported by many researchers<sup>1-7</sup>. Arsenic exposure mostly causes mutagenic, carcinogenic, and teratogenic problems<sup>8-10</sup>. Literature survey indicates that several techniques were developed and studied for the removal of arsenic and largely these technologies are based on oxidation, sedimentation, coagulation, sorptive, and membrane filtration. Although the technologies based on these are known to be effective but not far from disadvantages<sup>11-13</sup>. The serious consequences of arsenic poisoning and expensive technologies available for arsenic mitigation have led many researchers to explore a substitute technology. In that effort bio-sorption is one of the known and emerging technologies that have gain momentum in removing heavy metals from aqueous solution.

Biosorption is explained in detailed by Mohan and Pittman<sup>12</sup> as a passive immobilization of metals by biomass. Various adsorbents were tested for arsenic removal. Some of them are mixed metal oxide impregnated chitosen beads (MICB) by Jamila et al.<sup>14</sup>; clays, laterites, soils, lime stones; natural organic based sorbents by Jochen et al.<sup>15</sup>; ferrihydrite, granular ferric

hydroxide, zirconium oxide, fly ash, activated carbon, zeolite, activated alumina were detailed reviewed by Gary et al.<sup>16</sup>. One of the least studied biosorbent for arsenic mitigation is dried hyacinth root (DHR). Dried hyacinth roots, being cheap and locally available is considered as one of the most promising adsorbent for mitigating heavy metals from aqueous solution<sup>17-24</sup>.

The endeavor of this study is to explore the morphological structure in order to indentify the adsorptive capacity and also investigate the adsorption kinetics of arsenite by dried hyacinth root at different temperatures. Results were used to appraise the effectiveness of an adsorbent DHR for arsenic removal. This research article is organized as follows: first the morphological structure is indentified using SEM and elemental analysis were conducted by EDX followed by application of various kinetic models in an attempt to probe into the suitability of kinetic model to describe the adsorption processes involved in arsenic-DHR system.

### Material and Methods

**Materials:** Dried hyacinth root powder was prepared in laboratory of Department of Civil and Environmental Engineering, Birla Institute of Technology, Mesra, Ranchi. After the preparation of DHR powder sieving with a sieve stack was conducted to extract different sizes. Three different sizes 0.212, 0.106, and 0.063mm were obtained. A Stock solution of arsenite (As III) was prepared using Sodium arsenite 'Excel R'  $\text{NaAsO}_2$  (mol. wt. 129.91).

**Batch Experiments:** Kinetic experiments were carried out in a set of 200 ml beaker containing 100 ml of aqueous adsorbate solution with an initial concentration of 2 ppm. Adsorbent dried hyacinth root powder was added to the aqueous As (III) solution in the amount of 1 gm, and the mixture was stirred at an agitation speed of 300 rpm using a magnetic stirrer in temperature ranging from 4°C to 36°C. At different contact time from 12 minute to 192 minute, 10 ml aliquots were withdrawn and the adsorbent was separated from the adsorbate by using syringe filter of 0.2 µm. The arsenite concentration of supernatant was analysed by using inductively coupled plasma-optical emission spectrometry (ICP-OES) at a wavelength of 193.696 nm.

## Result and Discussion

**SEM-EDX analysis:** The microanalysis concerning the structure and elemental composition of dried hyacinth root before and after arsenic exposure was studied by SEM-EDX (Model JSM 6390 LV, JELO). SEM analysis was carried out at three different magnifications of 500X, 2000X, and 5000X

respectively. For comparison of all three magnifications of DHR before and after exposure to arsenite is depicted in figure-1a and 1b. SEM was used to image As (III) on dried hyacinth roots. Dried roots of hyacinth were found to be contaminated with arsenite as shown by white spots in figure-1b. These micrographs categorically show that As (III) is concentrated on the external surface of the roots (figure-1b).

Energy-Dispersive X ray spectroscopy was conducted to determine the elemental composition of DHR. The EDX spectrum of fresh dried hyacinth root shows the presence of sulphur at 2.31, 2.46 KeV; oxygen at 0.53 KeV; phosphorous at 2.02, 2.14 KeV; silicon at 1.75 KeV; nitrogen at 0.33 KeV; and carbon at 0.28 KeV but did not show the characteristics signal of As (III) on the surface of dried hyacinth roots as depicted in figure-2a. After exposing DHR to initial concentration of 2 ppm arsenite, the EDX spectrum shows the characteristic peaks for arsenite at 1.12, 1.15, 1.28, 10.54, and 11.72 KeV as depicted in Figure 2b. This explicitly shows the binding of arsenite to the dried hyacinth root surface.

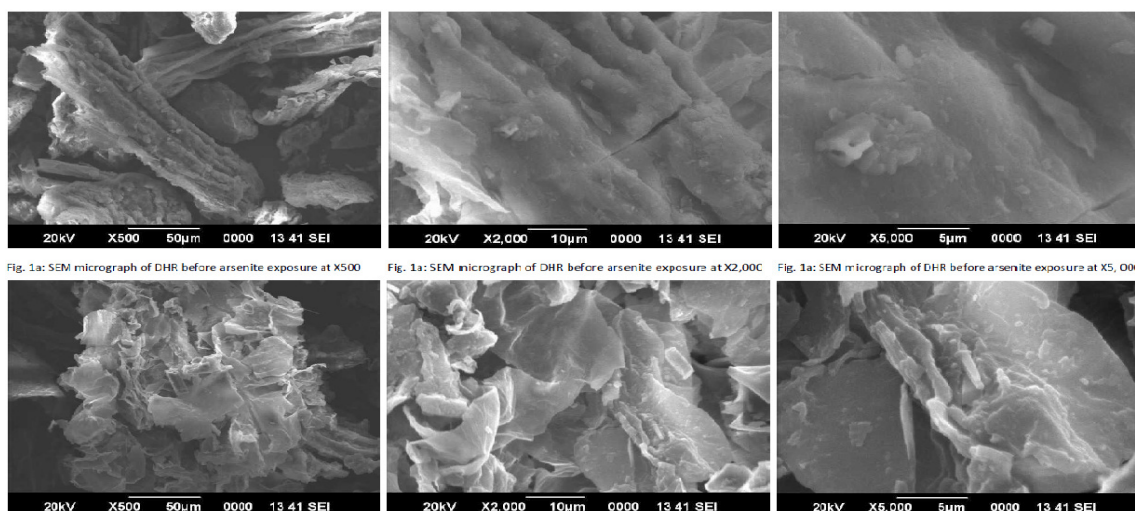


Fig. 1a: SEM micrograph of DHR before arsenite exposure at X500

Fig. 1a: SEM micrograph of DHR before arsenite exposure at X2,000

Fig. 1a: SEM micrograph of DHR before arsenite exposure at X5,000

Figure-1

(a) DHR before arsenite exposure (b) DHR after arsenite exposure

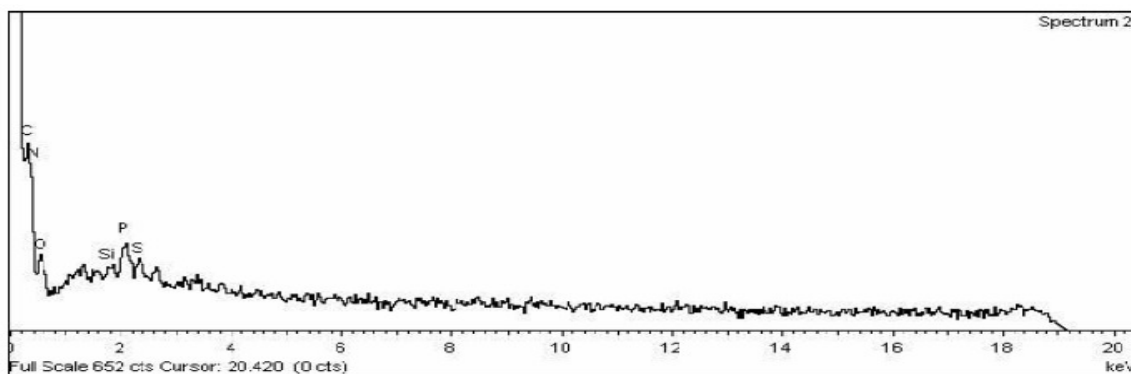
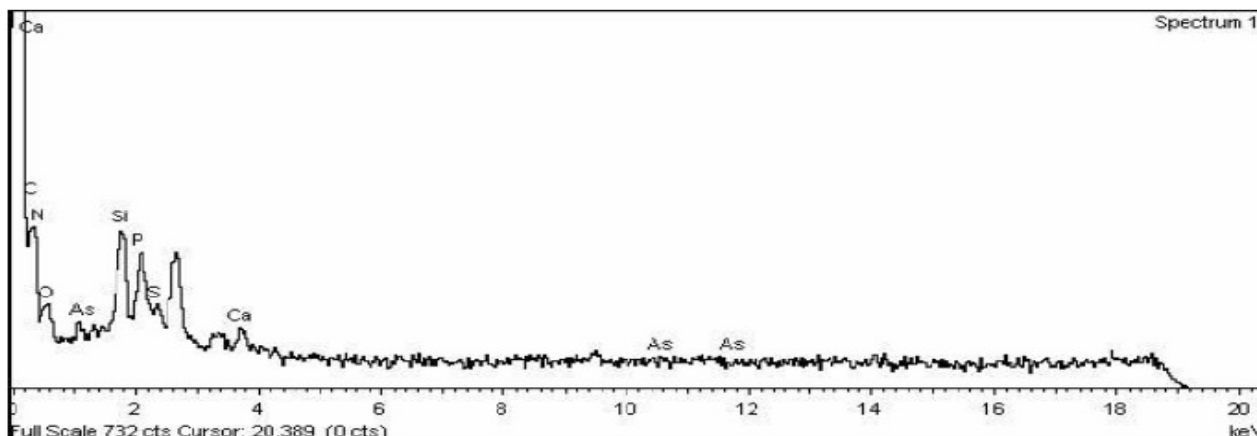


Figure-2a

EDX of DHR before arsenite exposure



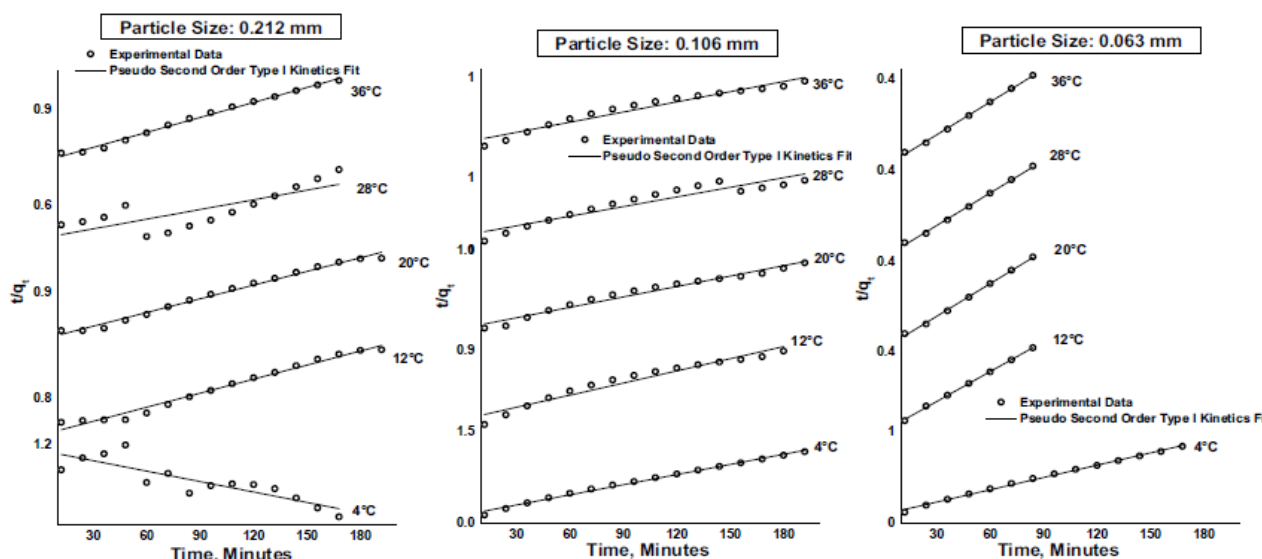
**Figure-2b**  
 EDX of DHR of after arsenite exposure

**Kinetic Studies:** Literature survey illustrates various kinetic models to describe adsorption processes<sup>25,26,27</sup>. In this study kinetic first order, pseudo first order and second order, pseudo-second order Type I, Type II, Type III, and Type IV along with elovich equation were applied to explain the kinetics of the adsorption process of varied sized DHR. The suitability of model is based on normalized standard deviation percentage and coefficient of determination ( $R^2$ ). By comparing all kinetic models it was deduced that kinetic first order, pseudo first order and second order was completely not applicable to explain adsorption process. However, comparing all types of pseudo-second order and elovich model, it was inferred that these models are capable to explain adsorption process. This article, therefore, focused only on all types of pseudo-second order and elovich model. However the comparison of all kinetic models is depicted in table-3.

**Pseudo-Second Order Kinetic Model:** Blanchard et al. in 1984 proposed pseudo-second order model to illustrate the adsorption kinetics of ammonium ion by natural zeolite. The modified version of pseudo-second order was later on given by HO and McKay in 2002 which is linearly expressed in Equation 1 to describe the sorption of copper (II) ion on to peat.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (1)$$

Where  $q_t$  is the amount of solute adsorbed on adsorbent (mg/g) at any time (t);  $q_e$  is the amount of solute adsorbed at equilibrium (mg/g); and  $K_2$  is the constant of pseudo-second order kinetic model (g/mg/min);  $K_2 q_e^2$  (mg/g/min) is the initial adsorption rate.



**Figure-3a**  
 Pseudo-second-order Type I kinetics plots for biosorption of arsenite (As III) onto Dried Hyacinth Root (DHR)

The pseudo-second order model is based on the assumption that one adsorbate ion adsorbed onto two sorption site of an adsorbent. The value of  $K_2$  and  $q_e$  (cal) were calculated from the slopes and intercepts of the linear plots of all pseudo-second order Type I ( $t/q_t$  versus  $t$ ) depicted in figure-3a, Type II ( $1/q_t$  vs.  $1/t$ ) in figure-3b, Type III ( $q_t$  vs.  $q_t/t$ ) in figure-3c and Type IV ( $q_t/t$  vs.  $q_t$ ) in figure-3d. Comparing the value of experimental equilibrium ( $q_e$  exp.) and calculated value of equilibrium ( $q_e$  cal) shows marked deviation for pseudo second order Type I and Type III as depicted in table-1, whereas the  $q_e$  (exp) and  $q_e$  (cal) values for pseudo-second order Type II and Type IV were in

good agreement with each other as shown in table-1. For pseudo-second order Type I and Type III, the experimental data deviate considerably from the calculated data suggests that the adsorption of arsenite on dried hyacinth root did not follow it, in spite of high value of 0.99 for coefficient of determination ( $R^2$ ). Pseudo-second order Type II and Type IV shows good agreement between the experimental and calculated values and also the coefficient of determination ( $R^2$ ) over the entire range of temperatures indicates that this model was appropriate for illustrating the adsorption process of arsenite ion.

Table-1

Comparison of Pseudo-second order Type I, Type II, Type III and Type IV Rate constant & other parameters at varied temperature of varied sized DHR

Size mm	Tmp °C	$q_e$ exp mg/g	Pseudo-second-order kinetic equation											
			Type I			Type II			Type III			Type IV		
			$q_e$ (cal) (mg/g)	$K_2$ (g/mg.min)	$R^2$	$q_e$ (cal) mg/g	$K_2$ (g/mg.min)	$R^2$	$q_e$ (cal) mg/g	$K_2$ (g/mg.min)	$R^2$	$q_e$ (cal) (mg/g)	$K_2$ (g/mg.min)	$R^2$
0.212	4	190	-653	$1.9 \times 10^{-6}$	0.82	190	$3.4 \times 10^{-7}$	0.99	504	0.821	0.80	192	$-2.11 \times 10^{-6}$	0.94
	12	155	242	$3.5 \times 10^{-5}$	0.98	154	$1.9 \times 10^{-5}$	0.99	240	2.079	0.95	152	$-3.13 \times 10^{-5}$	0.97
	20	155	221	$4.7 \times 10^{-5}$	0.98	155	$3.6 \times 10^{-5}$	0.99	216	2.386	0.95	157	$-5.0 \times 10^{-5}$	0.90
	28	199	238	0.00014	0.85	199	$2.6 \times 10^{-6}$	0.98	262	4.162	0.81	196	$-2.62 \times 10^{-6}$	0.91
	36	140	202	$6.2 \times 10^{-5}$	0.99	140	$5.0 \times 10^{-5}$	0.99	199	2.612	0.96	143	$-6.2 \times 10^{-5}$	0.88
0.106	4	163	179	0.00236	0.99	163	0.00061	0.82	159	13.595	0.83	162	-0.00038	0.82
	12	199	249	$7.1 \times 10^{-5}$	0.95	199	0.00023	0.90	200	7.041	0.82	198	-0.00011	0.90
	20	199	263	$5.9 \times 10^{-5}$	0.96	198	0.00011	0.97	229	5.083	0.85	198	$-7.8 \times 10^{-5}$	0.97
	28	199	160	0.00039	0.90	200	0.00051	0.88	179	12.986	0.81	197	-0.00015	0.88
	36	199	268	$4.8 \times 10^{-5}$	0.95	198	0.00011	0.97	223	4.534	0.82	198	$-6.8 \times 10^{-5}$	0.97
0.063	4	199	221	0.000236	0.99	199	0.00061	0.94	205	13.59	0.89	199	-0.00038	0.99
	12	199	227	0.000071	0.99	199	0.00023	0.97	222	7.04	0.95	198	-0.00011	0.99
	20	199	212	0.000059	0.99	198	0.0001	0.90	216	5.08	0.87	199	-0.00007	0.99
	28	199	212	0.00039	0.98	200	0.0005	0.91	218	9.98	0.88	199	-0.00015	0.98
	36	199	208	0.00008	0.99	199	0.0001	0.88	215	5.53	0.85	197	-0.00068	0.99

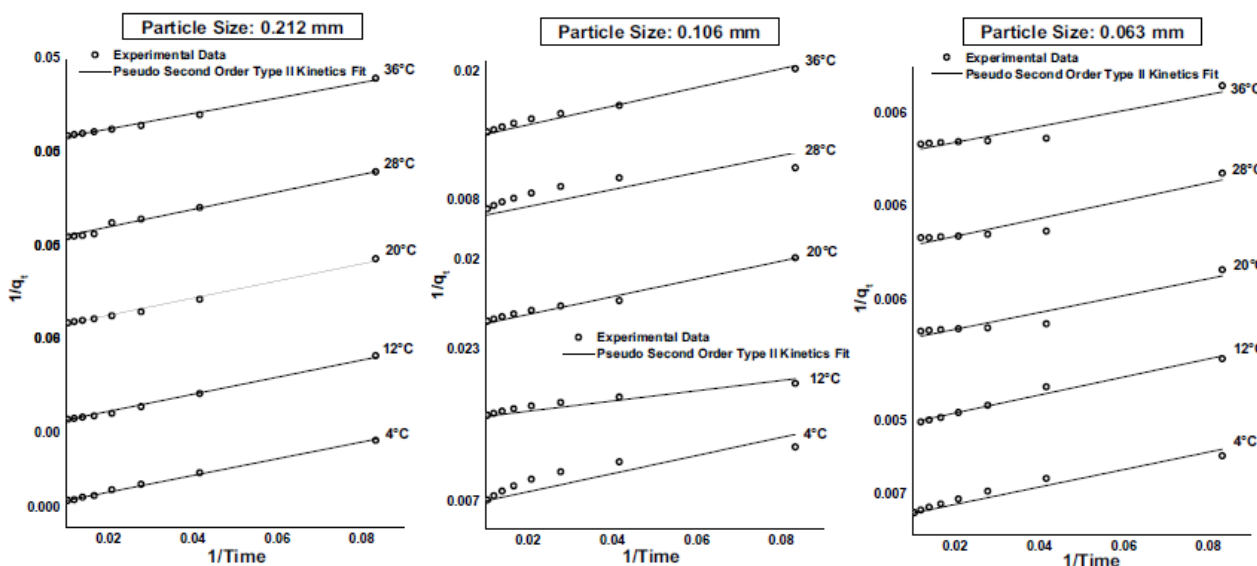


Figure-3b

Pseudo-second-order Type II kinetics plots for biosorption of arsenite (As III) onto Dried Hyacinth Root (DHR)

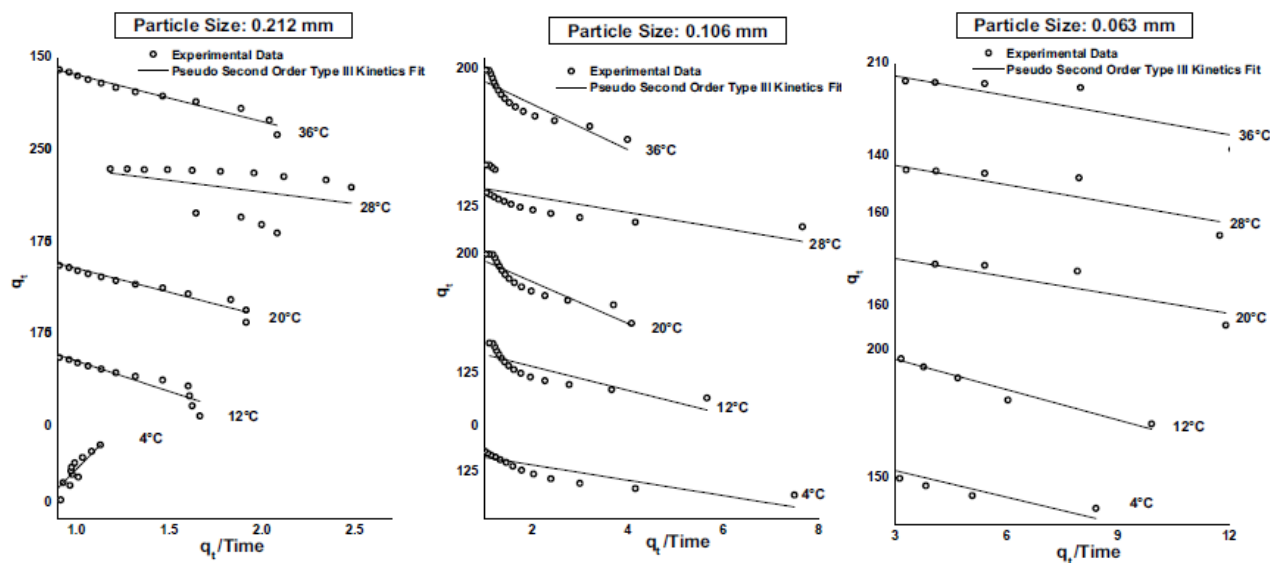


Figure-3c

Pseudo-second-order Type III kinetics plots for biosorption of arsenite (As III) onto Dried Hyacinth Root (DHR)

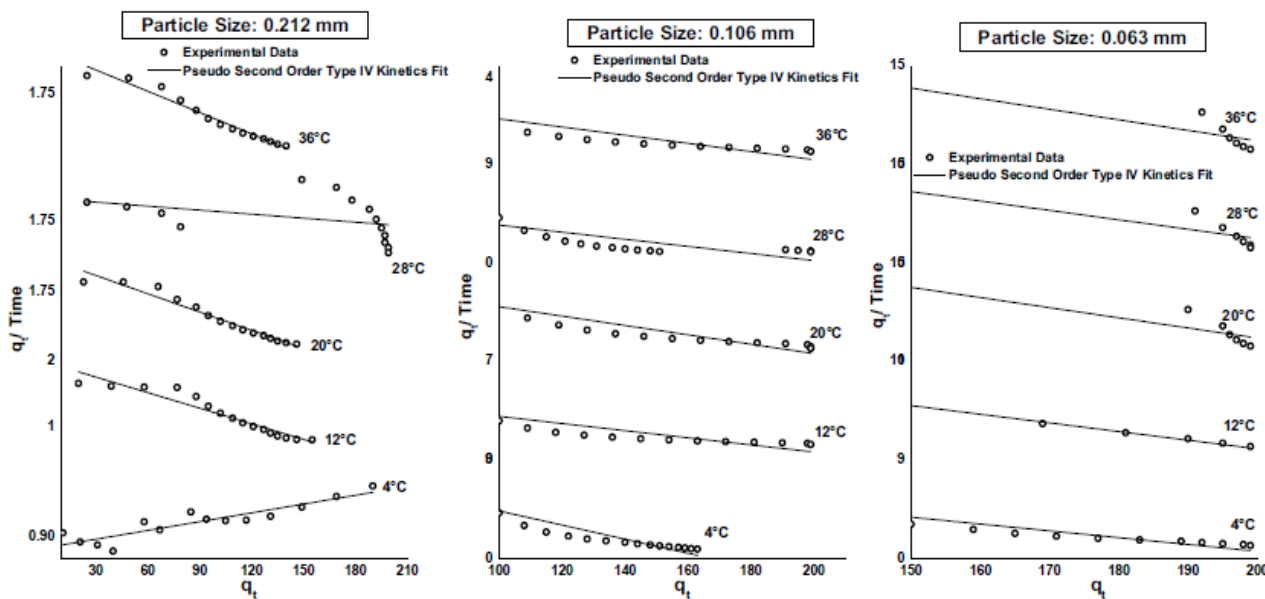


Figure-3d

Pseudo-second-order Type IV kinetics plots for biosorption of arsenite (As III) onto Dried Hyacinth Root (DHR)

**Elovich Model:** The Roginsky- Zeldovich or Elovich equation is generally expressed as follows in equation-2a;

$$\frac{dq}{dt} = \alpha \exp(-\beta q) \quad (2a)$$

Where  $\alpha$  is the initial adsorption rate (mg/g min) and  $\beta$  is desorption constant (g/mg) energy. This equation is further simplified to;

$$q_t = \frac{1}{\alpha \ln(\alpha \beta)} + \frac{1}{\beta \ln(t)} \quad (2b)$$

The plot of  $q_t$  versus  $\ln(t)$  yields a linear relationship with a slope and an intercept within the varied temperature depicted in figure-4, and this suggests arsenite fits the elovich model. The value of experimental  $q_e$  (exp.) and calculated  $q_e$  (cal.) were found to be in good agreement with each other along with highest coefficient of determination ( $R^2$ ) in the range of 0.91 to 0.99 within the varied temperature studied depicted in table-2. Besides, the Elovich model constant  $\alpha$  (mg/g min) and  $\beta$  (g/mg) primarily increased with temperature but after certain interval at highest temperature it started decreasing.

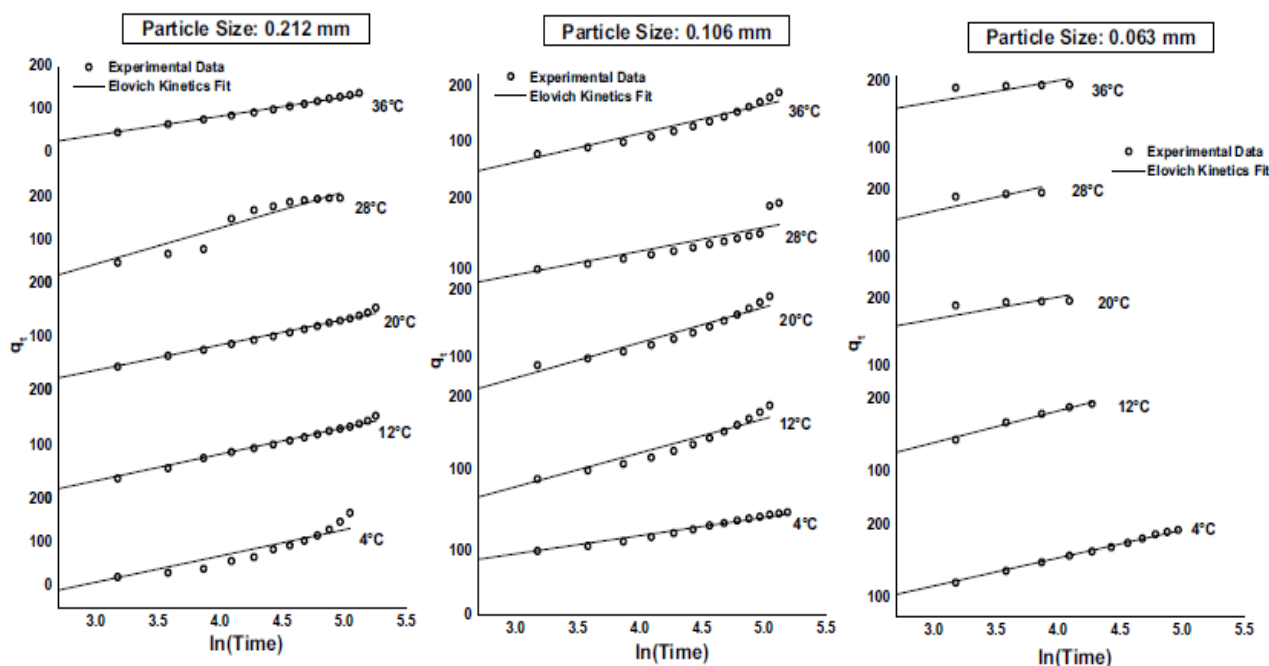


Fig. 4 Elovich equation plots for biosorption of arsenite (As III) onto Dried Hyacinth Roots (DHR)

**Figure-4**  
**Elovich equation plots for biosorption of arsenite (As III) onto Dried Hyacinth Roots (DHR)**

This indicates that the initial sorption rates and the amount of surface of DHR covered by arsenite ion primarily increases with temperature up to 28°C and after that decreases with further rise in temperature at 36°C.

**Validity of Kinetic Model:** Based on comparison of experimental and calculated value of equilibrium it was found that the best suited model to describe adsorption process was pseudo-second order Type II and Type IV followed by elovich model. The applicability of these models were further validated by applying normalized standard deviation,  $\Delta q_t$  (%), which is defined in Equation 3 according to Tan et al<sup>28</sup>.

$$\Delta q_t(\%) = \sqrt{\frac{\sum (q_e(\text{exp}) - q_e(\text{cal}))^2}{q_e(\text{exp.})}} \times 100\% \quad (3)$$

Where, N is the number of data points. The  $\Delta q_t$  (%) value for pseudo second order Type I, Type II, Type III and Type IV models along with Elovich model are depicted in table-3.

Average value of  $\Delta q_t$  (%) for pseudo second order Type II and Type IV along with elovich model was found to be lowest among all described models. This lowest value of standard deviation percentage confirms pseudo-second order Type II and Type IV followed by elovich model as best fit model to describe the adsorption process of arsenic-DHR system.

## Conclusion

Arsenic is a major pollutant found in groundwater and various researches have been conducted hitherto for mitigating arsenic. Several adsorbents were explored but the need of present is to investigate sustainable biosorbent for removing arsenic. Dried hyacinth root is one such adsorbent found to be effective and efficient. This study was conducted to explore the adsorption kinetics of arsenite ion on dried hyacinth root. Based on SEM-EDX analysis it was confirmed that arsenite is adsorbed on the surface of dried hyacinth root. Further on the basis of average lowest standard deviation percentage of pseudo second order type II, and IV followed by elovich model found to be suitable best-fit model to describe the adsorption process of arsenic-dried hyacinth root system among all kinetic models. By comparing all kinetic models, this study concludes that chemisorption is the rate-limiting step on the basis of lowest normalized standard deviation and highest coefficient of determination for explaining adsorption kinetics of arsenic on dried hyacinth root system.

## Acknowledgement

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**Table-2**  
**Elovich model of varied sized DHR at varied temperature**

Size(mm)	Temp°C	q <sub>e</sub> (exp) (mg/g)	α (mg/g. min.)	β (g/mg)	q <sub>e</sub> (cal) (mg/g)	R <sup>2</sup>
0.212	4	190	5.2x10 <sup>-6</sup>	30	192	0.839
	12	155	0.0012	45	155	0.986
	20	155	0.00015	46	153	0.986
	28	199	0.0053	63	198	0.911
	36	140	4.2x10 <sup>-5</sup>	43	141	0.992
0.106	4	163	1.6x10 <sup>-6</sup>	28	161	0.968
	12	199	0.00011	37	198	0.928
	20	199	0.00019	48	198	0.961
	28	199	0.00076	53	199	0.974
	36	199	4.2x10 <sup>-5</sup>	43	197	0.944
0.063	4	199	5.6x10 <sup>-5</sup>	35	198	0.961
	12	199	0.0005	42	197	0.991
	20	199	0.0002	47	196	0.973
	28	199	0.0002	49	199	0.977
	36	199	1.4x10 <sup>-7</sup>	31	199	0.970

**Table-3**  
**Comparison of Normalized Standard Deviation Percentage Value of various Kinetic Model and Elovich Model**

Size (mm)	Temp°C	Kinetic Models							Elovich model
		First order	Pseudo-first-order	Second-order	Pseudo-second-order (Type I)	Pseudo-second-order (Type II)	Pseudo-second-order (Type III)	Pseudo-second-order (Type IV)	
<b>0.212</b>	4	38	165	95	243	1.02	748	3	32.0
	12	1	54	41	56	3.42	95	1.4	2.0
	20	3	12	39	42	5.63	56	4	4.0
	28	123	31	91	19	1.01	348	3	4.0
	36	16	42	77	44	5.0	56	2	3.0
$\Delta q_t$ (%)		36.2	60	68.6	80.8	3.2	260	2.7	9.0
<b>0.106</b>	4	14	232	92	9	4.0	2	4	1.21
	12	1	62	96	25	0.5	11	6	3.5
	20	5	40	96	32	5.0	22	1.1	4.0
	28	112	350	98	19	1.2	4	1.7	2.5
	36	0	45	96	34	1.0	21	3	9.0
$\Delta q_t$ (%)		26.4	145	95.6	23.8	2.3	12	3.2	4.0
<b>0.063</b>	4	32	36	97	11	3	5	1.1	1.0
	12	15	15	94	14	2.1	12	1.4	1.5
	20	11	11	97	6	2	12	5	2.0
	28	10	10	10	6	4	13	3	3.0
	36	22	22	5	4	3	11	4	4.5
$\Delta q_t$ (%)		18	18.8	60.6	8.2	2.8	10.6	2.9	2.4

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