

Remediation of arsenic from water by utilizing waste of Jatropha seed cake as low cost and ecofriendly bio-adsorbent

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Abstract:

A low- cost, eco-friendly and highly efficient activated bio-adsorbent (*AC-JSC*) is prepared by carbonization of waste Jatropha seed cake. The prepared *AC-JSC* bio-adsorbent has been utilized for the removal of arsenic from contaminated water without any chemical modification. Various experimental parameters, including adsorbent dose, initial arsenic concentration, contact time and pH of the medium, were investigated to evaluate the performance efficiency. The experimental results revealed that the *AC-JSC* has significant removal efficiency for arsenic and pH of the solution has influential effect on the sorption process. The *AC-JSC* could successfully reduce the arsenic concentration as per permissible limit (WHO: 10µg/L). The adsorption isotherm models, Langmuir ($b = 146$ for As^V , and $b = 96.1$ for As^{III}) and Freundlich ($K_f = 0.671$, $n = 0.350$) for As^V and ($K_f = 0.964$, $n = 0.250$) for As^{III} were calculated to describe the adsorption kinetics. The thermodynamic studies of the present system indicates the spontaneous process of adsorption (ΔG : -8.58 KJ/mol and -8.60 KJ/mol) for As^V and As^{III} respectively. The results reveals that bio adsorbent derived from the industrial waste generated from bio-fuel industry would be a potential low-cost adsorbent for the remediation of arsenic from contaminated water.

Key Words: Waste Jatropha seeds cake, Adsorption, Arsenic removal, Kinetic and Isotherm model

Introduction

Water is an essential natural resource for sustaining life and environment which have been thought to be available in abundance and gratuitous gift of nature. It has been reported that

more than 80 countries around the world encounter severe water shortage and about 25% of the population do not have adequate access to fresh water with satisfactory quantity and quality. [1,2]. Apparently, groundwater, being the main source of drinking water worldwide is contaminated with various types of toxic contaminants via natural as well anthropogenic sources[3]. Arsenic has been found one of the most toxic pollutants among others contaminants due to its carcinogenic and toxic effect on living beings. High arsenic concentrations have been reported in various pockets of the globe (approximately 21 countries) such as USA, China, Chile, Bangladesh, Mexico, Argentina, Poland, Canada, Hungary, Japan and India [4-6]. The largest population at risk among the various countries with known ground water arsenic contamination is in Bangladesh, followed by West Bengal in India [7]. Since, these populace are heavily dependent of ground water sources for drinking water, are suffering from the big health issue called arsenicosis.

In natural water, arsenic is present in both organic as well as in inorganic forms. The inorganic form of arsenic is more fatal compared to organic form as it can deactivate more than 200 enzymes responsible for the DNA synthesis and involve in cellular energy pathways whereas organic arsenic bio- transform and detoxifies through methylation. In the inorganic forms of arsenic As^{III} is 60 times more lethal than As^V . The long term intake of high concentration of both forms of arsenic causes chronic intoxication of various parts of body such as liver, skin and results in the various types and level of cancers along with the damage the central nervous system, [8]. The World Health Organization (WHO) has set the maximum safe concentration of arsenic in drinking water to be 0.01 mg/L [9]. Various remediation techniques, such as adsorption [10], membrane separation, [11, 12] coagulation and precipitation, and lime softening [13] have been so far explored for the removal of arsenic from water. Among various techniques, adsorption is considered as most promising and feasible technique for removal of different types of organic and inorganic pollutants because of its simplicity, cost-effectiveness and removal-effectiveness, especially convenient for application in rural areas [10]. A wide range of sorbent materials such as clay minerals, zeolites and metal oxides, activated carbons polymeric adsorbents and resins have been used for the removal of arsenic from water [14]. Moreover, the utilization of green adsorbent (bio-adsorbents) derived from industrial and agricultural waste streams have emerged as economically viable, eco-friendly and sustainable water treatment technology, which has several advantages compare to other conventional adsorbent materials including cost efficacy, efficiency minimization of chemical or biological sludge, requisite of adsorbent nutrients, and regeneration of bio adsorbent with possibility of metal recuperation[15,16].

Various adsorbent derived from certain agricultural and industrial by-products have been explored as bio-adsorbents to adsorb cationic, anionic and neutral metal species [17] such as waste tea fungal biomass [18] rice husks [19] red mud [20] and fly ash [21] etc., have also been utilized as good and inexpensive sorbents for arsenic. Nevertheless, use of *Jatropha* plant material as bio adsorbent for remediating arsenic from water is still scares.

Jatropha curcas is a non-edible, oil bearing and draught hardy shrub, belongs to the Euphorbiaceae family, comprising of approximately 8000 species belonging to 321 genera. *Jatropha curcas* is economically advantageous for the production of biofuel in several countries worldwide [22]. In the recent years, the plantation of *Jatropha*, as a commercial crops has been increased abundantly due to its increase in biodiesel demand. After extracting oil from the seed large amounts of solid seed cake has resulted as waste residue [23]. This huge amount of waste residue is disposed of into the open land fill or can be used as fertilizer as it contains lignocellulosic compounds, water, minerals and proteins. Otherwise, the waste residue has no economic value. Thus, utilization of agro-industrial wastes (waste cake) as bio adsorbent could be a viable option for the removal of hazardous ions from water due to low costs, lack of any treatment, and derivation from renewable sources. The utilization of *Jatropha* waste as green adsorbent has been still scares except few for the removal of cadmium [24, 25] which would be an excellent and environmental friendly approach. Moreover, to date no study has been reported on the removal of arsenic carbon derived from waste cake of *Jatropha* seed.

In this work, we have utilized activated carbon derived from *Jatropha* waste seed cake after extracting oil from the seed as bio adsorbent (*AC-JSC*) for the removal of arsenic from water.. The *Jatropha* seed cake waste, generated by the biofuel industry can be considered as a potential low-cost sorbent for the abstraction of arsenic. To evaluate the removal efficiency of *AS-JSC*, for arsenic various experimental parameters such as adsorbent dose, feed solution's concentration, pH, contact time. The adsorption kinetics were evaluated by adsorption isotherm, thermodynamics etc., for the adsorptive process.

Experimental

Materials and Methods:

Jatropha seed cake obtained from the biodiesel unit, CSIR-CSMCRI, G.B. Marg, Bhavnagar, Gujarat India. This is the raw material used to prepare the adsorbent has no economic value. It's just as a waste residue after removing oil from the *Jatropha* seeds and generally dumped in the open land fil. Deionised water having conductivity: 2.9 $\mu\text{S/m}$, pH: 7.0 \pm 0.1 and total

dissolved solids (TDS): 2.0 mg/L was used in all the experiments. Sodium arsenate (Na_2HAsO_4) and Sodium Arsenite (NaAsO_2) have been purchased from Sigma-Aldrich, USA. A stock solution of arsenic (As^{V} : 1000 mg/L, As^{III} : 1000 mg/L) was prepared by dissolving 4.16 gm of Na_2HAsO_4 and 1.733 gm of NaAsO_2 in deionised water and further diluted to the desired concentration levels.. Sodium chloride (NaCl), sodium bicarbonate (NaHCO_3), sodium sulphate (Na_2SO_4) and sodium nitrate (NaNO_3) were used as purchased from Fisher Scientific, India.

Preparation of the bio- sorbents (AC-JSC)

The bio-adsorbent was prepared by simple and eco-friendly method. First, the waste Jatropha seed cake (JSC) was collected from oil expeller unit at Chemical Shed CSIR-CSMCRI, Bhavnagar Gujarat, India. The collected seed cake was thoroughly washed with hot water to remove soluble components. The washed seed cake was filtered out and air dried followed by oven dried at $85 \pm 10^\circ\text{C}$ until reaching a constant weight. The dried seed cake was crushed into powdered form and carbonized in a muffle furnace at $600 \pm 5^\circ\text{C}$ for 6 hrs. After carbonization, the carbonized jatropha seed cake (AC-JSC) was again thoroughly washed with distilled water till to attain neutral pH, then filtered out followed by air dry. Subsequently obtained product (AC-JSC) was oven-dried at 100°C for 24 hrs to volatilize any organic impurities, sieved to a particle size of 250–500 μm [60–35 mesh ASTM (American Society for Testing and Materials)], and kept in an air-tight container. This AC-JSC was directly used as bio-adsorbent without any chemical modification to evaluate its performance for removal of arsenic. The preparative steps for the bio-adsorbent is shown in the Fig. 1

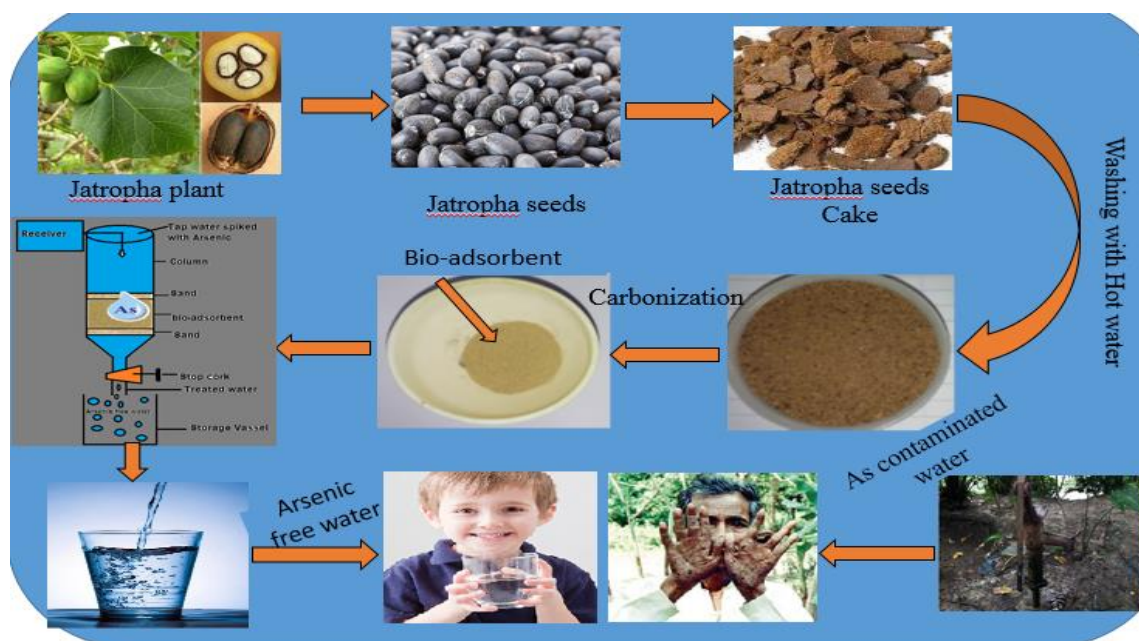


Fig. 1: Schematic process flow of adsorbent preparation

Adsorption experiment

The performance evolution study of prepared AC-JSC to remove arsenic was carried out by both batch and column method. The stock solution of As^V (1000 mg/L) and As^{III} (1000 mg/L) prepared in distilled water was used for this study.

Batch adsorption experiments

Preliminary, batch adsorption equilibrium study was carried out, to evaluate the adsorption of As^V using AC-JSC in aqueous solution. In batch mode of operation, the experiments were carried out by varying experimental parameters such as time (10 to 250 minutes), dose of adsorbent (0.1 to 1.5 gm/L), initial concentrations (100 to 700 $\mu\text{g/L}$), pH (2.0 ± 0.1 - 12.0 ± 0.1) and temperature ($30^\circ\text{C} \pm 1.0^\circ\text{C}$) of the medium while keeping other parameter constant such as agitation speed (120rpm). 1.0 gm of dry AC-JSC was added into the reaction vessel of 1.0 L containing 100 mL arsenic solution separately of known concentrations. The mixture was kept on constant stirring (120 rpm) to minimize the effect of bulk mass transfer on the reaction rate until maximum uptake was achieved. The samples were collected at a fixed time interval and filtered through syringe filter (syringe driven filter: 0.22 micron) before analysing the residual arsenic concentration using ICP-MS. All batch adsorption experiments were carried out at ambient temperature ($30 \pm 1.0^\circ\text{C}$). To decrement the experiment error, each adsorption experiment was conducted three times. The amount of arsenic adsorbed at equilibrium per unit mass of the bio adsorbents (q_e , $\mu\text{g/g}$ and mg/g) was calculated using the equation.

$$\text{Adsorption capacity}(q_e) = \frac{(C_0 - C_e) \left(\frac{mg}{L}\right) \times V(L)}{m(g)} \dots\dots\dots (1)$$

Where q_e is the adsorption capacity (mg/g) in the solid at equilibrium; C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of Arsenic (mg/L), respectively; V (L) is the volume of the aqueous solution and m is the mass (g) of adsorbent used in the experiments.

Fixed bed column adsorption experiment

Continuous Up-flow column adsorption experiments were conducted in a fixed bed using glass column with a total length of 1.0 m and an internal diameter of 0.015 m. 10.0gm of AC-JSC was packed in glass column in between two small layers of glass wool. Feed water of arsenic (As^V and As^{III} - 250 μ g/L) was passed through the columns with the fixed flow rate of 5.0 BV till breakthrough.

Reusability after Desorption experiment

The reusability of any adsorbent is one of the important parameter from the economics as well as environmental point of view, as it help to reduce the cost as well as environmental impact of disposal. Hydrochloric acid has been used as desorption agent for this desorption study. Once the bio-adsorbent (AC-JSC) was exhausted. 1.0 gm of exhausted AC-JSC was added into 0.1N HCl (200mL) and kept it for 24 hrs. To test the reusability of the adsorbent, same adsorbent were washed with degionised water and desorption process were reiterated for five times. The amount of As^V ion relinquished from AC-JSC after washing process again analysed. The (%) desorption of arsenic from AC-JSC was calculated by percentage of the deduction amount of As^V ions adsorbed on AC-JSC to the concentration of arsenic in the desorption medium.

The adsorption efficiencies after regeneration (q_r) of AC-JSC adsorbent of different consequent cycle of regeneration was evaluated using equation (1), whereas desorption efficiency (% DE) of AC-JSC for each consecutive cycle of operation was calculated as-

$$DE(\%) = \frac{C_0 - C_e}{C_0} 100 \dots\dots\dots (2)$$

Where, C_0 and C_e are initial and equilibrium concentrations of Arsenic (μ g/L) of each consecutive cycle of adsorption and desorption respectively, while q_r and q_e represent adsorption efficiencies of regenerated and pristine adsorbent respectively.

Characterization

The *Jatropha* seeds cake raw and carbonized both were characterized by instrumental techniques. Fourier transform infra-red spectroscopy (FTIR) (Perkin Elmer Spectrum GX FT-IR Microscope), were done to analyse the organic function groups of the adsorbent Spectra were obtained by transmittance with potassium bromide pellets (KBr). The surface morphology and element composition of *AC-JSC* powder, before and after adsorption of arsenic were examined with a FESEM-EDX (JEOL JSM 7100 F, Japan). Element composition in terms of sulphur, carbon, hydrogen, oxygen and nitrogen was measure using CHNSO Elemental Analyser, vario MICRO cube, Germany. The pore size and specific surface area of carbonised *Jatropha* seeds cake (*AC-JSC*) were measured by BET, in the presence of N₂ atmosphere (Micromeritics ASAP2010, USA).

Presence of arsenic in the water before and after adsorption, collected at different time interval were filtered out with syringe driven filter (PVDF hydrophilic membrane: 0.22 micron) to analyse the residual arsenic in water using Inductive Couple Plasma Mass Spectrometer (ICP-MS, ThermoFisher Scientific, iCAP RQ, Europe). Minimum and maximum limit of arsenic detection is 5 to 100 µg/L. The pH of the samples were analysed by Eutech PC 700 with pH electrode.

Result and discussion

Synthesis

After carbonization the ready to use *AC-JSC* adsorbent has grey colour appearance, having high average surface area of 481m²/g. Generally the activation of any bio-adsorbent is carried out by chemical (acid and alkaline treatment) and thermal treatment to improve the surface area which would further results in improved adsorption process with increased rate of reaction. For this materials, we adopted thermal activation approach to activate the adsorbent to improve surface area for enhanced adsorption. Post treatment of water is required to adjust the pH of final treated water while using adsorbent after chemical treatment which required technical skill at field. Another, drawback associated with the chemical treatment approach is that it can alter the structural moiety of adsorbent. The average pore size of *AC-JSC* was observed to 2.19 nm and total pore volume was observed to 0.73 cm³/g. The adsorbed average pore volume increased with an increase in P/P₀. The elemental composition of *AC-JSC* analysed as C (%): 51.9, H (%):8.06, O (%): 43.1, N (%): 2.51, which is comparable with the values reported earlier. [26]

Table 1: Characterises of bio-adsorbent (*AC-JSC*)

Adsorbent	Characteristics
Appearance	Grey colour
Physical form	Powder
Density (g /cm ³)	1.0
Average Surface Area (m ² /g)	481
Average pore volume (cm ³ /g)	0.73
Average pore size (nm)	2.19
Nature	Porous
Elemental composition	C(%): 51.9, H(%): 8.06, O(%): 43.1, N(%): 2.51

Structural, Morphological and Thermal Characterization

FTIR shows (Fig 2) infrared spectra of raw Jatropha seed cake (*Raw-JSC*) and carbonised Jatropha seed cake (*AC-JSC*). The FTIR spectra of JSC before carbonization show bands at 3424 cm⁻¹, 1636 cm⁻¹, 1398 cm⁻¹ and 1123 cm⁻¹ and 3149-3031 cm⁻¹ might be due to presence of stretching vibration of O-H group (carbohydrates, fatty acids, proteins, lignin units, cellulose present plant) and adsorbed water, amide linkage, (C=O, C-O functional groups) and symmetric and asymmetric C-H stretching of CH₂ and CH₃ groups respectively. The band at 770 cm⁻¹ might be due to presence of nitrogen group. After the carbonization, most of the functional groups of JSC, especially the oxygenated groups were escaped except the band at around 3400 cm⁻¹ (relatively low from raw JSC) and 1401 cm⁻¹ due to presence of -OH, C-H and S=O groups which can be attributed to the high contents of polyphenolic tannins, flavonoids, suberin, etc., in woody plants [25, 27].

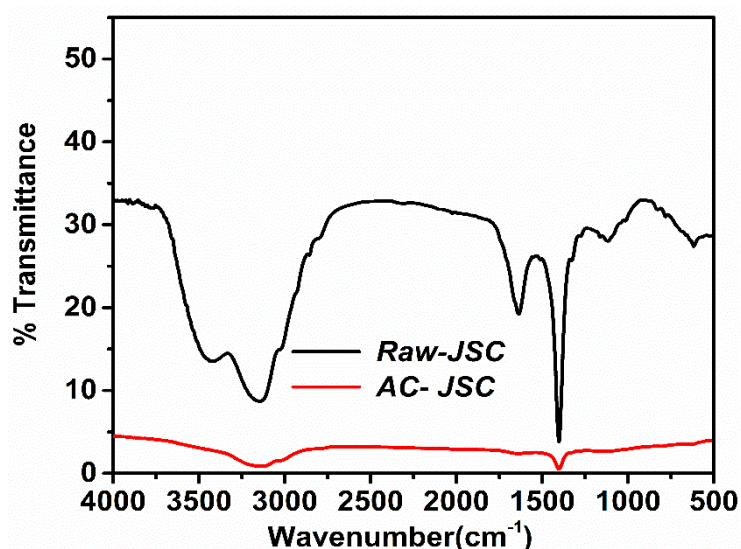


Fig. 2: Fourier transform infrared spectroscopy (FT-IR) Spectrum of *Raw-JSC* and *AC-JSC*

SEM and EDX analysis of *AC-JSC* was conducted by a Field Emission SEM instrument to understand the morphologies of *AC-JSC* pre- and post-adsorbed specimens (Fig. 3). The samples were prepared by grinding the *AC-JSC* to very fine powder. The surface morphology of *AC-JSC* before (*AC-JSC* 3a, b) and after adsorption (*AC-JSC* 3c, d) shows coral type structure with numerous voids on the surface. The high surface area and amorphous nature of material can be attributed to the voids inside the adsorbent. The average pore volume for *AC-JSC* was found to be 0.73 cm³/g, and average pore size is measured as 2.19 nm. The porous structure of adsorbent is favourable for the adsorption of arsenic as it allows the faster diffusion of pollutants through pores. The EDX spectrum and element mapping of *AC-JSC* revealed the presence of arsenic (3d), after adsorbed by *AC-JSC* while absence (3b) before arsenic adsorption. In the element mapping (3f) the distribution of arsenic can be clearly visible, the presence of red dots indicating adsorbed arsenic whereas green and violet colours indicating the presence of oxygen, carbon.

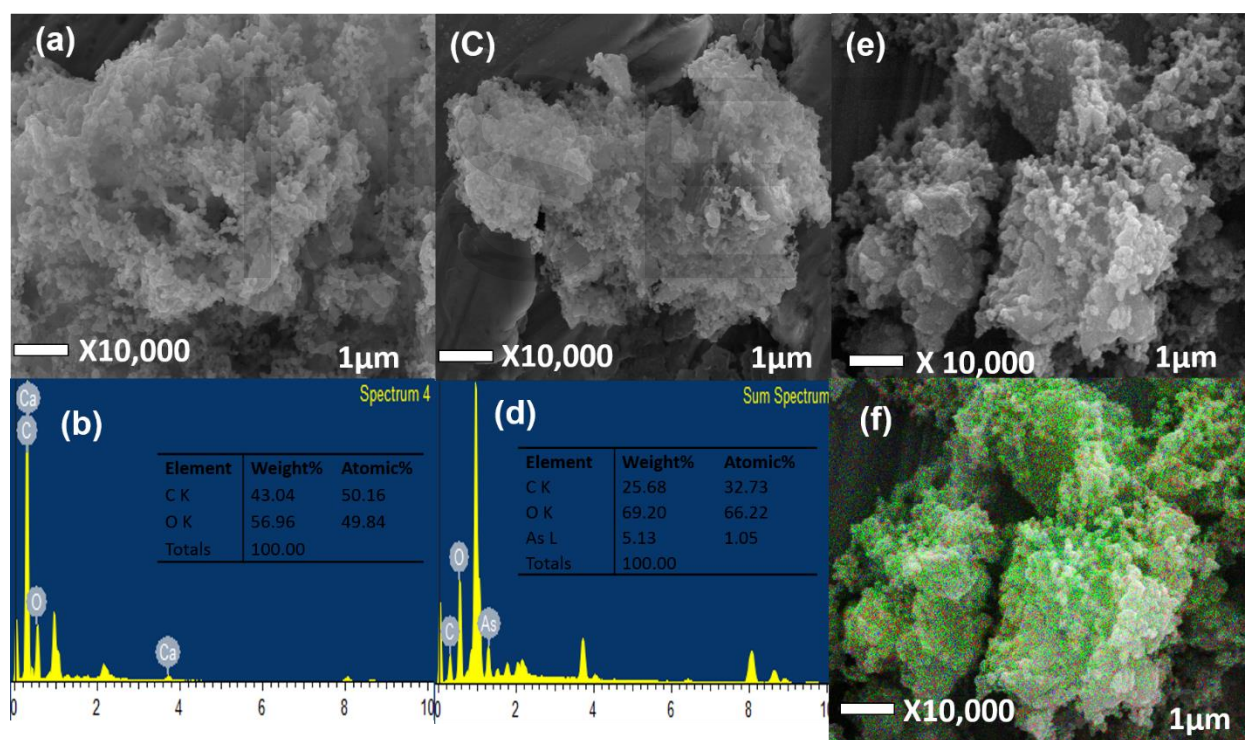


Fig. 3: FESEM-EDX (Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy) (a) images of *AC-JSC* before adsorption. (b) EDX of *AC-JSC* before adsorption (c) FESEM-EDX images of *AC-JSC* after adsorption of arsenic. (d) EDX of *AC-JSC* after adsorption. (e) Mapping of elements (f) Distribution of element onto *AC-JSC* adsorbed arsenic (red), oxygen (green) and carbon (violet).

Adsorption study

Effect of time on adsorption

To investigate the minimum time required to reach equilibrium, the effect of contact time on the adsorption of arsenic onto *AC-JSC* was studied under fixed experimental condition (dose: 1.0g/L, As^V and As^{III} : 250 $\mu\text{g/L}$ (separate solution of As^V and As^{III}), pH: 7.0 ± 0.1 , rpm: 120, equilibrium time: 3hrs and temperature: $30^\circ\text{C}\pm 1.0^\circ\text{C}$). It can be seen that very rapidly within the first 30 minutes of initiation of adsorption, >40% of arsenic (As^V and As^{III}) were adsorbed by the *AC-JSC*. Thereafter, rate of adsorption gradually slow down with the ~90% removal within 90 minutes followed by reaching equilibrium within 100 minutes. The *AC-JSC* can significantly remove both forms of arsenic very rapidly as per the WHO permissible limit, which can be ascribed due to the availability of an astronomically immense number of active sites on *AC-JSC* which gradually got saturated as time proceeded. Thus, at equilibrium (~100 minutes) can be observed as optimum contact time for the maximum uptake of arsenic and subsequent experimental work.

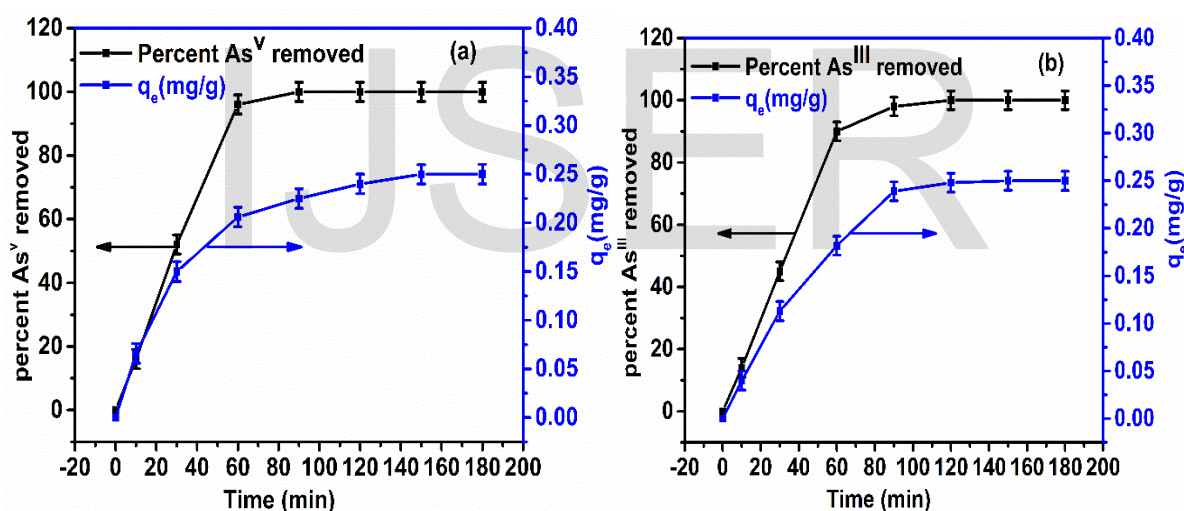


Fig. 4: Plot of adsorption capacity of *AC-JSC* as a function of time (minute) (a) As^V : 250 $\mu\text{g/L}$, (b) As^{III} : 250 $\mu\text{g/L}$, dose: 1.0g/L, pH: 7.0 ± 0.1 , rpm: 120, temperature: $30^\circ\text{C}\pm 1.0^\circ\text{C}$.

Effect of adsorbent dose

The amount of the adsorbent is a consequential parameter for cost-efficacious and important process to get the trade-off between the adsorbent dose and the percentage removal resulting in an optimum amount of adsorbent. Thus, the amount of adsorbent dose was optimize from 0.1g/L to 1.5g/L to bring down arsenic concentration below its permissible limit, while other parameter kept fixed i.e., As^V and As^{III} 250 $\mu\text{g/L}$, pH: 7.0 ± 0.1 , rpm: 120 rpm, contact time: 3hrs and temperature: $30^\circ\text{C}\pm 1.0^\circ\text{C}$. The percentage of arsenic abstraction distinctly

incremented from 17 to 80% with increase in dose of adsorbent from 0.1 to 1.5 g/L, while the equilibrium adsorption capacity (q_e) per unit mass was found to decrease for As^V is 0.45 to 0.166 mg/g and for As^{III} is 0.4 to 0.166 mg/g, which might be due to their more active sites and increase surface area for the sorption of arsenic. On further increasing the dose to 0.8 g/L, relatively less adsorption (96%) of arsenic is observed which has been reached to steady with 100 % removal on further increase to 1.5 g/L. The maximum equilibrium adsorption capacity ($q_{e \text{ max}}$) per unit mass is near about 0.66 mg/g for As^V and 0.63mg/g for As^{III} with the dose of 1.0g/L. Though, adsorbent dose of 0.9g/L is efficient to bring down arsenic ~96% within WHO permissible limit, however, 1.0g/L of has been chosen as fixed dose for all further Arsenic removal studies.

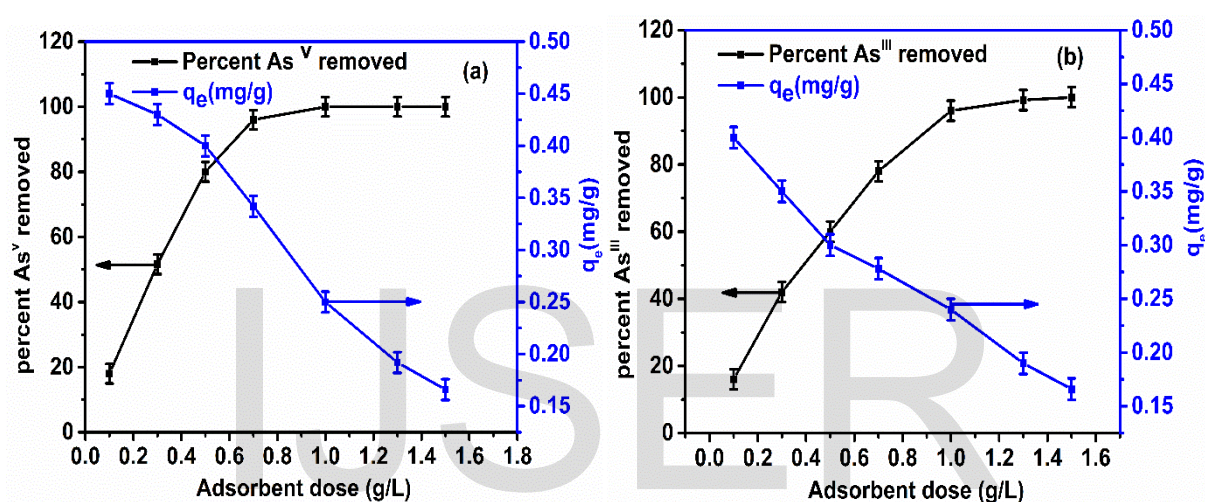


Fig. 5: Plot of percent removal of arsenic as a function of adsorbent dose (1.0g/L) at As^V 250 μ g/L and As^{III} 250 μ g/L, pH: 7.0 \pm 0.1, rpm: 120, equilibrium time: 3hrs and 30 $^{\circ}$ C \pm 1.0 $^{\circ}$ C.

Effects of initial Arsenic concentration on Arsenic adsorption

It is reported that the facility of a bio adsorbent to capture the sorbate could be invigorated by incrementing the initial aqueous concentration of the target at the sorbent and sorbate interface. Ergo, the effect of the initial concentration of arsenic on the adsorption and uptake of arsenic from solution by AC-JSC was evaluated by varying the concentration of arsenic in feed solutions from 100 to 700 μ g/L while keeping other parameter fixed (adsorbent dose: 1.0 g/L, pH: 7.0 \pm 0.1, rpm: 120, equilibrium time: 3hrs and temperature: 30 $^{\circ}$ C \pm 1.0 $^{\circ}$ C). It has been revealed that on increasing the feed concentration from 100 to 700 μ g/L the percentage removal efficiency decreases from 100 to 95% for As^V and 100 to 90.5% for As^{III} whereas, the adsorption capacity (q_e) per unit mass of AC-JSC increased from 0.1 to 0.66 mg/g for As^V and 0.1 to 0.63 for As^{III} . This may be due to greater number of arsenic ions remain available for the

adsorption by the AC-JSC hence supports faster and more efficient adsorption of arsenic. Moreover, the residual arsenic concentration could be reduced to below 10.0µg/L. Most adsorbent remove only As^V from water, only few adsorbents have been reported to remove both As^V and As^{III}. AC-JSC bio-adsorbent can effectively remove both As^V and As^{III} from contaminated water with high adsorption capacities of 0.66mg/g and 0.63mg/g respectively for As^V and As^{III}, which is higher than available bio-adsorbents. [26, 28, 29] A comparative study for removal of arsenic from water with other reported bio-adsorbents has been briefed in table no. 2.

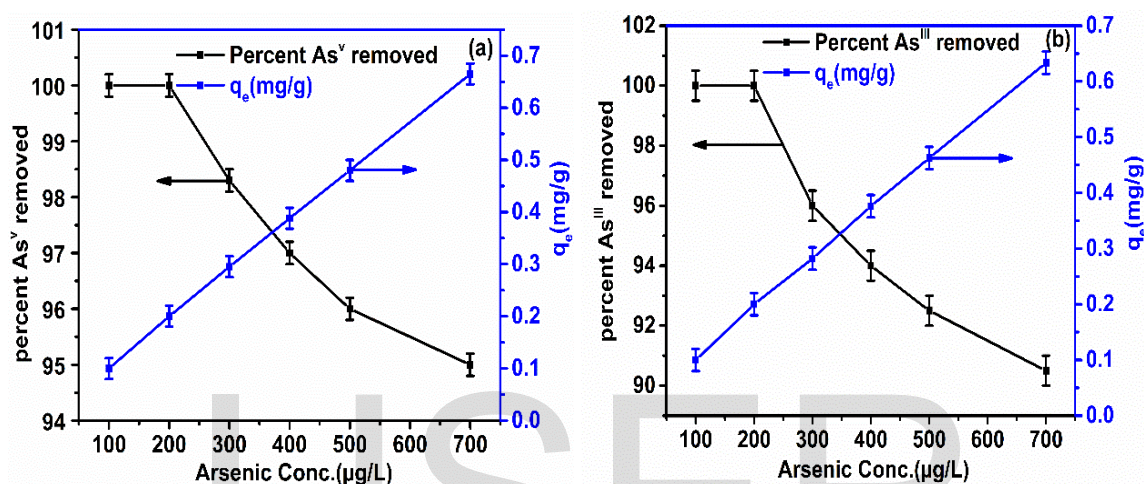


Fig. 6: Plot of percent removal of arsenic as a function of feed concentration of arsenic As^V and As^{III} adsorbent dose: 1.0g/L, pH: 7.0±0.1, rpm: 120, equilibrium time: 3hrs and temperature: 30°C±1.0°C.

Table. 2: Comparative study of different bio-adsorbent for arsenic removal

Adsorbent	Dose	pH	Capacity		Reference
			As ^V	As ^{III}	
1.AC-JSC	1g/L	7.0±0.2	0.66(mg/g)	0.63(mg/g)	Present work
2.Ca–Fe(III) alginate beads	5 g/L	6.0	0.12(mg/g)	0.36(mg/g)	[28]
3.Potato peel and rice husk (PPRH) ash	10g/L	7.0	2.17 µg/g	-----	[29]
4.Activated Carbons Prepared from Solvent Extracted Olive Pulp and Olive Stones	10g/L	7.0	-----	0.21(mg/g)	[26]

Effect of pH on arsenic adsorption

The effect of pH on adsorption has a significant impact on uptake of contaminant ions by adsorbent as, it determines the surface charge of the adsorbent. Thus, the effect of pH on adsorption of arsenic was studied at various solution pH values (ranging from 1.0 ± 0.1 to 12 ± 0.1), keeping other parameters constant (adsorbent dose: 1.0g/L , As^{V} and As^{III} $250\ \mu\text{g/L}$, (separate solution of As^{V} and As^{III}), pH: 7.0 ± 0.1 , rpm: 120, equilibrium time: and temperature: $30^{\circ}\text{C}\pm 1.0^{\circ}\text{C}$). The percentage adsorption was found to vary with the initial pH of solution. It has been revealed the percentage removal efficiency increased distantly from 50 to 100% from pH 2.0 ± 0.1 to 7.0 ± 0.1 which remains same till pH 8.0 ± 0.1 . The percentage removal efficiency decreased from 100% to 50% in alkaline pH from 8.0 ± 0.1 to 12.0 ± 0.1 . The highest removal efficiency of *AC-JSC* is observed in pH 7.0 ± 0.1 to pH 8.0 ± 0.1 , which is generally the pH of ground water level and the treated water can be utilize without any post treatment. Generally, the adsorbents prepared via chemical activation route works at extreme pH (acidic or alkaline) conditions for particular pollutants removal [30], wherein the post adjustment of pH of treated water is required at the end of process which is not recommended for the real water applications. The developed *AC-JSC* can dispenses the aforementioned drawbacks, concomitant have highest removal efficiency at ground water pH level.

Point of zero charge (pH_{pzc}) determination

The point of zero charge (pH_{pzc}) was determined to understand the surface chemistry of developed *AC-JSC*. When value of pH_{eq} is equal to the value of $\text{pH}_{\text{initial}}$, it shows the point of zero charge (pH_{pzc}) of adsorbent *AC-JSC*. For this experiment, accurately weighed *AC-JSC* (100 mg) was added into 50 ml deoxygenated aqueous solutions NaCl (0.01 M) under stirring for 24 hrs at 250 rpm at room temperature ($30^{\circ}\text{C}\pm 1.0^{\circ}\text{C}$). After 24hrs stirring, the final pH of solutions and blanks (without *AC-JSC*) were measured. The pH_{pzc} value of *AC-JSC* for As^{V} and As^{III} were calculated as 7.80 and 7.92 respectively. This indicates that below these values, the surfaces of *AC-JSC* is positively charged and above these values the surfaces is negatively charged for As^{V} and As^{III} respectively. Therefore it can be found that >98% arsenic removal were observed when initial pH of the solution was less than pH_{pzc} due to positively charged surface, which has been reduced once exceed above pH_{pzc} , for As^{V} and As^{III} as the surface of adsorbent become negatively charged. Generally, it has been is observed, that the pH levels of arsenic contaminated ground water varies between pH 6.0-8.0. Thus, the *AC-JSC* adsorbent would offer high practical utility in the area of water purification as low and eco-friendly bio-adsorbent with high removal efficiency at ground water pH level.

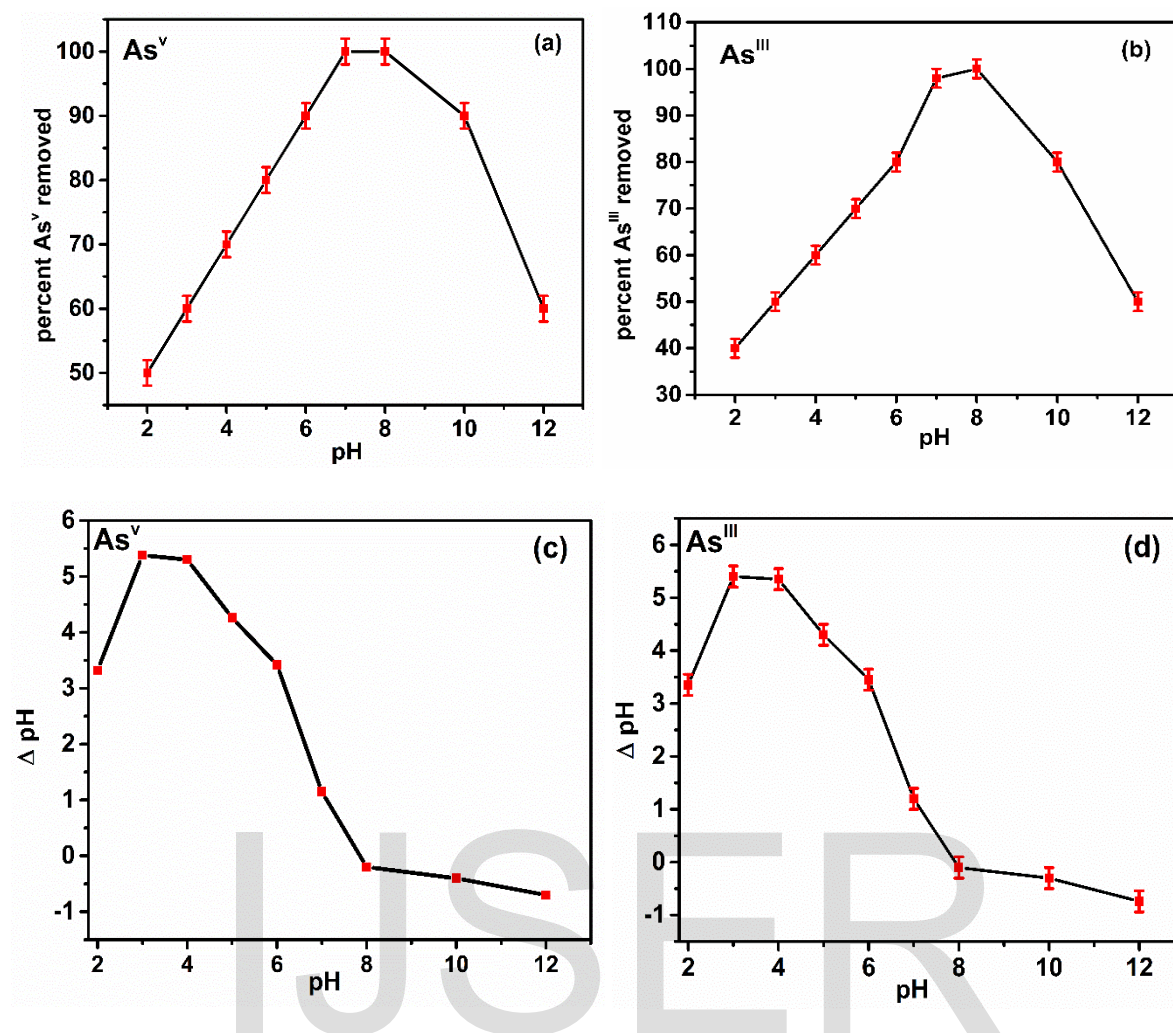


Fig. 7: Plot of percentage removal of arsenic as a function of pH (a) As^V (250μg/L), (b) As^{III} (250μg/L), and Plot of initial pH vs Δ pH (c) for As^V (250μg/L) and (d) for As^{III} (250μg/L) at adsorbent dose: 1.0g/L, pH: 7.0±0.1, rpm: 120, time: 3hrs and temperature: 30°C±1.0°C.

Column adsorption study:

Breakthrough curves was evaluated for the removal of As^V and As^{III} at an initial concentration of 250 μg/L by adsorption onto AC-JSC. 20 gm of AC-JSC bio-adsorbent was packed in the column in between two small layers of cotton. Arsenic containing feed water of spiked (As^V and As^{III}: 250μg/L separately) was passed through the both the columns with the fixed flow rate of 5.0 BV till breakthrough. It has been observed that breakthrough at 15 litre for As^{III} and 20 litre for As^V was found with spiked water samples with the residual arsenic concentration of <10 μg/L in treated water, which is within the permissible limit for arsenic as per WHO, which indicates its high removal efficiency for arsenic (Fig.-6).

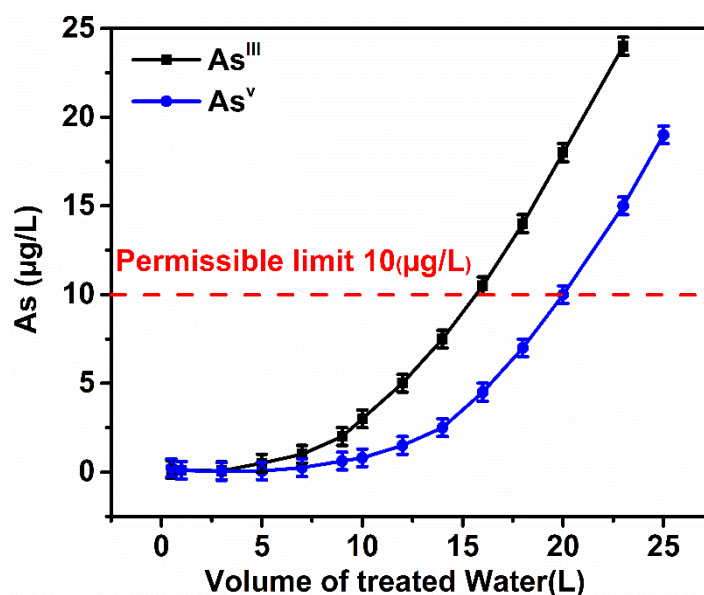


Fig.8: Breakthrough curves for the removal of As^V and As^{III} via column mode of operation

Sorption-Desorption and Regeneration Experiments

Hydrochloric acid (HCl) has been used as regenerating agent to desorb arsenic from the AC-JSC. Approximately 0.5g of arsenic exhausted adsorbent from previous experiment was kept into 0.1N HCl (100ml) solution under stirring condition for 6 hrs. The desorbed AC-JSC was filtered out with Whatman filter paper (No. 43). The filtrate was again filtered out with syringe-driven filter (PVDF Hydrophilic membrane- 0.22 micron) and analysed for desorbed arsenic using IC-MS. After desorption AC-JSC was washed with water till neutral pH for further reuse. Similar experiments were repeated to evaluate the adsorption-desorption and regeneration efficiency of AC-JSC for 3 times. The desorption ratio (%) of arsenic using AC-JSC was calculated by the equation-2.

The arsenic removal efficiency decreased slightly with regeneration (q_r) of AC-JSC as 0.28 (q_{r1}), 0.26 (q_{r2}) and 0.22 (q_{r3}) mg/g with successive sorption cycles. Apparently, for the aforementioned sorption cycles, desorption efficiencies (% DE) were found to decrease as 95, 87 and 74, respectively. The slight decrease in removal efficiencies might be due to presence of trace amount of trapped arsenic inside the pores. However, the arsenic concentration of the treated water was found below 10 µg/L from initial feed concentration of 250µg/L for even up to 3 consecutive cycles of sorption without any performance degradation indicates the potentiality of the developed adsorbent for the removal of arsenic. (Fig.9)

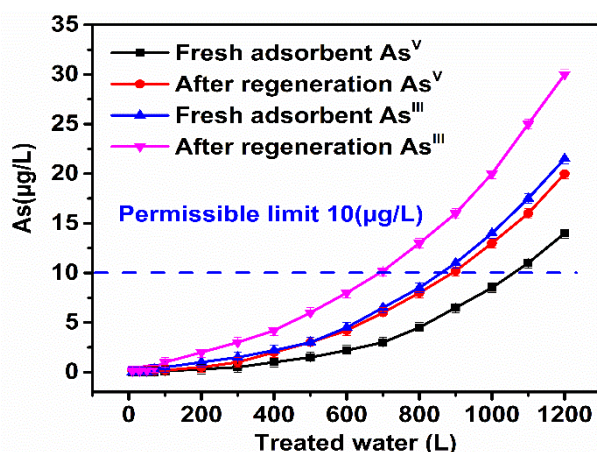


Fig.9: Regeneration of AC-JSC for repeated use

Possible adsorption mechanism

The possible adsorption mechanism for the removal of arsenic onto AC-JSC can be supposed to occur via two routes. Firstly, affinity adsorption and secondly, by anion exchange between the arsenic in the water and the carbon surface of the AC-JSC. The Affinity adsorption simply relates to the surface behaviour of AC-JSC, whereas anion exchange relates to the existing forms of the arsenic species.

The Affinity adsorption is related to the surface behaviour of AC-JSC, whereas anion exchange relates to the existing forms of the arsenic species. It has been generally found that OH groups are generated on the surface carbon during the activation process. The mechanism of adsorption of anions onto activated carbon is generally well explained by electrochemical theory: Carbon in contact with water reduces oxygen to a hydroxyl group and thus, the carbon loses electrons and becomes positively charged. The surface charge (Electrical neutrality) is maintained with hydroxyl ions, resulting in their adsorption. Though the AC-JSC utilized for the removal of arsenic in the present work has not been subjected to any chemical and/or physical activation treatment, however, possibility of presence of a large number of OH groups on the surface of the AC-JSC after the drying process, which might have facilitated the adsorption of arsenic onto AC-JSC as soon as carbon of AC-JSC comes in contact with arsenic solution and the latter are adsorbed [31]. Moreover, as the results of pH_{pzc} value of AC-JSC, as 7.80 and 7.92 for As^V and As^{III} respectively, indicates that the surfaces of AC-JSC are positively charged and become negatively charged above these values. Thus, >98% of arsenic removal was observed at neutral pH due to positively charged surface concomitantly higher surface area and porous texture of adsorbent which has favoured the higher removal efficiency for both forms of arsenic.

Adsorption kinetics

Lagergren pseudo first-order and pseudo second-order kinetic models

Adsorption kinetics were followed to presage the adsorption rate and understand the mechanism of arsenic adsorption. Mainly, two types of kinetics models, namely Lagergren pseudo-first-order and pseudo-second-order kinetics models, were evaluated to describe the kinetics of arsenic adsorption on the AC-JSC adsorbent in this study.

Lagergren pseudo-first-order and pseudo-second-order kinetics models can be linearly expressed as eq (3) and (4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots (3)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \dots (4)$$

Where $h = k_2 q_e^2$

Where k_1 and k_2 are the rate constants of pseudo-first-order and pseudo-second-order kinetics, respectively; q_t and q_e are the amount of adsorbent Arsenic at any time and at equilibrium state, respectively.

The adsorption kinetics of both the aforementioned is shown in Fig. 10(a) and Fig. 10(b) and the parameter values obtained by curve-fitting kinetics data are listed in table 2. Lagergren pseudo- second-order kinetics models proved to be more suitable in describing the adsorption kinetics of arsenic based on the correlation coefficient ($R^2 > 0.94$) for As^v and ($R^2 > 0.99$) for As^{III} , suggesting that a chemisorption step might be rate determining in the arsenic adsorption process [32]. The higher correlation coefficient values observed with the pseudo-second-order model indicates the applicability of this model. Furthermore, it could be seen that the adsorption capacities (q_e) obtained by theoretical (0.250 mg/g) and experimental value for As^v and As^{III} is (0.306 mg/g) and (0.350 mg/g) respectively .

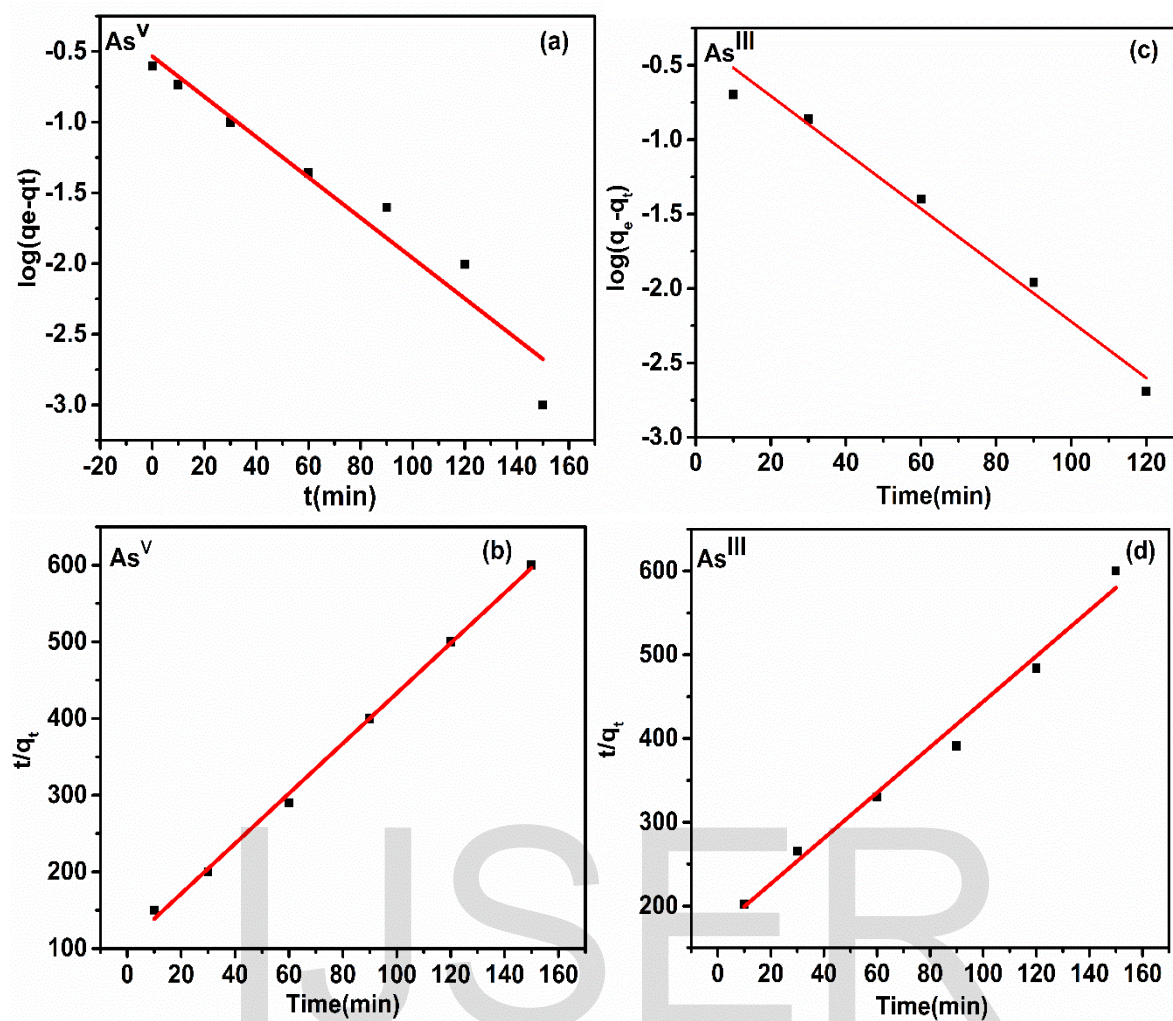


Fig. 10: Lagergren pseudo-first-order kinetics $\log(q_e - q_t)$ versus time (min) for (a) As^V (b) As^{III} and pseudo-second-order kinetics time (min) vs t/q_t for (c) As^V (d) As^{III}

Table 3: Lagergren pseudo-first-order and pseudo-second-order kinetic models constants for adsorption of arsenic on AC-JSC adsorbent.

Initial Arsenic Conc. (250 μ g/L)	Adsorption Capacity (Experimental) (mg/g)	Pseudo first order model			Pseudo second order model		
		K_1 (min ⁻¹)	q_e (mg/g)	R^2	K_2 (min ⁻¹)	q_e (mg/g)	R^2
As^V	0.250	0.032	0.293	0.94	0.1006	0.306	0.99
As^{III}	0.240	0.043	0.394	0.99	0.0474	0.350	0.99

Adsorption Isotherm

Adsorption isotherms are very important for understanding the nature of the interaction between the applied adsorbent and the concentration of sorbate at a constant temperature. The

Langmuir and Freundlich models are most commonly used isotherms to represent the equilibrium distribution of adsorbate from a liquid phase onto a solid phase [33, 34]. Langmuir isotherm equation is predicated on monolayer adsorption on the active sites of the adsorbent. The Langmuir isotherm in its linear form is represented by equation below:

$$\text{Langmuir isotherm models: Langmuir model: } \frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_e \dots (5)$$

Where b is a constant related to the affinity of the binding sites and q_m is the maximum amount of the arsenic ion per unit weight of *AC-JSC* to form a complete monolayer on the surface bound at high C_e . The Langmuir constants for As^V and As^{III} , q_m and b were calculated from the slope and intercept of the plot C_e/q_e versus C_e and were found to be 0.686 mg/g, 0.667 mg/g and 146 L/g, 96.40 L/g respectively, with regression coefficient (R^2) of 0.94 and 0.92 respectively (Fig. 11 (b) and 11 (d), Table 4).

The Freundlich isotherm model is regarded as adsorption on a heterogeneous surface, which is considered to be appropriate for describing both multilayer sorption and sorption on the heterogeneous surface, mathematically it is given by the following linearized equation ((Fig. 11 (a) and 11(c), Table 4).

$$\text{Freundlich isotherm models: } \log q_e = \log K_f + \frac{1}{n} \log C_e \dots (6)$$

Where C_e (mg/L) and q_e (mg/L) are the concentration and adsorption capacity at equilibrium, respectively; b (L/mg) is the adsorption equilibrium constant that relates to the adsorption energy, and q^m (mg/g) is the amount of the arsenic weight of bio-adsorbent, which estimates the maximum uptake of adsorption. The value of q^m and b can be calculated from the slope and intercept of plot $\frac{C_e}{q_e}$ vs. C_e . The value of K and $1/n$ represent adsorption capacity and adsorption intensity, respectively and can be calculated from the intercept and the slope of the straight line for the log-log plot of q_e and versus C_e

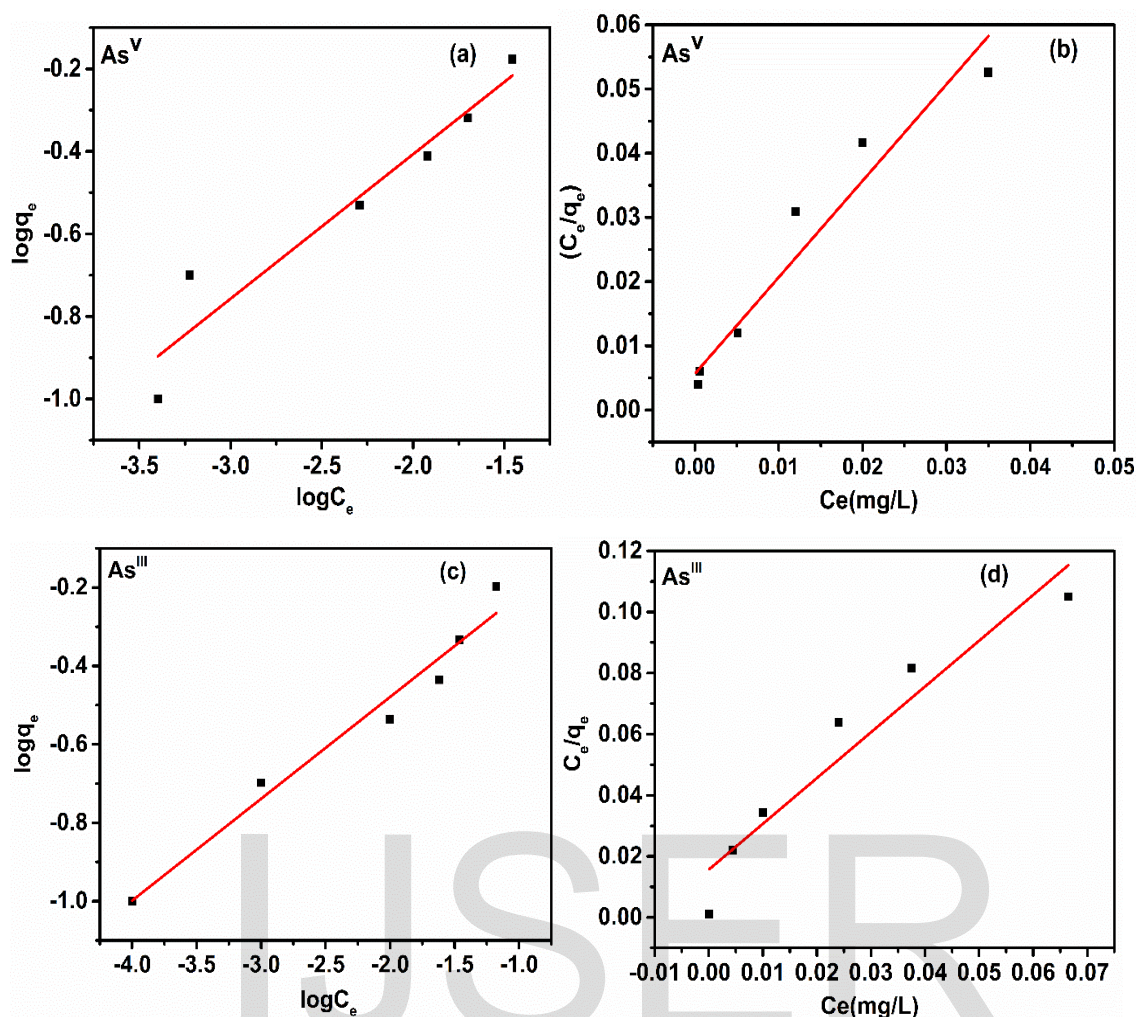


Fig. 11: Plot of (a, c) $\log(C_e)$ versus $\log(q_e)$ Freundlich adsorption isotherm and (b, d) plot of C_e versus C_e/q_e Langmuir isotherm plot for arsenic using AC-JSC.

The higher value (2.85) As^V and (3.86) As^{III} of Freundlich coefficient ($1/n$), ranging from 1 to 10, supports the favourable sorption of Arsenic onto the adsorbent [35]. Higher values of both K_f (0.671) As^V and (0.964) As^{III} and n (0.350) As^V and (0.259) As^{III} by Langmuir isotherm indicate the effective sorption Arsenic by adsorbent surfaces. Thus, it can be concluded that the adsorption data are best supported to Freundlich model with R^2 values 0.92 and 0.96 for As^V and As^{III} respectively and for Langmuir model with R^2 values 0.94 and 0.92 for As^V and As^{III} respectively; showing that arsenic adsorption on AC-JSC could be described by these models.

Table 4: Langmuir and Freundlich isotherm constants for adsorption of arsenic on AC-JSC.

AC-JSC	Langmuir Isotherms			Freundlich isotherm		
	q_m (mg/g)	b (L/g)	R^2	$1/n$	K_f (mg/g)	R^2
As^V	0.686	146	0.94	2.85	0.671	0.92

As ^{III}	0.667	96.105	0.92	3.86	0.964	0.96
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Adsorption thermodynamics

Temperature has an important role in adsorption process as it exerts the great influence on the rate of adsorption process. Indeed, an increase in temperature provides an increase in the amount of available energy and accelerates the adsorption process. Hence, elevated temperature can reduce processing cost by increasing rate of adsorption and concomitantly by reducing time required to complete adsorption [36]. The effect of temperature in adsorption of arsenic by AC-JSC is recorded at different temperatures i.e., 298, 303, 308, 313, 318 and 323 K, while all other parameters i.e.; adsorbent dose 1.0g/L, pH: 7.0±1.0, rpm: 120, feed concentration: 250 µg /L and contact time : were kept constant.

The experimental result reveals the increase in percentage adsorption of arsenic as temperature increased. The arsenic adsorption capacity (q_e) of AC-JSC increases from 0.240 to 0.250 mg/g, for both arsenic with increasing temperatures from 298 to 323K with 250 µg/L of initial arsenic concentration. The increase in q_e value with temperature indicates an endothermic adsorptive process and temperature seems a significant parameter. Thermodynamic parameters were calculated using the Van't Hoff equation –

$$\log q_e/C_e = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \dots\dots\dots (8)$$

$$\Delta G = \Delta H - T \Delta S \dots\dots\dots (9)$$

Where ΔS is the entropy change, ΔH is the enthalpy change, and (q_e/C_e) is the adsorption affinity.

The enthalpy change ΔH and the entropy change ΔS calculated from the intercept and slope of the plot of $\log (q_e/C_e)$ vs $1/T$ were found to be 177.5KJ/mol and 0.629 KJ/mol, with regression coefficient (R^2) of 0.99 (Fig. 12, Table 5). The positive values of both ΔH and ΔS denoted the endothermic nature and corresponds to increase in degree of freedom of the adsorbed species respectively. Moreover, the negative value of ΔG calculated as -8.58 KJ/mol for As^V and -8.60 KJ/mol for As^{III}, at 303 K confirm the feasibility of the adsorption process and the spontaneous nature of adsorption. The values of enthalpy of sorption process may be acclimated to distinguish between chemical and physical sorption [37]. For chemical sorption, enthalpy values range from 83 to 830 KJ mol⁻¹, while for physical sorption they range from 8

to 30 KJ mol⁻¹. Thus, the value ΔH (177.5) more the 83 confirms the possibility of chemisorption adsorption as with increase in temperature of the system.

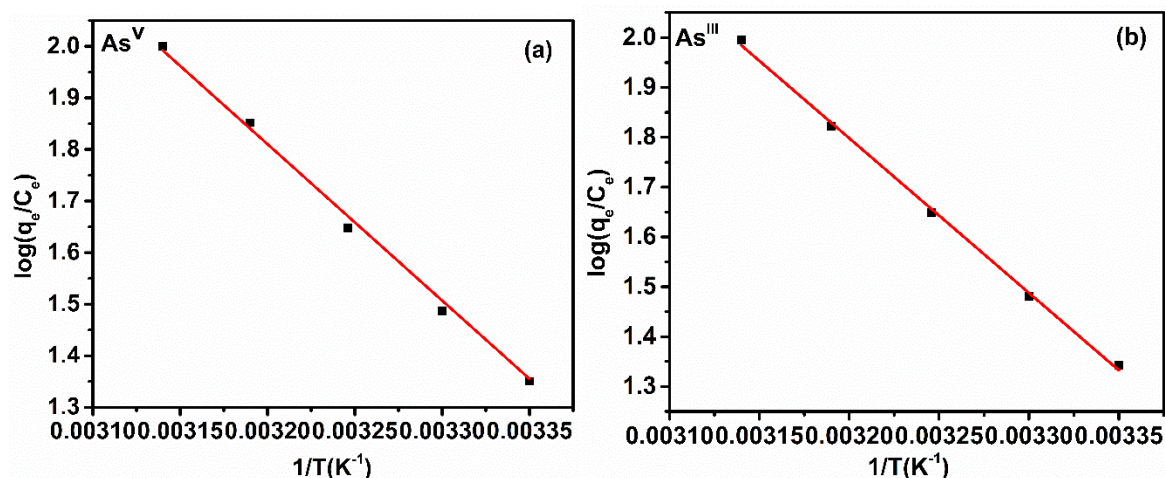


Fig. 12: Plot of thermodynamics of the adsorbent $\log(q_e/C_e)$ vs $1/T (K^{-1})$ for (a) As^V (b) As^{III}

Table 5: Thermodynamic parameters for arsenic adsorption by AC-JSC

	ΔH (KJ/mol)	ΔS (KJ/mol)	R^2	ΔG (KJ/mol)					
				298	303	308	313	318	323
As^V	58.079	.220	0.99	-7.48	-8.581	-9.681	-10.787	-11.881	-12.981
As^{III}	59.42	0.22457	0.99	-7.481	-8.603	-9.726	-10.848	-11.971	-13.093

Conclusion

Bio-adsorption is eco-friendly and cost effective process to encounter the hazardous ions from water. AC-JSC derived from the industrial waste has been utilized for the removal of arsenic at laboratory scale without any chemical modification. The experimental results of present investigation revealed, AC-JSC has better efficiency towards abstraction of arsenic from contaminated water. The abstraction of arsenic was found to be very rapidly and most of the arsenic was removed during 10–60 min and reaches to maximum of 99% at 3hrs. The experimental data well fitted to the Freundlich and Langmuir equations, with good correlation coefficients. The experimental data also showed that intra-particle diffusion is significant in the sorption rate determination. The adsorption process was spontaneous and increased with increase in temperature. The AC-JSC works well at wide pH range of 2.0 ±1.0-10.0±1.0, however maximum removal efficiency is found the in the range of 6–8, reflects high practical utility for the field water application without any further chemical treatment. Thus, AC-JSC

derived from the industrial waste has tremendous potential as bio adsorbent for the remediation of arsenic from water

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