



Arsenic Removal using Silver-Impregnated *Prosopis spicigera* L. wood (PSLW) Activated Carbon: Batch and Column Studies

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ABSTRACT: Silver-impregnated carbon (SIC) and its precursor (un-impregnated) derived from an easily available low cost plant material *Prosopis spicigera* L. wood (PSLW) carbon was investigated for their ability to remove arsenic from aqueous solutions in batch and column experiments. Arsenic uptake has no regular trend with increasing pH; contains two adsorption maxima, the first adsorption maximum at pH 4.0 and a second adsorption maximum at pH 10.0. The extent of As (III) removal increased with increase in temperature. As (III) sorption kinetics was well fitted by pseudo second order with pore diffusion as rate determining step. The applicability of Langmuir isotherm suggests the formation of monolayer coverage of As (III) at the outer surface of the adsorbent. Thermodynamic parameters show that the adsorption was spontaneous and endothermic in nature. Column experiments were done using Thomas model, the maximum adsorption capacity of SIC was found to be 9.36 mg/g.

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Ground water is the prime source of drinking water and meets the needs of households' worldwide. Arsenic is known to be one of the naturally occurring element in ground water which is associated with adverse health effects. Arsenic concentration in water varies from less than 0.05 to more than 5000 µg/L depending on the source of arsenic and the arsenic concentration in drinking water is of great human health concern in some regions of Bangladesh, India, Nepal, Mexico and Argentina (Wagle and Shipley, 2016). Recent literature reveals that As(III) and As(V) oxyanions with varying concentration have been distributed regionally across the United States (USA) (Sorg et al., 2014). The potable water is considered to be safe for human consumption if the concentration of arsenic in water is 10 µg/L. Therefore it is essential to remove arsenic from potable water resources.

The important process listed for the removal of arsenic are oxidation-reduction, precipitation, co-precipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, ion floatation, coagulation and biological processing (Zhao et al., 2012; Bilici Baskan and Pala, 2010; Sen et al., 2010; Shobana et al., 2014; Pio et al., 2015;

Sneh Lata and Samadder, 2016; Overah and Odiachi, 2017). Among the techniques, adsorption by activated carbon is accepted to be the best available technology for the removal of pollutants. The main disadvantage of activated carbon adsorption technology is its high cost. This can be overcome by preparing activated carbon from renewable biomass in nature and tailoring the carbon surface to enhance the removal capacity (Hoskins et al., 2002).

In our previous work (Jansi Rani et al., 2014) activated carbon prepared from a low cost biomass *Prosopis spicigera* L. wood (PSLW) carbon was used to remove arsenic from aqueous solution. In the present work, the PSLW carbon impregnated with silver known as silver-impregnated carbon (SIC) was employed to remove arsenic from aqueous solution. The physical and chemical characterization of SIC by scanning electron micrographs (SEM), Fourier transform infra-red spectroscopy (FT-IR), Energy-dispersive X-ray (EDX) and Boehm estimation were conducted and further the potential of the SIC was evaluated for As(III) removal. The study was to examine As(III) adsorption capacity of SIC by batch studies and to investigate the As(III) uptake characteristics of SIC by column studies.

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MATERIALS AND METHODS

Preparation of PSLW activated carbon and silver impregnation: PSLW plant material used in the present work was collected from the dry land area of Tiruchendur in Thoothukudi district, Tamil Nadu state, India. Activated carbon was prepared from the collected plant material as follows. The branches and roots of the tree were cut into pieces and piled up on a firing hearth. Before firing, the heaped wood pieces were enclosed by fresh plantain pith and the whole mass was covered and plastered with layers of wet clay. This arrangement prevented the direct-entry of air into wood pieces and hence prohibited burning of wood and becoming ash. After 48h of continuous firing and subsequent natural cooling, the activated carbon was obtained. After removing non-carbonaceous materials like plantain pith, clay-mud etc., carbon was isolated, crushed into fine powder and sieved to 75 micron particles. Silver impregnation was carried out using the following simple procedure. 5 g of carbon was suspended in 100 ml of 0.1 N AgNO₃ solution. To this 100 ml of 0.2 N glucose solution was added and mixed thoroughly, heated for an hour in water bath and then cooled to room temperature. Silver-impregnated carbon (SIC) was filtered and washed with distilled water to remove the excess of glucose. It was dried and sieved to 75 micron particle and stored in air tight bottle and used for adsorption study.

Adsorbent characterization: Surface areas of PSLW carbon and the SIC was estimated using methylene blue dye adsorption method on a per gram basis at 30 °C as described in literature. A SEM (Hitachi S 450 Japan) was used to study the surface characteristics of the sorbent materials before and after adsorption of arsenic. Elemental mapping of the adsorbents' surfaces were conducted with Energy-dispersive X-ray (EDX) (Thermo NORAN system Vantage).

Potentiometric titration with acid/alkali was used to determine the p*H*_{zpc} (zero point charge) of the adsorbents. Selective neutralization of acidic/basic surface groups by varying strength of acid/base were determined by Boehm method. This method was used to determine the surface functional groups such as carboxyl, lactone and phenolic groups etc. Fourier Transform Infra-Red (FT-IR) spectroscopic study of adsorbents was performed with Jasco FT-IR 410 spectrophotometer to find the nature of the functional groups. As(III) ion in aqueous solution was estimated using Atomic Absorption Spectrophotometer (Shimadzu, AA-6300). A portable digital pH meter with glass electrode (model LT-120 ELICO) was utilized for the measurement of pH values.

Batch adsorption studies: The arsenic stock solution (1000 mg/L As₂O₃) was diluted to desired concentration of experimental As(III) solution. An adsorbent dose of 2 g/L was kept constant for all the batch experiments. The initial pH of As(III) solution was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. Batch adsorption equilibrium experiments were performed using 0.1 g of SIC (particle size 75 micron) in 50 mL of As(III) solution and agitated in a thermostatic shaker. After adsorption, the adsorbent was separated by filtration and the concentration of As(III) in the filtrate was investigated using Atomic Absorption Spectrophotometer (Shimadzu, AA-6300). The batch experiments were performed to study the effect of various parameters such as pH (1-10), contact time (5-120 min) and temperature (30-45 °C). The amount of As(III) adsorbed per unit mass of the adsorbent (q) was calculated using equation (1),

$$q = [(C_i - C_f) V] / W \quad (1)$$

where, C_i and C_f are the initial and free concentrations of As(III) in mg/L respectively; V is the volume of As(III) solution in mL and W is the weight of the adsorbent in g.

Column study: In column study, 5 g of SIC (particle size 75 micron) was washed with distilled water to remove carbon fines and then packed evenly in a glass column (1.5 cm diameter) by tapping to reduce air voids in the carbon bed for a bed height of 7.1 cm. As(III) solution (500 mg/L) was drawn into the column at a rate of 0.5 mL/min from a separating funnel. Effluents were collected at regular intervals of time and analyzed. The column flow was terminated when the As(III) concentration ratio of the effluent to influent reached a value of 0.8.

RESULTS AND DISCUSSIONS

Adsorbent characterization of SIC

Energy-dispersive X-ray (EDX) analysis shows the percent of impregnation of silver is 9.77 weight % of carbon. Surface area of SIC is slightly higher than the PSLW carbon indicating the segregation of carbon particle after silver impregnation. There are evidences from the SEM study that the carbon surface is segregated and smoothed in the SIC. SEM analysis (Figure 1) shows that the impregnation of silver as white patches on the surface of carbon. The observed decrease in the basic sites and cation exchange capacity may be due to adsorption of Ag⁺ ion onto the basic sites. Further, it is shown that there is a significant increase in lactone and the amount of phenolic groups after impregnation which shows the oxidation of carbon surface. The p*H*_{zpc} values of

PSLW carbon and SIC are found as 6.98 and 7.06 respectively.

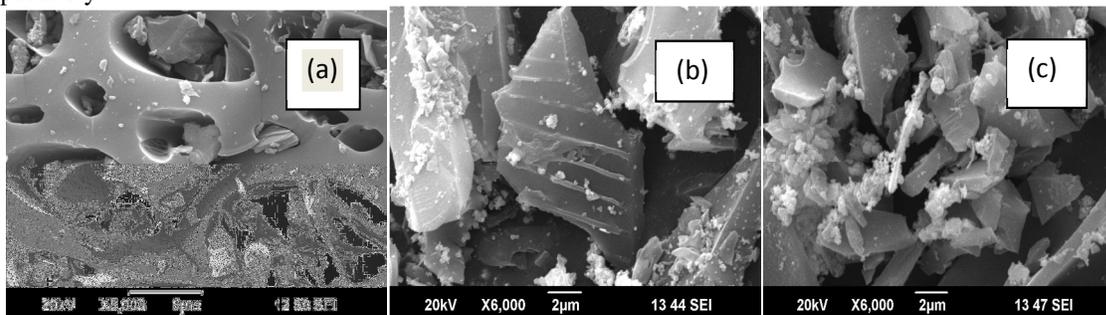


Fig. 1: SEM images of (a) PSLW carbon (b) SIC and (c) As(III)-loaded SIC (x 6000 magnification).

The slightly higher pH_{zpc} value of SIC shows the presence of more acidic sites on SIC than PSLW carbon. Thus the SIC differ significantly from PSLW carbon in physical and chemical characteristics due to silver impregnation.

Effect of pH: The experiments were carried out to investigate the effect of pH on the adsorption of As(III) onto SIC. Arsenic adsorption onto any adsorbent depends on the arsenic valence as well as pH of the solution. Figure 2 depicts the effect of pH over a range of 1-10.0. Though no regular trend in adsorption is seen with pH, the figure shows two maxima, one at pH 4.0 and another at about pH 10.0. For an initial As(III) concentration of 1000 mg/L the maximum adsorption capacity of As(III) at pH 4.0 is 98.2 mg/g and at pH 10.0 it is found to be 207.5 mg/g. It was postulated that under acidic condition

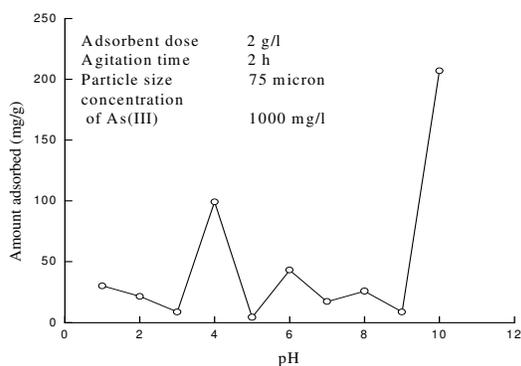
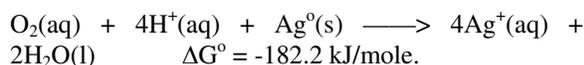


Fig. 2: Adsorption of As(III) on SIC as a function of pH.

the metallic silver get oxidized in aqueous solution according to the following reaction (Hoskins et al., 2002).



From the SEM and EDX analyses it is evident that the silver on the surface of SIC exists as metallic silver (i.e. Ag^0). Therefore it is assumed that at pH 4.0, Ag is oxidized to Ag^+ ion which reacts with AsO_3^{3-} to give Ag_3AsO_3 precipitate and gets adsorbed on the surface of SIC. As the pH rises the formation of Ag^+ is limited and at alkaline pHs silver exists as $AgOH$ and the following reaction may occur.

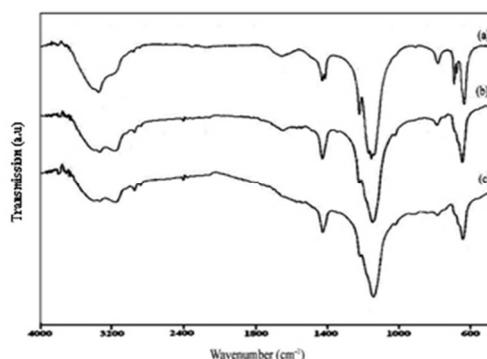
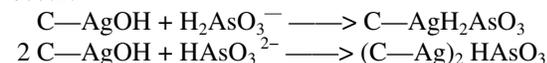


Fig. 3: FT-IR spectra of (a) PSLW carbon (b) SIC and (c) As(III)-loaded SIC.

Further at alkaline pHs, the Na^+ ions may also bind to the negatively charged surface of SIC and neutralize the charges partially (Mehta and Chaudhari, 2015). Therefore in the alkaline pH the $H_2AsO_3^-$ and $HAsO_3^{2-}$ species may also be bound to the surface of SIC carbon by vander Waals forces in addition to the above process. Further the FT-IR study shows the surface of SIC consists of lactone and phenolics

groups (Figure 3). These surface groups may form complex with As(III) which is evident from the IR spectroscopy. The in plane bending of -OH group occurs at 2273 cm^{-1} is blue shifted and C-O stretching at 1160 cm^{-1} in SIC disappeared at As(III) loaded-SIC.

Effect of contact time and temperature: Contact time is a significant yardstick in determining the rate and equilibrium time of adsorption process.

Table 1: Langmuir constants at different temperatures

Temp (°C)	Q _o (mg/g)	b (10 ³) (L/mg)	R _L
30	32.39	1.90	0.3448
35	34.72	1.93	0.3415
40	44.64	2.15	0.3174
45	59.17	2.40	0.2920

The characteristics of SIC and its available adsorption sites affect the course of time to reach the equilibrium. As(III) removal increases with increasing contact time; an initial rapid uptake of As(III) followed by a gradual/slowed uptake at later stage. The removal rate gradually slows down and equilibrium reaches at 120 min. After reaching the

state of equilibrium, there is no remarkable increase in the adsorption capacity. The maximum adsorption capacity of As(III) was found to be 196.43 mg/g for an initial concentration of 1000 mg/L. Temperature plays a key role in determining the adsorption capacity and in this study temperature was varied from 30 to 45 °C. It shows the variation of adsorption capacity with temperature, which increases with increase in temperature. Thus, increase in adsorption capacity with temperature clearly demonstrates that the adsorption of As(III) on SIC is an endothermic process.

Isotherm analysis: The adsorption data were analyzed with two well-known adsorption isotherm models namely Langmuir and Freundlich models.

Table 2: Comparison of pseudo-first order and pseudo-second order model parameters

As(III) (mg/L)	T °C	Pseudo-first order model				Pseudo-second order model			
		q _e (exp) (mg/g)	k ₁ (min ⁻¹)	q _e (cal) (mg/g)	R ²	k ₂ ×10 ² (g/mg/min)	q _e (cal) (mg/g)	R ²	
1000	30	196.43	0.0279	140.799	0.9805	2.82	219.05	0.993	
	35	199.15	0.0338	131.009	0.9976	4.12	218.82	0.997	
	40	224.10	0.0334	139.740	0.9866	4.45	242.72	0.998	
	45	235.05	0.0453	140.472	0.9957	5.58	250.16	0.999	

The experimental data did not fit well with the Freundlich model but linear correlation is obtained with Langmuir model. This is evident from the linear plots of C_f/q against C_f for the adsorption of As(III) on SIC (Figure 4).

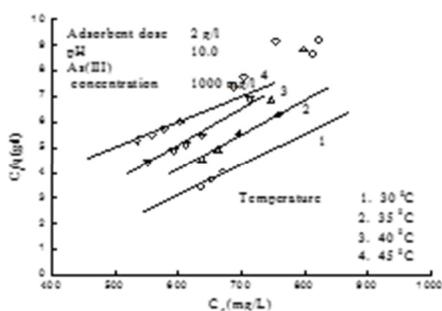


Fig. 4: Langmuir plot at different temperatures.

The Q_o and b can be determined from the slope and the intercept of the linear plots and are given in Table 1. All these facts prove that As(III) is adsorbed in a monolayer on the surface of the adsorbent. The Langmuir constant, b, is used to assess the affinity between the adsorbate and adsorbent which steadily increases with temperature. Further dimensionless

separation factor (R_L) is calculated. It is observed that the R_L values (Table 1) lie between 0 and 1, which establishes the truth that the adsorption isotherm is favorable under the studied conditions.

Adsorption kinetics: The kinetics of As(III) adsorption on SIC was examined with pseudo-first order and pseudo-second order kinetic models which are expressed in equations (2) and(3),

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

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

where, q_e and q_t are the amount of As(III) adsorbed (mg/g) at equilibrium and at time 't' (min), respectively. k₁ (L/min) and k₂(g/mg min) are the adsorption rate constants of first order and second order adsorption.

In addition, the initial adsorption rate, h (mg/g/min) equal to k₁q_e or k₂q_e² was also calculated. For the studied initial concentrations and temperatures, the rate constants (k₁ and k₂), theoretical equilibrium adsorption capacities, q_e (cal) calculated from the slope and intercept of the linear plots of the pseudo-

first order and pseudo-second order kinetic model and the co-efficient of linear correlation (R^2) at different temperatures are given in Table 2. An analysis of the values in Table 2, particularly the agreement between q_e (exp) and q_e (cal) and the value of R^2 towards unity between pseudo first-order and pseudo-second order models clearly reveals that pseudo-second order model fits better to the data than the pseudo-first order model. Therefore it is inferable that the adsorption of As(III) on SIC is a second order type process.

Thermodynamic behavior: The thermodynamic constants, standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were determined to know the thermodynamic feasibility of the adsorption process. The negative values of ΔG° indicate the spontaneous nature of adsorption process. The increase in adsorption capacity with increase in temperature from 30 °C to 45 °C demonstrates the endothermic nature. Therefore ΔH° needs to be positive for a spontaneous process and the same has been observed true (0.472 kJ/mol). The positive value of ΔS° (16.65) shows the affinity of the adsorbent towards As(III) species and suggests the possibility of some structural changes in the solvent cluster around the As(III)-SIC complex.

Intra-particle diffusion: To determine whether the intra-particle diffusion is the rate determining step or not, the data were analysed using Finkiam diffusion law. The intra-particle diffusion constant, k_i value is calculated from the slope of the plot of q_t vs $t^{1/2}$. The plots do not pass through the origin, which indicate that the above diffusion law is applicable. The pore diffusion constants are 12.4076, 12.8549, 17.7870 and 23.0400 (mg/g/min) at different temperatures. The increase in k_i values with increase in temperature, clearly demonstrates that the intra-particle diffusion becomes easier at higher temperature. The plot also indicated that intra-particle diffusion is not the only rate-controlling step because it did not pass through the origin. The linearity of the plots demonstrated that intra-particle diffusion plays a significant role in the uptake of the adsorbate by adsorbent.

Column study: Column adsorption process is vital to industrial process for waste water treatment. The observed data fit to the linearised form of the Thomas model (Thomas, 1948) and are given in equation (4),

$$\log(C_0/C_e - 1) = kq_0M/Q - kC_0V/Q \quad (4)$$

where, C_0 and C_e are the influent and effluent As(III) concentrations (mg/L) respectively. k stands for the Thomas rate constant (mL/min/mg); q_0 is the

maximum solid phase concentration of solute (mg/g); M is the mass of the adsorbent (g); and V is the throughput volume (mL/min). For an initial concentration of As(III) 500 mg/L, the concentrations of As(III) in effluent was found to be zero for the first 65 bed volumes, approximately 85% of As(III) was retained for 5 bed volumes, 68% for another 10 bed volumes and as evident from the curve, the retention of As(III) by the column gradually declines as the bed volume increases. The values of k and q_0 are computed from the slope and intercept of the linear plot of $\log(C_0/C_e - 1)$ versus V and they are found as 5.311×10^{-2} mL/min/mg and 9.36 mg/g. Thus from column analysis it has been shown that can be used in industrial processes for the removal of As(III) from aqueous systems.

Desorption study: Desorption was carried out by placing 0.1 g of As(III) loaded SIC in 50 ml of 0.1 N HCl at 30 °C. The percent desorption was 86.4. During the experiment, leaching of Ag was not observed because the solution tested with potassium chromate did not give any characteristic colouration.

Conclusions: In this study, silver impregnated carbon (SIC) was prepared from PSLW carbon and its adsorption capacity was investigated using batch and column study. Silver content of carbon and pH play vital role in the adsorption process. Metallic silver impregnated on SIC is oxidized under acidic conditions. The adsorption at pH 4.0 is due to coulombic interaction between As(III) and Ag^+ ion while at higher pH 10.0 the sorption is due to vander Waals interaction and complex formation of As(III) with surface functional groups. It was found that desorption of As(III) is possible with 0.1 N HCl. This work provides way for developing other silver impregnating adsorbents for As(III) removal.

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