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Research Article

Adsorption Studies for Arsenic Removal using Activated *CASSIA TORA*

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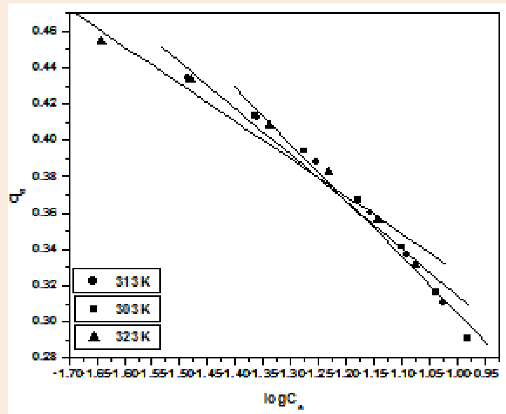
Abstract

New low cost adsorbent, activated *cassia tora* has been developed for aqueous arsenic removal. Batch experiments were revealed that Arsenic removal was up to 82.7% using activated *cassia tora*. Isotherm studies revealed that Langmuir and Temkin isotherm were followed with a better correlation than the Freundlich isotherm. The recently developed cost-effective novel bio sorbent, activated *cassia tora* can be used as household level to mitigate the arsenic problem.



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Introduction

Heightened awareness of arsenic toxicity and regulatory changes has prompted considerable research efforts toward developing methods for arsenic removal from drinking water [1]. Naturally occurring arsenic contaminates groundwater in many countries including Argentina, Australia, Chile, China, Hungary, India, Mexico, Peru, Taiwan, Thailand, and the United States. Several techniques effectively lower arsenic concentrations in aqueous solutions: coagulation/precipitation, reverse osmosis, ion exchange, and adsorption. Coagulation and softening with metal ions such as aluminum and ferric salts require use of large-scale facilities for implementing water treatment. Adsorbent materials studied for arsenic removal include activated alumina, fly ash, pyrite fines, manganese greensand [2], amino-functionalized meso porous silicas[3], aluminum loaded Shirasu-zeolite[4], clinoptilolite, and other zeolites[5]. However, there is still a strong challenge in developing economical and commonly available bio sorbents for Arsenic removal. Therefore, we focused on the characterization and bio sorption efficiency of a cheapest and easily available indigenous biomass taken from the leaves of c*assia tora*. *cassia tora* is a legume belonging to the *Caesalpiniaceae* family. It is a wild crop and grows in most parts of India as a weed. *cassia tora* leaves are used for various soup preparations in some parts of northern Nigeria.

According to Ayurveda the leaves and seeds are acrid, laxative, anti periodic, anthelmintic, ophthalmic, liver tonic, cardio tonic and expectorant. The leaves and seeds are useful in leprosy, ringworm, flatulence, colic, dyspepsia, constipation, cough, bronchitis, cardiac disorders.

The aim of this research work is therefore to prepare activated carbon from c*assia tora* and to carry out the equilibrium studies of Arsenic on the activated c*assia tora*.

Materials and methods

Fresh and healthy leaves of c*assia tora* were chosen. Prior to analysis, the samples were air dried (away from sunlight). The preparation of activated carbon from all the four adsorbents consisted of carbonization of the plant material. Dried raw leaves were cut into small pieces and the carbonization was conducted in a muffle furnace at

400°C. The heating period was 20minutes, then powdered well and finally activated at a temperature of 800°C for a period of 10 minutes. The activated carbon obtained was kept in a desiccator.
All chemicals were of analytical grade (>99%) and were purchased from Sigma-Aldrich. Water used in the study was tap water of Sivanthipuram (a direct ground water supply).The water was spiked with As(III)using sodium arsenite($NaAsO_2$).

Batch sorption experiments

Batch sorption experiments were conducted to study the effect of contact time, initial As(III) concentration, pH, dose and concentration of various co-existing ions on As(III) sorption by adsorbent. The kinetics experiments were carried out at room temperature (30±1°C). Adsorbent samples were added to 250 ml Erlenmeyer flasks containing 100ml of As(III) solution. The flasks were kept for shaking at 120rpm in a thermostatically controlled orbital shaker (Remi, India) at 30±1◦C. Samples were withdrawn at predetermined time intervals and analyzed for residual As(III) concentrations. The initial pH of the samples was adjusted using dilute NaOH or HCl. Effects of contact time and initial As(III) concentration on sorption were tested with four different As(III) concentrations (0.25,0.5, 0.75 and 1mg/L). Samples were withdrawn from the reactor at small time intervals and analyzed for residual arsenic concentration.

Adsorption isotherms

Isotherm studies were performed in four 250 ml Erlenmeyer flasks. Each flask was filled with 100 ml of As(III) solutions of different initial concentrations (5-20 mg/L) and pH was adjusted to 7.0. To each flask, 1.2 g of adsorbent was added, and solutions were agitated at a speed of 120 rpm for 140 min.

The bio-sorption data have been subjected to Langmuir, Freundlich and Temkin isotherm models.

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in linear form:

$$C_e/q_e = (1/q_m)\,C_e + 1/(K_a\,q_m) \qquad (1)$$

Where, q_m is the monolayer bio-sorption saturation capacity (mg/g) and K_a represents the enthalpy of bio-sorption (L/mg), independent of temperature.

On the other hand, the Freundlich equation is represented by the following:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (2)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of As adsorbed (mg/g), K_f and n are Freundlich constants.

The Temkin isotherm the simple form of an adsorption isotherm model has been developed considering the chemisorption of an adsorbate onto the adsorbent is represented as:

$$q_e = a + b \log C_e \qquad (3)$$

Where, q_e and C_e have the same meaning as noted previously and the other parameters are called the Temkin constants. The plot of q_e versus log C_e will generate a straight line. The Temkin constants a and b can be calculated from the slope and intercept of the linear plot.

Results and discussion

The effect of contact time and adsorbate concentration

Figure 1 show the effect of initial concentration of Arsenic and contact time on adsorption uptake. The experiment was carried with initial concentrations 0.25, 0.50, 0.75 and1 mg/L of As(III) solution (100ml) and agitated with 0.5 g of c*assia tora* at 303K. The adsorption at different As(III)concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption. The uptake of As(III) onto c*assia tora* nearly reaches equilibrium in 120 min. The time beyond no significant change in adsorption takes place has been fixed as equilibrium time [6].Based on the results, 120 min was fixed as equilibrium time throughout the study. More than 80% of As(III) adsorbed with initial concentrations ranging from0.25-1mg/L for 2hr equilibrium time. The rate of percent removal is higher in beginning due to larger surface area of the adsorbents available for the adsorption of the As(III). The percentage removal, however, decreased with increase in initial concentration of the As(III). The slower adsorption was likely due to the decrease in adsorption sites on the surface of the adsorbents [7, 8].

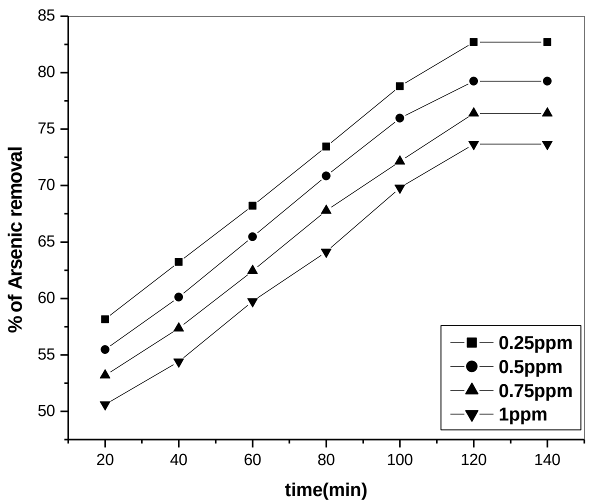

Figure 1 Effect of contact time

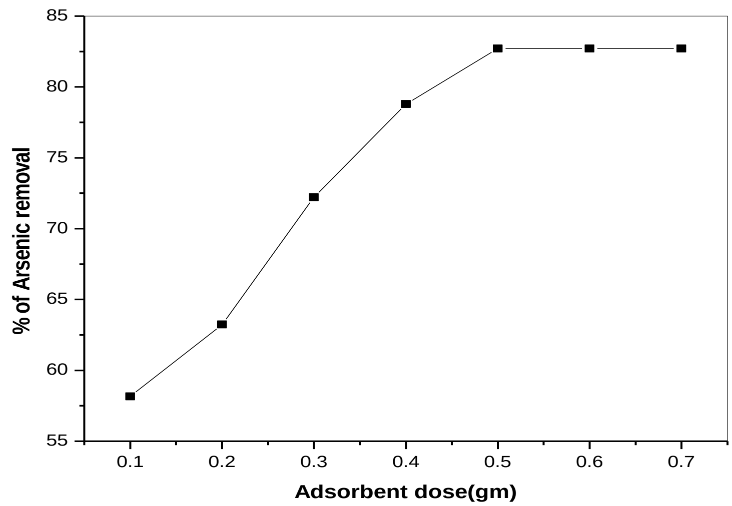

Figure 2 Effect of adsorbent dose

The effects of absorbent dosage

The results of experiments to determine the effects of adsorbent dosage on As(III) removal are shown in Fig. 2 and reveal that the removal efficiency of As(III) ion by the c*assia tora* increased with an increase in adsorbent dosage. It rose from 58.16% to 82.74% with the increase of adsorbent dosages ranging from 0.1 g/ml to 0.7 g/ml. While a rapid increase was observed at adsorbent dosages ranging between 0.1g/ml to 0.5g/ml, a plateau was seen at those ranging between 0.6g/ml and 0.7g/ml. Increasing adsorbent dosage above 0.5g/ml had negligible effect on the increase in removal efficiency of As(III) ions. This may be attributed to the formation of aggregates at higher solid/liquid ratios or to precipitation of particles [9].

Adsorption isotherms

Adsorption of As(III) ions by c*assia tora* was modeled using the Freundlich, Langmuir and Temkin isotherms with the quality of the fit assessed using the correlation coefficient. Langmuir isotherm parameter fits (Table1) for As(III) adsorption on c*assia tora* yielded isotherms that were in good agreement with observed behaviour(r^2 ≥0.99). The As(III) adsorption capacity on c*assia tora* at room temperature (303K) was 26.62mg/g. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = 1/1 + k_aC_o \quad (4)$$

Where, C_o (mg/L) is initial concentration of adsorbate and k_a (L/mg) is Langmuir constant. **Figure 3a** shows the variation of separation factor (R_L) with initial Arsenic concentration. The R_L values were in the range of 0–1 at 303K, indicating that the sorption of As(III) onto c*assia tora* is favorable. The 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 (Fig.3b). In this study n values are greater than unity indicating chemisorption (Table1) [10]. Isotherms with n > 1are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption [11]. The Freundlich constant, K_F, which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic.

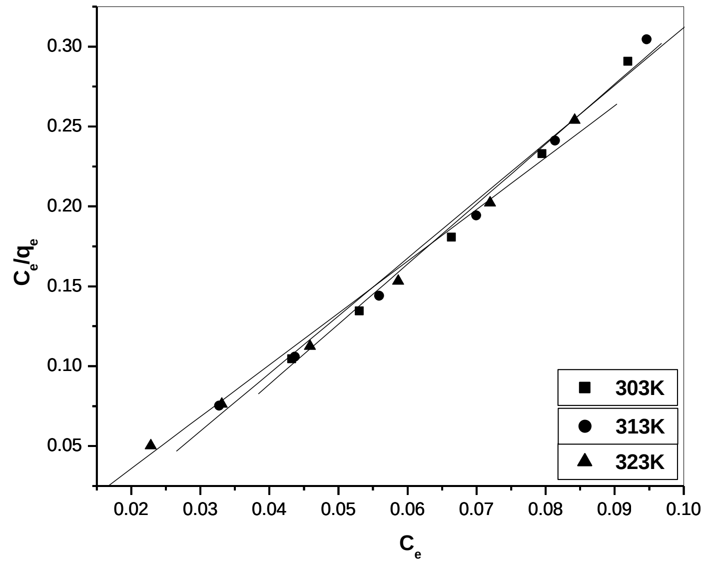

Figure 3 Plot of the Langmuir isotherm

Linear plots for Temkin adsorption isotherm(Fig.3c), which consider chemisorptions of an adsorbate onto the adsorbent[12], fit quite well with correlation coefficients ≥0.99 (Table1).This further supports the findings that the As(III) adsorption on c*assia tora* is a chemisorptions process.

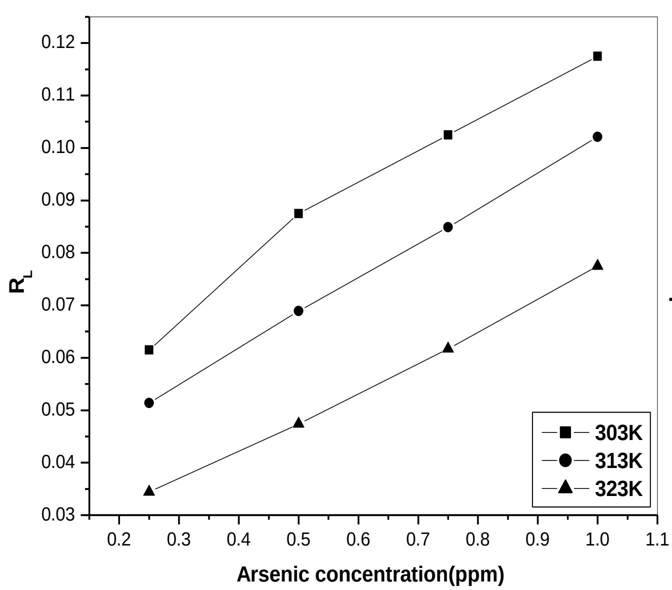

Figure 3a Separation factor R_L values versus initial Arsenic concentration

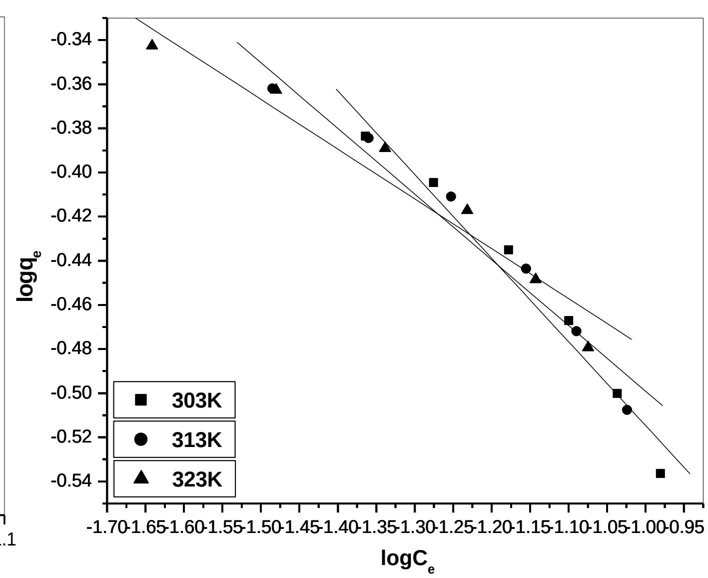

Figure 3b Plot of the Freundlich isotherm

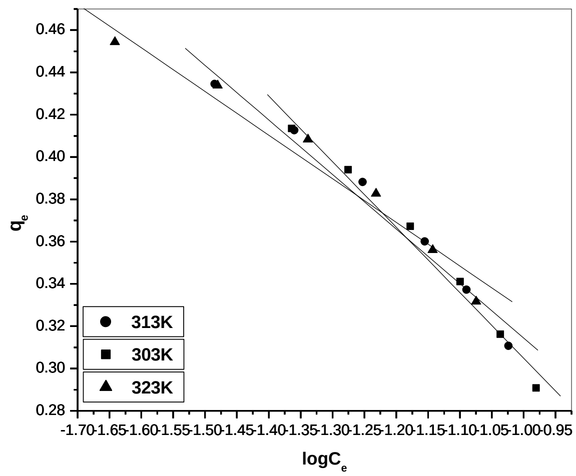

Figure 3c Plot of the Temkin isotherm

Table 1 Equlibrium constants of various isotherm models for the adsorption of Arsenic on activated c*assia tora*

Isotherm	**Isotherm constants**	**Temperature**		
		303K	**313K**	**323K**
Langmuir	K_a(L/mg)	0.6107	0.7377	1.1222
	q_{max}(mg/g)	26.62	27.72	30.83
	r^2	0.9973	0.9956	0.9962
	SD	0.0061	0.0089	0.0075
Freundlich	K_f(mg/g)(mg/L)$^{-1/n}$	0.1278	0.1710	0.1971
	n	2.6392	3.3579	4.4307
	r	0.9864	0.9824	0.9769
	SD	0.0107	0.0115	0.0125
Temkin	a(L/mg)	0.0049	0.0564	0.1215
	b (mg/g)	0.3098	0.2579	0.2063
	r^2	0.9931	0.9899	0.9850
	SD	0.0062	0.0075	0.0091

Table 2 R_L values at different temperatures, which were calculated using Langmuir constants

Arsenic concentration	**Temperature (K)**		
(mg/L)	**303**	**313**	**323**
0.25	0.0615	0.0514	0.0344
0.50	0.0875	0.0689	0.0474
0.75	0.1025	0.0849	0.0617
1	0.1175	0.1021	0.0775

Conclusion

This study focused on the bio sorption of As(III) onto bio sorbent material(c*assia tora*) from aqueous solution. *cassia tora* sorption on Arsenic was studied in batch mode and found to be strongly dependent on pH value of solution, adsorbent dosage, and temperature .The adsorbent had a high removal capacity towards As(III). Maximal adsorption capacities were 26.62 mg/g at pH 8.0. The adsorption mechanism was found to be chemi sorption and the rate-limiting step was mainly surface adsorption. The Langmuir isotherm showed a better fit than the Freundlich isotherm, thus, indicating the applicability of monolayer coverage of Arsenic on increasing the temperature increased the Arsenic adsorption rate. The equilibrium data were also well described by the Temkin equation further supporting Arsenic adsorption on c*assia tora* as a chemisorptions process.

Based on all results, it can be concluded that c*assia tora* is an effective and alternative biomass for removing As(III) from aqueous solution due to high bio sorption capacity, easy availability and environmental friendly.

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