Removal of Arsenic from Aqueous Solution Using Iron(III)-loaded Sugarcane Bagasse

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Abstract

The adsorption of As(III) and As(V) from aqueous media onto novel bioadsorbent prepared from sugarcane bagasse i.e. Fe(III) loaded charred sugarcane bagasse (FeCSCB) has been studied by batch equilibration method under different experimental conditions. Effects of pH, adsorbent dose, adsorbate concentration and contact time were studied. The concentration of As(III) and As(V) was determined spectrophotometrically by molybdenum blue method. Maximum adsorption was observed at pH 8 and pH 5 for As(III) and As(V) and at optimum contact time of 4 hrs and 3 hrs, respectively at an initial concentration of 5 mg/L. Maximum adsorption capacity (q_{max}) value of FeCSCB was found to be 25 mg/g and 70 mg/g for the adsorption of As(III) and As(V), respectively. Kinetics and isotherms modeling studies demonstrated that the experimental data best fitted with pseudo second order kinetic model and Langmuir isotherm model, respectively. This study revealed that FeCSCB can be used as an efficient, ecofriendly and economic material for the adsorptive removal of As(III) and As(V) from aqueous system.

Keywords: Arsenic(III), arsenic(V), adsorption, biosorption, sugarcane bagasse.

Introduction

Arsenic, a ubiquitous element in nature, is a naturally occurring contaminant of drinking water. Arsenic contamination in ground water has been emerged as a major problem of catastrophic proportions. It is notorious as king of all poisons. Severe arsenic contamination of ground water was first reported in Bengal delta (Bangladesh and West Bengal, India) in the early 90's[1]. In 1999 it was reported first in Nepal. The most stable species of dissolved arsenic in water are the anionic species of arsenite [As(III)] and arsenate [As(V)]. However, the predominant form between pH 3 and pH 7 is $H_2AsO_4^-$, and that between pH 7 and pH 11 is $HAsO_4^{2-}$, are the most prevalent in well oxidized waters, while under reducing environments it occurs as a neutral, undissociated species H_3AsO_3, as in natural ground. In natural waters As(V) is the prevalent species. The toxicity of arsenic depends on its chemical form, arsenite [As(III)] is more toxic than arsenate [As(V)] and mobilized in the environment. The WHO guideline value for arsenic in drinking water is 10 µg/L [2]. Provisional guideline value of arsenic in drinking water in Nepal is 50 µg/L including Bangladesh and China[3].

The technologies for removal of arsenic are oxidation/reduction, adsorption, coagulation – precipitation, ion exchange, membrane filtration or biological removal processes[2]. The adsorption process offers flexibility in handling and in many cases produces treated effluent suitable for reuse, free of color and odor[4]. Adsorbents based on biomaterials usually called bio-adsorbents have been studied as cost effective and environmentally benign means to remove pollutants. Sugarcane bagasse in a sugar industry is a waste byproduct which is available in large quantities at no cost and can be used for the development of adsorbent.

The sugarcane bagasse contains the following ingredients as cellulose (46.0%), hemicellulose (24.5%), lignin (19.95%), fat and waxes (3.5%) and other elements (1.7%). The polysaccharides found in sugarcane bagasse are biopolymers containing many hydroxyl and phenolic groups that can be chemically modified to form new compounds with changed properties[5]. The effectiveness of native biomass or its modified forms towards the removal of arsenic has been studied by many researchers[6-10]. A number a papers have been published in this field[11-13].

The main objective of this investigation is to prepare a low cost bioadsorbent from sugarcane bagasse and to investigate its adsorption capacity for the sorption of As(III) and As(V) from aqueous media.

Material and Methods

Chemicals: All chemicals As_2O_3, $Na_3AsO_4.12H_2O$, H_2SO_4, and $FeCl_3.6H_2O$ used were of reagent grade. All the solutions were prepared in distilled water.

Preparation of Adsorbent from Raw Sugarcane Bagasse (RSCB): Raw sugarcane bagasse in this work was collected from the juice shop located at Nayabazar, Kirtipur, Kathmandu, Nepal and thoroughly washed with distilled water to remove the remaining sugar. Then the bagasses were dried in sunlight for 5 days to remove moisture. The dried bagasses were grinded into

powdered form using mechanical grinder at Central Department of Chemistry and was sieved to the particle size of 250 μm. The adsorbent is designated as RSCB.

A volume of 200 mL of concentrated sulfuric acid was taken in a plastic container adding 100 g of raw sugarcane bagasse (RSCB). The suspension was left for 48 hrs at room temperature to accomplish the charring reaction. The suspension was further treated with distilled water several times and supernatant was removed carefully to achieve the pH of the suspension almost to neutrality. Thus obtained solid adsorbent was dried below 80^0C in hot air oven for 6 hrs and sieved to pass the particle size of 250 μm. This powder is named as CSCB. By charring, the surface of the adsorbent gets modified due to ring opening of sugar units as shown in scheme-1 first and increases the active sites at the surface of adsorbent.

20 g of charred sugarcane bagasse (CSCB) was brought in contact with 500 mL of 0.2M hydrated ferric chloride; $FeCl_3.6H_2O$ solution in 500 mL of beaker, and stirred using magnetic stirrer for 6 hrs and was kept in contact for 24 h rs. Then, the upper supernatant was carefully poured and the residue left was washed with distilled water in portion several times till litmus neutrality was achieved. The solid product was dried in an oven for 12 hrs at 80^0C and was named as Fe(III) loaded charred sugarcane bagasse (FeCSCB). Fe(III) is loaded onto ring opened structure as shown in scheme-2.

Then powdered FeCSCB was stored in clean and dry polythene bottle safely. The dried material was further used as the sorbent in the adsorptive removal of arsenic from aqueous solution.

Sorption Tests: In all the batch tests, synthetic arsenic (III and V) solutions of predetermined concentration and adsorbents, FeCSCB were used. The working solutions of various required concentrations were prepared by diluting 1000 mg/L of arsenic solutions.

Firstly, pH of the 50 mL of arsenic solutions was adjusted by using 0.1M HCl and 0.1M NaOH in 250 mL of beaker. Then 25 mL of pH adjusted working solution was kept in 50 mL of conical flask with help of burette in which 25 mg of Fe(III) loaded charred sugarcane bagasse (FeCSCB) was already weighed out. Then conical flasks were shaken for definite length of time in a mechanical shaker to attain equilibrium. The equilibrated suspensions were filtered with the help of ordinary filter paper. Then, arsenic concentrations before and after adsorptions were determined by the spectrophotometric molybdenum blue method using WPAS 104 Spectrophotometer. All experiments were carried out in duplicate and average results were reported.

Cellulose unit   Compound formed by ring opening
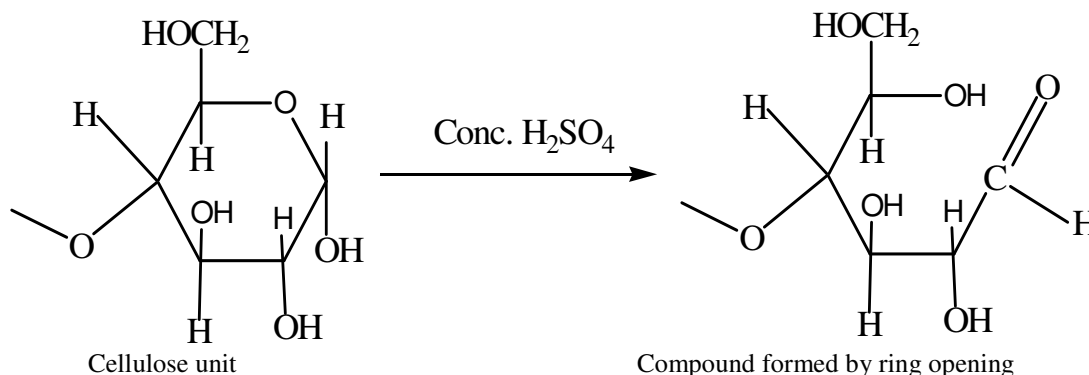
Scheme-1
Plausible mechanism for the charring process of monomeric unit of cellulose contained in sugarcane bagasse[5]
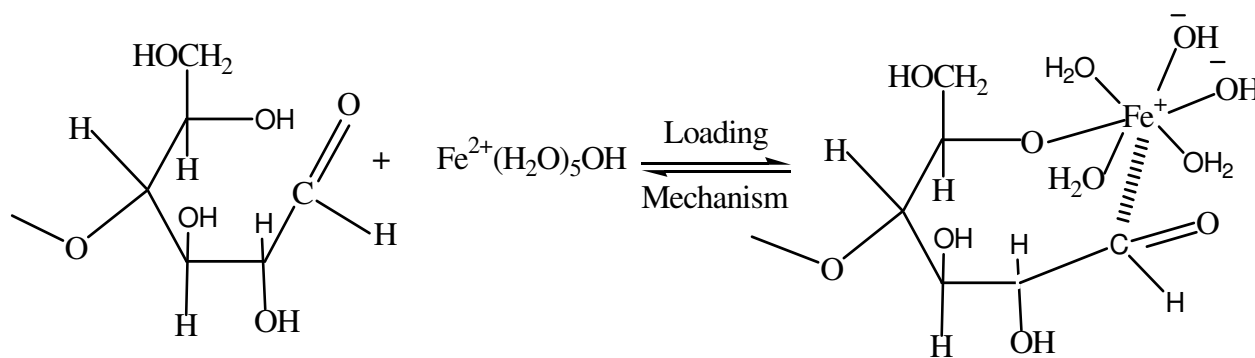
Scheme- 2
Mechanism showing loading of Fe(III) onto ring opened structure of cellulose unit

The percentage removal is determined by equation-1.

$$\text{Removal \%} = \frac{c_i - c_e}{c_i} \times 100\% \tag{1}$$

Where: c_i = Initial concentration of arsenic, c_e = Equilibrium concentration of arsenic. The amount of adsorbate adsorbed in mg/g at equilibrium is determined by equation-2.

$$q = \frac{(c_i - c_e)V}{W} \text{ mg/g} \tag{2}$$

Where: V = Volume of adsorbate solution in liter, W = Weight of adsorbent in g, c_i = Initial concentration of arsenic, c_e = Equilibrium concentration of arsenic.

Results and Discussion

Effect of pH: The effect of pH on removal efficiency of As(III) and As(V) is shown in figure-1 which shows that maximum removal of As(III) occurred at pH 8 and maximum removal of As(V) occurred at pH 5 for FeCSCB.

This may be owing to the fact that in the pH range 0-9, As(III) predominantly exists as the neutral H_3AsO_3[2,10,14] and in the pH range 3-6, As(V) exists as oxyanion $H_2AsO_4^-$ [2, 14]. The adsorption of As(III) may be due to ligand exchange between neutral H_3AsO_3 and neutral water molecules contained in the coordination spheres of loaded metal ion from adsorbent surface as mentioned in scheme-2 and adsorption of As(V) may be due to ligand exchange between oxyanion $H_2AsO_4^-$ and hydroxyl ion existing in the metal coordination spheres as shown in scheme-3.

Effect of Adsorbent Dose: The effect of adsorbent dose on the adsorption efficiency of As (III) and As(V) by FeCSCB is shown in figure-2 which shows that removal of As (III) and As(V) increases with increasing adsorbent dose. The removal remains almost constant after adsorbent dose 200 mg for As (III) and 100 mg for As(V) onto FeCSCB. Increase in removal efficiency with increase in adsorbent amount is due to the availability of sufficient vacant sites and large surface area of adsorbent. At low dose, the adsorbent surface becomes saturated with As (III) and As(V) and the corresponding residual As (III) and As (V) ion concentration in the solution is high.

Effect of Contact Time: The effect of contact time on the batch adsorption of 5 mg/L As(III) and As(V) with 25 mg of adsorbent, FeCSCB is shown in figure-3 which shows the equilibrium contact time for the adsorption of As(III) and As(V) onto FeCSCB reached within the first 240 minutes and 180 minutes respectively, beyond which saturation level is obtained.

From the results, it is clear that the adsorption rate is initially rapid due to the presence of large number of adsorptions sites or complexation sites. The rate decreases gradually as the available sites are occupied by the arsenic metal ions, which is illustrated in the figure-3 as there is no significant increase in adsorption thereby reaching the saturation point. Higher adsorption efficiency of FeCSCB towards As(V) compared to As(III) could be attributed to the higher availability of different oxyanionic species selective surface functional groups obtained by chemical modification of adsorbent.

Effect of Initial Concentration: The effect of As(III) and As(V) concentration is shown in figure-4. It shows that removal of As(III) and As(V) increases with increase in initial concentration of As(III) and As(V) and attains equilibrium which is due to the availability of limited sorption sites.
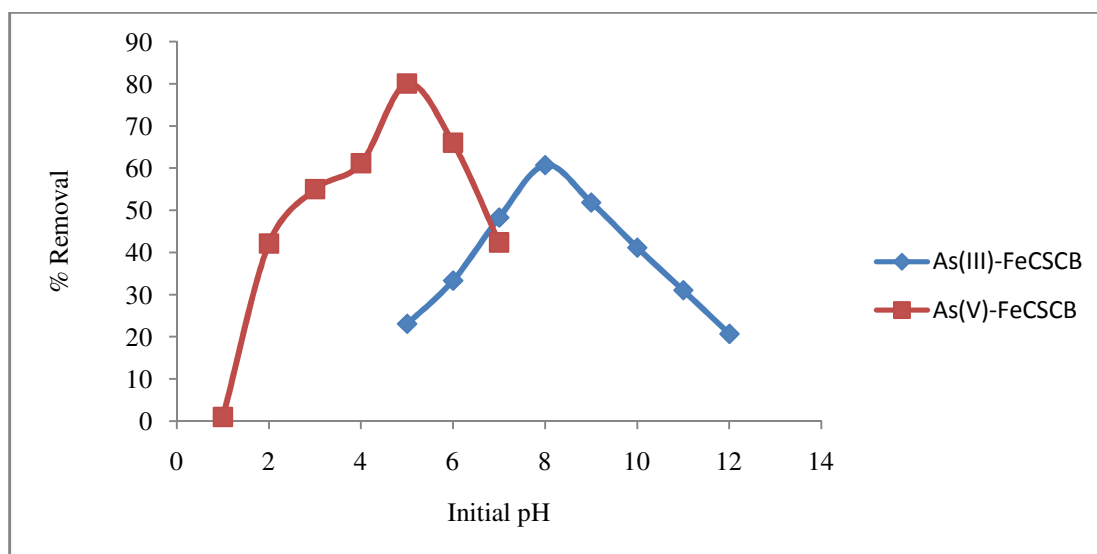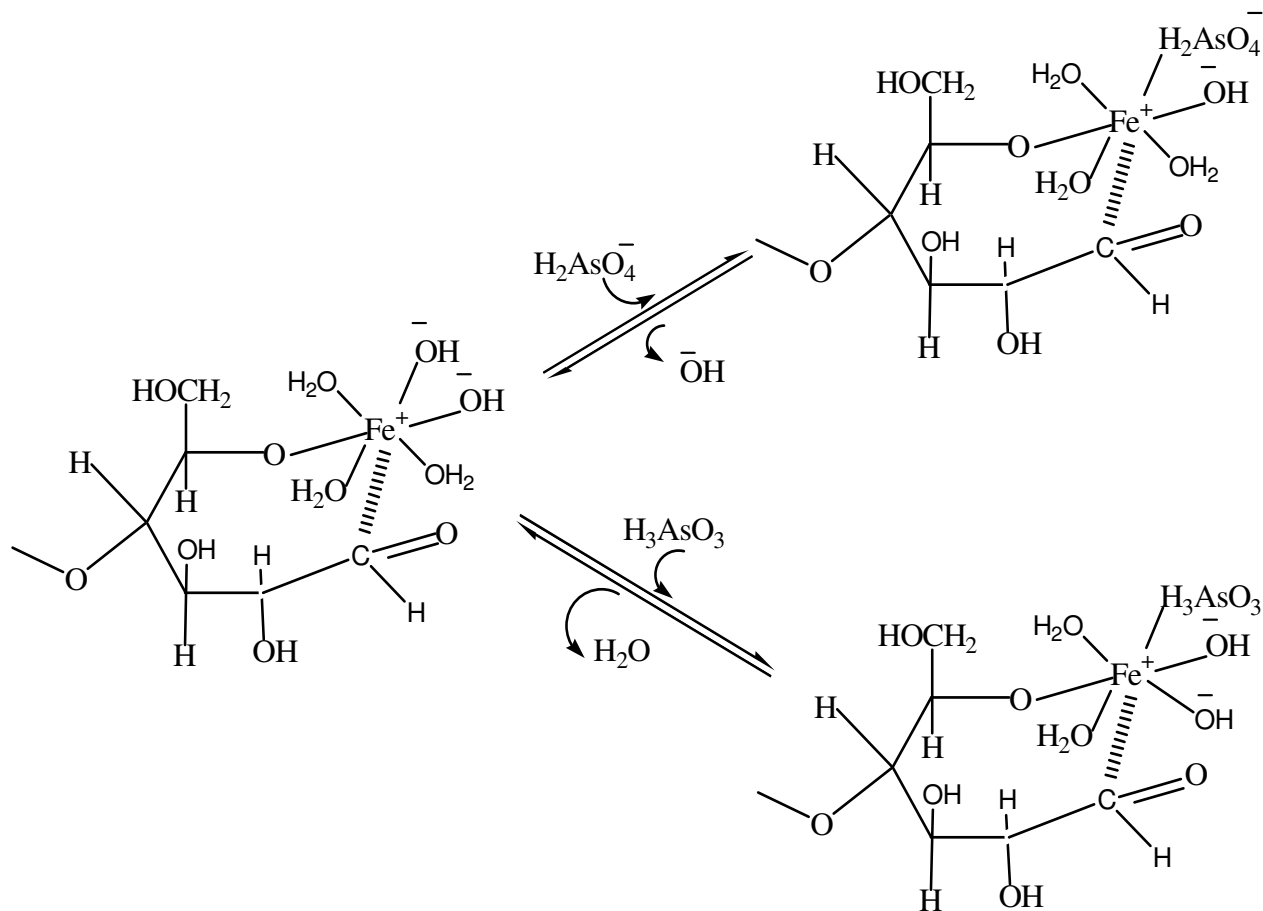

Figure-1
Effect of pH in the adsorption of As(III) and As(V) onto FeCSCB

Scheme-3
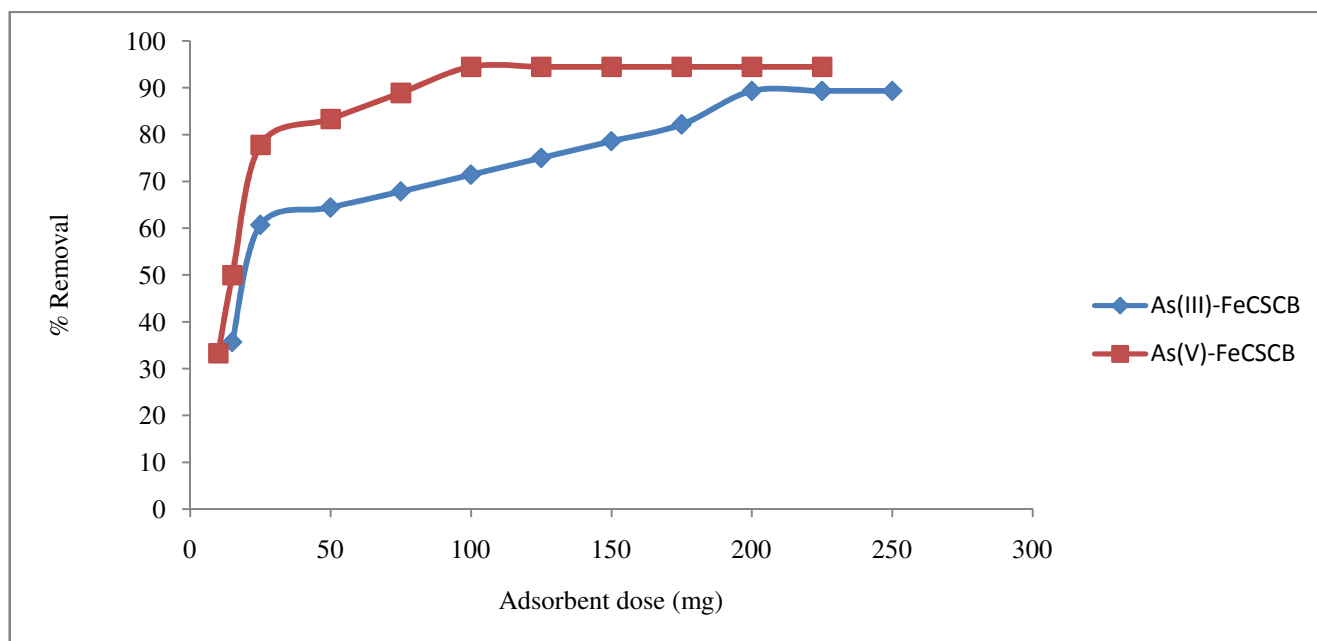**Inferred mechanism of ligand exchange for arsenic adsorption onto FeCSCB[6]**

Figure-2
Effect of adsorbent dose in the adsorption of As(III) and As(V) onto FeCSCB
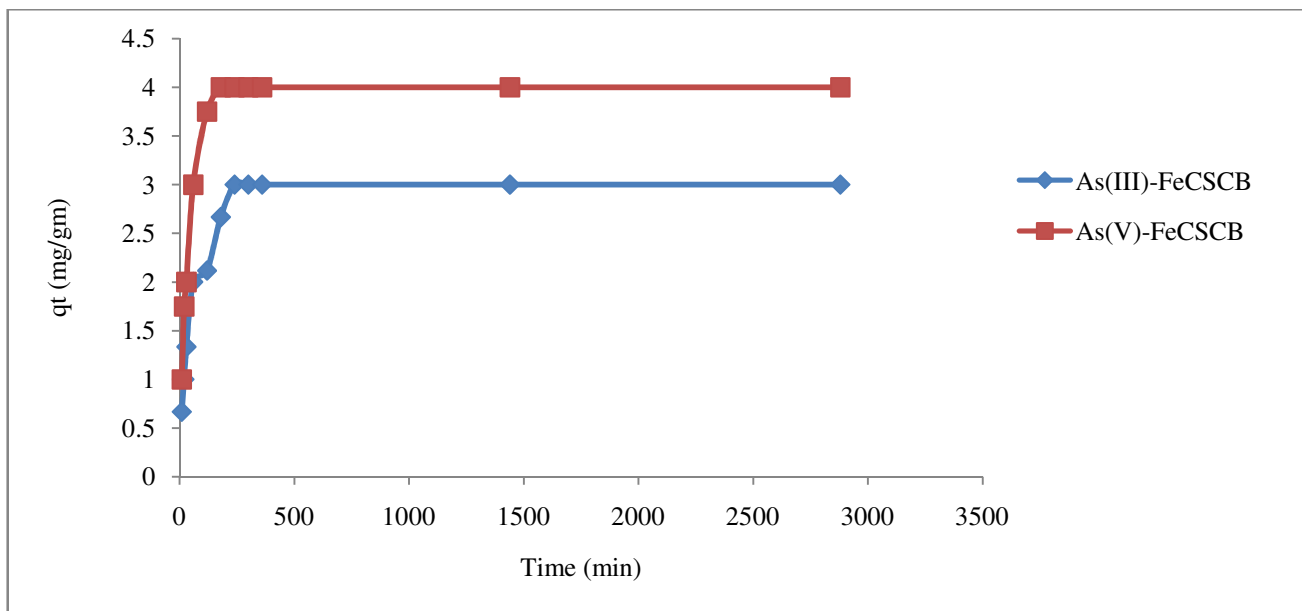
Figure- 3
Effect of contact time in the adsorption of As(III) and As(V) onto FeCSCB

Figure-4
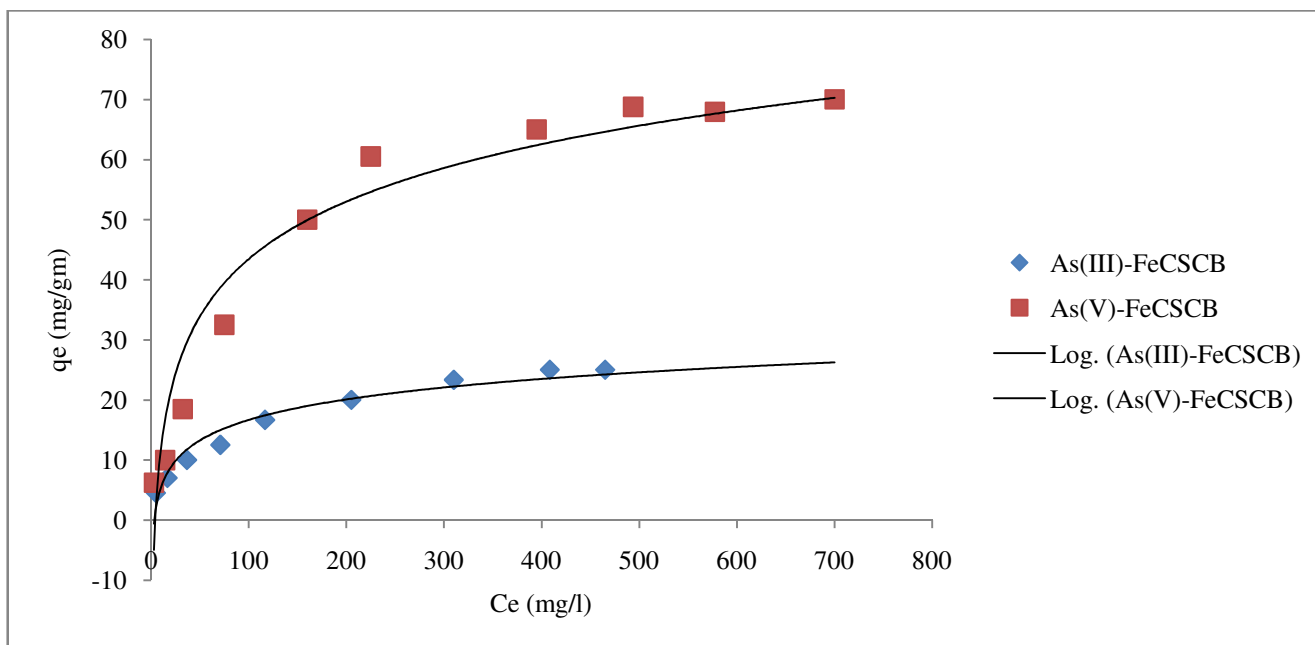**Adsorption isotherm for the adsorption of As(III) and As(V) onto FeCSCB**

The increase in concentration of As(III) and As(V) increases the mass transfer driving force and therefore increases the rate at which As(III) and As(V) ions pass from the bulk solution to the particle surface that would results in higher adsorption.

From the results it is clear that on changing the initial concentration of As(III) from 9.33 mg/L to 490 mg/L, the amount adsorbed increased from 4.5 mg/g to 25 mg/g and for As(V) from 9.25 mg/L to 770 mg/L, the amount adsorbed

increased from 6.25 mg/g to 70 mg/g at corresponding optimum pH for FeCSCB signifying that the bioadsorbent prepared was found to be more efficient for adsorptive removal of As(V) than As(III).

Adsorption Isotherms: The experimental data for the adsorptive removal of As(III) and As(V) from aqueous media was analyzed by using Langmuir and Freundlich isotherm models as shown in figures-5 and 6.
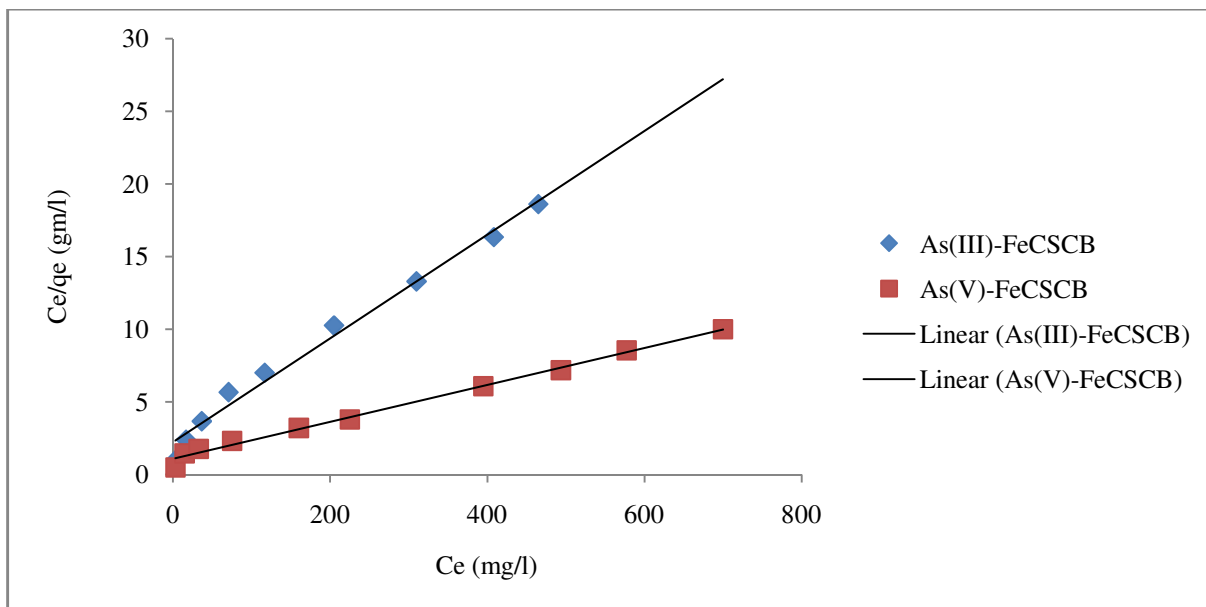
Figure-5
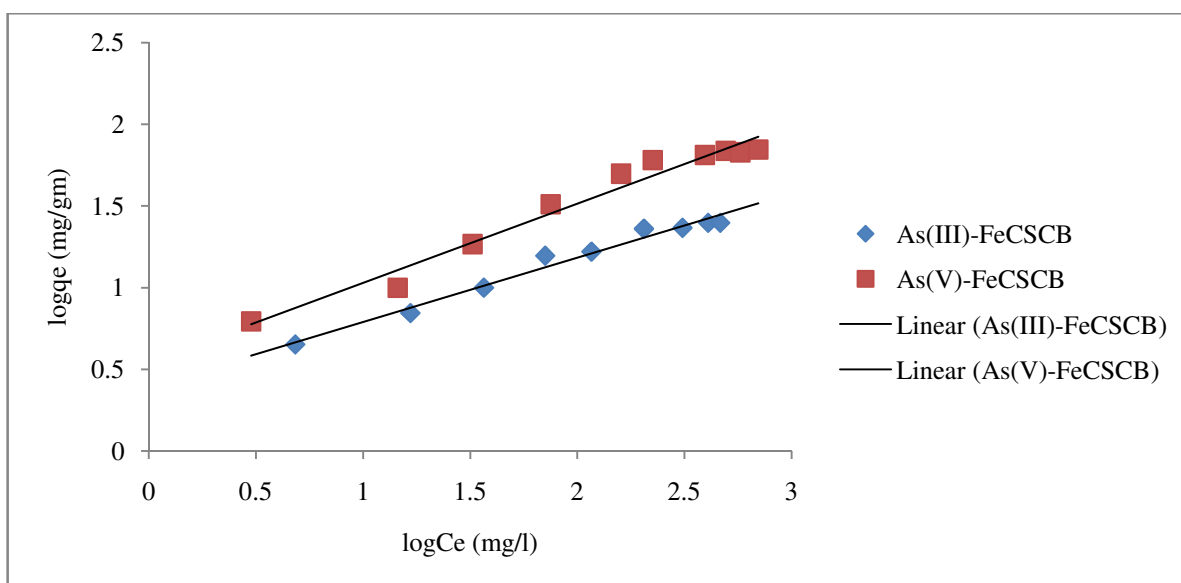**Langmuir adsorption isotherm for the adsorption of As(III) and As(V) onto FeCSCB**

Figure-6
Freundlich adsorption isotherm for the adsorption of As(III) and As(V) onto FeCSCB

Table-1
Langmuir and Freundlich parameters for the adsorption of As(III) and As(V) onto FeCSCB

Species	Adsorbent	Experimental value q_{max} (mg/g)	Langmuir parameter			Freundlich parameter		
			q_m (mg/g)	b (l/mg)	R^2	K(mg/g)	1/n	R^2
As(III)	FeCSCB	25.0	28.57	0.016	0.99	2.45	0.39	0.98
As(V)	FeCSCB	70.0	76.28	0.011	0.99	3.51	0.48	0.97

Langmuir and Freundlich parameters shown in table-1 were determined from the slope and intercept of their respective plots. The values of Langmuir equilibrium parameters which lie between 0 and 1 indicated that equilibrium data fits well with Langmuir adsorption isotherm. The values of 1/n lies between 0 and 1 indicated that adsorption process was favorable.

The correlation coefficient values for Langmuir isotherms were found to be greater than that of Freundlich isotherms indicating that the adsorption process is better defined by the Langmuir adsorption isotherm model than by the Freundlich, which indicated the homogenous distribution of active sites on the adsorbent surface. The monolayer sorption capacities of FeCSCB for As(III) and As(V) were found to be 28.57 mg/g and 76.28 mg/g respectively.

Kinetic Modeling: The kinetics for the adsorption of As(III) and As(V) onto FeCSCB were analyzed by using pseudo first order, pseudo second order and second order models.
From the kinetic plots for the adsorption of As(III) and As(V) onto FeCSCB it was found that the linear correlation coefficients, R^2 for pseudo second order kinetic model were found to be higher than that of pseudo first order kinetic model and second order kinetic model onto FeCSCB adsorbent.

According to pseudo second order kinetic model, the plot of t/q_t versus t gives a straight line with positive slope value. Therefore adsorption of As(III) and As(V) onto FeCSCB follows the pseudo second order kinetic model.

Comparison of the Maximum Adsorption Capacity (q_{max}):
Table-2 shows the comparison of maximum adsorption capacity

(q_{max}) of the FeCSCB with other previously reported adsorbents. The results reveal that the prepared sugarcane bagasse possesses higher potentiality towards the removal of As(III) and As(V) from aqueous solution.

Table-2
Comparison of the maximum adsorption capacity (q_{max})

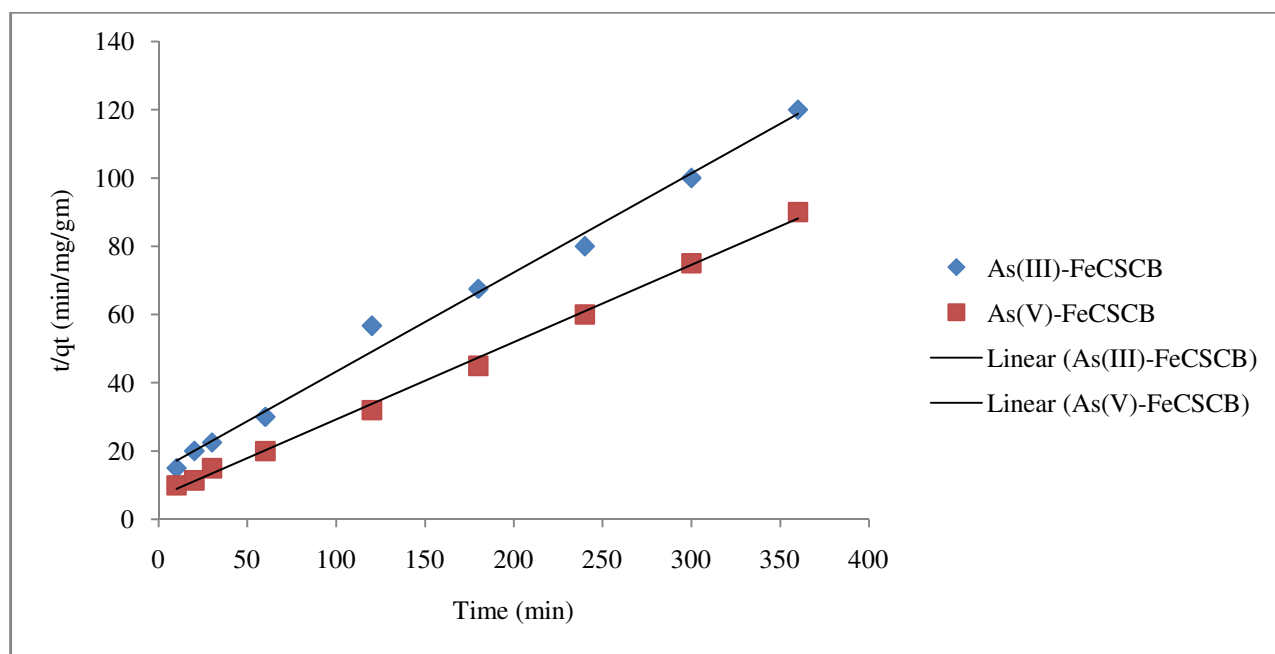| Species and adsorbent	q_{max} (mg/gm)	References
As(III), multi functionalized cellulose	5.71	14
As(V), multi functionalized cellulose	75.13	14
As(V), sugarcane bagasse treated with ferric oxide	22.1	15
As(III), *Cinnamomum zeylancium*	36.311	16
As(V), palm bark	2.23	10
As(III), iron oxide impregnated activated alumina	12	7
As(III), FeCSCB	25	Present work
As(V), FeCSCB	70	Present work

Figure -7
Pseudo second order kinetic model for the adsorption of As(III) and As(V) onto FeCSCB

Conclusion

Iron loaded chemically modified sugarcane bagasse showed appreciable affinity towards adsorptive removal of As(III) and As(V). Basic adsorption experiments indicated that the adsorption of As(III) and As(V) by FeCSCB was an adsorbate, adsorbent dependent phenomena and the optimum adsorption capacity for the FeCSCB were achieved at pH 8 and pH 5 for As(III) and As(V) respectively, at an initial concentration of 5 mg/L. The equilibrium contact times for the sorption of As(III) and As(V) were 240 minutes and 180 minutes respectively. The optimum dose of FeCSCB for As(III) and As(V) were 200 mg and 100 mg respectively. The maximum adsorption capacities were found to be 25 mg/g and 70 mg/g for As(III) and As(V) respectively, signifying that the adsorbent prepared was more efficient for adsorption of As(V) than As(III). The isotherm result revealed that the Langmuir adsorption isotherm model was found to be more applicable than Freundlich adsorption isotherm for the better description on the adsorption behaviour of the As(III) and As(V) ions onto FeCSCB, signifying the surface homogeneity with respect to active sites. The kinetic data was analyzed by pseudo second order, pseudo first order and second order kinetic models and it was found that the obtained data were best fitted by the pseudo second order kinetic model. Comparisons of maximum adsorption capacity of FeCSCB with earlier investigated adsorbents have shown that bioadsorbent prepared in this work possesses higher potentiality towards the adsorptive removal of As(III) and As(V) from aqueous media. Thus, it is concluded that the sugarcane bagasse can be used as an efficient and economical material for the adsorptive removal of As(III) and As(V) from aqueous system.

Acknowledgement

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