

Original Research Article

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Application of Chemically Modified Chitosan for Removal of Arsenic from Water: A Column Bed Experiment

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ABSTRACT

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A low cost column mode device was designed and fabricated for removal of trivalent and pentavalent arsenic from water. The chemically modified chitosan was entrapped in polyurethane matrix and used as a column bed for adsorption for both the forms of arsenic. The chemical modification of chitosan was achieved by pre-treatment with ferrous oxide manganese oxide. The column bed exhibited 75% of As(III) and 72 % of As(V) removal at 1000 ppb concentration. The flow rate of the arsenic solution through column matrix directly influenced the removal and the flow rate of 100 mL min⁻¹ showed two to three folds higher removal of arsenic as compared to 200 mL min⁻¹. The design and the process of preparation of chemically modified chitosan are the novel findings of the study.

Introduction

There is a growing concern about contamination of ground and surface water in developing countries. The use of arsenic in various industries such as semiconductor manufacturing industries and wood preservative industries has led to the contamination of water (Choon *et al.*, 2007). The concentration higher than guideline value of arsenic in natural water is well documented in countries such as America, France,

Bangladesh, China, India and Mexico (Lee *et al.*, 2017). The drinking water consumed by at least 140 million people in 50 countries is contaminated with arsenic at levels above the World Health Organization (WHO) guideline value of 10 µg L⁻¹ (Ravenscroft *et al.*, 2009). The dominant inorganic forms of arsenic are function of pH and redox potential of water. Based on oxidation state the different forms of arsenic are arsenate [As(V)], arsenic [As(0)] and arsenite [As(III)]. Arsenate and arsenite are the most prevalent species of

arsenic, commonly encountered in water (Pouset *et al.*, 2015). Higher cytotoxicity, genotoxicity, mobility and solubility have led to higher toxicity of arsenite compared to arsenate (Singh *et al.*, 2015). Many treatment methods were tried for removal of arsenic from water but adsorption is the most preferred method due to availability of variety of low-cost adsorbent, low waste generation and ease of operation (Kabir and Chowdhary, 2017).

Chitosan is a polysaccharide obtained by hydrolysis of chitin using alkali. It is non-toxic, renewable and hydrophilic compound (Elwakeel, 2010). Chitosan is considered as a better adsorbent than chitin due to the presence of many amino (-NH₂) groups which act as reaction sites for binding with arsenic (Annadurai *et al.*, 2008). It is also considered as a low-cost adsorbent due to the availability of its raw material in plenty and also as a by-product of crustacean shell and fungal biomass

The present study aimed to fabricate a low-cost column mode device by using PVC pipe. The adsorbent bed of the column was prepared by chemical modification of chitosan using ferrous oxide and manganese oxide and used for arsenite [As(III)] and arsenate [As(V)] removal from water. The efficacy of the column was evaluated through column experiments on the basis of the parameters such as removal efficiency, adsorption capacity and breakthrough ratio.

Materials and Methods

Design of column

The filtration unit used for the present study was developed and fabricated from locally available material. Low cost and locally available materials like polyurethane foam, PVC pipes and plastic containers were used

for the fabrication of the unit. The unit consisted of two compartments (upper and lower), and a column consisting of adsorbent materials which was placed at the junction of both the compartment with a vertical orientation. The column was in contact with an untreated arsenic solution of the upper compartment through the inlet channel. The treated water was discharged into the lower compartment after passing through the column. The simplified column is shown in (Fig. 1).

Packing material of column for arsenic removal

The column packing material was prepared by entrapping the chemically modified chitosan into the polyurethane foam. The foam was cut into a cylindrical shape. Two foams entrapped with the chemically modified chitosan were used to prepare the column for the experiment. The dimension (diameter x height) of foam material used in the experiment was 7.5 and 6.5 cm respectively.

The packing material for the column was prepared by soaking the polyurethane foam with the chemically modified chitosan which was prepared by the following procedure of Zhang *et al.*, (2007) and Miller and Zimmerman (2010) with a slight modification. The total weight of adsorbent for each polyurethane foam was 10 g. The polyurethane foams are then soaked in 0.01 M NaOH and washed with distilled water until the filtrate becomes neutral. Polyurethane foams were then dried and kept for later use in the experiment.

Column experiment

Column experiment for removal of As(III) and As(V) was conducted using column consisting of polyurethane foam entrapped with the chemically modified chitosan. The

required working test concentration of As(III) and As(V) was prepared from the stock solution of both forms of arsenic and filtered through the column.

The experiment was conducted by passing 1000 ppb of As(III) and As(V) solution through the designed column for 180 min at a flow rate of 100 mL min⁻¹. The effect of the flow rate of the column on its performance was also studied at 100 and 200 mL min⁻¹. The samples were collected at 15, 30, 45, 60, 90, 120, 150, and 180 min post operational from the column and filtrate was analyzed for arsenic content. The removal efficiency, adsorption capacity and breakthrough ratio were calculated and compared for As(III) and As(V) at each time period. The arsenic concentrations before and after adsorption were estimated. Further, the removal efficiency of the column was computed using the standard equation (Das and Mondal, 2011).

$$\text{Removal efficiency} = [(C_0 - C_e)/C_0] \times 100$$

Where C_0 and C_e are the concentration of arsenic before and after the treatment.

The adsorption capacity ($q_e = \text{mg g}^{-1}$) of the column for each concentration of arsenic [As(III) and As(V)] at equilibrium was also determined by using the following equation (Das and Mondal, 2011):

$$\text{Adsorption capacity} = \frac{[(C_0 - C_i)V]}{M}$$

Where,

V is the volume of solution (L) and M is the mass of the adsorbent (g).

The breakthrough ratio of As(III) and As(V) during the column experiment at various time interval was calculated by taking the ratio of

effluent concentration (C_e) and influent concentration (C_0) against time. The ratio value of 1.0 denoted the breakthrough point.

Arsenic analysis

As(III) and As(V) in the water before and after treatment were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Briefly, a Perkin Elmer ELAN DRC instrument was used with a meinhart nebulizer and silica cyclonic spray chamber and continuous nebulization. The operating conditions were Nebulizer Gas flow rates: 0.95 L min⁻¹; Auxiliary Gas Flow: 1.2 L min⁻¹; Plasma Gas Flow: 15 L min⁻¹; Lens Voltage: 7.25 V; ICP RF Power: 1100 W; CeO/Ce = 0.031; Ba⁺⁺/Ba⁺ = 0.016.

Results and Discussion

Removal efficiency of column with increase in time

The result showed that the removal efficiency of column (Fig. 2) decreased with increase in time for both As(III) and As(V). The removal efficiency decreased from 75 to 9 % in 15 to 180 min period for As(III). A similar trend was observed for As(V) where the decrease in removal efficiency was 72 to 4% in 15 to 180 min column operation time. It was also observed that removal efficiency of the column for As(III) was higher at all the time (15 to 180 min) when compared for As(V). The overall decrease in column removal efficiency with increase in time for both As(III) and As(V) is due to reduction in vacant sites of adsorbents with increase in time.

Adsorption capacity of column with increase in time

The result showed there was an increase in adsorption capacity of column in the initial

phase but a gradual decrease in adsorption capacity was evident after initial 15 minutes (Fig. 3). The adsorption capacity increased 0.05 to 0.09 mg g⁻¹ till 60 min of operation of the column for As(III). Also the adsorption capacity started decreasing after 60 min of column operation time and reached from 0.09 to 0.05 mg g⁻¹ at the end of the column experiment (180 min). The same trend was also observed for As(V), but the increase was found only upto 30 min of column operation time and after that it gradually decreased. The adsorption capacity increased from 0.05 to 0.9 mg g⁻¹ till 30 min and then decreased to 0.02 at the end of experiment (180 min). The above trend is due to shortening of mass transfer zone after a initial time period which resulted in a decrease in adsorption capacity after attaining maximum value.

Breakthrough ratio of column with increase in time

The breakthrough ratio of the column showed that it increased with the column operation time (Fig. 4). The breakthrough ration increased from 0.25 to 0.91 in 15 to 180 min of column operation time for As(III). The same trend was also observed for As(V) where the breakthrough ration increased from 0.28 to 0.96 in 15 to 180 min of column

operation time. It was also observed that the breakthrough ration was always higher for As(V) when compared for As(III). The increase in breakthrough ratio is due to the increase in amount of adsorbate (arsenite and arsenate) on the column bed, which reduces the capacity of adsorption of the adsorbent.

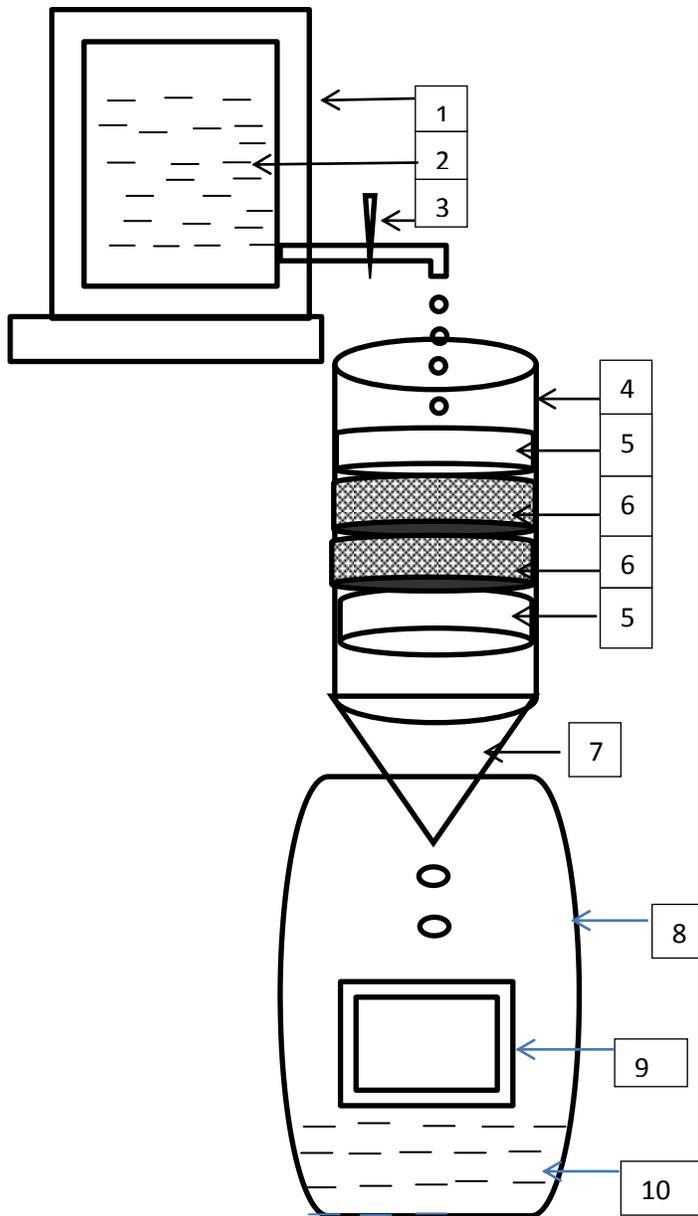
Effect of column flow rate on removal efficiency of column

It was noticed that with increase in flow rate of the column, there was decrease in removal efficiency of the column (Table 1) for both As(III) and As(V). The removal efficiency of column decreased from 80 to 30% at flow rate of 100 mL min⁻¹, while it reduced from 32 to 10.2 % at flow rate of 200 mL min⁻¹ for As(III) between 15-180 min. In case of As(V) the removal rate decreased from 76 to 26 % at 100 mL min⁻¹ and 30 to 8 % at 200 mL min⁻¹ between 15-180 min. The result showed that there was almost two to three-fold decrease in removal efficiency of column for both As(III) and As(V) due to increase in flow rate from 100 mL min⁻¹ to 200 mL min⁻¹. The decrease in removal efficiency with increase in flow rate is due to availability of insufficient time for both forms of arsenic to interact with the column bed (Nidheesh *et al.*, (2012).

Table.1 Removal efficiency (%) of column at different flow rate for As(III) and As(V) at different time period. [Adsorbent mass: 20g, Initial concentration: 500 ppb, pH: 7± 0.5, Temperature: 27 ± 2 °C]. Data are presented in Mean± S.E, n=2.

Time (min)	As(III)		As(V)	
	100mL min ⁻¹	200mL min ⁻¹	100mL min ⁻¹	200mL min ⁻¹
15	80±0.0022	32.0±0.0033	76.0±0.0028	30.0±0.0043
30	76±0.0030	28.0±0.0020	72.0±0.0031	26.0±0.0040
45	72±0.0035	24.8±0.0015	68.0±0.0030	23.0±0.0015
60	66±0.0039	22.0±0.0029	62.0±0.0038	21.0±0.0069
90	54±0.0056	20.0±0.0031	50.0±0.0023	18.0±0.0021
120	46±0.0023	18.0±0.0049	38.0±0.0027	14.0±0.0029
150	38±0.0035	13.6±0.0052	32.0±0.0019	10.0±0.0032
180	30±0.0058	10.2±0.0016	26.0±0.0024	8.0±0.0036

Fig.1 Diagram of column



- | | |
|-------------------------------|-------------------------------------|
| 1- Water tank | 6- Treated polyurethane foam |
| 2- Arsenic contaminated water | 7- Funnel plastic for effluent exit |
| 3- Water flow regulator | 8- Water container |
| 4- PVC pipe | 9- Window for collection of sample |
| 5- Polyurethane foam | 10- Treated water |

Fig.2 Removal efficiency of column for As(III) and As(V) at different time period [Adsorbent mass: 20g, Initial concentration: 1000 ppb, pH: 7 ± 0.5 , Temperature: 27 ± 2 °C, Flow rate: 100mL min^{-1}]. Data are presented in Mean \pm S.E., n=2

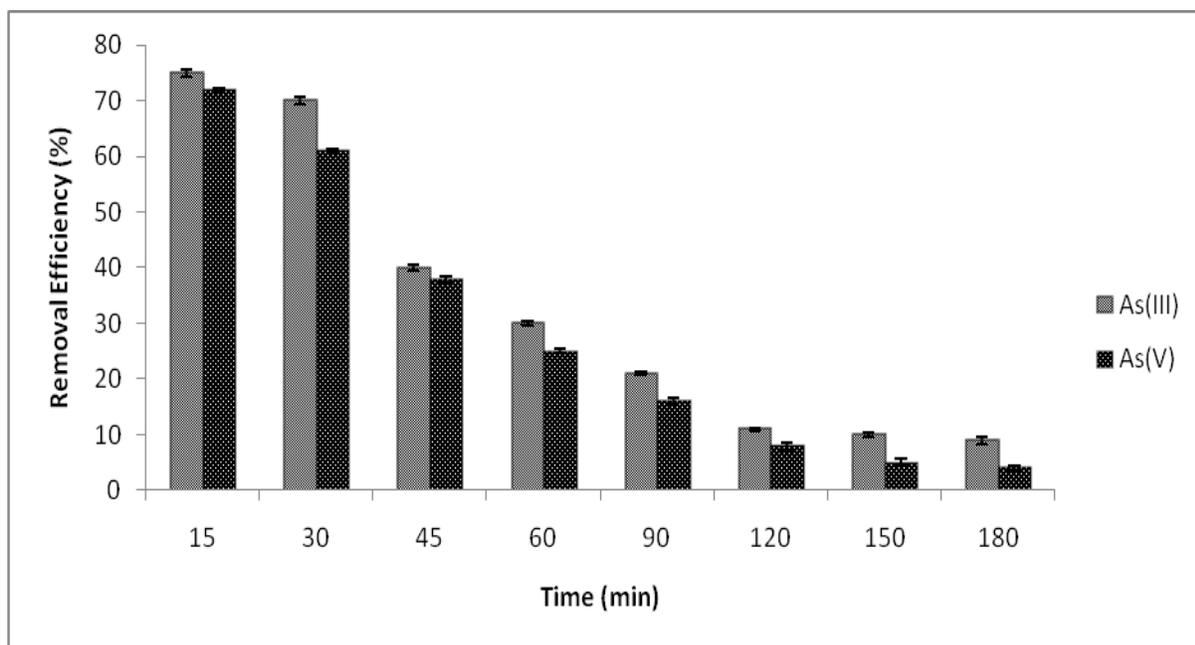


Fig.3 Adsorption capacity of column for As(III) and As(V) at different time period [Adsorbent mass: 20g, Initial concentration: 1000 ppb, pH: 7 ± 0.5 , Temperature: 27 ± 2 °C, Flow rate: 100mL min^{-1}]. Data are presented in Mean \pm S.E., n=2

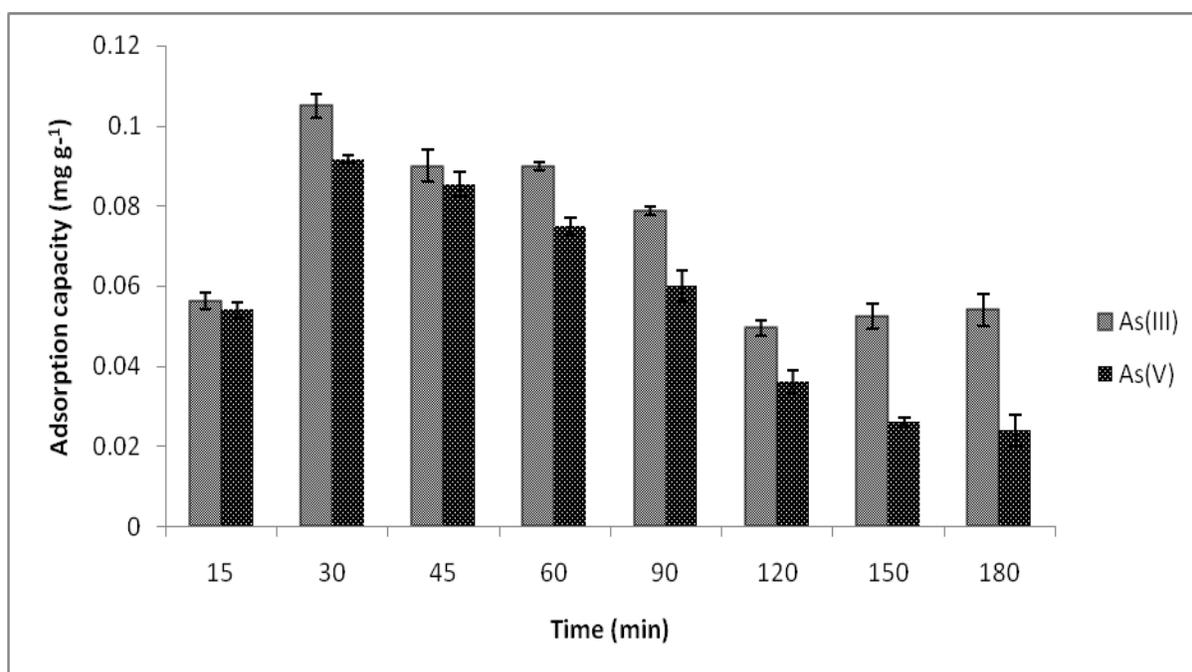


Fig.4 Breakthrough ratio of column for As(III) and As(V) at different time period [Adsorbent mass: 20g, Initial concentration: 1000 ppb, pH: 7 ± 0.5 , Temperature: 27 ± 2 °C, Flow rate: 100mL min^{-1}]. Data are presented in Mean \pm S.E., n=2

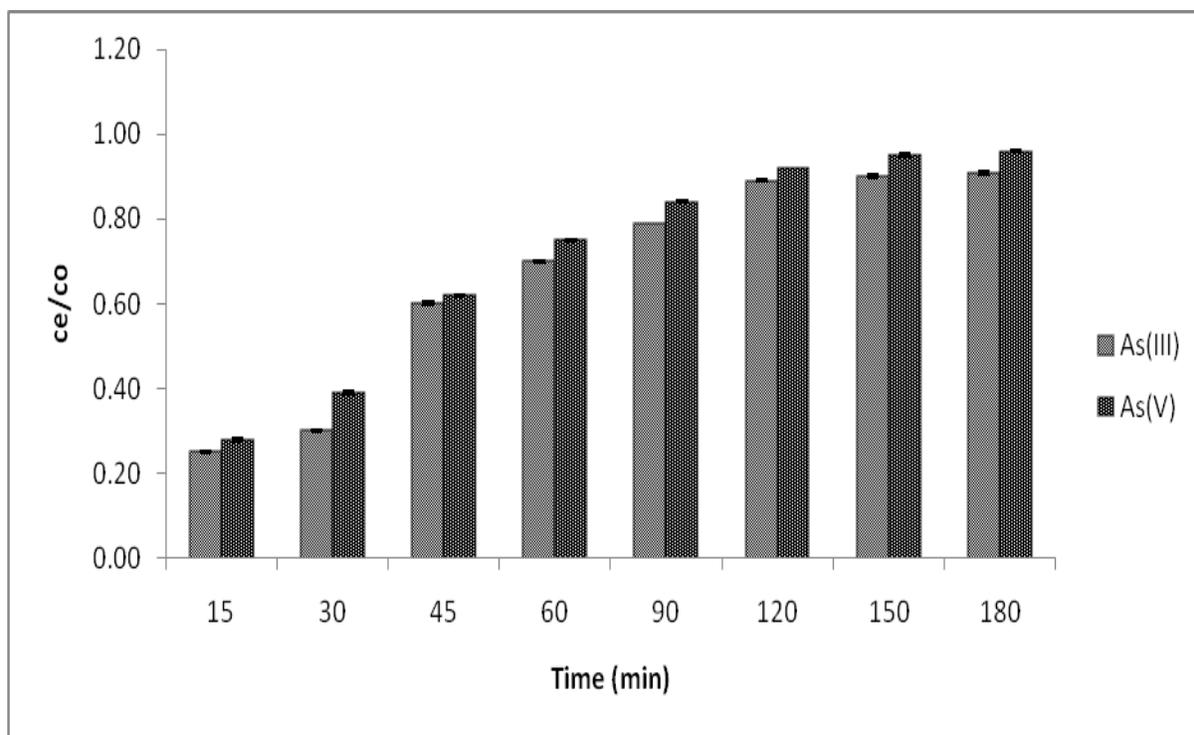


Fig.5 Adsorption capacity of column at different flow rate for As(III) and As(V) at different time period. [Adsorbent mass: 20g, Initial concentration: 500 ppb, pH: 7 ± 0.5 , Temperature: 27 ± 2 °C]. Data are presented in Mean \pm S.E., n=2

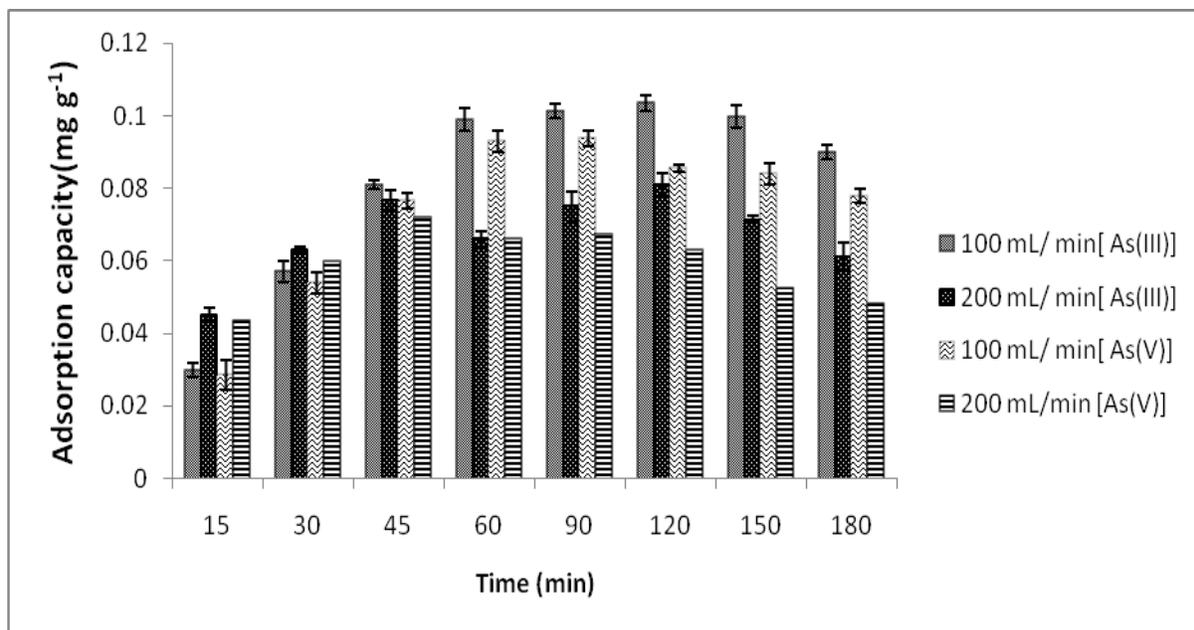
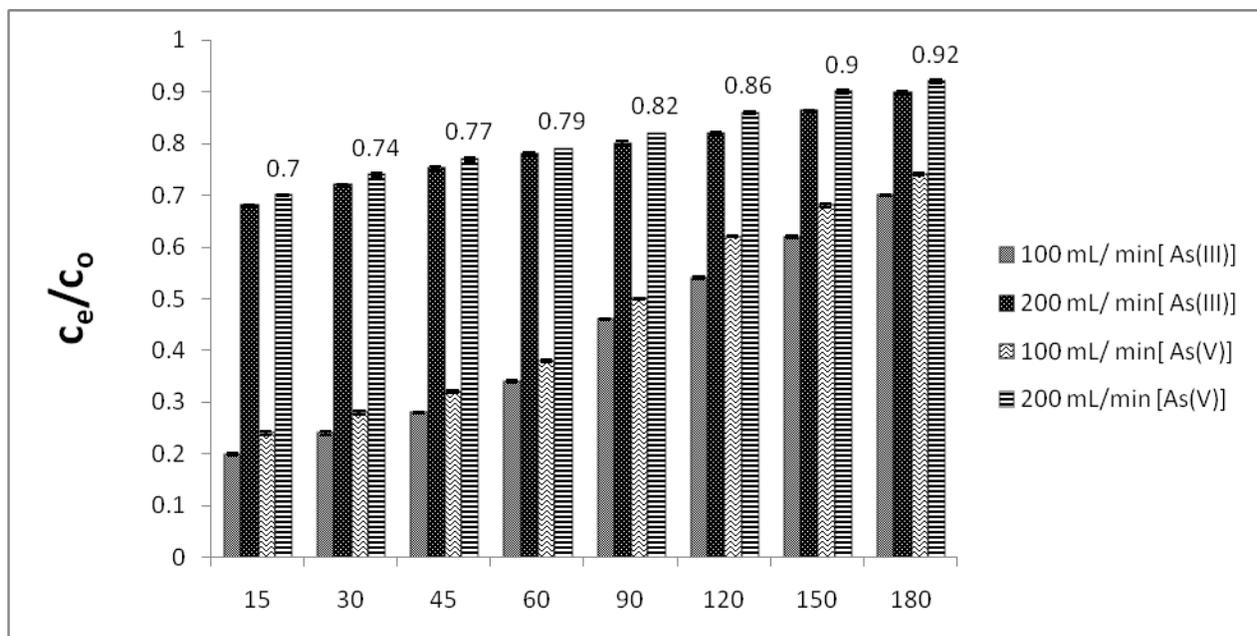


Fig.6 Breakthrough ratio of column at different flow rate for As(III) and As(V) at different time period. [Adsorbent mass: 20g, Initial concentration: 500 ppb, pH: 7 ± 0.5 , Temperature: 27 ± 2 °C]. Data are presented in Mean \pm S.E, n=2



Effect of column flow rate on adsorption capacity of column

It was found that with increase in flow rate from 100 to 200 mL min⁻¹, the adsorption capacity decreased after 30 min of column operation for As(III). The adsorption capacity was found to be higher at 200 mL min⁻¹ till 30 min of column operation time when compared to flow rate of 100 mL min⁻¹(Fig. 5). The adsorption capacity increased from 0.03 to 0.10 (15-120 min) and then decreased to 0.09 (180 min) at 100 mL min⁻¹ for As(III). But at 200 mL min⁻¹ for As(III), the adsorption capacity increased from 0.04 to 0.08 (15 -120 min) and then decreased to 0.06 (180 min). The same trend was also observed for As (V) where the adsorption capacity was higher at flow rate of 200 mL min⁻¹ till 30 min of column operation. A gradual decrease in the adsorption capacity of the column at 200 mL min⁻¹ was recorded after 30 min. The adsorption capacity was 0.02 mg g⁻¹ at 15 min, 0.09 at 90 min and then finally reached

to 0.07 after 180 min for As(V) at flow rate of 100 mL min⁻¹. In case of As(V) , flow rate of 200 mL min⁻¹ showed that the adsorption capacity increased from 0.04 mg g⁻¹ (15 min) to 0.07 mg g⁻¹ (45 min) and then decreased to 0.04 mg g⁻¹ (180 min). The increase in adsorption capacity up to certain time is attributed to the higher availability of vacant sites on the adsorbent. The decrease in removal efficiency of column might be also due to decrease in bonding capacity of arsenic ions onto the adsorbent surface with increase in flow rate. Similar findings were reported by Roy *et al.*, (2013) who stated that adsorption capacity decreased when the flow rate increased from 3 to 7 mL min⁻¹.

Effect of column flow rate on breakthrough ratio of column

The breakthrough ratio shows it was comparatively higher for both As(III) and As(V) at 200 mL min⁻¹ of column flow rate . The breakthrough ratio increased from 0.2 (15

min) to 0.7 (180 min) at flow rate of 100 mL min⁻¹, while the increase was from 0.68 (15 min) to 0.89 (180 min) for 200 mL min⁻¹ (Fig. 6) for As(V). At flow rate of 100 and 200 mL min⁻¹ for As(V), the breakthrough ratio increase from 0.24 (15 min) to 0.74(180 min) and 0.7 (15 min) to 0.92 (180 min) respectively. The increase in breakthrough ratio with increase in flow rate is explained by the fact that as the flow rate increased, the time required for the adsorbate (arsenic) to interact with the column bed decreases and thus the concentration of arsenic after treatment decreases slowly. It was also observed that at higher flow rate saturation of column will occur more slowly when compared to lower flow rate. Rouf and Nagapadma, (2015) also reported that at higher flow rate saturation of column was delayed in case of azo dye adsorption on chitosan impregnated with a cationic surfactant.

In conclusion, chemical modification of Chitosan showed an improved efficiency for the removal of trivalent and pentavalent arsenic from water. The entrapment of the chemically modified chitosan in the column matrix exhibited an appreciable extent of removal of arsenic from water. The column bed device was fabricated from widely available low-cost materials therefore, the developed device offers an effective solution for remediation of arsenic contaminated water.

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