

## Adsorption of As (III) on surface modified coconut husk in fixed bed column

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Column studies with iron impregnated coconut husk (IICH) were carried out to demonstrate its potential and for practical suitability as an adsorbent for treatment of water containing arsenic (III) i.e. As(III) at industrial scale. The required experimentations were performed and using the data generated, the breakthrough curves were prepared depicting the adsorption of As (III) on IICH at different concentration (10-100 mg/l), different bed depth (10-30 cm) and different flow rate (1-4 ml/l) with the constant initial pH of influent solution 7.5. On analyzing the data, the breakthrough time was observed to decrease with increase in initial As (III) concentration and flow rate but it increases with an increase in bed height. The higher value of bed height is not recommended. The experimental data obtained during this work were fitted with Thomas model at different experimental conditions of inlet concentration, bed height and flow rate. The experimental breakthrough curves were close to the predicted by Thomas model.

Keywords: As (III), fixed bed column, RCH and IICH, breakthrough curve.

### Introduction

As (III) is a common trace organic and inorganic pollutant in drinking and industrial water is extremely detrimental to many organism and human being. The standard of arsenic determined by EPA, The permissible level of arsenic contamination in drinking water is 10 ppb. In Recent day epidemiological evidences on arsenic both acute and carcinogenicity suggest if the arsenic level is above its permissible limits. Acute & sub acute Impacts include development of nonspecific gastrointestinal effects such as diarrhea, cramping, pain in stomach, vomiting, nausea, etc. Such symptoms may further lead to coma and even death if intake is high enough. Not only this, several other chronic health effects such as Hypertension, various type of cancer,

Peripheral and Cardiac vascular diseases, Breathing diseases, failure of kidney, liver, bladder, and Malignancies in skin have also been observed due to exposure to Arsenic (III) contamination. Even in some cases, genetic effects have also been detected<sup>1</sup>.

Because of its simplicity and ease of applicability in rural as well as in urban areas, the adsorption process is maintaining its importance in water treatment processes. So, the researchers working in this area are continuously trying to find out cheap but effective adsorbents to deal with the day-by-day aggregating ground water contamination by arsenic. Therefore, technically viable and cheaper approach for removal of arsenic is necessary. The study presented in this work is reliable and pretty efficient for removal of

complex inorganic and organic As (III) than many conventional treatment methods<sup>2</sup>. Iron Impregnation is a common coating of many bio adsorbent such as coconut husk, bagasse, rice husk etc. and has a high capacity for removal of As (III).

The column operation has a unique advantage over batch operation, as in column operation the adsorption rate depends on the solute concentration of the solution under treatment<sup>3</sup>.

Considering the above, this study was performed to assess the feasibility of using a controlled column system with variables conditions. Various parameters affecting the process such as depth of the column bed, flow rates of influents, initial concentration of influent to treat the arsenic contaminated water have been studied. Also, the models fitting the data generated were identified and kinetic coefficients and breakthrough time were calculated. Finally, the results obtained are compared with reported literature.

## **Experimental Methods**

### *Reagent*

Analytical/ technical grade materials and chemicals are used in this study. For the removal of Arsenic (III), modified adsorbent (IICH) were prepared in the laboratory.

### *Preparation of Adsorbent*

The Coconut husk used in this study was bought from the local market near MNNIT Allahabad. Firstly, the procured adsorbent were washed using tap water and then several time washed by distilled water to remove the impurities such as dust and foreign substances, and after this process, it was put in oven at 105 °C overnight, and then were kept at room temperature for cooling. The coating was developed by evaporating a ferric nitrate solution in presence of adsorbent in glass beakers, a 200 gram of the dried adsorbent was mixed with 200 ml of ferric

nitrate solution containing 2.5% by weight Fe<sup>+3</sup>. The pH was adjusted to ~12 by adding NaOH solution. The modified adsorbent was filtered and washed several time to remove the extra iron from the modified husk. This modified form of the coconut husk was then dried at 105 °C temperature overnight to get the adsorbent. The adsorbent prepared through this is termed as Iron Impregnation Coconut Husk (IICH).

### *Analytical procedures*

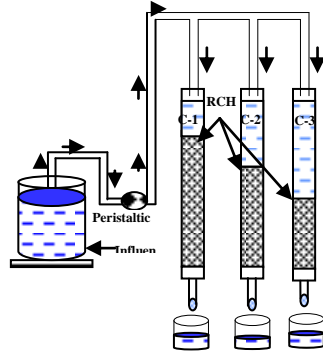
During experimentation, precise measurements of various parameters were quite important. A double beam UV spectrophotometer (Shimadzu, Japan; model UV570453) was used to record the concentration of As (III) concentrations. The wavelength ( $\lambda_{max}$ ) used was 865 nm. Further, a digital pH meter (model 420A+, Thermo Orion, USA) was used to monitor another crucial parameter, the pH of the arsenic contaminated water.

### *Experimentation*

Adsorptive removal of arsenic from synthetic arsenic solution by raw and modified coconut husk was examined at room temperature under unsteady state condition in a continuous column. The effect of important parameter such as different concentration (10-100mg/l), bed height (10-30 cm), flow rate (1-4 ml/min) and a fixed bed diameter (2.54 cm) at 6.5 pH<sub>0</sub>. The adjustment in this pH value was done using the 0.1M dilute aqueous solutions of NaOH or HCl. The performance of continuous column in the form of breakthrough curve was obtained and tested using linear form of Thomas model.

### *Specification of the column.*

The schematic diagram of the continuous columns setup used in this investigation is shown in Fig. 1 and the technical specifications are provided in the Table 1. Further, the details related to bed porosity, specific gravity of packed column is given in Table 2.



**Fig.1.** Schematic diagram the continuous columns setup

**Table 1:** Details of column and operation conditions for column study

Parameter	Dimension
Diameter of column	2.54 cm
Height of the column	120 cm
Glass wool used	1 gram
Area of column	957.67 cm <sup>2</sup>
Bed Volume of column	607.7 cm <sup>3</sup>
Initial As (III) concentration	10 -100 mg/l
Height of the column	10-30 cm
Glass wool used	1 gram
Flow rate used	1-4 ml/L
Peristaltic pump used	Miclins

**Table 2:** The details of bed porosity, specific gravity and formula used

Parameters	RCH	IICH
Bed Porosity	0.03829	0.1439
Dry density (g/cm <sup>3</sup> )	0.1345	0.2511
Wet density (g/cm <sup>3</sup> )	0.25	0.32
Specific gravity (g/cm <sup>3</sup> )	0.1345	0.2511

## Result and discussion

### *Characterisation of adsorbents*

The characterization of the raw and modified coconut husk was done using standard methods. IICH were characterized by using standard methods. The characterization result is published in our previous research paper<sup>4</sup>.

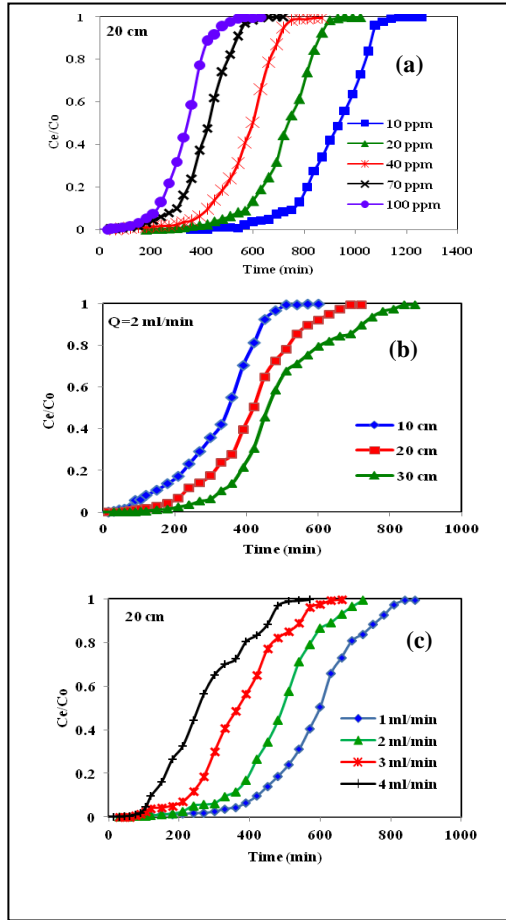
### *The effects of initial arsenic concentration*

The relevant breakthrough curve for adsorption As (III) at different influent concentration onto IICH is shown in Fig. 2(a). The figure depicts that as the initial As (III) concentration is increased, the break through point time decreased. When the initial As (III) concentration was higher, the value of breakthrough time was smaller and the slope of the breakthrough curve was steeper. Studies carried out by other investigators also support this finding that the breakthrough curves become steeper and the breakthrough time decreases with increasing the influent concentration<sup>5</sup>. Further, when concentration in the inlet increases then the adsorbed quantity increased. This is due to an increase in the concentration gradient so that the more driving forces available surrounding the adsorption phase<sup>6</sup>.

### **3.2 The Effects of the column bed depth**

The breakthrough curve for As (III) removal at three different heights (10, 20 and 30 cm) at constant flow rates (1 to 4 ml/min) and fixed influent As (III) concentration (40 mg/l) with the initial pH of influent solution 7.5 maintained by 1 N HCl and 1 M NaOH solution. Fig. 2(b) shows the breakthrough curves for the adsorption of As (III) onto IICH at three different bed heights. It was found that the breakthrough volume and adsorption capacity increases with an increase in the bed depth because the increase in binding site for adsorption and the intra-particle diffusion in to the inner pores of the adsorbent. The results shows that increase in bed depth enhances the availability active adsorption sites and also comparatively more volume of aqueous solution available for contact with adsorbent<sup>7,8</sup>. In this study, breakthrough times were found 200 to 1050 min for As (III) removal using IICH with increasing bed height, respectively. Further, with rise in the bed depth from 10 to 30 cm, the breakthrough time of As (III) increases and also an increase in the flow rate

at different height was found to decrease the breakthrough time.



**Fig. 2:** Evaluation of breakthrough curve for As (III) adsorption (a) different concentration at  $Q=1$  ml/min  $H=20$  cm (b) different height at  $Co=40$  mg/l,  $Q=2$  ml/min (c) different flow rate at  $Co=40$  mg/l,  $H=20$  cm

#### The Effects of Flow Rate

The breakthrough ( $C_e/C_0$  vs. time) curves obtained for As(III) on the continuous column using IICH at different flow rates (1-4 ml/min) at constant depth (10-30 cm) and fixed influent concentration of 40 mg/l with the initial pH of influent solution of 7.5 are shown in Fig. 2(c). It can be observed from the figures that the breakthrough time of As (III) adsorption in column decreases with an increase in the flow rate. The breakthrough time in case of modified coconut husk was in the range of 190

to 490 min. Breakthrough time decreased with an increase in the flow rate and decrease in the bed depth. This is due to the fact that with at increased influent flow rate, the molecules of arsenic were having less time to diffuse into the inner pores of the adsorbent<sup>9</sup>. Also, there is possibility that higher flow rate might desorb some As (III) molecules already adsorbed on the surface with weak and reversible bonds. It is therefore, resulted with an earlier breakthrough time<sup>10</sup>. On the other hand, the adsorptions of As (III) in the fixed bed at low flow rates were beneficial. These observations are in line with the previous reported studies in the literature<sup>11,12</sup>. The data presented in Table 3 reveals that the methodology adopted for removal of the As (III) in the present study has higher adsorption capacity than that of the other adsorbents reported in the literature.

#### Thomas model kinetics parameters evaluation

The Thomas model<sup>13</sup>, one of the extensively used theoretical methods to describe the performance a column, has been used in this investigation to fit the data obtained.

For each set of experimental data, regression analyses were to determine adsorption capacity ( $q_0$ ) and Thomas constant ( $K_{Th}$ ). The plot of  $\ln[(C_0/C_e) - 1]$  vs. time (t) gives the value of  $q_0$  and  $K_{Th}$ , which are presented in Table 3.

#### Different influent concentration:

The results shown in Fig. 3(a) reveal that the value of  $K_{Th}$  decreases but  $q_0$  increases with increase in As (III) concentration for IICH adsorbent

The reason for increase in  $q_0$  is that, the driving force for this process is the difference between concentrations the As (III) on the surface of the adsorbent and in the solution. Thus, an increased difference in As (III) concentration causes the improved performance of the column<sup>11</sup>.

Further, the value of  $K_{Th}$  was decreased due to the lesser mass transfer rate in the column at increased concentration of As (III), which results in lengthening the contact time between solute and adsorbent. These results are in line with the data reported in literature for uptake of As (III) by modified wheat straw<sup>14, 15</sup>.

*Different Bed depth:*

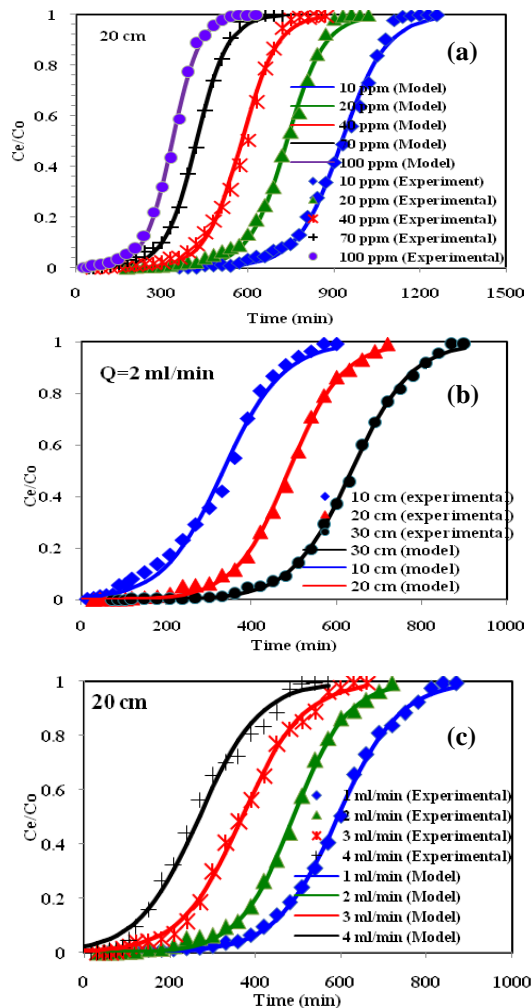
The rise in bed depth from 10 to 30 cm the breakthrough time of As (III) increases. In this analysis, we have found that on increasing the flow rate at different height the breakthrough time decreases. Data generated by using Thomas model at different height is represented in Table 3.

The data presented in the table indicates that that when the bed height increased from 10 to 30 cm, the  $K_{Th}$  value decreased and  $q_0$  value increased for experiment, Fig. 3(b). The increase in  $q_0$  is due to increase in availability of more binding sites for adsorption because of increased adsorbents surface area. Further, with increase in contact time and height, the diffusion into the inside pores of the adsorbent particle also increases. Finally, for larger bed, more As (III) ions get adsorbed and thus the removal percentage and adsorption capacity increase<sup>16</sup>. In case of adsorption with IICH, the value of  $K_{Th}$  increases from 10 cm to 20 cm and then decrease from 20 cm to 30 cm. The time needed for the effluent to attain the breakthrough point increases with increasing bed height.

**Table 3.** Kinetics parameters for As (III) adsorption onto IICH by using Thomas model (a) different concentration at  $Q= 1\text{ml}/\text{min}$   $H=20\text{ cm}$  (b) different height at  $Co=40\text{mg}/\text{l}$ ,  $Q= 2\text{ml}/\text{m}$  in (c) different flow rate at  $Co=40\text{mg}/\text{l}$ ,  $H=20\text{ cm}$

Kinetic parameters	Different concentration at $Q= 1\text{ml}/\text{min}$ $H=20\text{ cm}$				
	10 mg/l	20 mg/l	40 mg/l	70 mg/l	100 mg/l
$k_{Th}(\text{ml}/\text{min}/\text{mg})$	$1.26 \times 10^{-3}$	0.9976	0.9986	0.9988	0.9986
$q_T(\text{mg}/\text{g})$	1106.46	$7.54 \times 10^{-4}$	$4.05 \times 10^{-4}$	$2.58 \times 10^{-4}$	$2.07 \times 10^{-4}$
$R^2$	0.9986	1752.2	2611.05	3518.69	4016.13
	Different height at $Co=40\text{mg}/\text{l}$ , $Q= 2\text{ml}/\text{min}$				
	10 cm	20 cm	30 cm	-	-
$k_{Th}(\text{ml}/\text{min}/\text{mg})$	$1.41 \times 10^{-3}$	$7.82 \times 10^{-4}$	$3.55 \times 10^{-4}$	-	-
$q_T(\text{mg}/\text{g})$	2046.23	5992.56	15612.12	-	-
$R^2$	0.9978	0.9987	0.9994	-	-
	Different flow rate at $Co=40\text{mg}/\text{l}$ , $H=20\text{ cm}$				
	1 ml/min	2 ml/min	3 ml/min	4 ml/min	-
$k_{Th}(\text{ml}/\text{min}/\text{mg})$	0.00138	$7.88 \times 10^{-4}$	$6.95 \times 10^{-4}$	$6.98 \times 10^{-4}$	-
$q_T(\text{mg}/\text{g})$	1816.67	5992.56	2639.48	1672.54	-
$R^2$	0.9991	0.9994	0.9986	0.9936	-

-NA



**Fig. 3.** Compression of experimental and theoretical breakthrough curve for As (III) adsorption onto IICH by using Thomas model (a) different concentration at  $Q=1\text{ ml/min}$   $H=20\text{ cm}$  (b) different height at  $C_o=40\text{ mg/l}$ ,  $Q=2\text{ ml/min}$  (c) different flow rate at  $C_o=40\text{ mg/l}$ ,  $H=20\text{ cm}$

#### Different Flow rate:

The Thomas model kinetics  $q_0$  and  $K_{Th}$  at different flow rate are presented in Table 3. The results shown in Fig. 3(c) indicates that the  $q_0$  value first increases and then decreases, also values of  $K_{Th}$  first increased and then decreased with an increase in the flow rate for both RCH and IICH adsorbents. The initial increase in  $q_0$  is because of the increased driving force for adsorption and later decrease in  $q_0$  is because of exhaustion of the

bed depth in very less time. Whereas the decrease in  $K_{Th}$  can be explained using the same reasons as discussed in previous section.

#### Conclusions

Present study deals with remediation of As (III) contaminated aqueous solutions by adsorbent IICH through continuous column analysis. The results indicates that IICH is an effective adsorbent for the removal of As(III). The breakthrough time was observed to decrease with increase in initial metal ion concentration and flow rate but increased with an increase in bed depth. The shape and gradient of the breakthrough curve differed slightly from one another for different bed depth. As bed height increased the curves shape changes from steep concave to flatter concave. An ideal S-shape was found to occur at a bed height of 20 cm. Over all conclusions the experimental breakthrough curves were very close to the predicted by Thomas model.

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