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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 and 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[1].

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[2]. Iron impregnation is a common coating of iron on many bio adsorbent such as coconut husk, bagasse, rice husk etc. which 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[3].

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

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 g of the dried adsorbent was mixed with 200 ml of ferric nitrate solution containing 2.5% by weight Fe^{3+}. 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 (λ_{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 (10–100 mg/L), bed height (10–30 cm), flow rate (1–4 ml/min) and a fixed bed diameter (2.54 cm) at 6.5 $pH_{0.}$ The adjustment in this pH value was done using the 0.1 *M* 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.

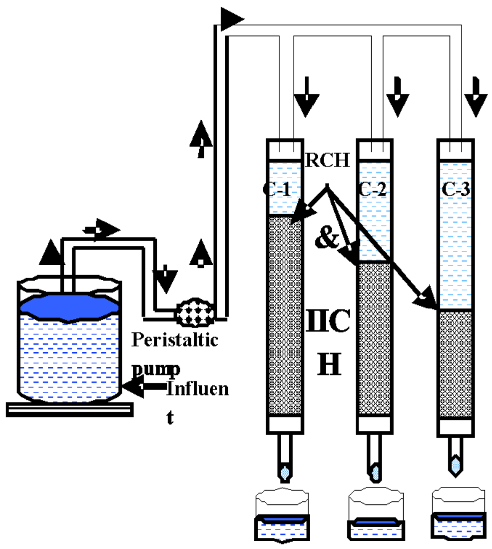

Fig. 1. Schematic diagram the continuous columns setup

Table 1. Details of column and operation conditions for column study

Parameter	Dimension
Diameter of column (cm)	2.54
Height of the column (cm)	120
Glass wool used (g)	1
Area of column (cm^2)	957.67
Bed volume of column (cm^3)	607.7
Initial As(III) concentration (mg/L)	10–100
Height of the column (cm)	10–30
Glass wool used (g)	1
Flow rate used (ml/L)	1–4
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^3)	0.1345	0.2511
Wet density (g/cm^3)	0.25	0.32
Specific gravity (g/cm^3)	0.1345	0.2511

Results 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[4].

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(I) concentration is increased, the breakthrough 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[5]. 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[6].

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

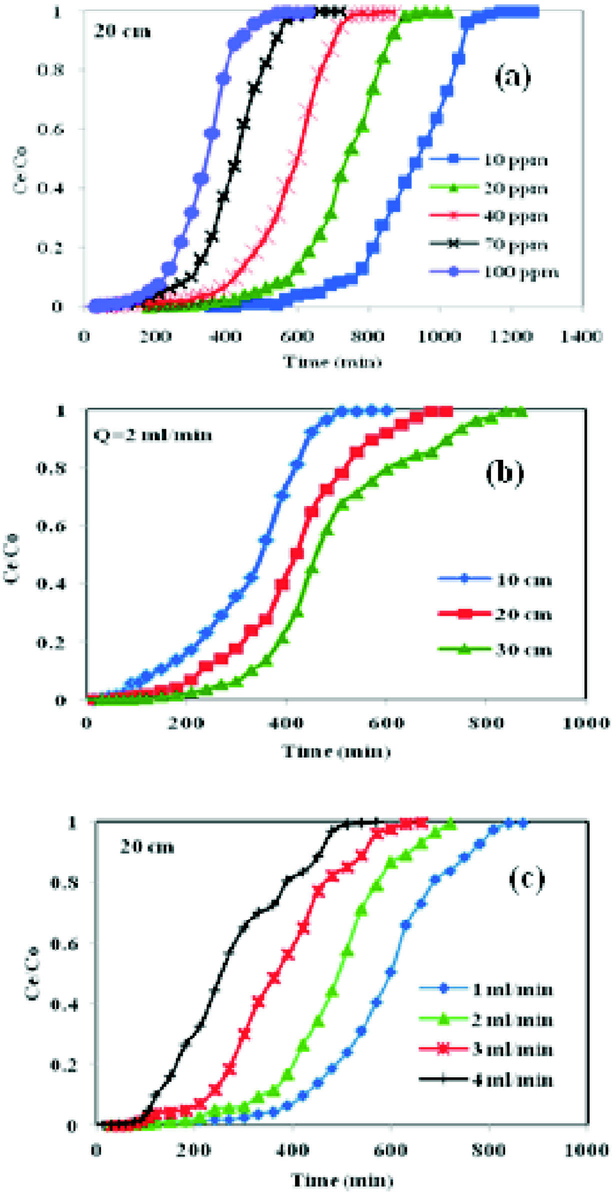

Fig. 2. Evaluation of breakthrough curve for As(III) adsorption, (a) different concentration at Q = 1 ml/min, H = 20 cm, (b) different height at C_o = 40 mg/L, Q = 2 ml/min and (c) different flow rate at C_o = 40 mg/L, H = 20 cm.

comparatively more volume of aqueous solution available for contact with adsorbent[7,8]. 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.

The effects of flow rate:

The breakthrough (C_e/C_o vs time) curves obtained for As(III) on the continous 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. Breakthrought time decressed with an increse 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[9]. 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[10]. 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[11,12]. 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[13], 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_o) and Thomas constant (K_{Th}). The plot of vs time (t) gives the value of q_o 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_o increases with increase in As(III) concentration for IICH adsorbent.

The reason for increase in q_o 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[11]. 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[14,15].

Different bed depth:

The rise in bed depth from 10 to 30 cm the breakthrough

Table 3. Kinetics parameters for As(III) adsorption onto IICH by using Thomas model: (a) different concentration at Q = 1 ml/min, H = 20 cm, (b) different height at C_o = 40 mg/L, Q = 2 ml/min and (c) different flow rate at C_o = 40 mg/L, H = 20 cm

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

– NA

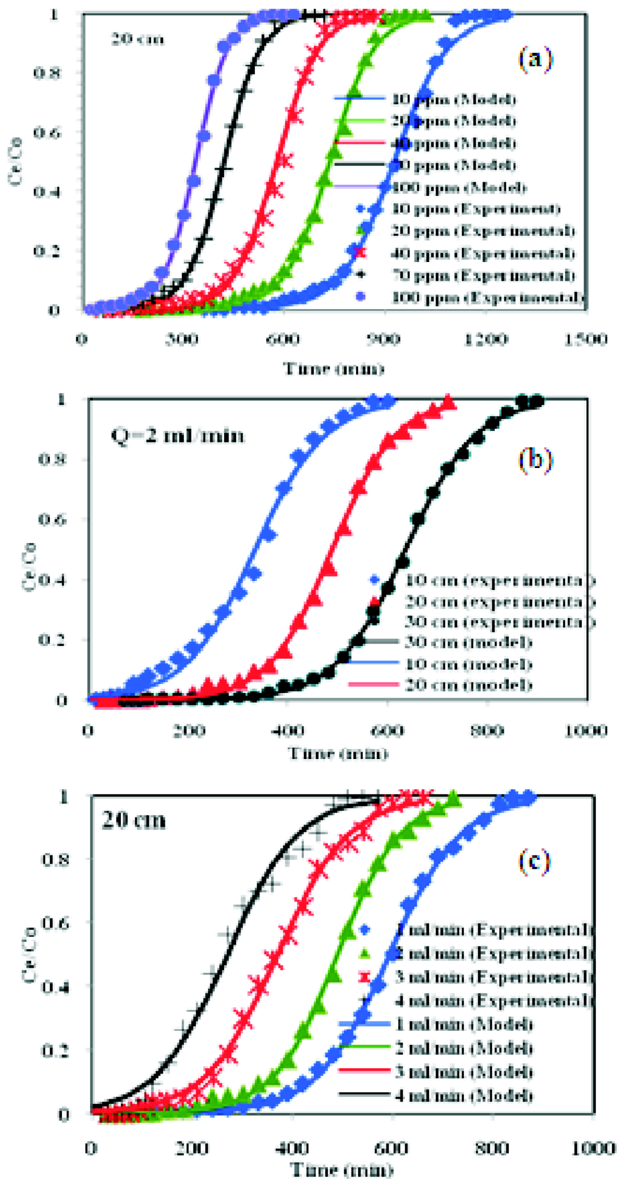

Fig. 3. Compression of experimental and theoretical breakthrough curve for As(III) adsorption onto IICH by using Thomas model: (a) different concentration at Q = 1 ml/min, H = 20 cm, (b) different height at C_o = 40 mg/L, Q = 2 ml/min and (c) different flow rate at C_o = 40 mg/lL, H = 20 cm.

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 when the bed height increased from 10 to 30 cm, the K_{Th} value decreased and q_o value increased for experiment, Fig. 3(b). The increase in q_o 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[16]. 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.

Different flow rate:

The Thomas model kinetics q_o and K_{Th} at different flow rate are presented in Table 3. The results shown in Fig. 3(c) indicates that the q_o 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_o is because of the increased driving force for adsorption and later decrease in q_o 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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