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Investigation on fixed bed column performance of fluoride adsorption by sugarcane charcoal

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Abstract

The present study explores the potentiality of sugarcane charcoal for fluoride removal from synthetic fluoride solution. Column adsorption experiments with respect to variation of flow rate, pH, initial concentration, and column depths were carried out. Sugarcane charcoal exhibited almost consistent scavenging capacity at various bed depths with a flow rate 4.34 ml min^{-1}. Maximum adsorption capacity of sugarcane charcoal was recorded 7.33 mg g^{-1}. The adsorption studies were simulated using Thomas and Bed depth service time model. Both the models consistently predict its characteristic parameters and describe the breakthrough profiles in the whole range of sorption process.

Key words

BDST model, Column adsorption, Fluoride adsorbent, Sugarcane charcoal, Thomas kinetic model

Introduction

Minute quantity of fluoride (F) is essential for normal mineralization of bones and formation of dental enamel (Mohapatra *et al.,* 2009). However, high concentrations of F occurring naturally in groundwater, and eventually in drinking water, have caused widespread fluorosis (both dental and skeletal) throughout many parts of the world (Arora and Mahaeshwari, 2007).Today, in India, the F contamination in groundwater has been detected in more than 20 states, of which 66.64 million of people are suffering from fluorosis (Susheela *et al.,* 1993; Ayoob *et al.,* 2009).

Due to negative impact of F on human health, the World Health Organization (WHO, 2011) has recommended maximum permissible limit of 1.5 mg l^{-1} F in drinking water. This limit has posed a challenge for research of new technologies capable of selectively removing low level of F.

In order to treat F in water systems, developing cost-effective technologies to remove F from water drew great attention in the last 20 years. Several physioco-chemical techniques, such as ion exchange, electrochemical degradation, precipitation–coagulation, biodegradation and adsorption have been applied to remove F from aqueous system (Chen *et al.,* 2011). Among these technologies, adsorption technology is mainly used because it is very simple, cost effective and eco-friendly nature (Ranjan *et al.,* 2009; Chen *et al.,* 2011). The technique is also popular due to its availability of a wide range of adsorbents.

Among all types of conventional and non-conventional adsorbents, there has been an increase in the use of numerous waste materials like fly ash (Chidambaram *et al.,* 2003), wood ash (Makhado *et al.,* 2006), tea ash (Mondal *et al.,* 2012a), different coal-based adsorbents (lignite, fine coke, bituminous coal) (Sivasamy *et al.,* 2001), bagasse and cotton jute carbon (Jamode *et al.,* 2004), rice husk (Wahecd *et al.,* 2009; Mondal *et al.,* 2012b), eggshell powder (Bhaumik *et al.,* 2012), as adsorbents for the removal of F from aqueous solutions. Sugarcane bagasse is an

example of such type of a non-conventional waste biomaterials.

But in the present study, carbonized sugarcane bagasse i.e. sugarcane charcoal (SCC) was used as F adsorbent inspite of raw bagasse of sugarcane because the powder carbons shows more extended surface area, micro/ mesoporous structure which are significant for adsorption capacity. Only a few works on SCC have been conducted as an adsorbent (Dhungana and Yadav, 2009; Kalderis *et al.,* 2008) but not a single study has been reported on defluoridation of F solution by SCC under continuous flow conditions. This study sought to investigate SCC as an alternative fluoride adsorbent with the following objectives: (i) to perform breakthrough studies on fixed bed system (ii) to perform fixed bed operations to examine F adsorption using SCC (effect of initial fluoride concentration, flow rate, pH bed depth and adsorption isotherm) and (iii) to evaluate the column adsorption performance by using bed depth service time (BDST) and Thomas model.

Materials and Methods

Adsorbent preparation and characterization: To prepare SCC as an adsorbent, raw sugarcane bagasse was collected from sugarcane juice shop, Burdwan town, West Bengal, India and cut in to small pieces after several washings with double distilled water. For charcoal making the dry pieces of the collected materials were burned in a muffle furnace (PTC1, Paragon made) at 500ºC in an oven for 20-25 min followed by several washing with double distilled water and drying at 100º C for a period of 24 hr. Further, 300 g of charcoal was treated with 3000 ml of 4 N HCl for 10 min and filtered and again treated with 3000 ml of 4 N NaOH and filtered through a filter paper (Whatman No. 41 grade) and washed several times with distilled water until pH 7 was attained and then dried in sunlight and finally the material was grinded and sieved (300 mesh) to get desired monoparticle size of 250 µm. The charcoal of sugarcane was stored in vacuum desiccators for future use. The stability of SCC as an adsorbent was determined by dipping the material over night in different solvents (water, dilute acids and bases) having pH range 2 to 12 and its loss on ignition was also determined by using hydrogen peroxide as per the method of Jamode *et al.*, 2004. The SCC was found to be stable within the pH range 2 to 12. The composition of the adsorbent was SiO_2 - 61.4%, Al_2O_3 - 14.6%, CaO - 2.45%, Fe_2O_3 - 4.9%, MgO - 0.74% and the ignition loss was evaluated to be 15.5% by weight. The bulk density and porosity were recorded to be 1.05 g cm^{-3} and 0.0032 µm respectively.

Adsorption studies in fixed bed system: Adsorption studies were carried out in a series of pre-cleaned glass column with 2% HNO_3 followed by rinsing with double distilled water and drying. A borosil glass column with an internal diameter of 4.0 cm and at total height of 25.0 cm was used as adsorption column. The SCC adsorbent was packed with glass wool. The variable concentration of fluoride solutions were prepared by dilution with double distilled from of 100 mg l^{-1} of F stock solution (Sodium fluoride; NaF; Merck, Germany). In determining the effect of initial concentration, the bed mass and flow rate were considered 35.64 g and 4.34 ml min^{-1}, respectively. The total volume of water treated to reach the breakthrough point was found to be 0.868, 0.651 and 0.217 l for the F concentrations of 3.0, 5.0 and 10.0 mg l^{-1}, respectively. A blank column operation has been carried out to make sure that the filter used would not change the F concentration of the inlet solution. The flow velocity was observed periodically by collecting 100 ml of the exiting solution and recording the time taken for the given volume. The effects of several variables such as bed mass, bed depth, initial F ion concentration, pH and flow rate were studied. Continuous flow adsorption experiments were conducted in laboratory condition at the temperature range 27±1º C in a glass column of 4.0 cm internal diameter. Different set experiments were conducted with various F concentration (3.0 mg l^{-1}, 5.0 mg l^{-1} and 10.0 mg l^{-1}); flow rates (17.6 ml min^{-1}, 4.34 ml min^{-1}, 8.97 ml min^{-1} and 13.94 ml min^{-1}); pH (2.0, 6.0 and 10.0) and column depths (4.5 cm, 8.2 cm, 12.6 cm, 16.7 cm and 20.0 cm). The amounts of SCC used were 12.05 g, 15.01 g, 27.54 g, 35.64 g and 50.82 g for the bed depths 4.5, 8.2, 12.6, 16.7 and 20.0 cm respectively. To carry out the continuous column operation, aqueous F solution were flowed to downward of the packed columns using water suction pump as a flow rate controller. At regular intervals effluent solutions were collected and their concentrations were analyzed by using fluoride ion selective meter (Thermo Orion 4 Star, pH –ISE Benchtop).

Thomas Model: The Thomas kinetic model is one of the most general and widely used methods in fix bed column studies. This column performance theory was developed to calculate the maximum solid phase concentration of the solute on adsorbent and the adsorption rate constant for continuous adsorption process in column studies (Zheng *et al*., 2008; Ayoob *et al.,* 2009; Chen *et al.,* 2011).

The bed-depth/service time analysis (BDST) model: A few mathematical models have been developed for the use in designing fixed bed column operation. Among them, the BDST model which is the modified form of Bohart-Adams model was used to compare the uptake capacity of adsorption columns. The BDST model works well and provides useful modeling equations of columns, operating under different process variable (Ranjan *et al*., 2009).

Error analysis: For non-linear fitting of kinetic data, the sum of squared error (SSE) analysis as per Han *et al*. (2007).

Performance indicators: During operation, the adsorbent is deactivated. The deactivation rate of the adsorbent will determine the frequency of replacement of adsorbent and hence operating the costs. The cost of the adsorption system for a fixed flow rate, feed concentration and adsorption characteristics were almost entirely dependent on number of bed volume (BV) and adsorbent exhaustion rate (AER) only (McKay and Bino, 1990).

Results and Discussion

Effect of initial fluoride concentration: Three different initial concentration (3.0, 5.0 and 10.0 mg l^{-1}) were used in this study. From the volumes processed at break through point, the AER (BV in parenthesis) values were computed and found to be 40 (4.14), 50 (3.10) and 160 (1.04) g l^{-1} for the initial concentrations of 3.0, 5.0 and 10.0 mg l^{-1}, respectively (Table 1). As the F concentration increased, adsorption efficiency of SCC decreased, the driving force for adsorption increased and the active sites were consumed faster. This led to the treatment of a smaller volume of water per unit mass of adsorbent, as depicted by the large AER value (Onyango *et al.*, 2009). The results showed that breakthrough time was increased at lower concentrations of F solutions. Therefore, adsorption efficiency of SCC decreased on gradual increase of influent F concentration. So the removal of F was efficient at lower concentration, (3.0 mg l^{-1}). At higher concentrations (5.0 and 10.0 mg l^{-1}), more adsorption site were covered that saturated the bed more quickly and hence decreased the breakthrough time (Ranjan *et al.*, 2009).

Effect of flow rate, pH and bed depth: This increase in breakthrough point at higher flow rate is due to the minimization of contact time between adsorbate and adsorbent that leads to an early breakthrough. Again the variation of adsorption efficiency may also be explained on the basis of mass transfer fundamentals. The increase in adsorption efficiency of SCC were more pronounced at the flow rate of 1.76 ml min^{-1}; whereas the effect was almost negligible at the flow rate of 13.94 ml min^{-1}. The different AER (BV in parenthesis) of water processed at breakthrough points were found to be 100 (1.68), 50 (3.1), 53 (3.21) and 51 (3.32) g l^{-1} for the flow rate 1.76, 4.34, 8.97 and 13.94 ml min^{-1}, respectively (Table 1). The increased volume, processed with an increased in flow rate, can be attributed to the reduce influence of external mass transfer resistance (Onyango *et al.*, 2009) that resulted to the faster movement of adsorption zone along the bed leading its quick saturation (Ayoob *et al.*, 2009).

The pH of the solution has been recognized as one of the most important factors influencing the kinetic study of adsorption (Chowdhury and Saha, 2011). For the experiment, the pH of F solution was adjusted by adding 0.1 (M) NaOH or HCl solution and the pH measurement was done by digital pH meter (Model No. Systronic-335). The result (Table 1) suggests that with decrease in pH, the adsorption capacities increased under experimental condition. So the removal of F from aqueous solution was

Table 1 : Effect of adsorbent mass, flow rate and initial concentration on adsorption capacity, bed volume, service time and adsorbent exhaustion rate

Parameters	Service time (min) t_b	Adsorption capacity (mg g^{-1}) q_b	EBRT (min)	BV processed	AER (g l^{-1})
Adsorbent mass (g)					
12.05	25	5.81	0.442	1.92	111
15.01	50	7.33	0.456	1.98	69
27.54	100	6.54	0.636	2.76	63
35.64	150	7.29	0.714	3.10	50
50.82	200	4.72	1.011	4.39	46
pH					
2.0	150	5.05	0.714	3.10	50
6.0	100	4.07	0.477	2.07	80
10.0	40	3.08	0.191	0.828	210
Different flow (ml min^{-1})					
13.94	50	3.08	0.238	3.32	51
8.97	75	3.37	0.358	3.21	53
4.34	150	4.49	0.714	3.10	50
1.76	100	5.05	0.955	1.68	100
Initial concentration (mg l^{-1})					
3.0	200	2.34	0.954	4.14	40
5.0	150	5.33	0.714	3.10	50
10.0	50	12.6	0.237	1.03	160

BV : Bed volume; AER : Adsorbent exhaustion rate

Table 2 : Calculated constants of BDST model for the adsorption of F using linear regression analysis (C_0 = 5.0 mg l^{-1}, v = 4.34 ml min^{-1})

C_0/C_t	a (min cm^{-1})	b (min)	Ka (L mg^{-1} min^{-1})	N_0 (mg l^{-1})	R^2	SSE
0.4	3.67	7.55	0.037	79.64	0.950	58.07
0.6	9.97	31.7	0.026	216.5	0.952	71.82
0.8	12.0	54.5	0.003	260.6	0.935	81.13

Table 3 : Predicted breakthrough time based on the BDST constants for a new flow rate (C_0 = 5.0 mg l^{-1})

C_0/C_t	a (min cm^{-1})	b (min)	v	v'	a'	Z (cm)	t_e (min)	t_c (min)
0.4	3.67	7.55	4.34	8.97	1.78	16.7	55.0	53.9
0.6	9.97	31.7	4.34	8.97	4.82	16.7	125.5	134.8
0.8	12.0	54.5	4.34	8.97	5.81	16.7	130.7	146.1

Table 4 : Predicted breakthrough time based on the BDST constants for a new influent concentration (v = 4.34 ml min^{-1})

C_0/C_t	a (min cm^{-1})	b (min)	C_0 (mg)	C_0' (mg l^{-1})	a'(min)	b'(min cm^{-1})	Z (cm)	t_e (min)	t_c(min)
0.4	3.67	7.55	5.0	3.0	6.120	6.290	16.7	94.5	95.91
0.6	9.97	31.7	5.0	3.0	16.62	26.41	16.7	201.5	251.1
0.8	12.0	54.5	5.0	3.0	20.02	45.42	16.7	251.4	288.9

Table 5 : Calculated constants of Thomas model at different conditions using regression analysis

C_0 (mg l^{-1})	v (ml min^{-1})	Z (cm)	K_{th} (ml min^{-1} mg^{-1})	q_0	R^2	SSE
3.0	4.34	16.7	0.047	18.24	0.871	0.028
5.0	4.34	16.7	0.035	19.33	0.982	0.015
10.0	4.34	16.7	0.024	19.42	0.945	0.029
5.0	8.97	16.7	0.352	13.87	0.961	0.024
5.0	13.94	16.7	0.458	13.73	0.953	0.045
5.0	1.76	16.7	0.044	8.41	0.891	0.028
5.0	4.34	4.5	0.031	11.75	0.911	0.098
5.0	4.34	8.2	0.042	21.88	0.922	0.730
5.0	4.34	12.6	0.039	19.92	0.934	0.028
5.0	4.34	20.0	0.028	14.41	0.944	0.106

more efficient at lower initial pH value. There are many reasons which may be attributed towards the F adsorption behavior of the adsorbent relative to solution pH. This can be explained on the basis of electrostatic force of attraction, operated between the negatively charged fluoride ions and positively charged the surface of SCC surface at lower pH (Han *et al*., 2007).

From the bed depth study (Table 1), it was found that increase in the F uptake in a column with increase of bed depth was due to an increase in longer time to contact with SCC for F adsorption. The decrease of breakthrough point with increasing bed height at fixed bed conditions resulted in a longer distance for mass transfer zone and therefore an increase in breakthrough. A higher F uptake was also observed at higher bed height due to increase in the surface area of SCC, which provided more fixation binding sites for the F adsorption (Zulfadhly *et al*., 2001; Vadivelan and Kumar, 2005).

Adsorption modeling : It can be observed that as the values of C_0/C_t increased, the rate constant (Ka) decreased while the adsorption capacity of the bed permit volume (N_0) increased (Table 2) which indicated the validity of BDST model for this system (Han *et al*., 2007). The values of R^2 and 'SSE' as listed in Table 2 also supported the validity of BDST model for the present study. The predicted values were in good agreement for the case of changed feed concentration and flow rate (Table 3 and 4). Thus the advantage of the model is that any experimental test can be reliable used to design (Ramesh *et al*., 2011) the column area over a range of feasible flow rates and initial F concentrations at C_t/C_0 = 0.4, 0.6 and 0.8, respectively. The present result indicates that the model can be applied to

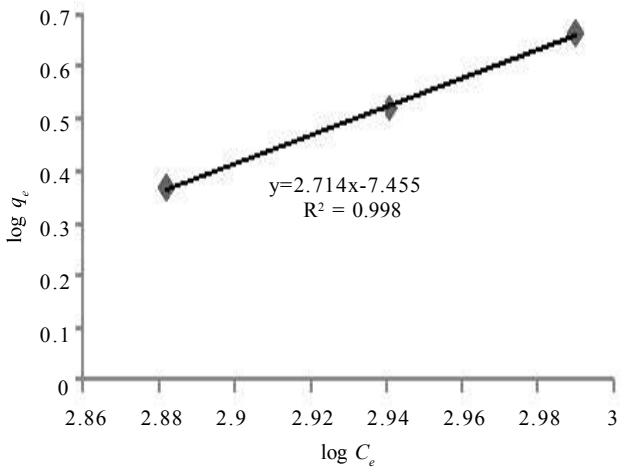

Fig. 1: Freundlich isotherm study

predict adsorption performance at other operating conditions for adsorption of F onto SCC.

Thomas model was applied to the experimental data with respect to influent concentration of F, flow rate and bed depth. It was observed that the value of q_0 increases with increasing influent concentration while the value of k_{Th} decreased (Table 5). The observation can be explained on the basis of the driving force of adsorption, which is the concentration difference between the F on the adsorbent and the F in the solution (Opeolu *et al*., 2009; Han *et al*., 2006). Thus the high driving force due to the higher F concentration resulted in better column performance. With increasing flow rate, q_0 decreased along with increased k_{Th}. As the bed depth increased, the value of q_0 increased with significant decrease of k_{Th}. So higher flow rate and higher influent concentration had disadvantage to adsorption of F on SCC column.

The Freundlich parameters, K_f and (1/n) was 3.5×10^{-8} and 2.71 respectively (Fig. 1). It is evident from the data that the surface of the adsorbent was made up of small heterogeneous adsorption patches which were very similar to each other in respect of adsorption phenomenon. Therefore, from the present study it can be concluded that SCC is an efficient adsorbent for effective removal of fluoride from aqueous solution.

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References

Arora, M. and R.C. Mahaeshwari: Investigation on the batch performance of fluoride adsorption by coconut shell carbon. *Asian J. Water Environ. Pollut*., **4**, 119-122 (2007).

Ayoob, S., A.K. Gupta and A.B. Basheer: A fixed bed sorption system for defluoridation of ground water. *J. Urban Environ. Eng*., **3,** 17-22 (2009).

Bhaumik, R., N.K. Mondal, B. Das, P. Roy, K.C. Pal, C. Das, A. Baneerjee and J.K. Datta: Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: Equilibrium, kinetic and thermodynamic studies. *E. J. Chem.,* **9**, 1457-1480 (2012).

Chen, N., Z. Zhang, C. Feng, M. Li, R. Chen and N. Sugiura: Investigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud. *Desalination,* **268**, 76–82 (2011).

Chidambaram, S., A.L. Ramnathan and S. Vasudevan: Fluoride removal studies in water using natural materials. *Water SA*., **29**, 339-344 (2003).

Chowdhury, S. and P. Saha: Adsorption thermodynamics and kinetics of malachite green onto Ca $(OH)_2$-treated fly ash. *J. Environ. Eng*., **137**, 388-397 (2011).

Dhungana, T.P. and P.N. Yadav: Determination of chromium in tannery effluent and study of adsorption of Cr (VI) on saw dust and charcoal from sugarcane bagasses. *J. Nepal Chem. Soc*., **23**, 93-101 (2009).

Han, R., Y. Wang, W. Yu, W. Zou, J. Shi and H. Liu: Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *J. Hazard. Mater*., **141**, 713-718 (2007).

Han, R., J. Zhang, W. Zou, H. Xiao, J. Shi and H. Liu: Biosorption of copper (II) and lead (II) from aqueous solution by chaff in a fixed-bed column. *J. Hazad. Mater*., **133**, 262-268 (2006).

Jamode, A.V., V.S. Sapkal and V.S. Jamode: Defluoridation of water using inexpensive adsorbents. *J. Indian Inst. Sci.,* **84**,163-171 (2004).

Kalderis, D., D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J. Olivares del Valle and C.Fernandez-Pereira: Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse. *Chem. Eng. J*., **144**, 42-50 (2008).

Makhado, R., T. Bologo and R. Knight: Fluoride removal from rural spring water using wood ash. S. *Afr. J. Sci*., **102**, 204 (2006).

McKay, G. and M.J. Bino: Simplified optimization procedure for fixed bed adsorption systems. *Water Air Soil Pollut*., **51**, 33-41 (1990).

Mohapatra, M., S. Anand, B.K. Mishra, D.E. Giles, and P. Singh: Review of fluoride removal from drinking water. *J. Environ. Manage*., **9**, 67-77 (2009).

Mondal, N.K., R. Bhaumik, T. Baur, B. Das, P. Roy and J.K. Datta: Studies on defluoridation of water by tea ash: An unconventional biosorbent. *Chem. Sci. Trans.,* **1**, 239-256 (2012a).

Mondal, N.K., R. Bhaumik, A. Baneerjee, J.K. Datta and T. Baur: A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash. *Inter. J. Environ. Sci.,* **2**, 1841-1858 (2012b).

Onyango, M.S., T.Y. Leswifi, A. Ochieng, D. Kuchar, F.O. Otieno,and H. Matsuda: Breakthrough analysis for water defluoridation using surface-tailored zeolite in a fixed bed column. *Indus. Engin. Chem. Res*., **48**, 931-937 (2009).

Opeolu, B.O., O. Bamgbose, T.A. Arowolo and M.T. Adetunji: Utilization of maize (*Zea mays*) cob as an adsorbent for lead (II) removal from aqueous solutions and industrial effluents. *Afr. J. Biotechnol*., **8**, 1567-1573 (2009).

Ranjan, D., M. Talat and S.H. Hasan: Rice polish: An alternative to conventional adsorbents for treating arsenic bearing water by up-flow column method. *Ind. Eng. Chem. Res*., **48,** 10180-10185 (2009).

Ramesh, S.T., R. Gandhimathi, P.V. Nidheesh, N. Badabhagni and K.S. Bharathi: Breakthrough data analysis of adsorption of Cd (II) on coir pith column. *Elec. J. Env. Agricult. Food Chem.,* **10**, 2487-2505 (2011).

Sivasamy, A., K.P. Singh, D. Mohan and M. Maruthamuthu: Studies on defluoridation of water by coal-based sorbents. *J. Chem. Technol. Biotechnol*., **76**, 717-722 (2001).

Susheela, A.K, A. Kumar and M, Bhatnagar: Prevalance of dental fluorosis with gastrointestinal manifestations in people living in some North-Indian villages, *Fluoride.* **26**, 97-104 (1993).

Vadivelan, V. and K.V. Kumar: Equilibrium, kinetics mechanism and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci*., **286**, 90-100 (2005).

Wahecd, S., S. Deshmukh, J. Attar and M.D. Waghmare: Investigation on sorption of fluoride in water using rice husk as an adsorbent. *Nature Environ. Pollut. Technol*., **8,** 217-223 (2009).

WHO, Guideline for drinking-water quality. 4rd Edn., Geneva, Switzerland, World Health Organization (2011).

Zheng, H., L. Han, H. Ma, Y. Zheng, H. Zhang, D. Liu and S. Liang: Adsorption characteristics of ammonium ion by zeolite *13 X, J. Hazard. Mater*., **158,** 577-584 (2008).

Zulfadhly, Z., M.D. Mashitah and S. Bhatia: Heavy metals removal in a fixed bed column by the macro fungus macro fungus *Pycnoporus sanguineus*. *Environ. Pollut*., **112**, 463-470 (2001).