



Defluoridation of Water by Biowaste Material – A Study of Adsorption Kinetics and Isotherms

K. Kiran Kumar*^{ORCID}, Ratnakaram Venkata Nadh**^{ORCID}†, Kaza Somasekhara Rao*** and G. Krishnaveni*^{ORCID}

*Department of Chemistry, KBN College, Vijayawada-520001, Andhra Pradesh, India

**Industrial Chemical Product Development and Analysis Centre, Department of Chemistry, GITAM Deemed to be University, Bengaluru Campus, Bengaluru-561203, Karnataka, India

***Department of Chemistry, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur-522510, Andhra Pradesh, India

†Corresponding author: Ratnakaram Venkata Nadh; doctornadh@yahoo.co.in

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 04-02-2023

Revised: 01-04-2023

Accepted: 07-04-2023

Key Words:

Defluoridation

Adsorption kinetics

Citrus limon

Citrus nobilis

Pithecellobium dulce

Bombax malabaricum

ABSTRACT

Human beings experience adversative effects due to the large fluoride concentrations present in potable water. Because of the low cost and simple operation, the extensively acknowledged process is adsorption. The objective of this study is to investigate the performance of some of the prepared carbons from bio-waste materials viz., *Citrus limon*, *Citrus nobilis*, *Pithecellobium dulce*, and *Bombax malabaricum* sheaths in defluoridation. Initial concentration, particle size, agitation time, adsorbent dose, and pH were the different parameters chosen to study their effect on adsorption. Studied the adsorption kinetics. Further suitability to adsorption isotherms was reviewed.

INTRODUCTION

Prolonged exposure to fluoride at higher concentrations leads to disease – Fluorosis, a serious health concern in several portions of the world, wherever drinking water contains higher than the permissible limits (1 to 1.5 ppm) of fluoride (Choubisa 2018). Crippling fluorosis, dental fluorosis, and skeletal fluorosis are the various manifestations of fluorosis. Fluoride at higher levels affects bone mineralization and collagen synthesis (Antonarakis & Moseley 2014).

It involves diminishing the function of the soft tissue of the animals intoxicated by fluoride due to crossing the cell membrane and entering soft tissues. Inhibition of enzymes (involved in energy producing and transferring, synaptic transmission membrane transport) by it causes affecting the muscle and brain (Yan et al. 2016). It also inhibits enzymes associated with pathways (like myosin-ATPase and pentose) and antioxidant defense systems. In addition, deactivates glutathione peroxidase, superoxide dismutase, and other enzymes that scavenge the free-radical. A decrease in GSH levels and improved ascorbic acid and MDA activity causes elevated oxidative stress in three to ten-year-old children (Hamza et al. 2015).

Human beings are exposed to fluoride in many ways, like inhalation of fluorine-laden air, exposure to dental products, and consumption of fluoride-rich drinking water, food (fish, fruits, and vegetables), and beverages (tea). Out of the total fluoride exposure, air has minor responsibility. The production of phosphate fertilizers that burn coal containing fluoride contributes to fluoride concentration in the air (Choubisa & Choubisa 2016). Dental products are used for the demineralization of enamel (Dental varnishes) and to lessen dental caries in adults and children (fluoride-containing toothpaste, gels, and tablets) (Shen et al. 2016). Fluoride mounts up in the bones and protein concentrates of fish.

Similarly, vegetables and fruits cultivated in industrial areas with high emissions of fluoride. Leafy parts of plants are found to have more amounts of accumulated fluorine than roots. For example, high fluoride levels in tea leaves (400 mg.kg⁻¹ dry weight) (Zohoori & Duckworth 2016). The chief contribution of fluorosis is fluorine-laden drinking water. High amounts of fluoride were reported in potable water supplied in various countries (Balasubramanian & Umaranib 2014). In lakes' surface waters, fluoride hoards

up due to high evaporation and leaches from the lava, tephra, alkalic rocks, and minerals like fluorspar and fluorapatite (Bosshard-Stadlin 2017). The influence of contiguous rocks is responsible for high amounts of fluorine in groundwater compared to surface water. Other origins are seepage from proximate saline formations and low recharging of groundwater (Li et al. 2018). Higher fluoride concentrations recorded in rainwater samples were attributed to nearby industrial areas containing aluminum smelters and glass and ceramics manufacturing units (Rodrigues et al. 2017).

Various techniques used for defluoridation, like Precipitation/coagulation, Membrane processes (Reverse osmosis, Nano-filtration, Electrodialysis), Ion exchange, and adsorption, have their advantages and limitations. However, adsorption has a very good potential for defluoridation due to various factors like cost effectiveness, regeneration ability (to reuse the adsorbent), high elimination capacities, and simple operation (Yadav et al. 2018). For the defluoridation of water, different adsorption materials were used. For example, carbon adsorbent materials (derived from agricultural by-products), Waste carbon slurry, concrete adsorbent materials (Cement paste, Lightweight concrete materials, quick lime), biosorbent materials (chitosan adsorbent materials (Natural chitosan, Magnetic chitosan, Chitin), clay materials and other adsorbent materials (ligand exchange cotton cellulose loaded with iron(III), alum producing unit waste residue, novel Fe–Al–Ce tri-metal oxide, MgAl-CO₃ layered double hydroxides, Mg/Al hydrotalcite-like compounds as well as calcined products from them) (Mondal & George 2015). Continuous availability of raw materials and reduced cost of production/biowaste disposal (Wong et al. 2018, Mokkaapati et al. 2015, Ramya et al. 2016a, 2016b, 2015) encouraged the researchers to explore the possibility of usage of biowaste (*Citrus limon*, *Citrus nobilis*, *Pithecellobium dulce*, and *Bombax malabaricum*) to prepare charcoals for their usage in defluoridation of water.

The prime objectives of the current research work are (i) to learn the influence of physico-chemical parameters such as carbon amount, initial fluoride concentration, pH, and agitation time in batch biosorption, (ii) to evaluate the adsorption efficiency of this carbon by employing adsorption kinetics and isotherm and (iii) to compare their adsorption potential with the already existing biomaterials.

MATERIALS AND METHODS

Analytical reagent-grade chemicals were procured and used in the present research work. The apparatus used is the Elico UV-Visible Spectrophotometer (Model SL 171) and Elico pH Meter.

Preparation of Activated Carbon from Biowaste

Bio-waste materials viz., *Citrus limon*, *Citrus nobilis*, *Pithecellobium dulce*, and *Bombax malabaricum sheaths* were the starting materials to prepare the activated carbons and then utilized as adsorbents for defluoridation. Fruits vending shops and agriculture fields of Nuzvid Mandal, Andhra Pradesh, India, were the sources to collect the bio-waste materials of the current study. The adhered dust on the above-gathered bio-waste was removed by washing it with water and dried out by exposing it to sunlight for three days. Then crushed, the above-dried material was followed by carbonization at 600°C in an electrically heated horizontal tube furnace under the flow of nitrogen for 4 h for all conditions, followed by activation in the stream at 850°C; the activated sample was obtained directly under steam pyrolysis of 600°C to 700°C. Then these carbons were cooled to ambient temperature and collected as uniform particles by sieving. Mostly, the chemical or structural integrity of the biosorbents is modified by diverse methods, viz., chemical grafting, alkali or acid modification, and oxidation, to enhance the adsorption capacity (Li et al. 2010, Xue et al. 2012). Increased chemical reactivity and improved active surface area are due to the above activating techniques, which cause the creation of surface functional groups. Hence, chemical bonding with the ions in an aqueous solution occurs due to the chemical reactivity.

Hence, these carbons are treated with 1N HNO₃ and can settle for 2-3 h, filtered, and dried at 120°C for 2 h in an air oven. Then the above contents were brought to the ambient temperature. Clean air-tight vessels were used to store the above-prepared activated carbons and further used in the experiments with batch adsorption. The obtained acid-activated carbons are designated as *Citrus limon*, *Citrus nobilis*, *Pithecellobium dulce*, and *Bombax malabaricum sheaths*.

Batch Adsorption Studies

Pipetted out 5 ppm fluoride standard aqueous solution (50 mL) into a flask. The batch mode was adopted by engaging ambient temperature (30 ± 1°C) and constant pH to carry out the adsorption studies. REMI shaker was used to maintain a mechanical stirring at 240 ppm after adding the above-prepared carbons at a 0.5 g.L⁻¹ dosage. Equilibrated the fluoride aqueous with these carbons in each experiment and then centrifuged the withdrawn solution. Then Zr-SPADNS method was employed to measure the final concentration of fluoride (Bellack & Schouboe 1958). The standard curve and the colored solution's absorbance value were used to learn the fluoride concentration in the defluoridized sample.

Each experiment was carried out by adopting the same procedure by changing the experimental conditions in the following ranges: (i) agitation time (from 10-120 min), (ii) adsorbent dosage (from 1.0 to 9.0 g.L⁻¹), (iii) pH of the initial standard fluoride solution (ranging from 3 to 9) (iv) initial concentration of fluoride solution (ranging from 1 to 7 ppm) and (v) carbon particle size (45 to 150 μ). The given below mathematical equations were used to get the % of defluoridation and adsorbed fluoride amount (in mg.g⁻¹)

$$q_e = \frac{(C_0 - C_e) \times V}{W} \dots(1)$$

$$\text{Percent removal of nickel (II)} = \frac{(C_0 - C_e) \times 100}{C_0} \dots(2)$$

In the present case, C₀ and C_e are the initial and final concentrations of fluoride ions in aqueous solution before and after adsorption, q_e (mg.g⁻¹) is the adsorption capacity of the adsorbent at equilibrium, V and W are the fluoride solution volume, and mass of carbons.

RESULTS AND DISCUSSION

The adsorption potential of the prepared carbons from bio-waste materials for the defluoridation of water was studied by carrying out the adsorption experiments. The influence of various parameters (adsorbent dose, contact time, particle size, and initial fluoride concentration) was determined. Further studied the adsorption kinetics and isotherms.

Effect of Adsorbent Dose

To appraise the sorption efficiency on the defluoridation, studied the adsorbent (CLC, CNC, PLDC, and BMC) dose effect on the fluoride ion removal. The increase in the

adsorbent dose resulted in the exponential increase in % of fluoride removal (Fig 1.a.). It may be explained based on the improvement of available sites due to a hike in the effective surface area at larger adsorbent doses (Gupta & Sharma 2002).

Then, attained equilibrium after a certain dose. The relative percentage removal of fluoride after the doses of 5, 3, 3, and 3.5 g for CNC, BMC, PLDC, and CLC, respectively, are found to be insignificant and fixed as optimum doses. Overcrowding of biosorbent particles has resulted due to the biosorbent dosage escalation and hence observed an overlap of the adsorption sites (Garg et al. 2008). It is responsible for the decline in unit adsorption (Fig 1.b.).

Effect of Agitation Time

A significant role is played by the contact time in the adsorption studies, which may be further experimental parameters that can influence the kinetics of adsorption. By changing the agitation time, i.e., contact time between adsorbent and fluoride water (5 - 120 min) at the constant conditions of other parameters like temperature (30 ± 0°C), initial fluoride concentration (5 ppm), and adsorbent dose at optimum conditions, the extent of defluoridation was studied to learn about the dynamics and kinetics of fluoride adsorption by different adsorbents. Fig. 2 shows the extent of defluoridation due to a change in agitation time. The % of fluoride removal by the present adsorbent carbons is quick at the beginning. Still, its sluggishness was observed later and then nearly constant values with a further enhancement in the contact time. The availability of ample surface area of these carbons explains the higher rate of defluoridation at the initial time. A drop in adsorption rate with a rise in time can be attributed to the drop in the accessibility to the active sites. A hike in % of defluoridation with a surge of contact time can be understood from the known information

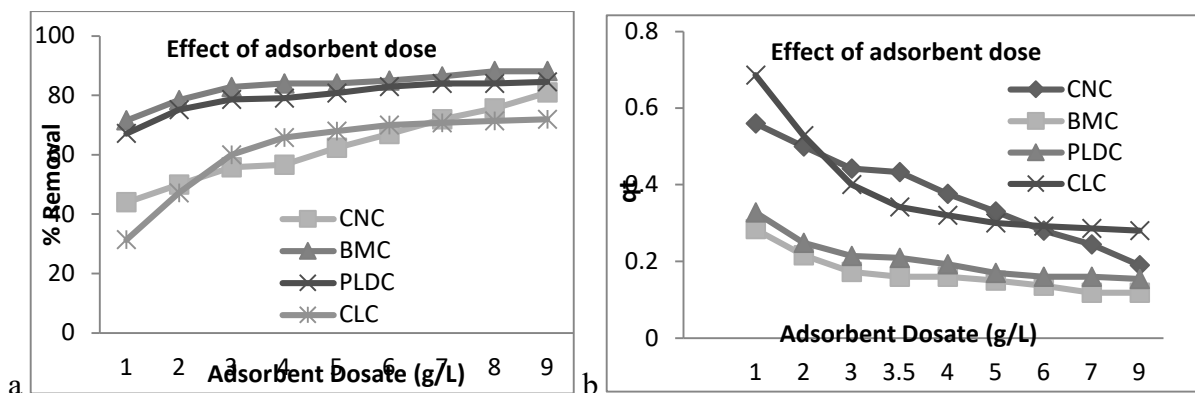


Fig. 1: Effect of biosorbent dose on (a) percent removal and (b) unit adsorption capacity in defluoridation.

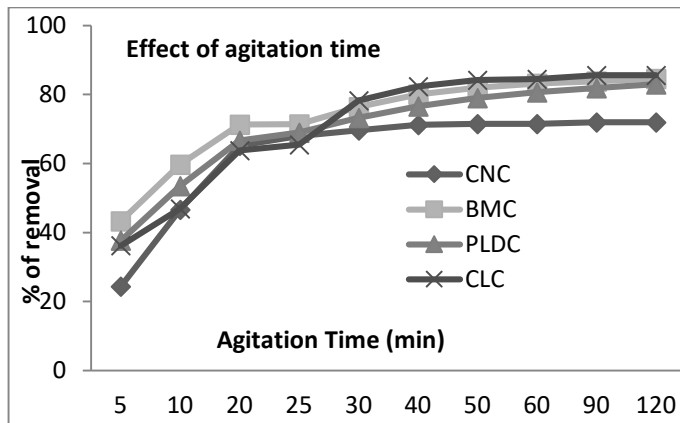


Fig. 2: Effect of agitation time during defluoridation.

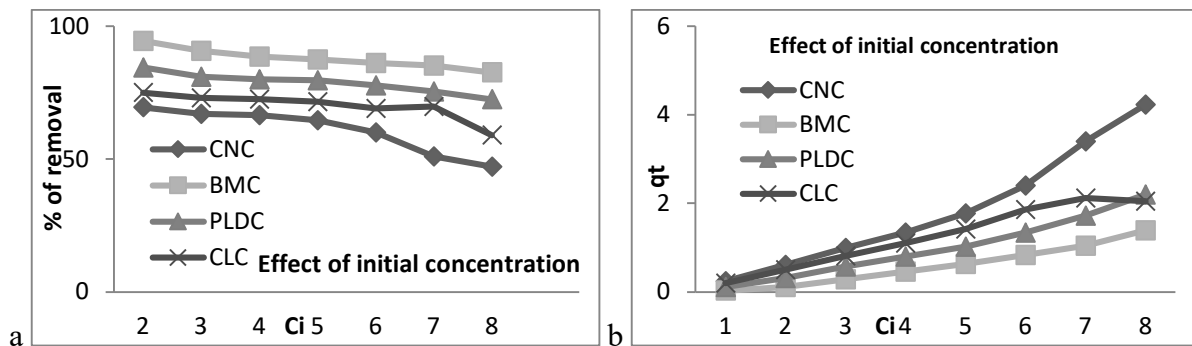


Fig. 3: Effect of initial fluoride ion concentration on (a) percent removal and (b) unit adsorption capacity in defluoridation.

that more time acquaints the fluorides to adsorb on these carbons (Bhattacharya et al. 2006). In the case of all carbons, forty minutes was when the highest % of adsorption was observed, and then a drop was noticed. Involvement of 3 steps can be proposed in the entire sorption mechanism from the observations in the % of defluoridation with time (Fig. 2). Those three steps can be listed as (i) film diffusion or molecular diffusion where an external mass transfer is involved, i.e., fluoride ions are transferred to the adsorbent's external surface from the aqueous solution (ii) fluoride ions adsorption takes place on the surface of particles; and (iii) intraparticle diffusion where the adsorbed fluoride ions transfer to the carbon particles internal surfaces (Li et al. 2010, Moradi 2011).

Effect of Initial Concentration of Fluoride Ions

A systematic study has been carried out to learn about the adsorption capacity of these four activated carbons with a variation in the fluoride ions' initial concentration. The prime factors involved in studying fluoride ions (adsorbate) concentration on these activated carbons are the untenanted adsorption spots and the accumulation of fluoride ions at

their upper concentrations (Min et al. 2004). In each case of these carbons, a firm fall in the % of defluoridation was detected with growth in opening fluoride ion concentration (Fig. 3a). The present trend of diminishing defluoridation can be made clear from an enhanced rivalry amongst the unadsorbed fluoride ions towards the leftover binding sites on these carbons' surface at the superior fluoride concentrations (Min et al. 2004). However, the value of q_t (uptake capacity) of fluoride ions enhanced with an intensification of the initial concentration of fluoride (Fig. 3b). It can be understood from the disposal of larger fluoride ions in the aqueous solution towards adsorption, which is a motivating force to overwhelm resistance against the mass transfer between these activated carbons and fluoride ions. Consequentially improves the collision probability between the activated carbons and fluoride ions (Rao et al. 2008).

Effect of pH

A deci normal NaOH or HCl was used to maintain the fluoride-containing aqueous solution at various pH levels (3 to 9). Fig. 4 reveals the influencing nature of the pH of the medium on the defluoridation. An increase in the pH of

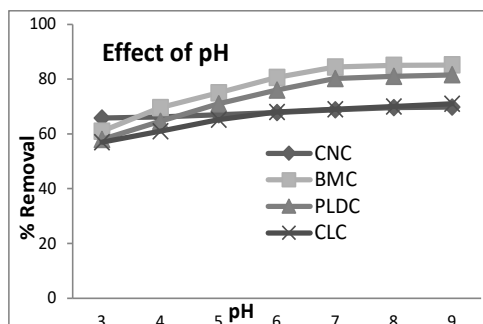


Fig. 4: Effect of pH on the % removal of fluoride.

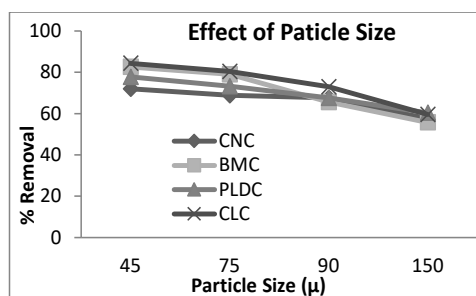


Fig. 5: Effect of particle size on the % removal of fluoride.

a high number of small-size particles with the same amount of biowaste adsorbent.

Adsorption Kinetics

Pseudo-first-order (Lagergren 1898) (Eq. 3) and pseudo-second-order (Ho & McKay 1999) (Eq. 4) kinetic equations are used to investigate the defluoridation mechanism using these four adsorbents.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{t}{q_e} \right) \tag{4}$$

In the above equation, the quantities of fluoride ions adsorbed on these carbons at equilibrium and time t are denoted by q_e and q_t , respectively. k_1 and k_2 represent the corresponding rate constants of pseudo-first-order and second orders. Fig. 6a and 6b, respectively denote the linear plots of pseudo first and second-order kinetics and present the values of corresponding parameters in Table 1.

In the current study of fluoride removal by the prepared carbons, the kinetic data, i.e., determination coefficient (R^2) values, agree with the pseudo-second-order that of the pseudo-first-order. Further used the Elovich equation (Eq. 5) to learn about its suitability for the adsorption of fluoride ions (Sparks 1986). In equation 5, q_t , α , and β symbolize respectively the removed amount of fluoride at a time t, the rate of defluoridation at the beginning, and a constant pertaining to desorption (Table 1).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{5}$$

The significant interactions between these activated carbons and fluoride ions are intra-particle transport, pore diffusion, and film diffusion. Among the above three factors, the first and the latter are the prime steps in rate limiting. But, in a continuous flow system, film diffusion is the likely rate-

the medium has resulted in an improved defluoridation up to pH 7 and then unchanged in the present investigation. The optimum pH is 7.

Effect of Particle Size

A decrease in these carbons' particle diameter resulted in improved fluoride ions uptake (Fig. 5). A diminished external mass transfer resistance and availability of a large surface area for defluoridation have resulted from the accessibility of

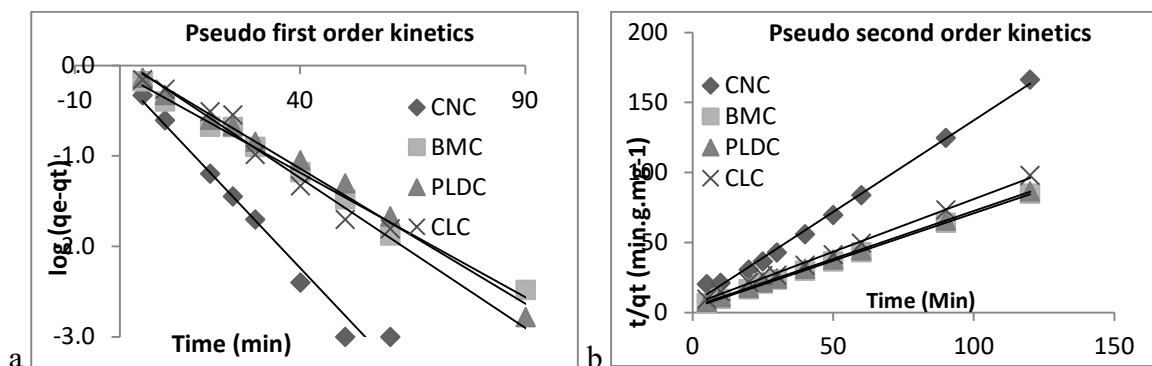


Fig. 6: Linear plots of (a) pseudo-first-order kinetics and (b) pseudo-second-order adsorption kinetics.

Table 1: Defluoridation kinetic parameters and values of kinetic models using 15 g.L⁻¹ CFP and SSP as biosorbents.

Kinetic adsorption model	Parameter	CLC	CNC	PLDC	BMC
Pseudo-first-order	q _e [mg.g ⁻¹]	1.0912	0.8835	1.0595	0.9234
	k ₁ [min ⁻¹]	0.0332	0.0528	0.0299	0.0276
	R ²	0.9691	0.9761	0.9875	0.9906
Experimental	q _e [mg.g ⁻¹]	1.083	0.858	1.213	1.2
Pseudo-second-order	q _e [mg.g ⁻¹]	1.3243	0.7627	1.4613	1.4738
	k ₂ [g.mg ⁻¹ .min ⁻¹]	0.0995	0.2677	0.1111	0.1418
	R ²	0.9966	0.9952	0.9998	0.9997
Elovich's kinetic model	α [mg.g ⁻¹ .min ⁻¹]	0.478	0.398	1.010	2.049
	β [g.mg ⁻¹]	4.034	7.107	4.186	4.65
	R ²	0.9067	0.7672	0.9299	0.9116
Weber intraparticle diffusion model	K _d [mg.g ⁻¹ .min ^{1/2}]	0.081	0.043	0.077	0.069
	θ [μy.γ ⁻¹]	0.518	0.369	0.689	0.798
	R ²	0.750	0.543	0.760	0.743
Boyd kinetic model	R ²	0.9691	0.9671	0.9875	0.9906

limiting step (Goswami & Ghosh 2005). Therefore, further analysis was forwarded with Weber's model concerned to intra-particle diffusion (Eq. 6). Table 1 shows the calculated concerned statistic parameters like θ (a constant value with regard to the thickness of the boundary layer) and K_d (a rate constant related to intra-particle transport) (Sousa et al. 2007).

$$q_t = K_d t^{1/2} + \theta \quad (6)$$

In addition, the Boyd kinetics model (Eq. 7) was used to analyze the adsorption data. In this model, F denotes the fluoride ions fraction adsorbed at any time (t min), which tells about the deviance of the fluoride ions' occupation on the adsorbent from the aqueous system. It indicates that external mass transport governs the adsorption mechanism (Kumar et al. 2011).

$$B_t = -0.4977 - \ln(1 - F) \quad (7)$$

Adsorption Isotherms

To understand the nature of the interaction of the fluoride ion on the surface of these carbons and to reveal the adsorption mechanism, adsorption isotherms are very useful. In the present study, to evaluate the adsorption of fluoride onto CNC, BMC, PDLC, and CLC, three adsorption isotherms (Langmuir, Freundlich, and Temkin models) were studied by variation of C_i (initial fluoride ion concentration). It is a well-known fact that Langmuir and Freundlich's isotherms describe monolayer and multilayer adsorptions (Fig. 7a & 7b). Table 2 lists the coefficient of determination (R^2) values and parameter values (K_D , K_L , K_F , A_T , n, B, q_D , and q_m), which are characteristics of these three isotherms. R_L

is the Langmuir isotherms characteristic. It is denoted as an equilibrium parameter or separation factor, a dimensionless constant.

$R_L = 1/[1+K_L C_o]$ was the equation used to derive values of these parameters. In this equation, initial fluoride ions concentration and Langmuir constant are represented respectively by C_o and K_L . The R_L values give Langmuir adsorption isotherm characteristics. Irreversible, favorable, unfavorable, and linear adsorptions can be expected from R_L values 0, 0 to 1, 1, and greater than 1, respectively (Tewari et al. 2005). R_L parameter values for different adsorbents are found to be CNC (0.577, 0.327, 0.255, 1, 1, 1, 1, 1), BMC (0.304, 0.155, 0.264, 1, 1, 1, 1, 1), PDLC (0.573, 0.140, 0.26, 1, 1, 1, 1, 1) and CLC (0.814, 0.103, 0.369, 1, 1, 1, 1, 1) at different initial concentrations of 1 to 8 mg.L⁻¹ with one unit increment. These values show that defluoridation by these adsorbents is favorable at lower initial concentrations and linear higher concentrations. Additionally, the values of $n > 1$ from Freundlich isotherm also reflected the favorable adsorption conditions (Crini & Ndongo Peindy 2006).

K_L is the sorption energy representing the Langmuir constant; K_F and n are the interactions between fluoride ions and carbons at a given temperature measured by these Freundlich constants. T represents the Kelvin-measured absolute temperature; B is the heat of sorption related to the Temkin constant; and A_T is the equilibrium binding constant for the Temkin isotherm.

Preferred monolayer adsorption is evident in CNC from the calculated R^2 values in the adsorption isotherms studied in Table 2. However, in the case of other adsorbents (BMC, PDLC, and CLC), both the mono and multilayer adsorptions

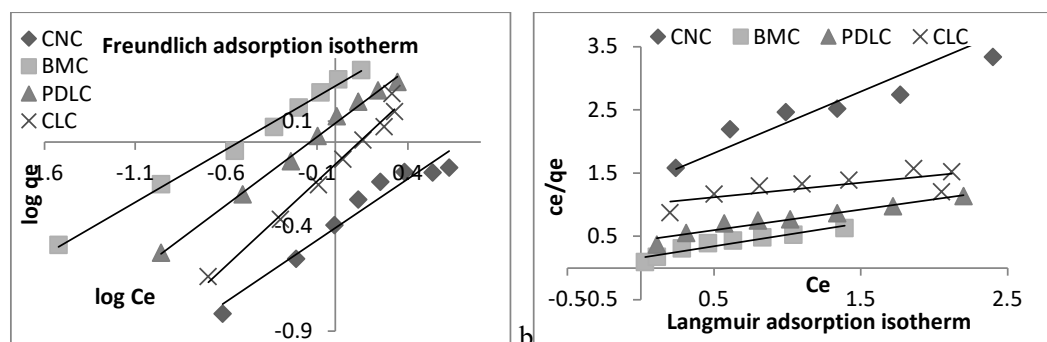


Fig. 7: Linear plots of (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm on fluoride adsorption.

Table 2: Fluoride ion adsorption isotherm parameters at 5.0 pH, 303 K, and 200 rpm agitation speed.

Isotherm	Linear form of adsorption isotherm	Parameter	Parameter values for adsorbents			
			CLC	CNC	PDLC	BMC
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	K_L [L.mg ⁻¹]	0.228	0.732	0.746	2.286
		q_m [mg.g ⁻¹]	4.365	1.028	3.069	2.725
		R^2	0.570	0.972	0.948	0.927
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	n	1.243	1.711	1.541	1.988
		K_F [mg.g ⁻¹] [L.mg ⁻¹] ^{1/n}]	0.784	0.389	1.228	1.849
		R^2	0.982	0.946	0.996	0.995
Temkin	$q_e = B \ln A_T + B \ln C_e$	B [J.mol ⁻¹]	0.56	0.23	0.57	0.49
		A_T [L.g ⁻¹]	5.27	7.01	10.56	39.51
		R^2	0.84	0.95	0.93	0.90

can be considered with a preference for the latter. An even distribution of binding energies can be expected in all these carbon adsorbents with more inclination by CLC, as evident from Temkin isotherm (Kaewsarn & Yu 2001). For these models, the finest appropriate order can be concluded as given below.

Langmuir > Temkin > Freundlich : for CNC

Freundlich > Langmuir > Temkin: for BMC and PDLC

Freundlich > Temkin > Langmuir: for CLC

Compared to the adsorption capacities of some of the adsorbents like activated rice husk ash (0.426 mg.g⁻¹) (Mondal et al. 2012), banana peel (0.3123 mg.g⁻¹), and coffee husk (0.2946 mg.g⁻¹) (Getachew et al. 2015), the present study carbons – CNC (0.7 mg.g⁻¹) BMC (1.4 mg.g⁻¹), PDLC (1.3 mg.g⁻¹) and CLC (1.2 mg.g⁻¹) shown good defluoridation capacities. In view of the good sorption capacities of biomaterials in literature (Wong et al. 2018, Li et al. 2010, Ramya et al. 2015) and the present study, they can be effectively used to remove different pollutants.

CONCLUSION

In the defluoridation of water using activated carbons prepared from bio-waste materials as adsorbents, the optimum dose for CNC, BMC, PLDC, and CLC are 5, 3, 3, and 3.5 g L⁻¹, the optimum time is 40min, the optimum pH is 7 at 30±1°C. In the optimum pH conditions and dose of adsorbents, the percentage of defluoridation from synthetic samples is 71, 80, 76.6, and 82% for CNC, BMC, PLDC, and CLC, respectively. Different kinetic models (Elovich, Boyd, Webers) and kinetic orders (pseudo-first and second orders) were utilized to explore the adsorption mechanism. These results indicate that BMC and PLDC can be utilized as potential adsorbents for the defluoridation of water. Fluoride removal was 70 to 80% from potable water samples with 3-4.5 ppm fluoride under optimized conditions. The selected carbons successfully defluorinated potable water to the permissible limit. Hence, considering the fact that the selected biomaterials are abundantly available in nature and have a negligible cost involved in processing, these highly efficient carbons seem to have a rosy path for potable water

defluoridation and also can be practically used at household level by all populations including those who are without having any scientific knowledge.

REFERENCES

- Antonarakis, G.S. and Moseley, R. 2014. Waddington RJ. Differential influence of fluoride concentration on the synthesis of bone matrix glycoproteins within mineralizing bone cells *in vitro*. *Acta. Odontol. Scand.*, 72(8): 1066-1069. doi: 10.3109/00016357.2014.882982.
- Balasubramaniana, T. and Umaranib, R. 2014. A study on the health hazards of consuming high fluoride content potable water using fuzzy cognitive maps-A Data mining Approach. *Women*, 520: 52.
- Bellack, E. and Schouboe, P.J. 1958. Rapid photometric determination of fluoride in water. Use of sodium 2-(p-sulfophenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonate-zirconium lake. *Anal. Chem.*, 30(12): 2032-2034. doi: 10.1021/ac60144a050.
- Bhattacharya, A.K., Mandal, S.N. and Das, S.K. 2006. Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chem. Eng. J.*, 123: 43-51. doi:10.1016/j.cej.2006.06.012.
- Bosshard-Stadlin, S.A., Mattsson, H.B., Stewart, C. and Reusser, E. 2017. Leaching of lava and tephra from the Oldoinyo Lengai volcano (Tanzania): Remobilization of fluorine and other potentially toxic elements into surface waters of the Gregory Rift. *J. Volcanol. Geother. Res.*, 332: 14-25. doi: j.jvolgeores.2017.01.009.
- Choubisa, S.L. 2018. A brief and critical review of endemic hydrofluorosis in Rajasthan, India. *Fluoride*, 51(1): 13-33.
- Choubisa, S.L. and Choubisa, D. 2016. Status of industrial fluoride pollution and its diverse adverse health effects in man and domestic animals in India. *Environ. Sci. Pollut. Res.*, 23(8): 7244-7254. doi: 10.1007/s11356-016-6319-8.
- Crini, G. and Ndongo Peindy, H. 2006. Adsorption of C.I. basic blue 9 on cyclodextrin-based material containing carboxylic groups. *Dye Pigm.*, 70: 204-211. doi: 10.1016/j.dyepig.2005.05.004.
- Garg, U.K., Kaur, M.P., Garg, V.K. and Sud, D. 2008. Removal of Nickel(II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresour. Technol.*, 99: 1325-1331. doi:10.1016/j.biortech.2007.02.011.
- Getachew, T., Hussen, A. and Rao, V.M. 2015. Defluoridation of water by activated carbon prepared from banana (*Musa paradisiaca*) peel and coffee (*Coffea arabica*) husk. *Int. J. Environ. Sci. Technol.*, 12(6): 1857-1866. doi: 10.1007/s13762-014-0545-8.
- Goswami, S. and Ghosh, U.C. 2005. Studies on Cr(VI) adsorption behavior onto synthetic hydrous stannic oxide. *Water SA*, 31: 597-602. doi: 10.4314/wsa.v31i4.5150.
- Gupta, V.K. and Sharma, S. 2002. Removal of cadmium and zinc from aqueous solutions using red mud. *Environ. Sci. Technol.*, 36: 3612-3617. doi:10.1021/es020010v.
- Hamza, R.Z., El-Shenawy, N.S. and Ismail, H.A. 2015. Protective effects of blackberry and quercetin on sodium fluoride-induced oxidative stress and histological changes in the hepatic, renal, testis, and brain tissue of male rat. *J. Basic Clin. Physiol. Pharmacol.*, 26(3): 237-251. doi: 10.1515/jbcpp-2014-0065.
- Ho, Y.S. and McKay, G. 1999. Pseudo-second order model for sorption processes. *Process Biochem.*, 34: 451-465. doi: 10.1016/S0032-9592(98)00112-5.
- Kaewsarn, P. and Yu, Q. 2001. Cadmium(II) removal from aqueous solutions by pre-treated marine alga *Padina* sp biomass. *Environ. Pollut.*, 112:209-213. doi: 10.1016/S0269-7491(00)00114-7.
- Kumar, P.S., Ramalingam, S. and Kirupha, S.D. 2011. Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism, and process design. *Chem. Eng. J.*, 167: 122-131. doi:10.1016/j.cej.2010.12.010.
- Lagergren, S. 1898. On the Theory of So-called Adsorption Solutes. The Royal Swedish Academy of Sciences, Handlingar, pp. 1-39.
- Li, D., Gao, X., Wang, Y. and Luo, W. 2018. Diverse mechanisms drive fluoride enrichment in groundwater in two neighboring sites in northern China. *Environ. Pollut.*, 237: 430-41. doi: 10.1016/j.envpol.2018.02.072.
- Li, X., Zheng, W. and Wang, D.B. 2010. Removal of Pb(II) from aqueous solutions by adsorption onto modified areca waste: kinetic and thermodynamic studies. *Desalination*, 258: 148-153. doi: 10.1016/j.desal.2010.03.023.
- Li, Xming., Zheng, W., Wang D.B., et al. 2010. Removal of Pb(II) from aqueous solutions by adsorption onto modified areca waste: kinetic and thermodynamic studies. *Desalination*, 258: 148-153. doi: 10.1016/j.desal.2010.03.023.
- Min, S.H., Han, J.S., Shin, E.W. and Park, J.K. 2004. Improvement of cadmium ion removal by base treatment of juniper fiber. *Water Res.*, 38: 1289-1295. doi:10.1016/j.watres.2003.11.016.
- Mokkapat, R.P., Ratnakaram, V.N. and Mokkapat, J.S. 2018. Using agro-waste to remove toxic hexavalent chromium: surface interaction and mass transfer studies. *Int. J. Environ. Sci. Technol.*, 15: 875-886. doi: 10.1007/s13762-017-1443-7
- Mondal, N.K., Bhaumik, R., Banerjee, A., Datta, J.K. and Baur, T. 2012. A comparative study on the batch performance of fluoride adsorption by activated silica gel and rice husk ash. *Int. J. Environ. Sci.*, 2(3): 1643-1661.
- Mondal, P. and George, S. 2015. A review on adsorbents used for defluoridation of drinking water. *Rev. Environ. Sci. Biotechnol.*, 14(2): 195-210. doi: 10.1007/s11157-014-9356-0
- Moradi, O. 2011. The removal of ions by functionalized carbon nanotube: Equilibrium, isotherms, and thermodynamic studies. *Chem. Biochem. Eng. Q.*, 25: 229-240.
- Ramya, P.M., Jayasravanthi, Dulla, B.J. and Venkata Nadh, R. 2015. Chemical oxygen demand reduction from Coffee Processing wastewater – A comparative study on the usage of biosorbents prepared from agricultural wastes. *Global NEST J.*, 17(2): 291-300.
- Ramya, P.M., Jayasravanthi, M. and Venkata Nadh, R. 2016a. Kinetic, thermodynamic, and equilibrium studies on removal of hexavalent chromium from aqueous solutions using agro-waste biomaterials, *Casuarina equisetifolia* L. and *Sorghum bicolor*. *Korean J. Chem. Eng.*, 33(8): 2374-2383. doi: 10.1007/s11814-016-0078-6.
- Ramya, P.M., Jayasravanthi, M. and Venkata Nadh, R. 2016b. Kinetic, isotherm, and thermodynamics investigation on adsorption of divalent copper using agro-waste biomaterials, *Musa acuminata Casuarina equisetifolia* L. and *Sorghum bicolor*. *Pol. J. Chem. Technol.*, 18(2): 68-77. doi: 10.1515/pjct-2016-0031.
- Rao, K., Mohapatra, M., Anand, S. and Venkateswarlu, P. 2011. Review on cadmium removal from aqueous solutions. *Int. J. Eng. Sci. Technol.*, 2: 81-103. doi:10.4314/ijest.v2i7.63747.
- Rodrigues, A.A., Vasconcelos-Filho, S.C., Mendes, G.C., Rehn, L.S., Rodrigues, D.A., Rodrigues, C.L. and Muller, C. 2017. Fluoride in simulated rain affects the morphoanatomy and physiology of *Eugenia dysenterica* (Mart.) DC. *Ecol. Indic.*, 82: 189-195. doi: 10.1016/j.ecolind.2017.07.005.
- Shen, P., Bagheri, R., Walker, G.D., Yuan, Y., Stanton, D.P., Reynolds, C. and Reynolds, E.C. 2016. Effect of Calcium phosphate addition to fluoride containing dental varnishes on enamel demineralization. *Aust. Dent. J.*, 61(3): 357-365. Doi: 10.1111/adj.12385.
- Sousa, F.W., Rosa, M.F., Tropical-ce, E.A. et al. 2007. The use of green coconut shells as adsorbents in the removal of toxic metals. *Quim. Nov.*, 30: 1153-1157. doi: 10.1590/S0100-40422007000500019.
- Sparks, D.L. 1986. Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry. CRC Press, Boca Raton.
- Tewari, N., Vasudevan, P. and Guha, B.K. 2005. Study on biosorption of Cr(VI) by *Mucor hiemalis*. *Biochem. Eng. J.*, 23: 185-192. doi: 10.1016/j.bej.2005.01.011.

- Wong, S., Ngadi, N., Inuwa, I.M. and Hassan, O. 2018. Recent advances in applications of activated carbon from biowaste for wastewater treatment: A short review. *J. Clean. Prod.*, 175: 361-375. doi: 10.1016/j.jclepro.2017.12.059.
- Xue, Y., Gao, B. and Yao, Y. 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. *Chem. Eng. J.*, 200-202: 673-680. doi: 10.1016/j.cej.2012.06.116.
- Yadav, K.K., Gupta, N., Kumar, V., Khan, S.A. and Kumar, A. 2018. A review of emerging adsorbents and current demand for defluoridation of water: Bright future in water sustainability. *Environ. Int.*, 111: 80-108. doi: 10.1016/j.envint.2017.11.014.
- Yan, N., Liu, Y., Liu, S., Cao, S., Wang, F., Wang, Z. and Xi, S. 2016. Fluoride-induced neuron apoptosis and expressions of inflammatory factors by activating microglia in rat brain. *Mol. Neurobiol.*, 53(7): 4449-4460. doi: 10.1007/s12035-015-9380-2.
- Zohoori, F.V. and Duckworth, R.M. 2016. Fluoride: Intake and metabolism, therapeutic and toxicological consequences. *Mol. Genet. Nutr. Aspects Major Trace Miner.*, 20: 539-550. doi: 10.1016/B978-0-12-802168-2.00044-0.

ORCID DETAILS OF THE AUTHORS

- K. Kiran Kumar: <https://orcid.org/0000-0001-8612-5776>
Ratnakaram Venkata Nadh: <https://orcid.org/0000-0003-0925-1132>
G. Krishnaveni: <https://orcid.org/0000-0003-1589-2497>