Defluoridation using pinecone-based activated carbon: Adsorption isotherm, kinetics, regeneration and co-ions effect investigation

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Abstract: In this work, cheap and locally available pinecones of *Pinus kiseya* were used as a precursor to prepare activated carbon using single-step KOH activation for the removal of fluoride from water. The prepared activated carbon's BET surface area, and total pore volume, were determined as 972.13 m^2 g^{-1} and 0.469 cm^3 g^{-1}, respectively. Batch adsorption studies were evaluated at different contact times, solution pH, adsorbent dose and concentration to obtain the optimum conditions for maximum adsorption. The adsorption data were fitted with the isotherm models (Langmuir, Freundlich ad Temkin isotherm model) and the adsorption kinetic models. The experimental data were found to best fit using the Langmuir isotherm which confirmed the formation of a monolayer coverage with a maximum adsorption capacity of 2.845 m^2 g^{-1}. The adsorption kinetics was well described by the pseudo-second-order model. A study on the effects of co-existing ions showed that fluoride adsorption capacity was observed to decrease in the order: $CO_3^{2-} > SO_4^{2-} > NO_3^- > Cl^-$. The regeneration studies were investigated to determine the reusability of the spent adsorbent. In summary, these findings demonstrated substantial evidence that the activated carbon can be prepared from *P. kiseya* cones as an eco-friendly adsorbent for the removal of ions such as fluoride from water.

Keywords: pinecone; activated carbon; fluoride; biomass; regeneration; water treatment.

INTRODUCTION

There is no doubt that fluorine is an essential element for the development of bones and teeth yet it is regarded as an element of "boon and bane". It is known

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to have healing characteristics, but exceeding its permissible limit of 1.5 mg L^{-1} (WHO guidelines) could ultimately result in serious health problems in the long run. The World Health Organization also recognizes the fluorides as the drinking water contaminants, alongside arsenic and nitrate, that contribute to significant health issues on a large scale.[1] Some of the problems associated with fluorides are dental and skeletal fluorosis, brittle bones, Alzheimer's syndrome and thyroid disorder, neurological damage, low haemoglobin levels, gastrointestinal problems and infertility.[2,3] The global prevalence of fluorosis is estimated to affect approximately 70 million individuals.[4] Fluorides enters water from various sources, including naturally the occurring geological sources such as fluorine-containing rocks and minerals (*e.g.*, granite, basalt, syenite, fluorite, biotites and topaz) as well as the industrial activities such as metallurgical, electrodeposition, phosphate production, electronics, brick and iron-works, and ceramics.[5,6] The elevated concentrations of fluorides are prevalent in many water sources, particularly in regions such as China, Sri Lanka, Rift Valley countries in Africa and India. In India, chronic fluorides levels of 12–18 mg L^{-1} have been reported with 17 states showing the excessive fluorides levels.[2,7]

Since the fluorides levels in drinking water is an issue of global health concern, it needs to be reduced below acceptable level to provide safe drinking water. To date, numerous technologies and methods have been applied for the removal of fluoride such as nanofiltration (NF), reverse osmosis (RO), ion--exchange method, electrodialysis and adsorption.[6,8–11] But, most of these techniques fail when it comes to the rural population because of their cost except the adsorption method. Adsorption is an ancient and widely used method because of its high efficacy, operational and budget-friendliness for the removal of fluoride and other pollutants as well from water.[2,12]

In this regard, adsorbent such as activated carbon from biomass origin has been widely used to investigate studies related to fluoride removal. Biomass--based carbon over the years has gained a significant place as an alternate adsorbent due to its high surface area and reactivity, low-cost, eco-friendly characteristics, and renewability.[3,13,14] For instance, Gebrewold *et al.* 2019 synthesised activated carbon from biomass of rice husk and corn cob for the removal of fluorides from groundwater with an adsorption capacity of 7.9 and 5.8 mg g^{-1};[15] Fito *et al.* 2019 also used *Catha edulis* as a potential precursor for the synthesis of activated carbon for the removal of fluorides from water;[16] Jayashree *et al.* 2021 studied the removal of fluorides from water using the activated carbon prepared from pods of *Bauhinia variegata* by both physical and chemical methods with BET surface area of 71.59 and 124.82 m^2 g^{-1}. They found that the chemically prepared activated carbon was having a higher fluorides adsorption capacity (15.74 mg g^{-1}) over physically prepared carbon by a difference of 5 mg g^{-1}.[17]

Therefore, the biomass materials such as pinecones that are often discarded as waste can be potentially utilised to obtain a value-added product like the activated carbon to remove fluoride from water. Our group have been working on the preparation of the activated carbon from locally available biomass – *Manihot esculenta*, *Schima wallichii* and *Mucina sp.*—for the removal of fluorides from water.[4,18,19]

Thus, in this piece of work, we explored the pinecone of *Pinus kesiya* as the precursor for the synthesis of activated carbon because of its easy availability, abundance and low cost for the removal of fluorides from water. The characterization of the adsorbent was analysed with various techniques to study the physicochemical properties, surface morphology and functionalities to access the capability of the adsorbent for the fluorides removal. Further, motivated by the presence and effects of existing co-ions on the adsorption efficiency, the prepared adsorbent was applied for defluoridation studies in the presence of various co--ions, using a batch method to understand the efficacy of the adsorbent in a real--time situation. The regeneration of the adsorbent was also explored in order to understand its recyclability.

EXPERIMENTAL

Materials

Pinecones were collected locally, washed, and grounded using a mixer grinder to fine particles. All other chemicals used in this work were of analytical grade.

Synthesis of pinecone activated carbon

For the synthesis of activated carbon, a single-step method published in our earlier work was followed.[4] In a typical method, the dried particles of pinecone biomass were grounded into finer particles in a ball mill. The dried biomass powder was then activated by carbonizing it in a muffle furnace at 600 °C for 2 h at a heating rate of 20 °C min^{-1} by mixing it with KOH at a 1:2 ratio. The black carbonized sample was then cooled and washed with hot water and finally with cold distilled pH of the wash solution becomes neutral. The sample was then dried in an oven overnight at 110 °C and stored in an airtight sealed container, labelled as Pc-AC (pinecone activated carbon) for further characterization and use.

The yield percentage of Pc-AC was calculated as:

$$\text{Yield} = 100 \frac{\text{Mass of final carbon after activation process}}{\text{Initial mass of the dry impregnated sample}} \tag{1}$$

Adsorbent's characterization

The prepared carbon was characterized through different analytical techniques. The carbon, hydrogen and nitrogen percentage in the prepared carbon were determined using an elemental analyzer (model: PE 2400 Series II, Perkin Elmer). The batch equilibrium method was employed to determine the zero point charge.[20] To measure the pHpzc, a 50 mL solution of 0.1 M KNO_3 was prepared in a conical flask, to which the prepared Pc-AC was added. The adsorbent suspended was kept in this 0.01 M KNO_3 solution until the pH reached a stable state. The initial pH values were adjusted in the range of 2 to 12 by adding HCl or NaOH. The mixture was continuously stirred for 2 days on a magnetic stirrer. Afterward, the final pH

values were measured, and the difference between the initial and final pH values (ΔpH = pHinitial – pHfinal) was plotted against the initial pH values (shown in Fig. S-1 of the Supplementary material to this paper). Surface functionalities of the prepared carbon was determined using the FT-IR spectrometer (model: Spectrum Two, Perkin Elmer) in the range 4000–400 cm^{-1}. Surface morphology was determined using the scanning electron microscopy (JSM-6360, JEOL). The BET surface area and pore volume were measured by using a BET surface area analyzer (Smart instrument, SS93/02).

Preparation of standard fluoride stock solution

The standard fluoride solution was prepared by dissolving 2.178 g of NaF (Merck) in 1000 ml of double-distilled water in a 1000 ml volumetric flask. The solution was then further diluted to 100 mg L^{-1} of the fluoride solution. All test solutions of the desired concentrations were prepared by the successive dilutions of 100 mg L^{-1} fluoride solution to get the required initial experimental concentration (2, 5 and 8 mg L^{-1}). The pH of all the solutions was adjusted by adding 0.1 M HCl or 0.1 M NaOH before the addition of the adsorbent and was measured by pH meter (Eutech).

Fluoride adsorption by batch mode experiments

For any adsorption study, a batch adsorption experiment is vital as it provides information about the different parameters that control the adsorption process. This method helps to find out the optimum condition for the reaction to be carried out effectively. Thus, the adsorption parameters such as contact time, adsorbent dosage, pH, and the fluorides concentration are investigated by this method. An optimized condition is established from the different experimental data and enables us to fix the experimentally obtained optimal conditions to perform further experiments in the future.

In the current study, the batch mode experiments were accomplished by taking 50 mL of fluoride known solution in an Erlenmeyer flask, which was stirred with a known weight of pinecone activated carbon at 150 rpm in a rotary shaker. The solution was filtered after the adsorption equilibrium was achieved, and the unadsorbed fluorides concentration was measured with the help of a fluoride meter (model: Hanna Hi 98402 ISE Fluoride Meter). The effect of the adsorption parameters like pH (pH 2 to 12), activated carbon quantity (0.05 to 0.30 g), contact time (0 to 180 min), and the fluoride concentration of 2, 5, and 8 mg L^{-1} were conducted. The removal percentage efficiency and the defluoridation capacity (mg g^{-1}) for Pc-AC was determined as:

$$\text{Removal efficiency} = 100(C_0 - C_e)/C_0 \tag{2}$$

$$\text{Defluoridation capacity} (q_e) = V(C_0 - C_e)/M \tag{3}$$

where c_0 = initial fluoride concentration in mg L^{-1}; c_e = equilibrium fluoride concentration in mg L^{-1}; q_e = amount of adsorbate adsorbed at equilibrium in mg g^{-1}; M = mass of pinecone activated carbon in g; V = volume of fluoride solution in L.

RESULTS AND DISCUSSION

Pinecone-activated carbon characterization

The results indicated that the yield and ash content values of Pc-AC were 16.88 and 3.07 %, respectively; the carbon, hydrogen, nitrogen and oxygen content as determined by ultimate analysis was 87.69, 2.01, 0.72 and 6.51 %, respectively (Table I). The BET surface area and the total pore volume of Pc-AC

were 972.13 $m^2 g^{-1}$ and 0.469 $cm^3 g^{-1}$ as compared to the sample activated without any KOH which had a surface area of 108.54 $m^2 g^{-1}$ and the pore volume of 0.057 $cm^3 g^{-1}$. The higher BET surface area and the pore volume upon KOH activation could be attributed to the elimination and release of volatile matter from the carbon skeleton to form voids, leading to an increase in the availability of active sites for adsorption.

TABLE I. Properties of Pc-AC with and without KOH impregnation

Condition	Yield, %	BET Surface area, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$
Without KOH	35.13	108.54	0.057
With KOH	16.88	972.13	0.469

The pH of the zero point charge (pHzpc) of Pc-AC was found to be 6.93 reflecting the fact that the surface of the adsorbent was positive below this pH and negatively charged when pH > pH_{zpc}.[21] Fig. 1a shows the SEM image of the pinecone-activated carbon. The SEM analysis of the adsorbent indicates that the surface of the adsorbent was irregular and rough, with different pore sizes and shapes. The presence of such pore sizes is expected to influence the adsorption process and thus makes it appropriate for the adsorption of fluoride.

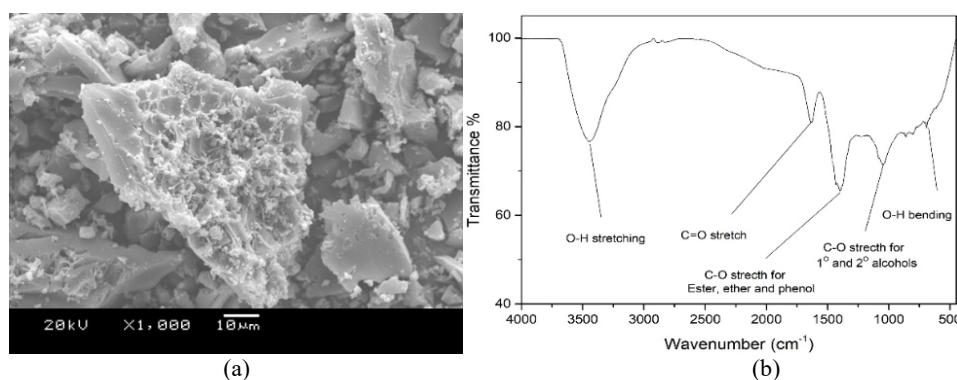
(a)   (b)

Fig. 1. a) SEM micrograph of Pc-AC; b) FTIR spectrum of Pc-AC.

FT-IR study was used to determine the major surface functionality on the Pc-AC surface. The FTIR is shown in Fig. 1b. A very prominent peak around 3450 cm^{-1} was observed for Pc-AC which is due to the O–H stretching mode of hydroxyl groups, –NH group. It is also due to the adsorption and presence of moisture on the PC-AC surface. The functional groups include alcohols, phenols, carboxylic acids and amine. The peaks around 1637 cm^{-1} account for the presence of C=O groups such as in carboxylic acids.[22] While the band appearing at 1435 cm^{-1} has been assigned to the aromatic structure of Pc-AC, that are coupled to the highly conjugated carbonyl groups or attributed to the stretching vibrations

of C=O moieties of conjugated systems.[23] Bands near 1395 cm^{-1} is assigned to C–O stretching vibration from ester, ether and phenolic functional groups.[24] While the bands around 1048 cm^{-1} account for C–O vibrational stretching for primary and secondary alcohols. Finally, bands at 700–900 cm^{-1} corresponds to =C–H bending of the substituted aromatic rings, while broad peaks at ~640 cm^{-1} account for O–H bending.[25] The FT-IR studies show that the various surface functionalities makes them an ideal adsorbent for adsorption study.

Batch adsorption studies

Effect of contact time and initial concentration. The effect of the contact time on the adsorption of fluoride at three different initial concentration were investigated and reflected in Fig. 2a. The adsorption in all cases is found to increase rapidly with time and becomes saturated as time continues, and an equilibrium is achieved. The rapid adsorption in the initial period is caused by the availability of active adsorption sites, but as time proceeds, these sites get accumulated with the adsorbate, which does not allow any further adsorption. The equilibrium time for maximum fluoride adsorption was found to be 120 min for Pc-AC.
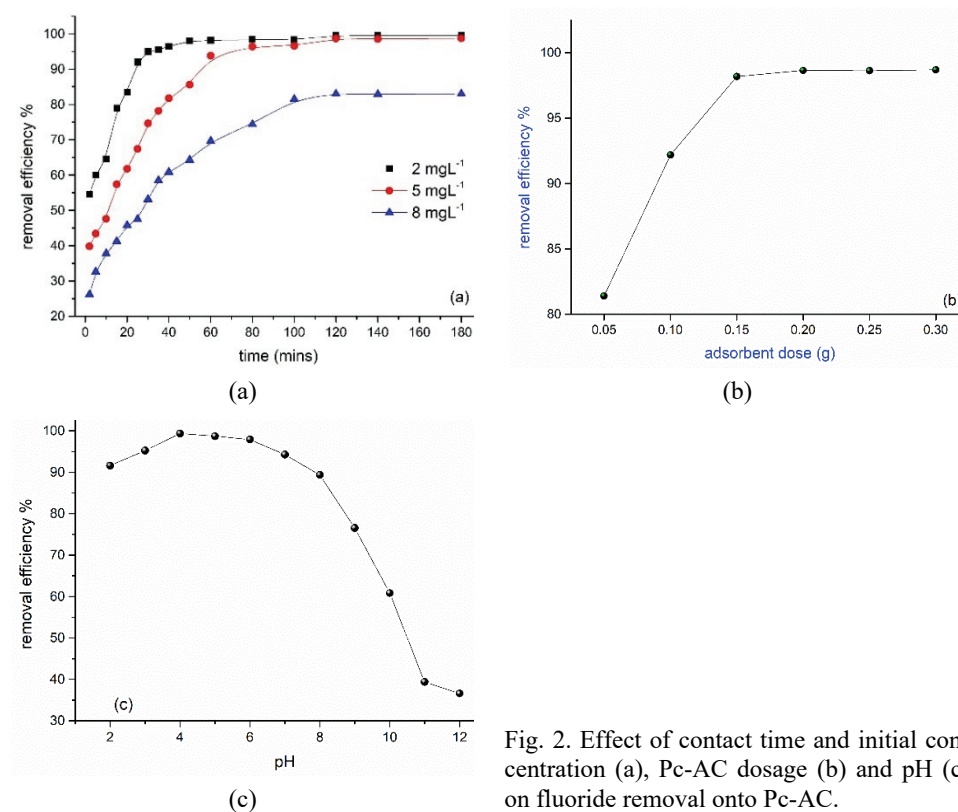

Fig. 2. Effect of contact time and initial concentration (a), Pc-AC dosage (b) and pH (c) on fluoride removal onto Pc-AC.

Moreover, it is well-known that adsorption depends on the relationship between the unoccupied adsorption sites and the concentration of fluoride. Accordingly, Figs. 2a and S-2a of the Supplementary material shows that, with the increasing initial concentration of fluorides, the removal percentage decreases (increase in the adsorption capacity). This was due to the saturation of the available adsorption sites on the adsorbent. It was observed that at 2 mg L^{-1} fluoride concentration, there seemed to be easy availability of the unoccupied sites, which led to the complete adsorption of fluoride from the solution. However, as fluoride concentrations increased, a decrease in the number of active sites was noticed due to the increased adsorption of fluoride on the surface of the active sites, which led to a reduction in the available active sites. It was found that the removal percentage of fluoride by Pc-AC, at concentrations of 2, 5 and 8 mg L^{-1} were 99.9, 98.7 and 83 %, respectively. Based on these observations, the fluoride concentration of 5 mg L^{-1} concentration was taken for all other experiments as the optimal concentration.

Effect of adsorbent dose. To confirm the proper dosage of the adsorbent, the adsorption process was conducted at different PC-AC dosages. Figs. 2b and S-2b show the effect of the adsorbent dosage (0.05–0.30 g) on the removal of fluorides by PC-AC. It was found that with an increase in the adsorbent dosage, the fluorides removal efficiency increased, but it reached the equilibrium at an adsorbent dosage of 0.15 g with no further increase in the removal percentage after that. The high removal percentage at this dosage was due to the availability of the active binding sites on the adsorbent as a result of its surface area.[26] The porous nature of the adsorbent also facilitates the fluorides adsorption, which is consistent with the observations obtained from the scanning electron microscopy (SEM) analysis. However, with a further increase in the adsorbent dose, there was no further increase in the removal rate (as there was a decrease in the adsorption capacity). This was due to the accumulation or the partial overlapping, which lead to a decrease in the total adsorption sites for fluorides.[27] Thus, for the subsequent studies, an adsorbent dose of 0.15 g was used.

Effect of solution pH. The pH of the solution is one of the basic parameters that affect the adsorption of fluorides. A study on the effect of pH on the adsorption of fluoride was done at different pH from 2 to 12 keeping the other parameters like adsorbent dose and the fluoride concentration constant (Fig. 2c). It can be seen that; the adsorption of fluoride was more significant at lower pH (acidic medium) when compared to the alkaline condition. This could be because at lower pH (pH < pHpzc) most of the surface becomes positively charged which further facilitates the adsorption of fluoride. The maximum fluoride adsorption was found to take place at pH 4. But below pH 4, the fluorides removal was found to decrease due to the formation of weak hydrofluoric acid.[28] On the other hand, when the solution pH was alkaline, there was a reduction in the adsorption

of fluorides because of the competition between the negatively charged surface hydroxyl ions and the fluoride ions on the active sites.[29]

Thus, for further studies, the optimum fluorides concentration was taken at 5 mg L^{-1} with the adsorbent dose of 0.15 g at 120 min. As the maximum fluorides removal takes place at pH 4, all further adsorption experiments were done at that pH value.

Isotherm studies

The study of the adsorption isotherms is important as it elucidates the most significant isotherm model that determines the interlaying relationship between the adsorbate and adsorbent, useful for the designing purposes. The experimental equilibrium data were modelled using three classical adsorption models: the Langmuir, Freundlich and Temkin isotherms. These models were employed to describe fluoride adsorption on Pc-AC. The equations and the calculated equilibrium isotherm parameters are given in Table II.

TABLE II. Different parameters of adsorption isotherm models for fluoride removal using Pc-AC; q_e = adsorption caPc-ACity at equilibrium (mg g^{-1}); C_e = residual concentration at the equilibrium state of the system (mg L^{-1}); Q_{max} = maximum adsorption caPc-ACity (mg g^{-1}) K_L = Langmuir constant; K_F = Freundlich constant (L mg^{-1}); R_L = separation factor (provides insight into the favourability of the adsorption process); $1/n_F$ = intensity of the adsorption, respectively; B_T = Temkin constant related to the heat of sorption (J mol^{-1}); A_T = equilibrium binding constant that corresponds to the maximum binding energy (L g^{-1})

Isotherm model	Equation	Parameters	Value
Langmuir	$C_e / q_e = 1/(Q_{max} K_L) + 1/(Q_{max} C_e)$	Q_{max}	2.845
		K_L	18.375
		R_L	0.011
		R^2	0.999
		χ^2	0.0001
Freundlich	$\log q_e = (1/n_F) \log C_e + \log K_F$	K_F	2.459
		$1/n_F$	0.221
		R^2	0.906
		χ^2	0.0060
Temkin	$q_e = RT/b_T (\ln A_T + \ln C_e)$	A_T	542.19
		B_T	0.358
		R^2	0.980
		χ^2	0.0174

The fitting of data with Langmuir isotherm for the adsorption of fluoride onto Pc-AC as shown in Fig. S-3a of the Supplementary material, gave the Q_{max} (maximum adsorption capacity) value of 2.845 mg g^{-1}. The correlation coefficient R^2 for Langmuir isotherm for the fluoride adsorption by Pc-AC was found to be 0.999 (Table II). Further, the separation (R_L), was found to be 0.011, thereby indicating the favourable adsorption of fluoride onto Pc-AC. The Freund-

lich isotherm, the plot of the model is shown in Fig. S-3b and the parameters calculated from the slope and intercept are given in Table II. It can be seen that, $1/n_F$, for the adsorption of fluoride by Pc-AC was found to be 0.22, thereby suggesting the favourability of the fluoride adsorption onto Pc-AC. It also indicates that the adsorption follows a normal Langmuir isotherm.[30] The correlation coefficient R^2 value for fluoride adsorption by Pc-AC for Freundlich isotherm was found to be 0.906, which, when compared to Langmuir isotherm is way much lower. While the fitting of the experimental data onto the Temkin isotherm model for fluoride adsorption by Pc-AC is shown in Fig. S-2c. The calculated parameters for the Temkin model are given in Table II. The heat of adsorption (B_T) was found to be 0.358 kJ mol^{-1}. The correlation value for Temkin isotherm for fluoride adsorbed onto PC-AC was 0.980.

For the determination of the appropriateness of the fit, the best adsorption isotherm model for the adsorption of fluoride by Pc-AC, chi-square analysis was performed on all the isotherm models, and the results are shown in Table II. For the adsorption of fluoride by Pc-AC, the chi-square value for the Langmuir isotherm model was found to be the least and therefore, the most suitable to describe the adsorption of fluoride. Since the Langmuir equation assumes that the surface is homogeneous, it indicates a homogeneous distribution of the adsorption sites on the adsorbent and the adsorption of fluoride by Pc-AC took place as a monolayer coverage on the carbon surface containing a finite number of adsorption sites of uniform energy. The isotherm study also suggests that there is no transmigration of adsorbate in the plane of the adsorbed site.

The fitness of the isotherm for fluoride adsorption by Pc-AC follows the order: Langmuir >> Temkin > Freundlich

Adsorption kinetics

The adsorption kinetics for the removal of fluoride by Pc-AC was investigated with pseudo first order, pseudo second order kinetic models and the intraparticle diffusion model using the equation provided in Table III. The graph of log (q_e–q_t) *versus t* was plotted for the pseudo-first-order while for the pseudo-second-order kinetics models the graph of t/q_t *versus t* was plotted and for the intraparticle diffusion model, q_t is plotted against $t^{1/2}$. Fig. S-4 of the Supplementary material shows the plot of the pseudo-first-order kinetics, the pseudo-second-order kinetics and the intraparticle diffusion model for the fluorides adsorption by Pc-AC. The results of the kinetic studies are listed in Table III.

Table III shows that the measured q_e value of the pseudo-first-order kinetic model do not tally with the experimental q_e values for the adsorption of fluorides and even the appropriateness of the fit was not satisfactory. In the case of the pseudo-second-order kinetics model, the measured equilibrium adsorption capacity, $q_{e,meas}$ of Pc-AC was found to be in good agreement with the experimental

data. A good correlation coefficient (R^2) value of 0.999, 0.997 and 0.991 was found for the pseudo-second-order kinetic model at 2, 5 and 8 mL^{-1} of fluoride concentration which in the case of pseudo-first-order model was 0.927, 0.930 and 0.918, respectively. Thus, the suitability of the pseudo-second-order kinetics model can describe the adsorption of fluoride onto Pc-AC, which suggests that the overall rate of adsorption is predominantly chemisorption.

TABLE III. Kinetic parameters for the adsorption of fluoride onto the pinecone-activated carbon; qe = the amounts of adsorbate (mgg−1) adsorbed at equilibrium; qt = amounts of adsorbate (mgg−1) adsorbed at a given time t (min); k1 = the rate constant of adsorption (min−1); k2 = pseudo-second-order adsorption rate constant (g/mg.min); *kipd* = intraparticle diffusion constant; C =intraparticle diffusion constant

C_0 mg L^{-1}	$q_{e, exp}$ mg g^{-1}	Pseudo-first-order kinetics[31] $\log(q_e - q_t) =$ $\log q_e - k_1/2.303t$			Pseudo-second-order kinetics[32,33] $t/q_t = 1/(k_2 q_e) + t/q_e$			Intraparticle diffusion[34] $q_t = k_{ipd}t^{0.5} + C$		
		$q_{e, meas}$ mg g^{-1}	k_1 min^{-1}	R^2	$q_{e, meas}$ (mg g^{-1})	k_2 g/(mg min	R^2	k_{ipd}	C	R^2
2	0.796	0.044	0.106	0.927	0.813	0.404	0.999	0.028	0.516	0.620
5	1.975	6.921	0.127	0.930	2.114	0.045	0.997	0.112	0.772	0.864
8	2.656	14.089	0.101	0.918	2.920	0.021	0.991	0.169	0.748	0.942

It was established through SEM analysis that the prepared adsorbent is porous; thus, it is essential to consider how fluoride diffuses into the pores of Pc--AC. The experimental data were therefore, examined using the intra-particle diffusion model to gain insights into the diffusion of fluoride adsorption onto Pc--AC. Fig. S-4c of the Supplementary material illustrates three distinct sections in the plot. The first straight portion corresponds to the rapid transport of the fluoride from the bulk liquid to the boundary layer, surrounding the adsorbent due to the readily available adsorbing sites on the adsorbent surface. It represents the fast adsorption of the fluorides on the external surface of pinecone activated carbon *via* macropore diffusion. The second linear portion accounts for the transport of the fluorides from the adsorbent surface into interior sites. The final step accounts for the slow diffusion of fluoride into micropores which are the less accessible sites of adsorption. It can also be seen that the proportion of C increases with the increase in the fluorides ion concentrations indicating an increase in boundary layer effects.

When compared to the pseudo-second-order kinetic model, the R^2 value for the intra-particle diffusion was lower, as evident from Fig. S-4c. Additionally, the intercept of the line does not pass through the origin, indicating that the adsorption mechanism of fluoride onto Pc-AC does not agree with this model. This observation adequately suggests that the chemisorption predominantly controls the

overall adsorption rate, following the pseudo-second-order kinetics. Similar results were also reported in the literature.[35–39]

Effect of co-ions on fluoride adsorption

The presence of co-ions like nitrate, sulphate, carbonate, chloride and bromide normally occurs in the fluorides-contaminated water. During the adsorption, these ions compete with fluorides for the adsorption sites, which results in a decrease in the adsorption capacity of the adsorbent.[40–42] Thus, it is important to study the effect of co-ions to understand the efficacy of the prepared adsorbent. Therefore, the adsorption of the fluorides in the presence of the competing anions such as bromides, chlorides, nitrates, carbonates and sulphates was investigated. For this study, 20 mg L^{-1} concentration of anions was stirred with an initial fluoride concentration of 5 mg L^{-1}; pH 7; contact time for 120 min for PC-AC, at temperature 303 K and an adsorbent dose of 0.15 g.

As an effect of the presence of co-ions, the adsorption capacity was observed to decrease for carbonate, followed by sulphate, nitrate and chloride, as depicted in Fig. 3. We found that the defluoridation efficiency reduces significantly in the presence of sulphate and carbonates, *i.e.*, for the sulphate adsorption of fluorides reduces from ~99 % (without any co-ions) to 84.17 %; for carbonate, the adsorption of fluorides reduces from ~99 to 72.13 %. The reduction in the removal efficiency could be because of a change in the pH of the fluoride solution because of the addition of the competing ions (the pH values of fluoride solution, pH 7, mixed with Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and CO$_3^{2-}$ increased for both the carbons as shown in Fig. 3). So as the pH increases, the pH of the solution shifts towards the alkaline end, thereby reducing the fluorides adsorption efficiency.
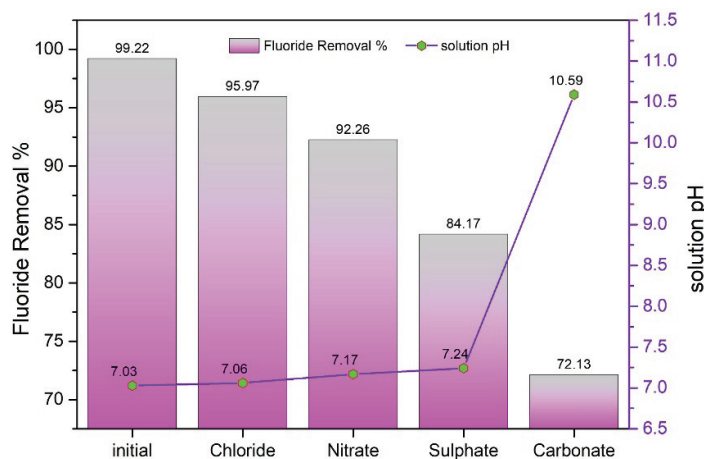

Fig. 3. Effect of co-ions on fluoride removal by PC-AC.

The reduced adsorption of fluorides in the presence of sulphate could be due to the formation of both outer-sphere and inner-sphere surface complexes.[43] On the other hand, the reduction due to the presence of carbonates could be because of the reduction of the positive charges on the active sites of the adsorbent by the carbonates and thus reduces the active sites for the adsorption of fluoride thereby lowering the removal efficiency.[44,45] But, the presence of chloride and nitrate showed a weaker effect on fluoride adsorption as compared to sulphate and carbonate. This might be due to the outer-sphere surface complex formation (for chloride and nitrate).

Regeneration study

In an adsorption process, the regeneration of the adsorbent is one of the crucial aspects as it reduces the cost and determines the cost-effectiveness of wastewater treatment. A regeneration study also allows a researcher to understand the economic viability of the adsorbent. In this study, the regeneration of the adsorbent saturated with fluoride was stirred in a 20 % NaOH solution for 1 h. It was then washed with distilled water until the pH of the desorbed carbon became neutral and oven-dried at 110 °C. For the estimation of the removal efficiency of the regenerated carbon, the adsorption experiments were repeated under the same conditions, *i.e.*, 0.1 g of the regenerated samples with 50 ml of 5 mg L^{-1} of standard fluoride solution was agitated for 120 min at a pH of 7. It was found that the removal efficiency of the regenerated carbon was 93.23 % in the first cycle, 90.14 in the second cycle, 86.45 in the third, and subsequently decreased to 79.83 % in the fourth cycle, as shown in Fig. 4. However, further studies are required in the future to increase the efficiency of the regenerated adsorbent in the subsequent cycles and also to explore the use of milder chemicals for the regeneration of the adsorbent.
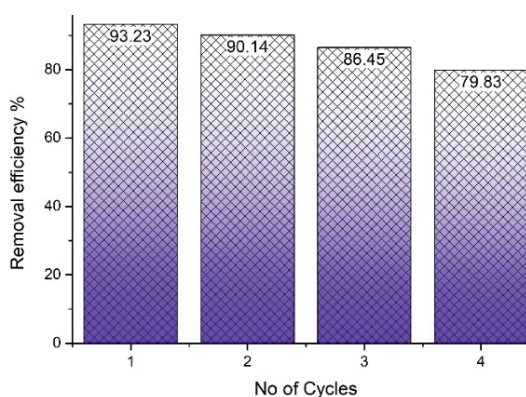

Fig. 4. Regeneration cycle of Pc-AC.

Comparison of Pc-AC with other adsorbents

The fluoride adsorption efficiency for the prepared activated carbon was compared with the other adsorbents reported in the literature and is listed in Table S-I of the Supplementary material.

CONCLUSION

The use of activated carbons derived from the locally abundant pinecone biomass was investigated for the fluorides removal from water in this study. The activated carbon exhibited an irregular surface and varied pores, as determined by the SEM micrographs. The FTIR analysis revealed the presence of different oxygen functionalities, including hydroxyl, ether, ester, carbonyls, *etc*. The batch adsorption experiments demonstrated that the fluorides adsorption was favourable at a pH of 4 and followed a monolayer adsorption type, with a chemisorptive mechanism and a maximum adsorption capacity of 2.845 mg g^{-1}. The presence of co-ions, specifically sulphates and carbonates, influenced the fluorides' adsorption process. The regenerated activated carbon using 20 % NaOH demonstrated promising results and could be used for the fluorides removal for a certain cycle. In summary, the results indicate that the pinecone-derived activated carbon exhibits to be a sustainable and efficacious adsorbent for the defluoridation purposes, particularly in the context of delivering the potable water to individual residences, small communities, and rural regions.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12451, or from the corresponding author on request.

И З В О Д
ДЕФЛУОРИДАЦИЈА КОРИШЋЕЊЕМ АКТИВНОГ УГЉА НА БАЗИ ШИШАРКИ: ИЗОТЕРМА АДСОРПЦИЈЕ, КИНЕТИКА, РЕГЕНЕРАЦИЈА И ИСПИТИВАЊЕ ЕФЕКАТА КО-ЈОНА

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У овом раду, јефтине и локално доступне шишарке *Pinus kiseya* коришћене су као прекурсор за припрему активног угља коришћењем једностепене KOH активације за уклањање флуорида из воде. BET површина припремљеног активног угља и укупна запремина пора су одређени као 972,13 m^2 g^{-1}, односно 0,469 cm^3 g^{-1}. Адсорпција је процењена за различита времена контакта, pH вредности раствора, дозу адсорбента и концентрацију, да би се утврдили оптимални услови за максималну адсорпцију. Подаци

о адсорпцији фитовани су са различитим моделима изотерми (Langmuir, Freundlich и Temkin модел) и кинетичким моделима адсорпције. Утврђено је да се експериментални подаци најбоље уклапају са Langmuir изотермом која је потврдила формирање једно-слојног покривања са максималним капацитетом адсорпције од 2,845 m^2 g^{-1}. Кинетика адсорпције је добро описана моделом псеудо-другог реда. Студија о ефектима коегзис-тирајућих јона је показала да је примећено да се капацитет адсорпције флуорида смањује по редоследу: $CO_3^{2-} > SO_4^{2-} > NO_3^- > Cl^-$. Испитиване су студије регенерације да би се утврдила могућност поновне употребе истрошеног адсорбента. Резултати су показали да се активни угаљ може припремити из шишарки *Pinus kiseya,* као еколошки прихватљив адсорбент за уклањање јона из воде, као што је нпр. флуорид.

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