Removal of fluoride from an aqueous solution by batch and column process using activated carbon derived from iron infused *Pisum sativum* peel: characterization, Isotherm, kinetics study

Naincy Sahu, Chandra Bhan, Jiwan Singh[†]

Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Lucknow-226025, India

ABSTRACT

The present study investigated the adsorption efficiency of magnetic activated carbon was synthesized by waste biomass of *Pisum sativum* (peel) and pyrolysis at 500°C temperature (MPPAC-500). Derived activated carbon was applied for removal of fluoride from aqueous solution. The MPPAC-500 was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), zeta potential, X-ray Diffraction (XRD) and Particle Size Analyser. The fluoride sequestration study was performed in both batch and column systems. The batch adsorption study was focused on parameter like, adsorbent dose, contact time, pH and initial fluoride concentrations. The maximum capacity of fluoride removal was $q_0 = 4.71$ (mg/g). Freundlich isotherm model ($R^2=0.995$) obeyed better than Langmuir ($R^2=0.979$) model. The R_L values observed between 0-1 ($R_L=0.057$) inferred the favourable adsorption. Pseudo-second-order model favoured well than pseudo-first-order in the whole experimental data. In case of column study was performed at two different bed height 5 cm and 10 cm having flow rate of 5 mL/min as well as 10 mL/min. The breakthrough curve and column data were interpreted by Thomas, Adams-Bohart, Yoon-Nelson and Clark model. These finding showed that MPPAC-500 has potential adsorptive capacity for fluoride removal from aqueous solutions in batch and column systems.

Keywords: Activated carbon, Adsorption, Column study, Fluoride removal, Pea peel

1. Introduction

Excessive and dearth presence of Fluoride (F⁻) in groundwater exposed more than two hundred million people across the world [1]. Many countries like China, India, Nigeria, Kenya, Pakistan, South America, Africa and Sri Lanka are facing severe problem of F⁻ contamination in groundwater [2, 3]. According to WHO [4] 1.5 mg/L is maximum concentration of fluoride in water for drinking purpose. Fluoride act as double edged sword like element in water as lower concentration of F⁻ is essential for human health, but its concentration more than 1.0 mg/L leads fluorosis related dental and skeletal in which teeth enamel and bone tissues get harmed because of its strong attraction with calcium found in teeth and bones [5].

Fluoride is naturally present in earth crust and rocks and it reached to the groundwater by slow leaching of fluoride containing

parent rocks (viz. granite, basalt, synginte etc.) and minerals such as biotite, fluorite topaz [6]. Therefore, the natural geological sources are eventually responsible for reaching of fluoride to groundwater. Besides natural sources pharmaceuticals, cosmetics, effluents from fertilizers, metal processing units, semiconductors, and glass manufacturing factories are also contributing in reaching of fluoride to the surface water and groundwater [7]. Globally about more than 20 developed and developing nations like USA, Africa and Asia, where fluorosis became endemic, wherever China, Sri Lanka, India and Rift Valley countries of Africa are badly affected. In India, it has been reported that about 17 states are prevalently affected by fluorosis specially Andhra Pradesh, Gujarat, Rajasthan, Haryana, Assam, Tamil Nadu and Uttar Pradesh [8]. At present about more than 1 million people of India are thought to be affected by endemic fluorosis [9]. Therefore, today defluoridation of water became a necessity for vital human health by feasible technologies. Defluorination of water has been conducted by applying different

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[†] Corresponding author

Email: jiwansingh95@gmail.com

Tel: +91-7376157206

ORCID: 0000-0003-3851-7331

conventional technologies such as membrane filtration, reverse osmosis, ion exchange, electrodialysis, flotation and adsorption. However, among these only few technologies can be applied at large scale because these technologies require high initial operating investment and maintenance. Therefore, there is a need to focus on cost effective and efficient technologies for the treatment of fluoride containing water. Adsorption is one of centre of focus of many researchers now days because of its cost-effectiveness, ease in operation, less chemical consumption, and better efficiency [10].

From the literature study, it is found that number of materials have been used for fluoride adsorption like oxides of Fe-Al [11], Al-impregnated carbon [12], activated charcoal, Mn-Ce oxide [13], composites of biopolymer [14], agricultural waste [15], algal biomass, leaf biomass, biochar [16]. Activated and modified carbon is well known adsorbent for removal of pollutants from the water and wastewater due to its large surface area, good porosity, stable chemical characters [17]. Impregnation of Fe(III) with activated carbon enhances the adsorption ability ion aqueous solutions. The Fe(III) containing material bound with carbonyl groups, amine, carboxylic and hydroxyl groups through complexation reaction [18]. The different adsorbents having their adsorption capacity were reported for fluoride adsorption such as Cerium impregnated activated carbon (4.6 mg/g) [1], activated carbon (6.5 mg/g) [19], Zirconium doped activated carbon (5 mg/g) at 4 pH [20], SnO₂ doped activated carbon (4.6 mg/g) [21] and CaCl₂ modified activated carbon (2.1 mg/g) [22].

In this study, authors attempt to prepare iron based activated carbon from the kitchen waste pea (pea peel) for the removal of fluoride by batch as well as column process that is the novelty of this research work.

2. Materials and Methods

2.1. Chemicals and Reagents

In this study magnetic adsorbent was prepared from the peel of pea (*Pisum sativum*) collected from the local vegetable market and grains separated from peel. The analytical grade chemicals and reagents were used in present study (sodium fluoride, solution of Ionic strength adjuster (ISA) solution, hydrochloric acid (HCl), ferric chloride (FeCl₃), sodium hydroxide (NaOH),) were acquired from sigma Aldrich and thermo fisher scientific.

2.2. Synthesis of Activated Carbon

Activated carbon prepared from the pea peel according to the method explained by Lung et al. [23]. The collected pea peel was washed several times to eliminate the dust particles followed by drying at 80°C for 24 h, after that it was ground and sieved in fraction of 0.25 mm mesh. The material was prepared in 1:10 ratio, 1 part is pea peel and 10 part is ferric chloride (FeCl₃) solution, then the mixture was stirrer for 240 mins and kept overnight for the mixing of FeCl₃ with pea peel powder. The excess iron solution was separated by vacuum filtration and the obtained solid material dried for 24 h at 80°C. The material was then filled in the quartz crucible with 100ml capacity and capped with fitted lid then pyrolyzed by using muffle furnace at 500°C temperature for 2 h.

The obtain Activated Carbon was washed number of times with distilled water and then oven dried for 12 h. The dried activated carbon homogenized and used for the removal of Fluoride. In this study synthesized pea peel magnetic activated carbon was termed as PPMAC-500.

2.3. Characterization of the Bioadsorbent

SEM (Scanning electron microscope), (JSM-6490 LV, JEOL, JAPAN) equipped with EDS used to determine surface analysis of the synthesized adsorbent (PPMAC-500). Surface functional group of the adsorbent observed by using Fourier- transform-infrared-spectroscopy (FTIR), (NICOLET 6700, Thermo Fisher Scientific, USA). X-Ray diffractometer (PW 3040/60 Pan Analytical Nether Land) was used for the analysis of crystalline structure of the activated carbon. The activated carbon scanned in the range 10° to 90° with 2° min⁻¹ speed rate. Zeta nano-sizer (model no-Nano-ZS90, Malvern Instrument) used for observation of stability and particles size distribution by after dissolving activated carbon in ethanol. Point zero charge on the surface of adsorbent was also analysed.

2.4. Experimental Batch Adsorption Design

All batch experiment performed by adding of decided MPPAC-500 doses (1 to 4 g/L) having 50 mL solution of fluoride with varying concentration (5 to 20 mg/L) in a 250 mL of Erlenmeyer flask. The flasks were shaken at constant speed (100 rpm) in an orbital shaker at ambient temperature. After adsorption, samples were collected at regular interval differences and then filtered, residual concentration of fluoride analysed by using fluorimeter (EUTECH ION 6+ THERMO SCIENTIFIC, U.S.A. Whole batch experiment was done at ambient temperature except (from temperature values 25°C to 55°C and pH study conducted with different pH (2 to 10 pH). A pH of the fluoride solution was maintained by 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solution. All batch adsorption studies were conducted in triplicates to minimize the error of the data. The removal percentage (Re) and adsorption capacity (q_e) of fluoride were determined by Eq. (1) and (2), respectively.

$$Re = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

$$Q_e = \left(\frac{C_o - C_e}{w} \right) \times V \quad (2)$$

Where, C_o; Initial concentration, C_e; final concentration, w; adsorbent mass, V; solution volume.

2.5. Experimental Column Design and Procedure

The continuous column adsorption performed for the removal of on MPPAC-500 borosilicate glass column at room temperature and neutral pH. Vertical glass column was used for fixed bed column study with 1.5 cm diameter and 38.3 cm length is shown in Fig. 1. Column were performed in downflow mode. Two different quantities of MPPAC-500 were packed at 5 cm and 10 cm bed height with used doses 4.8 g for 5 cm and 9.6 g for 10 cm bed depth.

Fig. 1. Experimental fixed bed column setup.

The MPPAC-500 was packed by the 1cm layer of glass wool and sieved with pore size 0.5 mm were placed at both side (up and down) of the column, which are used for the uniform flow. solution having 10 mg/L concentration was passed out from reservoir knob with 5 mL/min and 10 mL/min flow rate. The treated samples (5 mL) were collected at regular time interval. The main focus of column adsorption study to determined, how much volume of the effluent can treat at a time.

2.5.1. Column data analysis

2.5.1.1. Breakthrough curve

Breakthrough curve is used to check adsorption performance of the fixed-bed-column. The breakthrough point was taken until the outlet fluoride concentration reaches 99.5% of inlet fluoride concentration. The breakthrough curve was expressed by plotting C_{in}/C_{out} against contact time [24]. Where C_{in} is the starting fluoride concentration and C_{out} is the final fluoride concentration, respectively.

Total outlet volume, V_{eff} can be determined by the following Eq. (3).

$$V_{eff} = Q \times t_{total} \quad (3)$$

Where Q (mL/min); flow rate in volume, t_{total} ; total flow time (min).

Total adsorbed amount of fluoride concentration, q_{total} (mg) can be observed from the Eq. (4).

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (4)$$

Adsorption capacity denotes by q_e (mg/g) can be found by the formula as given below.

$$q_e = \frac{q_{total}}{m} \quad (5)$$

where m denotes dry amount of the adsorbent (g) filled in a column.

Total fluoride ions (M_{total}) delivered to the column is calculated

from Eq. (6).

$$M_{total} = C_o \times Q \times t_{total} \quad (6)$$

Total removal percentage of fluoride ions can be calculated from Eq. (7).

$$\text{Total fluoride removal \%} = \frac{m_{ad}}{m_{total}} \times 100 \quad (7)$$

Where m_{ad} is the dry amount of adsorbent sent to the column.

3. Results and Discussion

3.1. Characterization of MPPAC-500

3.1.1. SEM and EDX

The SEM and EDS analysis were conducted for morphological investigation of prepared adsorbent. Image shows that surface of iron modified biochar is rough and partially porous in nature as presented in Fig. 2(a). Surface roughness and porosity of adsorbent may determine the maximum adsorption sites that facilitate high adsorption of fluoride. After adsorption of fluoride the structure of adsorbent particle altered that is shown Fig. 2(b). The EDS analysis revealed that C, O, Cl, and Fe are present in adsorbent in different proportion as shown in Fig. 5(c) and (d).

3.1.2. FTIR

The FTIR spectra of MPPAC-500 before and after uptake of fluoride, are shown in Fig. 2(c). The spectra of materials were observed from scanning of wavenumber ranged from 400-4,000 cm^{-1} . The strong band observed 3,013.7 cm^{-1} in MPPAC-500 before fluoride adsorption and 3,046.8 cm^{-1} in MPPAC-5000 after adsorption represent the $-\text{CH}$ stretching vibration due to presence of methyl group. The peak ranged between 1,513.1 to 1,578.7 cm^{-1} are due to $\text{C}=\text{C}$ aromatic group [25]. The adsorption bands observed at 1,408.1 to 1,238.9 cm^{-1} could be assigned to $-\text{OH}$ (hydroxyl) group vibration mode. The shifting of wavenumber from 1,108.7-1,059.9 cm^{-1} represent the $>\text{C}=\text{O}$ (ketone) group functioning during adsorption of fluoride. The adsorption band between 400 cm^{-1} to 500 cm^{-1} attributed to the Fe-O vibrations. The presence of Fe-O shows that the iron was present on the synthetic adsorbent [26].

3.1.3. XRD

The XRD pattern of MPPAC-500 before adsorption is shown in Fig. 2(d). The XRD pattern observed in the 2θ range of 5-80°. The fine and sharp peaks of MPPAC-500 were found at 2θ range of 20-40°. Fig. 2(d) illustrates the XRD diffractogram pattern of iron coated adsorbent (MPPAC-500). The major and sharp peaks 23.58°, 31.04° and 35.7°, 40.48°, 49.06° and 53.72° are resembling the presence of Fe_3O_4 [27, 23]. Similar peaks i.e. 30.2°, 35.5° and 53.6° were reported for Fe_3O_4 [28]. A significant hump in the range of 20°-40° is depicted a crystalline graphitic structure [29].

3.1.4. Zeta Potential

Zeta potential of MPPAC-500 was studied at different pH (2- 10) by using the (Zeta Nano Zs90, Malvern Instrument). The value

Fig. 2. SEM and EDS of MPPAC500 (a) before and (b) after adsorption, (c) FTIR spectra of MPPAC500, (d) XRD analysis, (e) Zeta Potential and (f) Particle Size Analysis of MPPAC500.

of Zeta potential indicates the stability or instability of the material in dispersed medium [30]. Zeta potential was found to be +56 mV at pH-4 that is shown in Fig. 2(e). This value indicates that adsorbent is highly stable in acidic pH while at higher pH, Zeta potential value was observed + 10 mV. Therefore, it is clear that the adsorbent MPPAC-500 is stable for the application of fluoride.

3.1.5. PSA

Particle size distribution of adsorbent is measured by several techniques such as based on light, ultrasound, electric field and centrifugation. In this study we have used the light-based measurement particle size distribution (Zeta Nano ZS90, Malvern). Fig. 2(f) shows the average particle size range ~0.11 to 0.30 μm , for

first peak 20% particle in range $\sim 0.11 \mu\text{m}$ and second peak 80 % of particles in $\sim 0.30 \mu\text{m}$. Adsorbent MPPAC-500 has small average particle size distribution its mean synthesized adsorbent has high surface area that facilitate highest adsorption of adsorbate.

3.1.6. pH_{ZPC}

The pH_{ZPC} value of synthesized MPPAC-500 was measured according to a described method by Singh et al. [31]. pH_{ZPC} value was used to determine the surface charge of the adsorbent. Fig. S1 shows that pH_{ZPC} of MPPAC-500 was found to be 2.8 and this pH_{ZPC} value indicates that surface of adsorbent is dominated with cationic groups. It means the adsorbent is acidic in nature. When pH of the solution does below the pH_{ZPC} , surface of the adsorbent contains positive charge while above the pH_{ZPC} it contains negative charge.

3.2. Batch Study

3.2.1. Effect of adsorbent dose

Quantity of adsorbent plays crucial role in adsorption process. As given in Fig. 3(a) four varying doses 1, 2, 3, 4 g/L of MPPAC-500 were selected for the dose study for the removal of fluoride ions, while other parameters like starting concentration-10 mg/L, contact time- 470 min, at neutral pH in an ambient temperature were maintained. It was observed that with increasing the dosage of the adsorbent from 1 g/L to 4 g/L, the removal of fluoride increased from 78% to 99.5%. The highest adsorption capacity was achieved to be 2.48 mg/g, so that adsorbent dose 4 g/L was selected for the further study. The results revealed that percentage removal of fluoride was increased with increasing the amount of adsorbent because of more active sites are available on MPPAC-500 for the removal of fluoride ions.

3.2.2. Effect of pH

The pH of solution is the very crucial factor for adsorption process. In adsorption process, ionization potential, adsorbate speciation

and surface charge of adsorbent are strongly affected by pH of aqueous solution [32]. In present study the adsorption of Fluoride on MPPAC-500 was investigated with varying pH (2.0 to 10), while all other experimental parameters were remained same including dose-4g/L, concentration-10 mg/L, temperature- 25°C. Fig. 3(b) indicates that the maximum adsorption of Fluoride was achieved 100% at pH 2.0 and it slightly decreased with increasing pH of the solution. It was perceived that adsorption of fluoride ions is good in the pH values 2.0 to 7.0. At pH 7 the maximum adsorption efficiency was found to be 96%. The enhancement in adsorption efficiency may be happened due to fluoride ions are negatively charged and get attracted by the positively charged adsorbent. While at pH 10 adsorption efficiency was 90.4%. A slight decline in fluoride adsorption efficiency can be attributed due to OH^- ions enhancement, that form aqua-complexes in alkaline solution [33].

3.2.3. Effect of initial fluoride concentration with contact time on adsorption

The effect of fluoride concentration was assessed with varying the starting concentration, taken from 5 mg/L to 20 mg/L at the neutral pH and at ambient temperature. As shown in Fig. 3(c). It was obtained that adsorption rate was declined from 99% to 87% with enhancing the concentration of fluoride from 5 to 20 mg/L. The highest adsorption capacity was observed to be 4.35 mg/g. Further increasing the initial concentration of fluoride ions, removal percentage was decreased this may occur due to active sites on adsorbent surface were decreases after a saturation point [34].

To evaluate the effect of interaction time between fluoride ions and MPPAC-500, batch experiment was performed at several time intervals. Fig. 5(c) illustrates, the removal of fluoride increase with increasing contact time, after contact time of 300 min, there is no further increment in fluoride adsorption so adsorption equilibrium was achieved at 300 min at which removal rate of fluoride was constant because adsorption of fluoride ions in aqueous solution on the surface of MPPAC-500 is equal to the desorption rate.

Fig. 3. (a) Effect of adsorbent dose, (b) effect of pH on adsorption, (c) effect of initial concentration of fluoride, (d) effect of temperature on adsorption, (e) Plot of Freundlich adsorption isotherm for MPPAC500 and (f) Plots of pseudo second order kinetic.

3.2.4. Effect of Temperature

In an adsorption phenomenon temperature is a very important factor, which influence the reaction rate of it. The effect of the temperature was studied at different temperature range (25°C, 35°C, 45°C, and 55°C) for the adsorption of fluoride on MPPAC-500, while all other parameters were kept at optimum conditions such as dose-4 g/L, concentration-10 mg/L, pH-7, temperature- 25°C. As shown in Fig. 3(d) the removal percentage of the adsorbate was increased with increasing temperature, which proves that adsorption process is endothermic. The adsorption of fluoride was slightly increased from 95% to 99% with enhancing temperature from 25°C to 55°C, this happen might be due to various adsorbent required high temperature for activation of vacant sites on adsorbent at high temperature, many vacant sites are present on the surface of adsorbent, that need sometimes high or sometimes low temperature for activation [35].

3.3. Isotherm

An adsorption isotherm was applied to analysed the equilibrium relationship between adsorbate and adsorbent surface. Langmuir, Freundlich, Temkin were widely adapted for validity of adsorption phenomenon. The summarization of isotherm parameters is listed in Table 1.

Table 1. Parameters of Langmuir, Freundlich and Temkin Isotherm for the Fluoride Ions Removal on to AC-500

Langmuir Isotherm	$Q_o(\text{mg/g})$	4.717
	$B(\text{L/mg})$	3.355
	R_L	0.057
	R_2	0.979
Freundlich Isotherm	$K_F (\text{mg/g(L/mg)}^{1/n})$	3.206
	N	3.345
	R^2	0.995
Temkin Isotherm	K_T	29.254
	B	0.715
	R^2	0.945

3.3.1. Langmuir isotherm

Langmuir model illustrate the monolayer adsorption between the adsorbent and adsorbate due to presence of active sites on the surface of adsorbent. Langmuir isotherm presumes that adsorption force and chemical interaction are similar. Langmuir isotherm express by the given Eq. (8).

$$C_e/q_e = \frac{1}{Q_o b} + \left(\frac{1}{Q_o} \right) \quad (8)$$

Where, q_e denotes the quantity of fluoride adsorbed per unit gram of the adsorbent (mg/g) and C_e is the fluoride ion concentration at equilibrium (mg/L). Langmuir constant (Q_o) and highest adsorption capacity of MPPAC-500 and adsorption rate are represented by b . The value Q_o and b can be obtained from plot of C_e/q_e and C_e [36] shown in the supplementary Fig. S2. Table 1 show the

values of Langmuir isotherm parameter. R_L equilibrium parameter known as dimensionless constant that is significant characteristic of the Langmuir isotherm, expressed as following Eq. (9).

$$R_L = \frac{1}{1 + b C_o} \quad (9)$$

Where, C_o and b are stand for the starting fluoride concentration and Langmuir equilibrium constant, respectively. The R_L value express the Langmuir isotherm type could be favourable ($0 < R_L < 10$, ($R_L = 1$) linear, ($R_L > 1$) unfavourable, ($R_L = 0$) irreversible. The value of R_L was found to be 0.057 that is calculated by given Eq. (9).

3.3.2. Freundlich isotherm

This isotherm represents the heterogeneous layer formation on the surface of adsorbent due to adsorption. Freundlich model equation is expressed by the given Eq. (10)

$$\ln q_e = \ln K_F + \left(\frac{1}{n} \right) C_e \ln C_e \quad (10)$$

Where, at equilibrium quantity of fluoride (mg/g) and adsorbate concentration (mg/L) are denoted by q_e and C_e . The n value illustrates the Freundlich isotherm favouring or not favouring, whereas K_F represents the capacity ($\text{mg/g(L/mg)}^{1/n}$) of MPPAC-500 to adsorption fluoride. The heterogenous nature of adsorbent surface and adsorption intensity were calculated through the slope value between 0-1 was observed from the graph plotted $\ln q_e$ against $\ln C_e$. When the slope value is near about 0, indicate that the surface of adsorbent is highly heterogenous. Plotted graph is illustrated in the Fig. 3(e) and obtained values are listed in Table 1.

The Freundlich constant K_F value was 3.206 ($\text{mg/g(L/mg)}^{1/n}$), which shows the biosorption capacity of adsorbent. The value of ' n ' was also lying between 1 to 10 ($n=4.92$) which also favours the favourable adsorption process [37]

3.3.3. Temkin isotherm

This isotherm model gives information about interaction of adsorbent-adsorbate. This model assumes that adsorption heat of whole molecule will not remain same. Interaction between sorbate and sorbent decreases the heat during adsorption process due to uniform dispersal of binding energy [38]. Temkin isotherm represented in the Eq. (11).

$$q_e = B \ln(A_T) + B \ln C_e \quad (11)$$

Where, q_e represents the quantity of fluoride adsorbed on MPPAC-500 (g/L) and C_e is the concentration of fluoride. B_T is constant for Temkin isotherm related to the adsorption heat (L/g). A_T is Temkin isotherm equilibrium binding constant, which is dimensionless. Values of A_T and B presented in Table 1 and supplementary Fig. S3.

After comparing of these isotherm models, it is revealed that Freundlich model fitted well ($R^2 = 0.995$) than Langmuir model ($R^2 = 0.979$). Table 1 shows that Q_o value of MPPAC-500 was 4.717 mg/g which is quite higher than data available in literature, vitex negundo plant carbon 1.150 mg/g [30], treated banana peel 0.395 mg/g and treated coffee husk 0.416 mg/g [39]. The R_L values

Table 2. Values of Intraparticle Diffusion Model and Thermodynamic

Intraparticle diffusion model				Thermodynamic	
C ₀ (mg/L)	K _i (mg/g.min ^{1/2})	C(mg ⁻¹)	R ²	parameters	Temperature (K)
5	0.013	1.004	0.76	ΔG°(KJ/mol)	
10	0.032	1.818	0.71		298
15	0.054	2.415	0.955		308
20	0.104	2.399	0.965		318
					328
				ΔH (J/mol)	90.7889
				ΔS (J/mol K)	313.5209

was ranged between 0-1 (R_i-0.22) indicating the favourable fluoride adsorption onto MPPAC-500 [37].

3.4. Adsorption Kinetics

Adsorption kinetic quantifies the rate of reaction and adsorption mechanism involved in the uptake of fluoride onto MPPAC-500 [40]. Both kinetic models (pseudo-first-order and pseudo-second-order) and their parameters were applied for present experimental data. The rate constant of Fluoride adsorption is analysed from the reaction of Pseudo-first-order (PFO) given by Lagergren (1898) that is expressed by Eq. (12).

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.3030} \right) \cdot t \quad (12)$$

Where, q_e denotes amount of fluoride adsorbed on MPPAC-500 at a point of equilibrium, q_t is the amount of fluoride adsorbed at a time (min). K_1 is the fluoride adsorption constant rate. The K_1 value was obtained from the plot of $\log(q_e - q_t)$ and time (min) was given in supplementary Fig. S4.

The kinetics data of fluoride were also analysed through pseudo-second-order [31] and the equation for pseudo-second-order is given below.

$$t/q_e = 1/(k_2 q_e^2) + (1/q_e)t \quad (13)$$

Where, k_2 is stand for the pseudo-second-order constant (g/(mg min)) and q_e is the fluoride adsorption capacity. There values were found from the plot of t/q_t against t as represented in Fig. 3(f).

After comparing data of both kinetic models, it is confirmed that pseudo-second-order favoured better with adsorption data than pseudo-first-order. Values of both kinetics parameters are given in the supplementary Table S1.

3.5. Intraparticle Diffusion Model

Adsorption is considered as multi-step phenomenon because it includes transportation of solute from aqueous medium to the adsorbent surface and also solute diffusion through pores. Through the Intraparticle model, large amount of adsorbate present in solution are transferred to the adsorbent surface. The equation for Intraparticle diffusion model is expressed in the below.

$$q_t = k_i t^{1/2} + C \quad (14)$$

Where, K_i (mg/g min^{1/2}) represents to the rate constant and C is the constant, which related to thickness of boundary layer. Maximum value of constant indicates the maximum effect of boundary layer. The value of K_i and C can be determined from the m and C of the plot of q_t verses $t^{1/2}$. It was investigated from the Fig. 4(a) and Table 2, at each concentration linear plot of fluoride does not go through the origin, hence the diffusion rate was not only responsible for adsorption of fluoride. That means other mechanism may also affect the fluoride removal on MPPAC-500.

3.6. Thermodynamics

Thermodynamic study describes the role of temperature in adsorption process. Parameters related thermodynamic such as change in entropy (ΔS), change in enthalpy (ΔH) and change in Gibb's free energy (ΔG) for the adsorption of fluoride ions on adsorbent were determine by using following equation.

$$K_c = \frac{q_e}{C_e} \quad (15)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$$

$$\Delta G = \Delta H - T\Delta S \quad (17)$$

Where, K is the thermodynamic distribution coefficient constant, While T and R denote temperature (K) and universal gas constant, respectively in the reaction. C_e and q_e are fluoride ions in aqueous phase (mg/L) and adsorbed quantity of fluoride (mg/g) on MPPAC-500 at equilibrium. The changed entropy and changed enthalpy were obtained through the value of intercept and slope of the plot between $\ln K_c$ and $1/T$ (Fig. 4(b)). From the Table 2, it is evidenced that the reaction was spontaneous in nature due to negative value of Gibb's free energy. The positive value of enthalpy (ΔH) was 90.78 KJ/mol, it also stated that the fluoride uptake onto MPPAC-500 was endothermic in nature.

3.7. Column Experiment

3.7.1. Effect of packed column bed length

The breakthrough curve was obtained at two different bed depth 5 cm and 10 cm at a fixed flow rate 5 mL/min and starting concentration 10 mg/L. The breakthrough curve and other parameter are depicted in Fig. 4(c) and interpreted values of breakthrough param-

Fig. 4. (a) Plot of Intraparticle Diffusion Model, (b) Plot of Thermodynamic, (c) Breakthrough curve for effect of bed height on MPPAC-500, (d) effect of flow rate on MPPAC-500, (e) Thomas model of MPPAC-500 at 5 cm bed height, (f) Thomas model of MPPAC-500 at 10 cm bed height.

Table 3. Values of different fixed bed and Thomas model parameters

Column parameters								Thomas parameters		
C_0 (mg L ⁻¹)	Z (cm)	Q (mL min ⁻¹)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg/g)	V_{eff} (mL)	K _{TH} (mL min ⁻¹ mg ⁻¹)	Q ₀ (mg g ⁻¹)	R ²
10	5	5	360	18	17.9982	3.7497	1800	0.00354	3083.21	0.9588
10	5	10	105	10.5	10.4998	2.1878	1050	0.01168	1931.37	0.951
10	10	5	450	22.5	22.4998	2.3438	2250	0.0033	2327.7	0.9043
10	10	10	195	19.5	19.4998	2.0313	1950	0.0079	1829.38	0.8224

ter are presented in Table 3. When the bed depth was increased from 5cm to 10cm, saturation time from 345 min to 420 min and treated effluent volume from 1,800 mL to 2,250 mL and the breakthrough time from 135 min to 285 min were increased, which due to available adsorption sites of the adsorbent were increased for uptake of fluoride ions.

3.7.2. Effect of flow rate

To evaluate the effect of volumetric flow rate of inlet Fluoride ions on the capacity adsorption and breakthrough curve for MPPAC-500. The operational experiments were implemented at two different flow rates (5 mL/min and 10 mL/min), although experimental parameters were placed on concentration 10 mg/L and 10 cm bed height are constant. Obtained breakthrough curve shown in Fig. 4(d) and other breakthrough curve parameters such as breakthrough time, saturation time were appraised and treated volume was epitomized in Table 3. It is clear from the Fig. 4(d) that increasing the feed fluoride ions flow rate decreases the breakthrough time and exhaustion time, experimental results indicate when the flow rate increased which decreases breakthrough time and saturation time, because at high flow rate adsorbate have not enough time to contact with adsorbent bed in the column. The result show that higher breakthrough time,

saturation time, treated volume was found at lower flow rate because at low flow rate solute has more residence time to pores of the adsorbent.

3.7.3. Thomas model

Thomas model employed to predict column performance and breakthrough curves [41]. The model relied on with Langmuir kinetic of adsorption and desorption process [42, 43]. This model also describes constant separation factor which applied either favourable or unfavourable isotherms [41]. The linear Eq. (18) of Thomas model is given as below.

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{TH} q_e x}{Q} - k_{TH} C_0 t \quad (18)$$

Where, k_{TH} (mL/min.mg) is the rate constant for Thomas; Q (mL/min) is flow rate of the solution; q_e (mg/g) is the adsorption capacity and x (g) is the mass of adsorbent.

Fig. 4(e) shows the linear plot of $\ln[(C_0/C_t)-1]$ vs t . The values obtained from Thomas models were shown in Table 3. It can be stated that as increasing in flow rates from 5-10 mL min⁻¹ at bed height of 5 cm, the values of K_{TH} increased and q_0 decreased shown in Fig. 4(f). The reason of increased values of K_{TH} and decreased

value of q_o is due to the driving force between adsorbate and adsorbent. Similar results were also observed at 10 cm bed height for Fluoride adsorption in the solution [44]. These results revealed that lower the flow rates with higher bed height leads to maximum fluoride uptake on to adsorbent.

3.7.4. Adams-Bohart Model

This model assume that adsorption rate is proportional to the concentration of the adsorbate (fluoride) and residual capacity of the adsorbent. The equation of Adams-Bohart model in linear form is given in Eq. (19).

$$\ln\left(\frac{C_o}{C_t} - 1\right) = k_{AB} N_o \frac{z}{\mu_o} - k_{AB} C_o t \quad (19)$$

Where, N_o is the maximum uptake capacity of the adsorbent per unit volume in the column; k_{AB} is the rate constant for Adams-Bohart and μ_o is the linear flow rate of the influent solution (cm/min).

3.7.5. Yoon-Nelson model

Yoon- Nelson model stipulates the adsorption kinetic of a fixed bed. This model assumes that the rate decrease in the probability of adsorption for particular sorbate molecule is proportional to the probability of sorbate breakthrough and the probability of the sorbate (fluoride) adsorption. The linearized equation is presented as below.

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN} t - K_{YN} \tau \quad (20)$$

Where k_{YN} (1/min) is the rate constant for Yoon-Nelson and τ (min) is taken for 50% adsorbate breakthrough.

3.7.6. Clark model

This model introduced by Clark for fixed bed column adsorption. The mass transfer can be evaluated with the help of Freundlich parameter (n). Clark equation is presented as below.

$$\ln\left[\left(\frac{C_o}{C_t}\right)^{n-1} - 1\right] = \ln A - rt \quad (21)$$

Where, A and r (1/h) is the Clark constant, and n is the parameter of Freundlich. The value of these constant can obtain from the intercept and slope of the graph plotted $\ln[C_o/C_t]^{n-1} - 1$ vs time (min).

The parameters of Adams-Bohart, Yoon-Nelson and Clark models are given in supplementary data (Table S2, S3 and S4, respectively) and plot of these model is shown in Fig. S5, S6 and S7, respectively. Adams-Bohart model revealed that the rate constant increased as the bed depth of adsorbent increases. While, adsorption capacity (N_o) decreased. The rate constant (K_{YN}) of Yoon-Nelson and (time needed for 50% adsorbate breakthrough decreased with increasing flow rate, while increased with increasing adsorbent dose. The Clark parameter (r) increased with increasing flow rate.

4. Possible Fluoride Adsorption Mechanism on MPPAC-500

Adsorption mechanism leads to either physical or chemical adsorption in aqueous systems. Physical adsorption tends on the surface of adsorption due to Van der Waals force. Chemical adsorption occurs between adsorbent and adsorbate due to chemical bonding including ion exchange, complexation and electrostatic interaction that are generally taken place on adsorbent surface [45]. It is evident from Fig. 2(c) FTIR spectra both after and before adsorption, -CH (methyl), -OH (hydroxyl) and $>C=O$ (Ketone) groups are present, Wang et al. [46] reported that these groups play major role in F^- adsorption due to complexation mechanism. The ionic radius of fluoride and hydroxyl having same size, and the bonding affinity of F^- is higher than hydroxyl ion. Therefore, the ion exchange formation takes place by bonding between adsorbent and adsorbate [47]. Hydrogen bonding may occur between -OH group and fluoride ion. Based on EDX spectra (Fig. 2(a)), the presence of iron peak confirms the presence of iron in modified adsorbent and XRD analysis also confirm presence of iron in the MPPAC-500 by several peaks at 23.58° , 32.72° and 35.74° that are characteristic peak for presence of Fe in the form of iron and iron oxide. Reported that iron impart positive charged to the adsorbent that electrically attract the negatively charge fluoride ions. A proposed adsorption mechanism for fluoride on MPPAC500 is shown in Fig. 5.

Fig. 5. Possible adsorption mechanism of fluoride on MPPAC-500.

5. Conclusions

This work explored the applicability of waste pea peel as novel adsorbent for the elimination of fluoride ions from aqueous medium. The pea peel was modified with iron ($FeCl_3$) for enhancing its adsorption efficiency. Surface characterization explored the existence of heterogeneous structure, showing small and large pore, provides exchangeable sites for adsorption. Infrared Spectroscopy results demonstrated the role of hydroxyl, methyl and ketone groups were involved in the removal of fluoride. In batch study, the

maximum fluoride removal 99% was found at 5 mgL⁻¹ initial fluoride concentration at neutral pH, 4 gm/L dose, and 420 min contact time. Adsorption study favoured Freundlich isotherm model. Fluoride uptake was well described with pseudo-second-order kinetic model. Thermodynamic parameters indicated that the adsorption process was followed endothermic and spontaneous in nature. The column study results were fitted well with Adams- Bohart model followed by Thomas model. The maximum removal capacity at column system was found 3.75 mg/g. The present adsorbent shows the efficient adsorptive capacity for uptake of fluoride in batch and column systems, which may suggest for remediation of fluoride from groundwater and contaminated surface water by biomass based biosorbent is highly recommended.

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Author Contributions

Ms. N.S. (Project Assistant), has conducted all the experiments and writing work, Mr. C.B. (Ph.D) has drafted the manuscript and Dr. J.S. (Assistant Professor) has supervised the work and corrected the manuscript.

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