◑ Environmental Systems Research

Fluoride removal from aqueous solution onto activated carbon of *Catha edulis* through the adsorption treatment technology

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Abstract

Background: Nowadays freshwater quality deterioration and quantity depletion are rapidly increasing across the globe. Especially fluoride polluted groundwater is causing a severe shortage of water supply and public health problem. Hence, this study was designed to investigate the performance of activated carbon produced from the *Catha edulis* stem for the removal of fluoride from aqueous solution. A *C. edulis* stem sample was collected from dumping sites of Addis Ababa City and its activation and carbonation processes were performed using H_2SO_4 and a high temperature of 600 °C. The experimental study was designed to use a full factorial approach with a 3^3 which were the three factors with the three levels, namely pH (2, 7 and 9), contact times (60, 90 and 120 min) and adsorbent doses (0.5 g, 1.0 g and 1.5 g in 100 mL) at the initial fluoride concentration 30 mg/L which resulted in 81 experimental runs in triplicates.

Results: The calculated maximum adsorption capacity of 18 mg/g was found under the Langmuir isotherm, whereas the Freundlich model (R^2 0.98) better fitted the experimental data, which indicated that the adsorption process was multilayer and cooperative. The maximum fluoride removal of 73% was observed at the optimum condition of adsorbent dose of 1.5 g in 100 mL contact time of 60 min and pH 2, whereas the predicted value of the fluoride removal of 69% was calculated under the same experimental condition. Fluoride removal was positive and strongly influenced by the adsorbent dose, whereas the adsorption pH was negatively and weakly impacted on removal.

Conclusions: Generally, the performance of activated carbon for the removal of fluoride from aqueous solution is promising. The study also indicated that *C. edulis* activated carbon is a potential candidate for water treatment technology.

Keywords: Adsorbent, Environmental pollution, Experimental design, Freshwater, Pollutant removal, Water treatment

Background

Today, freshwater consumption is increasing rapidly at an unexpected rate due to the fast industrial advancement, world population explosion, mechanized agriculture expansion and progress of civilization (Fito et al. 2017a; Fito and Alemu 2019). Basically, in all nations across the globe, access to safe water and sanitation is recognized as a fundamental human right for all (Fito et al. 2019a). However, environmental crisis, particularly water pollution is a major contributor to water quality deterioration and quantity depletion, which is a global challenge to achieve sustainable development goals. In line with this, about 2.0–2.7 billion people are expected to face severe water shortage challenge by 2050 under current business and water consumption and management practices (UN-Water 2003). Furthermore, an estimated 4.8–5.7 billion people will live in potentially water scarce areas by 2050 (UN-Water 2015). It was also reported that water pollution poses serious concerns about human health and environmental risks in many developing countries, particularly those in sub-Sahara, including Ethiopia (Nienie

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et al. 2017; UN Water 2018; Fito et al. 2019b). Fluoride pollution of drinking water is very common, particularly in areas where groundwater is the only source of water supply (Sailaja et al. 2015).

Fluoride exists in rocks in different minerals such as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) (Mohapatra et al. 2009). High fluoride concentrations above 4 mg/L can cause various human health problems, such as dental fluorosis, skeletal fluorosis, decreased birth rates, lower intelligence quotient, thyroid gland injury and neurological disorders (Amalraj and Pius 2017; WHO 2017; Dehghani et al. 2018). Fluorosis is a very common and endemic disease in more than 25 countries worldwide in both developed and developing regions (Jagtap et al. 2012; Amalraj and Pius 2017; Bhattacharya 2017). Generally, the epidemiological studies show that drinking water contributes about 60% of fluoride ion of the total per capita daily intake (Jagtap et al. 2012). Fluoride concentration > 30 mg/L in groundwater was reported in many countries and regions, including China, India, Sri Lanka, West Africa (Ghana, Ivory Coast, Senegal), North Africa (Libya, Sudan, Tunisia), South Africa, the East African Rift Valley (Kenya, Uganda, Tanzania, Ethiopia and Rwanda), northern Mexico, and Central Argentina (Joshi et al. 2012). The highest fluoride concentration of 33 mg/L in drinking groundwater was reported in the Ethiopian section of the East African Rift Valley (Nigussie et al. 2007). However, in recently published papers, the average fluoride concentration in the range of 5 to 26 mg/L was reported (Mulugeta et al. 2015; Kebede et al. 2016). About 11–14 million people in the Ethiopian rift valley rely on fluoride polluted groundwater (Mulugeta et al. 2015; Kebede et al. 2016).

Fluoride-polluted water treatments have been performed using several purification techniques. The most common fluoride removal methods from drinking water are chemical precipitation, nanofiltration, membrane processes, ion exchange, reverse osmosis, electrocoagulation, and electrodialysis are expensive and thus non-sustainable for developing countries (Fito et al. 2019c). Additionally, these methods require high energy, chemical, operational and capital inputs and advanced technologies. These shortcomings of the various methods of defluoridation prompted researchers to find alternative treatment methods. In comparison with other aforementioned treatment techniques, adsorption of fluoride removal from drinking water is the most appropriate and widely used treatment technique. Flexibility, simplicity of design, relative ease of operation, cost-effectiveness, environmental considerations and production of high water quality are the major advantages of the adsorption treatment technology (Lavecchia et al. 2012; Nure et al. 2017). However, commercially developed activated carbon is a universal adsorbent and very expensive which makes adsorption unsuitable for developing countries.

The development of cost-effective and efficient adsorbent methods is still under investigation. In recent years, the use of inexpensive, easily available adsorbents with high carbon content and low inorganic composition have been used as potential raw material for the preparation of activated carbon. Special attention is given for locally developed adsorbents that are promising raw materials for the removal of contaminants from water and wastewater (Asaithambi et al. 2018). Hence, many studies are focused on adsorbents for fluoride removal from drinking water, such as an alum manufacturing process (Nigussie et al. 2007), alumina in bauxite (Lavecchia et al. 2012), activated alumina (Mulugeta et al. 2015), $CaCl_2$-modified *Crocus sativus* leaves (Dehghani et al. 2018), fired clay pots (Kofa et al. 2017), bark of *Morinda tinctoria* (Amalraj and Pius 2017), bark of the *Vitex negundo* plant (Suneetha et al. 2015), lanthanum-impregnated bauxite (Vardhan and Srimurali 2016), lapsi seed stone (Joshi et al. 2012), Al–Ce hybrid adsorbent (Liu et al. 2010) and iron ore (Kebede et al. 2016). However, researchers are still looking for practical and affordable adsorbents which can be applied at the commercial scale that leads to improving water supply quality in the regions of fluoride-saturated groundwater. Generally, adsorption is considered as an attractive, effective, convenient, easy to apply, simple to design, low cost and environmentally compatible technology (Loganathan et al. 2013).

Khat (*Catha edulis*), a dicotyledonous evergreen shrub of the family *Celastraceae* is a plant cultivated for the sedative effect in its leaves. In Ethiopia, *C. edulis'* stems are disposed of everywhere, especially around the khat market areas, streets and dumpsters. Thus *C. edulis'* stems are a major contributor to the huge amount of solid waste in larger Ethiopian cities. The use of *C. edulis* stems as a potential source of activated carbon was explored in this study. Employing this byproduct as an adsorbent for removal of fluoride from the water supply may thus be an environmentally friendly and practical waste conversion method (Fito et al. 2017b). However, very few studies have been conducted so far on the preparation of the activated carbon from *C. edulis*. Therefore, this study was designed to investigate the performance of activated carbon produced from *C. edulis* stems for the removal of fluoride from aqueous solution. Additionally, the experimental study was designed to use full factorial approach with a 3^3, which were the three levels of the three independent variables, namely: pH (2, 7 and 9), contact time (60, 90 and 120 min) and adsorbent doses (0.5 g, 1.0 g and 1.5 g in 100 mL). There are many advantages of such factorial experimental designs, some of which require low cost, minimum numbers of experiments, reduced

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treatment time and the possibility to investigate the main and interaction effects separately (Nure et al. 2017).

Materials and methods

Adsorbent development

Catha edulis stem samples were collected from dumping sites of the large Addis Ababa Merkato market, which is locally called "Khat terra". The sample was washed with distilled water and dried in an oven at 100 °C until completely dried. The stems were cut into pieces at the size of 10 mm. Carbonation and activation of *C. edulis* stem were performed using different activating agents, such as KOH, H_2SO_4 and H_3PO_4 at temperatures of 500 and 600 °C. Based on the prescreening, the activated carbon developed using H_2SO_4 at 600 °C was selected because it has a better fixed carbon composition and higher surface areas compared to the others. The procedure of the selected activating agent was started by soaking sample chips in concentrated H_2SO_4 for 24 h in order to achieve good carbon structure and a large surface area. The soaked sample was washed with distilled water and completely dried at 110 °C in an oven for 3 h. Then, the pyrolysis of the sample was operated at a temperature of 600 °C for 60 min in a muffle furnace (Ali et al. 2012). The activated carbon was washed thoroughly with 3 N HCl and heated to 50 °C to solubilize the mineral. Additionally, the activated carbon was washed with 1% $NaHCO_3$ to remove residual acid, and further washing was done

using deionized water until pH 7 of the activated carbon was achieved, which dried in an oven at 105 °C for 12 h (Shivayogimath et al. 2008). Finally, the activated carbon was passed through a 0.5 mm sieve and sealed in a polyethylene bag which was stored for further characterization and uses as indicated in Fig. 1 (Gupta and Suhas 2009).

Adsorbent characterization

Proximate analysis

In the determination of the proximate analysis of the *C. edulis* activated carbon (CAC), the moisture content, volatile matter, ash content and fixed carbon of the adsorbent were measured. The thermal drying method was applied for the proximate analysis of the adsorbent. The adsorbent sample of 1.0 g was weighed in triplicate and placed in a clean, dried, and weighed crucible in a preheated oven at 110 °C. The crucibles with samples were placed in an oven at 110 °C for 2 h. Then, the sample was cooled in desiccators at ambient temperature and its weight was measured again. Hence, the difference between the initial and the final mass of the CAC was used to determine the moisture content using Eq. 1.

$$Mc = \frac{W_w - W_d}{W_w} \times 100\% \tag{1}$$

where Mc is the moisture content of the CAC in percentage, Ww is the weight of the sample and Wd is the weight

Fig. 1 Different stages of the activated carbon production

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of the sample after drying (Milne et al. 1990; Anisuzzaman et al. 2015)

Similarly, for the determination of the ash content of the CAC, 1.0 g of CAC sample was put into a crucible and heated at 500 °C in a muffle furnace for 4 h and allowed to cool in a desiccator to room temperature. Finally, the CAC sample was weighed and the percentage of the ash content of the CAC was calculated using Eq. 2 (Anisuzzaman et al. 2015).

$$AC = \frac{W_1}{W_2} \times 100\% \tag{2}$$

where AC is the ash content in percentage, W_2 is the weight of the CAC sample and W_1 is the weight of the ash. For the determination of the volatile matter of the CAC, 1.0 g of the CAC sample was taken and placed in a pre-dried crucible and heated in a muffle furnace regulated at 800 °C for 8 min. Then, the crucible was cooled in desiccators and weighed (Aragaw 2016). Finally, the volatile matter of the CAC was calculated using Eq. 3.

$$Vm = \frac{W_2 - W_1}{W_2} \times 100\% \tag{3}$$

where Vm is the volatile matter in percentage, W_2 is the weight of the CAC sample and W_1 is the weight of CAC after heating. Fixed carbon content was determined by deducting the moisture, volatile, and ash content percentage using the Eq. 4 (Nwabanne and Igbokwe 2012).

$$\text{Fixed Carbon Content (\%)} = 100\% - (MC\% + VC\% + Ash\%) \tag{4}$$

where the MC% is moisture content in percent, VC% is volatile content in percent, Ash% is the ash content in percentage (Nure et al. 2017)

Determination of pH

A 1.0 g of CAC was added to 100 mL of distilled water in a beaker of 500 mL volume in order to determine the pH value of CAC adsorbent. Then, the beaker was covered with a watch glass and boiled on the hot plate for 5 min and set aside for a few minutes to settle the bulk of CAC particles. The supernatant liquid was poured off and cooled to the room temperature at a 25 °C. Finally, the pH value of the solution was measured by using a pH meter (Hach HQD Field Case Model 58258-00) (Dada et al. 2012)

Bulk density

The mass to volume ratio of CAC adsorbent was used to determine the bulk density. A measuring cylinder of a volume of 10 cm³ was weighted without and with the adsorbent sample. The difference between the initial weight of the container and the final weight was calculated. This mass difference was taken as the mass of the CAC adsorbent. Then, the bulk density was calculated from the relationship of mass to volume and determined using Eq. 5,

$$\text{Bulk Density}\left(kg/m^3\right) = \frac{M}{V} \tag{5}$$

where M is the mass of a sample (kg), whereas the V is the volume of the adsorbent sample (m³) (Dada et al. 2012)

Fourier transform infrared spectroscopy

CAC was characterized using Fourier transform infrared spectroscopy (FTIR). The CAC adsorbent was mixed with dry KBr in the ratio of 2:200 in mg and ground very well. The adsorbent sample was scanned over a wavelength of 400–4000 cm^{-1} using FTIR spectrophotometry (65 FT-IR PerkinElmer) (Dolphen and Thiravetyan 2011). This was designed to determine the availability of the functional groups on the surface of CAC.

Optimization of batch adsorption

In order to prepare a fluoride solution of 1000 mg/L, 2.21 g of NaF, salt was dissolved in 1 L of deionized water and the standard solution (30 mg/L) was prepared by diluting the stock solution with deionized water. The adsorption batch experiment was carried out using 100 mL of adsorbate solution into 250 mL conical flasks. This adsorption process was investigated using initial fluoride concentration 30 mg/L based on the maximum fluoride concentration in many places in Ethiopia, particularly in the Rift Valley. The fixed values of independent values were pH (2, 7 and 9), contact times (60, 90 and 120 min) and CAC doses (0.5 g, 1.0 g and 1.5 g in 100 mL) were selected (Tezcan et al. 2015). The design of this experiment was a 3³ full factorial design with 81 runs with triplicates at room temperature (Table 1). The pH of the solutions was adjusted using 0.1 N of HNO₃ and NaOH solutions. The flasks were agitated at 120 rpm

Table 1 Factors and their levels for removal of fluoride using full factorial design

Factors	Code	Minimum level	Intermediate level	Maximum level
Dosage (g/100 mL)	X_1	0.5	1	1.5
pH	X_2	2	7	9
Contact time (min.)	X_3	60	90	120

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using magnetic stirrers on an orbital shaker for specified contact times labeled. Then, the solution was left to settle for 2 min and the finer particles were removed using Whitman filter paper 42 (Hegazy et al. 2014; Nure et al. 2017). The filtrate sample was used for the analysis of fluoride removal. Finally, the reading of the electrode was made after the value stabilized for 15 min.

Adsorption equilibrium isotherms

The adsorption isotherm was determined by using adsorbent doses of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g which were added in 100 mL of the fluoride solution (30 mg/L) at constant values of pH 2 and contact time of 60 min. Equilibrium adsorption capacity (q_e, mg/g) is the ratio of the adsorbate per amount of the adsorbent at the equilibrium concentration (C_e), keeping the operational temperature constant (room temperature). This adsorption equilibrium is checked using the two commonly used Freundlich and Langmuir isotherm models (Nure et al. 2017). The amount of the adsorptive capacity was calculated using Eq. 6.

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V \tag{6}$$

General Langmuir isotherm equation was indicated in Eq. 7.

$$q_e = \frac{Q_O C_e b}{1 + C_e b} \tag{7}$$

where *Ce* equilibrium is the concentration (mg/L), Q_o maximum adsorption capacity (mg/g), q_e absorptivity capacity (mg/g), and *b* Langmuir isotherm constant (L/mg) (Tezcan et al. 2015).

The Freundlich isothermal model is expressed in Eq. (8).

$$q = K_f Ce^{1/n} \tag{8}$$

where the q (mg/g) is the adsorbed amount of the adsorbate per unit mass of the adsorbent, Ce (mg/L) is the equilibrium concentration in mg/L, K_f ((mg/g) (L/mg) 1/n) and 1/n are the Freundlich constants which represent adsorption capacity and adsorption intensity, respectively (Nure et al. 2017).

Statistical analysis

One-way analysis of variance (ANOVA) was used for means comparison of fluoride removal at the 95% confidence level. The removal of the fluoride through the treatment of the adsorption was also further supported by linear regression among the independent variables (pH, contact time and adsorbent dose) and dependent variable (removal efficiency).

Results and discussion

Characterization of activated carbon

The proximate analysis of the CAC with H_2SO_4 was analyzed and the results obtained were displayed in Table 2. Basically, the intention of the experiment was to determine the composition of fixed carbon and ash content. The high composition of the fixed carbon refers to the quality of the adsorbent which improves the surface area and adsorption performance. A very low value of the CAC moisture content of 4% was recorded, which is an indicator of its good quality. The volatile matter of the adsorbent was 25%, whereas the ash content was only 18%, which proved that the inorganic content was insignificant. In other studies of activated carbon derived from holm oak, high percentage of ash content of 70.6% was reported, which was much higher than that of activated carbon produced from *C. edulis* (Tezcan et al. 2015). The high content of ash can be explained as low quality of the raw material behavior for adsorbent preparation. This happened because the large amount of ash content is not favorable for activated carbon development and resulted in low carbon content, which in turn can lower the adsorption capacity and efficiency. Hence, adsorbent development with low ash content is one of the critical concerns of scientists and researchers working on water and wastewater purification processes through adsorption treatment technology.

Another most important parameter was fixed carbon, which was 53%, a significant amount for local prepared activated carbon. In another study of locally developed activated carbon, a moisture content of 4.0%, ash 36.0%, fixed carbon 42.2% and volatile substances of 16.8% were reported, which is in good agreement with the current study (Nure et al. 2017). Generally, the prepared activated carbon was a more carbonaceous material and a good precursor for adsorbent development, which contributed to water and wastewater purification at the industrial level.

The bulk density of CAC developed using H_2SO_4 and high temperature of 600 °C at the specific particle size of nearly 0.5 mm was determined. On average, a bulk density of 0.46 g/cm^3 was obtained. This value was found in the acceptable range of the carbonaceous materials

Table 2 Proximate analyses of CAC adsorbent after treatment with sulfuric acid

Proximate analysis	Mass in %
Moisture	4.0
Volatile matter	25.0
Ash content	18.0
Fixed carbon[a]	53.0

[a] The result was calculated by difference

Table 3 FTIR analyses, AC peak observed and corresponding functional groups

SN	Wave length in cm^{-1}	Peaks nature of AC		Functional groups
		Before	After treatment	
1	3300–3600	Small sharp peak	Diminished small sharp peak	Presence of O–H
2	2944	Small sharp peak	Small sharp peak	Stretching C–H
3	1500–1600	Long and broad peak	Diminished small peak	Carboxylate bond
4	1425	Small peak	Very small peak	C–C stretched (aromatic)
5	800	Sharp peak	No peak	C=CH stretched

of 0.35 to 1.2 g/m^3 as reported by many studies (Sunday et al. 2018). Normally, high bulk density is considered to be a good quality of the adsorbent materials. Hence, the CAC showed good material characteristics in terms of the bulk density value found in the recommendable range of the ideal adsorbent. Finally, the pH value of CAC that activated by sulfuric acid was found to be nearly neutral.

In an FTIR analysis of the *C. edulis*, three major peaks were observed and shown in Table 3. The first peak was found in the range of the wavelength 3300–3600 cm^{-1} indicates the presence of the hydroxyl functional group which could be associated to the organic acid, alcohol, or phenol functional group. The second group was found in the range of the 1500–1600 cm^{-1} wavelength related to the stretching of the carboxylate bond. These two broad and long peaks observed on the surface of the adsorbent were probably associated with the chemical activation process of the adsorbent. This particular surface modification might be attributed to hydrogen ion released from sulfuric acid and could be resulted in the development of the hydroxide functional group on the surface of the adsorbent. The last weak peak was found at the wavelength of 1425 cm^{-1} which was most likely associated with the functional group of the C–C stretching of the aromatic compound.

Fluoride removal analyses

The results of the fluoride removal from aqueous solution using experimental design of the factorial matrix and the corresponding predicted values are shown in Table 4 The adsorption efficiency was increased by 16% as the adsorbent dose shifted from low value (0.5 g) to a high value (1.5 g in 100 mL), but the efficiency was decreased by the same value as the pH of the solution shifted from 2 to 9, keeping other factors constant. However, the effect of raising the contact time from 60 to 120 min on the adsorption performance was insignificant. This indicated that the adsorption equilibrium was achieved at the lower contact time of the adsorption process. The overall effect of the independent factors on adsorption performance was investigated using the full factorial approach. The results obtained were considered both the main and

Table 4 Full factorial experimental matrix for fluoride removal displayed in percentage

Experiment #	Dose (mg/100 L)	pH	Time	Actual %	Predicted %
1	0.5	2	60	56.7	60.0
2	1	2	60	68.0	63.4
3	1.5	2	60	73.0	66.8
4	0.5	7	60	45.3	48.8
5	1	7	60	50.0	52.3
6	1.5	7	60	51.7	55.7
7	0.5	9	60	40.7	42.6
8	1	9	60	49.3	46.1
9	1.5	9	60	49.7	49.5
10	0.5	2	90	61.7	58.5
11	1	2	90	65.0	61.9
12	1.5	2	90	66.7	65.4
13	0.5	7	90	46.7	47.3
14	1	7	90	46.0	50.8
15	1.5	7	90	49.7	54.2
16	0.5	9	90	46.3	41.2
17	1	9	90	43.3	44.6
18	1.5	9	90	49.0	48.0
19	0.5	2	120	57.0	57.0
20	1	2	120	64.0	60.5
21	1.5	2	120	63.0	63.9
22	0.5	7	120	43.7	45.6
23	1	7	120	47.0	49.3
24	1.5	7	120	50.0	52.7
25	0.5	9	120	40.3	39.7
26	1	9	120	45.7	43.1
27	1.5	9	120	49.7	46.5

interaction effects, which represented the reality. Based on this fact, the maximum fluoride removal of 73% was observed at the optimum condition of adsorbent dose of 1.5 g in 100 mL, contact time of 60 min and pH 2 at the fixed and initial fluoride concentration operated at room temperature; the predicted value of 69% was calculated under the same experimental condition. Through all the

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adsorption experiments, the minimum adsorption of 40.7% was recorded at an adsorbent dose of 0.5 g, contact time 60 min and the pH of the adsorption solution was 9. In other studies, fluoride removal in the range of 50–99% at an initial fluoride concentration of 1–12 mg/L with the help of the barks of Vitex negundo activated carbon (Suneetha et al. 2015); 76% fluoride removal at an initial concentration of 25 mg/L using lapsi seed stone activated carbon (Sahira et al. 2013); adsorption capacity of 26 mg/g through the application of the bark of Morinda tinctoria as an adsorbent (Amalraj and Pius 2017); fluoride removal of 85% at initial solution 6.5 mg/L with the crocus sativus leaves adsorbent (Dehghani et al. 2018); and fluoride removal efficiency of 81% at an initial concentration of 1–5 mg/L with the modified sludge adsorbent (Li et al. 2018) were reported.

The main and interaction effects on adsorption

In this regression analysis, terms of the higher interaction effects such as three and four ways had no significant impact on adsorption performance. These terms were excluded from the regression analyses and from the model equation. The impacts of the main and two way interaction on the adsorption were investigated at 95% confidence level (Table 5). Basically, there are two important concepts in linear regression models, namely: the regression coefficient of determination (R^2), which is used to describe the degree of the variability explained by the regression model, and the *p* value which helps to check whether the main and interaction effects are statistically significant in the performance of adsorption.

Based on this principle, there were only two main effects, which were used to determine the influence on the adsorption treatment. Accordingly, only coefficient b_1 and b_2 were statically significant in this adsorption process and incorporated in the model Eq. (9). The R^2 value of the fluoride removal from aqueous solution was 92%, which was considered as 92% of fluoride removal was well explained by the liner regression model. This was a good indicator for the regression model goodness of fit. These statistically significant terms and their values were incorporated in the regression Eq. (9).

$$Y_{flouride} = 64.70 + 12.21X_1 - 3.4X_2 \qquad (9)$$

where $Y_{fluoride}$ was the predicted value of the fluoride removal in percentage; X_1 was adsorbent dose and X_2 was pH of the solution; the other main and interaction effects were not significant and removed from this equation. The regression coefficient of adsorbent dose was positive and enhanced the adsorption performance but increasing the pH value of the solution suppressed the adsorption performance as depicted by the negative coefficient in the model equation. The degree of impact on the adsorption process was $X_1 \gg X_2$, which basically depended on the magnitudes and the signs of the coefficients in the model equation. Generally, the adsorption performance was highly and positively influenced by the adsorbent dose but weakly and negatively influenced by the pH of the solution. Finally, the one-way ANOVA test showed that there were statistically significant differences among mean fluoride concentrations of the adsorption effluent after the treatment.

Table 5 The application of regression and ANOVA tests for fluoride removal

Variables	Coefficients symbol	Coefficients	Standard error	t Stat	p-value
Intercept	b0	64.70	7.32	8.83	3.73E−08
X1	b1	12.21	5.40	2.26	0.036
X2	b2	− 3.37	0.75	− 4.49	0.000
X3	b3	− 0.05	0.08	− 0.56	0.580
X1X2	b4	− 0.03	0.20	− 0.13	0.897
X1X3	b5	− 0.04	0.07	− 0.67	0.513
X2X3	b6	0.01	0.01	1.02	0.319
X1X2X3	b7	− 0.02	0.01	− 0.38	0.711
Regression statistics	**Multiple R**	**R square**	**Adjusted R square**	**Standard error**	**Observations**
	0.96	0.92	0.89	2.99	27
ANOVA	**df**	**SS**	**MS**	**F**	**Significance F**
Regression	7	1965.85	280.84	31.49	3.71E−09
Residual	19	169.43	8.92		
Total	26	2135.28			

Adsorption isotherms

The adsorption isotherm data were collected from adsorption capacity (q_e) and the equilibrium concentration of the fluoride (C_e). But the adsorption isotherms were investigated using the most commonly used adsorption models, namely Langmuir and Freundlich isotherms. The linearized form of the Langmuir Eq. 10 was used.

$$\frac{1}{q_e} = \frac{1}{Q_O} + \frac{1}{Q_O b C_e} \qquad (10)$$

Langmuir adsorption isotherm is based on the assumption that the adsorbent surface sites are capable of adsorbing one adsorbate at a time so that the layer of the adsorbent would have a mono layer thickness. Once the adsorbate matters occupy the sites, no further adsorption is expected. Langmuir isotherm was determined by plotting ($1/q_e$) versus ($1/C_e$), as indicated in Fig. 2. Based on this plot, the maximum adsorption capacity (Q_o) and Langmuir isotherm constant (b) were calculated from the intercept and slope of the Langmuir equation, respectively.

Langmuir isothermal adsorption constant (b) was found to be 0.05 L/mg and related to the free energy of adsorption, whereas the maximum adsorption capacity (Q_o) was 18 mg/g. Even though the highest value of the R^2 (0.96) indicated a satisfactory fit of the Langmuir isotherm with the experimental data, the maximum adsorption capacity deviated much from the observed data (33 mg/g). Therefore, the model couldn't well describe the mechanism of the adsorption process under the study condition. Based on the outcome of the Langmuir isotherm, it is difficult to make a decision on the prediction and improvement of the adsorbing surface chemistry. Therefore, the assumption of mono layer mechanism of the adsorption process has not well defined the phenomena, indicating the need to check it using other assumptions. However, the dimensionless constant parameter called separation constant (R_L) of the Langmuir adsorption process was also checked. The effect of the adsorption isothermal shape was determined by the value of the R_L to identify whether the adsorption system was favorable or unfavorable. Basically, this value can be calculated using Eq. 11,
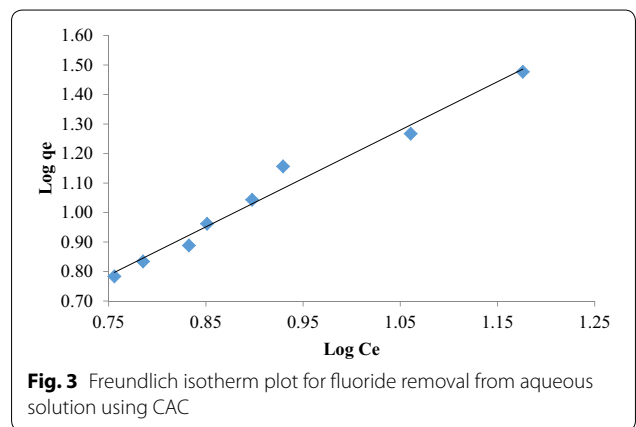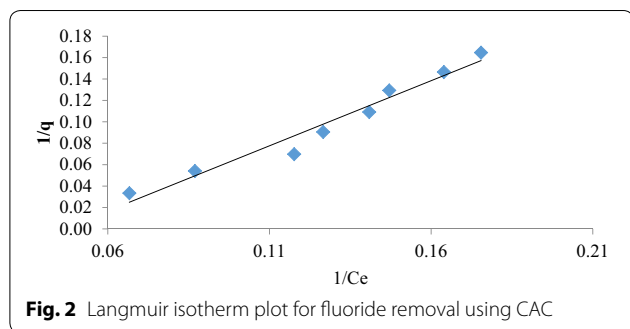
$$R_L = \frac{1}{1 + bC_o} \qquad (11)$$

where R_L is a dimensionless separation factor, C_O the initial fluoride concentration (mg/L) and b the Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm, which reflects when $R_L > 1$ (unfavorable); $R_L = 1$ (linear); $0 < R_L < 1$ (favorable) and when $R_L = 0$ is irreversible. Based on the above equation, the calculated value of R_L was 0.4. This value suggested that the adsorption process was categorized under the favorable adsorption group.

Freundlich isotherm

Similar to the Langmuir isotherm, the experimental data were checked against a linearized form of the Freundlich isotherm Eq. 12. The Freundlich isothermal plot of the linear equation is shown in Fig. 3. The adsorption isotherm is described by the relationship between the bulk aqueous concentration of fluoride and the adsorbed value on the surface of the adsorbent.

$$log q = log K_f + \frac{1}{n} \log Ce \qquad (12)$$

Freundlich isotherm is based on the assumption of heterogeneous surface composing of the different sites for adsorption. It doesn't forecast the adsorbent saturation level of the adsorbate which implies that the multilayer of adsorption phenomena is expected under such condition. Freundlich isotherm graph was sketched using log q_e vs log C_e. The values of K_f and n were obtained from the intercept and slope of the linearized form of Freundlich equation, respectively. Specifically, n is the degree of non-linearly between solution concentration and adsorption

Fig. 2 Langmuir isotherm plot for fluoride removal using CAC

Fig. 3 Freundlich isotherm plot for fluoride removal from aqueous solution using CAC

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capacity in addition to its relationship with the favorability of the adsorption process, whereas the K_f ((mg/g) (L/mg)$^{1/n}$) is an indicator of adsorption capacity.

Based on the Freundlich isotherm, Freundlich intensity (n) of 0.61 and the adsorption capacity (K_f) of 0.094 were calculated, which basically depend on the nature of the adsorbate and the temperature of the system. The value of $n = 1$ indicates that the equilibrium distribution between the solid and liquid phase is independent of the concentration, whereas the values of $1/n > 1$ or $1/n < 1$ show cooperative and normal adsorption, respectively (Nure et al. 2017). Moreover, the degree of the surface heterogeneity increases sharply as the value of 1/n decreases (Liu et al. 2015). Specifically, the Freundlich intensity (n) value indicated that the adsorption process was a cooperative, which was reported in several recently published journal articles (Nure et al. 2017). Generally, the Freundlich isotherm depicted that the adsorption process was heterogeneous and had multilayer surfaces, suggesting that the binding sites were not equivalent but with different adsorption layers. From the Freundlich equation, R^2 of 0.98 was found and could be considered as good fitness of the model to describe the adsorption mechanism. But the Langmuir maximum adsorption capacity showed a weak association between the calculated and the observed adsorption capacity, which was also further supported by its low value of R^2 compared to the Freundlich isotherm.

Conclusions

This study investigated the removal fluoride ions from aqueous solution using chemically (sulfuric acid) activated *C. edulis* stems under the batch adsorption mode. Four factors such as the adsorbent dose, contact time and pH of solution were used in factorial experimental design under adsorption study. The maximum fluoride removal of 73% was recorded at the optimum condition of adsorbent dose of 1.5 g in 100 mL, contact time 60 min and pH 2, whereas the model based predicted value of the fluoride removal under the same experimental condition was 69%. Fluoride removal was positive and strongly influenced by the adsorbent dose whereas the adsorption pH was negatively and weakly impacted on the removal. Removal of fluoride was effectively achieved using chemically modified of *C. edulis.* These results showed significant fluoride removal under the specific study condition. Experiment-based maximum adsorptive capacity was found to be 33.3 mg/g, whereas the predicted value under Langmuir isotherm study was 18 mg/g. *Catha edulis* was found to be a good precursor for activated carbon and have a good adsorption capacity. Freundlich isotherm (R^2 0.98) was better fitted to the experimental data, which indicated that the adsorption process was multilayer and cooperative. Generally, the performance of activated carbon for the removal of fluoride from aqueous solution is a promising which would make the CAC a potential nominee to be used in water treatment technology. However, further study of the treatment technology is expected in respect to the adsorbent recovery, adsorption kinetics and thermodynamics.

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