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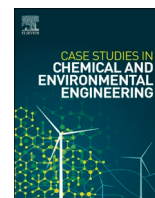
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Case Report

Adsorption of fluoride on a green adsorbent derived from wastepaper: Kinetic, isotherm and characterisation study



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ABSTRACT

The excessive concentration of fluoride (F^-) in water represents a grave problem for several countries, especially those that depend on groundwater as a main source of drinking water. Therefore, many treatment methods, such as chemical precipitation and membrane, were practised to remove F^- from water. However, the traditional methods suffer from many limitations, such as the high cost and the slowness. Hence, many studies have been directed towards developing novel and effective water defluoridation methods. In this context, the current study investigates the development of an eco-friendly adsorbent by extracting Ca, Al, and Fe from industrial by-products, precipitating them on sand particles, and using this new adsorbent to remove F^- from water. The removal experiments were commenced under different pH levels (3-10), contact times (0-240 minutes) and concentrations of F^- (7.5-37.5 mg/L). X-ray fluorescence (XRF), X-ray diffraction Investigator (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) methods were used to characterise the green adsorbent. Adsorption isotherm and kinetic studies were also conducted to define the adsorption type. The results confirmed that the new adsorbent could remove as high as 86% of F^- at pH, contact time, agitation speed and adsorbent dose of 10, 180 minutes, 200 rpm and 15 mg/L, respectively. The characterisation studies prove the occurrence of the sorption process and the suitability of the morphology of the adsorbent for F^- removal. Adsorption kinetics follow better with a pseudo-first-order model that indicates the predominance of physisorption, which agrees with the FTIR results. The isotherm study indicated that Langmuir isotherm is more suitable for representing data with an R^2 value of 0.992, which means the adsorption of F^- occurs as monolayer adsorption on homogeneous sites on the surface of the new adsorbent. In summary, it can be concluded that the developed adsorbent in this study could be a promising alternative to the traditional F^- removal methods.

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1. Introduction

Fluorine is defined as a monovalent member of the halogen family that can be found as Yellowish-green gas at room temperature and normal atmospheric, and it has atomic number 9.0 and a molecular weight of 18.998 g/mol. Fluorine compounds are characterised by an oxidation state of -1 . Fluorine has very high reactivity with a wide range of chemicals in nature because of its high electro-negativity, low dissociation energy, and great bond strength, forming different compounds. Generally, fluorine readily reacts with minerals in geological formations, forming fluoride, which leaches into the ambient environment due to weathering phenomena [1].

Fluoride (F^-) is one of the most common chemicals in nature (13th most plentiful element in nature), which can be found at high concentrations in many geological formations and water bodies, where its average concentration in soils is 611 mg/kg, and up to 0.3 mg/L and 35 mg/L in surface and groundwater, respectively [2]. For example, more than 8.0 mg/L of F^- was recorded in groundwater in some areas of China [3]; similar situations were observed in many other countries, such as India, Tunisia and South Africa [4]. Generally, there are two main sources of F^- in water: natural and anthropogenic. Fluoride-bearing minerals and volcanic sources represent the natural sources of fluoride. In terms of fluoride-bearing minerals, many studies showed that some minerals have high F^- concentrations. For example, fluorapatite and topaz contain 3.80 and 11.5 wt% of F^- , and some rare minerals, such as cryolite, contain higher F^- concentrations (up to 54.0%) [1,5]. Volcanic activities emit considerable amounts of gaseous F^- compounds that interact with the particulates and ashes that precipitate later on soil and surface water, causing high fluoride pollution [6]. Some studies classify seawater as another natural source of F^- because it contains, on average, 1.3 mg/L of F^- [1]. Generally, the natural sources of F^- are not significant compared to the anthropogenic sources because the latter produces huge volumes of F^- containing solutions. For example, Yadav et al. [7] demonstrated that the soils near a phosphatic fertilisers industry contain 90–23,700 mg/kg of F^- , and soils near brick industries contain extractable F^- concentration of 0.69–3.18 mg/kg. The excessive usage of F^- in industries such as bricks, ceramics, steel, fossil fuel and glass industries, along with natural sources, results in significant F-pollution of surface and groundwater in different parts of the world. For instance, the highest recorded concentration of F- in Lake Nakuru (Kenya), Lake Chitu (Ethiopia), and Mangochi district was 2800.0 mg/L, 250.0 mg/L, and 3.64 mg/L, respectively [8].

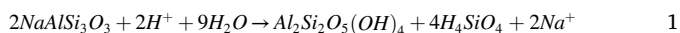
Although the daily intake of F^- is essential for the health of bones and teeth, excessive intake has serious impacts on human health; for instance, recent studies proved that excessive F^- intake leads to dental and skeletal fluorosis and kidney diseases [4,9]. In addition, some studies demonstrated that excessive F^- intake minimises the children's intelligence quotient (IQ) compared to healthy children [10,11]. For instance, Karimzade et al. [12] studied the relationship between the F^- intake and the IQ score of 39 children (aged between 9 and 12 years old) in Azerbaijan; 19 children drink water having 3.94 mg/L of F^- (high intake) and 20 children drink water with F^- concentration of 0.25 mg/L (healthy concentration). The authors found that the children who consume high concentrations of F^- have an IQ score of 81.21 ± 16.17 compared to 104.25 ± 20.73 for children who consume healthy concentrations of F^- . Generally, approximately 200,000,000 people in twenty-five nations are suffering from serious diseases due to the consumption of elevated concentrations of F^- . Therefore, controlling F^- concentration in water and wastewater became one of the top priorities of the water industry and became a hot topic for research. In this context, a wide spectrum of treatment methods has recently been developed and practised to minimise the F^- concentration in water to meet the limitations of the World Health Organization (WHO) (1.5 mg of F^- /L in drinking water) [9]. One of the commonly used methods for F^- removal is coagulation and precipitation (known as the Nalgonda technique) [13]. This method, which was developed for the first time in

India, depends on the addition of alum or lime into the contaminated water to achieve efficient removal of F^- via the coagulation-flocculation-sedimentation process. Although the Nalgonda technique enjoys many advantages, such as the ability to treat large volumes of water, it does not require expensive mechanical and electrical equipment and achieve uniform removal of F^- , it has several serious disadvantages, such as, but not limited to, the production of large quantities of sludge, high consumption of chemicals (alum) and the need for accurate control of pH [14]. Electro-defluoridation is another method that is used to remove F^- from solutions, and it uses metallic electrodes to generate destabilisation agents (such as Al^{3+} ions) through an anodic desolation process. This method has the ability to remove considerable amounts of F^- within a short treatment time; for example, Grich et al. [15] successfully removed 90% of F^- using the electro-defluoridation method. Hashim et al. [9] applied an aluminium-based electrocoagulation unit to remove F^- from water and optimised the effects of the initial pH, treatment time, current density and the distance between electrodes on the removal efficiency. It was found that the aluminium-based unit removed as high as 98% of F^- was removed within 25 min. However, the electro-defluoridation method also has some drawbacks, such as electrode passivation, the need for regular replacements of electrodes and sensitivity for organic matter [9, 16,17]. Reverse Osmosis (RO), a physical method that separates the pollutants using a semi-permeable membrane, has demonstrated a good ability to remove F^- from water. For instance, the literature shows that the RO removes as high as 98% of F^- within a very short time [18]; at the same time, the literature indicates that the RO has many serious drawbacks, such as the need for high-pressure, the high operational cost, high polluted rejected solution along with the need for complex technology are the main limitations of the wide use of the RO technology [19,20]. The adsorption method has overcome most of the drawbacks mentioned above of other methods; for instance, the literature confirmed the affordability, simplicity and efficiency of the adsorption method compared to other methods [21,22]. The literature is rich in the successful applications of different adsorbents for removing F^- from water. For example, Ramos-Vargas et al. [23] used aluminium-modified guava seeds as an adsorbent to remove F^- from groundwater samples, considering the effects of adsorbent dosage and pH. The results proved the good capacity of modified seeds for adsorbing F^- from groundwater (0.3445 mg of F^- per 1 g of the adsorbent), and the best pH and adsorbent dosage were 2 and 70 g/L, respectively. Tan et al. [24] prepared zirconium-based metal organic adsorbent and used it to remove F^- from water under different operating conditions, different treatment times and F^- concentrations. The results showed that the adsorption capacity of the developed adsorbent was 19.42 mg F^- /g. In fact, the adsorption technology recently received a big deal of attention due to its advantages, such as affordability, high removal efficiency and ease of operation. For example, the number of published documents in the Scopus database increased from about 1600 in 2012 to about 6700 in 2022 (four folds).

Based on the above mentioned attractive merits of the adsorption technology, the current study aims at the development of an eco-friendly adsorbent to remove F^- from water. The eco-friendliness of the new adsorbent is achieved through the extraction of the essential chemicals (Ca, Al, Fe, and Mg) for adsorbing F^- from the by-products of the paper industry.

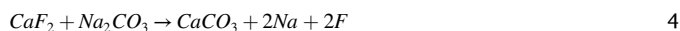
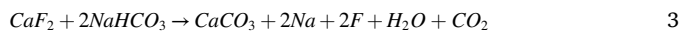
2. Mechanism of F^- release in water

The releasing rate and quantity of F^- from the geological formations into the water bodies depend on different factors, such as the type of rocks, dissolution activities of F^- minerals, and the residence time of water within the geological formations [8,25]. Generally, the release process F^- takes place when the hydrogen ions increase in the geological formation, as shown in the equations below [26]:



The main motivator for the increase of hydrogen ions is the concentration of CO_2 in the soil, which comes mainly from rainwater, bacterial activities in the soil, and oxidation of organic matter.

Notably, soil pH plays a significant role in the dissolving rate of F^- , where it has been reported that high pH levels improve the dissolving rate, while low pH levels improve the adsorbing F^- on clay [25,27]. Additionally, the presence of sodium bicarbonates or sodium carbonates increases the releasing rate of F^- [8,28]:



3. Materials and methods

3.1. Materials

Wastepaper sludge ash (WSA) was supplied by a local paper industry in the UK (Saica Paper UK Ltd.), and the chemicals (hydrochloric acid (32%), ferric chloride (≥ 98.0), sodium fluoride (≥ 99.99), sodium hydroxide (≥ 98.0), and Ethylene glycol ($\geq 99.75\%$)) were purchased from Merck, UK. The sand was provided by the construction laboratory at Liverpool John Moores University, UK.

All chemicals were used as supplied, while the sand sample was washed first using deionised water and then dried at 50°C using an oven. The dry sample was sieved using four sieves (from top to bottom: 3.55, 2.00, 1.18 and 0.60 mm), and the required amount of each size was taken according to the method stated by Alzeyadi [29].

3.2. Characterisation

Different characterisation technologies were used in this study to identify the key properties of the adsorbent and adsorption process. The used technologies are X-ray fluorescence (XRF) (Shimadzu 720 analyser), X-ray diffraction Investigator (XRD) (Shimadzu XRD-6000 analyser), Fourier Transform Infrared Spectroscopy (FTIR) (Agilent Technologies, Cary 360), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) (FEI Inspect-S (SEM) FEI Inspect-S). The XRF analysis was applied to the raw WSA to confirm the presence of Ca, Al and Fe in the chemical composition of the WSA, which indicates the ability of this material to sorb F^- ; XRD and EDX analyses were used to confirm the presence of F^- in used adsorbent that indicates the occurrence of the sorption process. SEM images were used to detect any morphological changes in the adsorbent (before and after treatment), while the FTIR analysis provides information about the changes in the functional groups, molecular structure, and chemical bonds due to the sorption process.

3.3. Manufacturing of adsorbent

Initially, the XRF analysis was used to characterise the chemical composition of the WSA sample to identify the content of the favourite ions for F^- removal, such as Ca, Al, Fe, and Mg [30,31]. The results showed that the WSA contains a considerable amount of CaO (about 34%), a moderate amount of Al_2O_3 (about 3.1%) and tiny amounts of Fe_2O_3 (0.473%) (Fe was spiked with FeCl_3). The extraction of the key chemicals from WSA was done using an acidic bath following the recommended procedures Dahan et al. [32], where 5 g of the WSA sample was mixed with 50 mL of HCl (32%) and agitated at a speed of 260 rpm for 270 minutes. The solution was then filtered at 0.45 μm filters and tested for concentrations of the mentioned chemicals.

The obtained solution was then mixed with 3.66 g of ferric chloride, 6 mL of Ethylene glycol and 3.66 g of clean sand. The mixture was

shaken for 180 minutes at a speed of 200 rpm and then filtered to separate the solid particles from the solution. The particles were dried at 95°C for 12 hours using a ventilated oven. The dry particles represent the new adsorbent (coated sand particles with Ca, Al and Fe ions).

3.4. F^- solution

Sodium fluoride (NaF) powder was used to prepare the F^- stock solution; 221 mg of the NaF powder was dissolved in 1000 mL of deionised water to have 100 mg/L of F^- . This concentrated solution was stored at 2°C and used to dilute smaller concentrations (7.5, 15, 22.5, 30 and 37.5 mg/L) before the experiments.

3.5. Adsorption kinetics and isotherms

Studying adsorption kinetics is essential to describe the sorption process and understand whether the sorption is controlled mainly by physical or chemical binding bonding (chemisorption or physisorption) [22,33]. Although several models can be used to study the adsorption kinetics, pseudo-first-order and pseudo-second-order models are the most commonly used for this purpose [34]. The adsorption process is described as chemisorption if the pseudo-second-order fits the data; otherwise, it is described as physisorption [35,36]. Pseudo-first-order and pseudo-second-order models are represented by the following two equations [34]:

A Pseudo-First-Order model

$$q_t = q_e (1 - e^{-k_1 t}) \quad 5$$

B Pseudo-Second-Order model

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2} + \frac{t}{q_t}\right)} \quad 6$$

Where q_e , q_t , t , k_1 and k_2 represent the adsorbed amount of the pollutant at the equilibrium conditions (mg/g), the adsorbed amount of the pollutant at a certain time (mg/g), measurement time (minutes), the Pseudo-First-Order adsorption rate (min^{-1}), and rate constant of the Pseudo-second-order model (mg/(mg. min)), respectively.

It is noteworthy to mention that the q_e value is calculated using the equation below [37]:

$$q_e = \frac{(C_i - C_e)}{W} \times V \quad 7$$

Where C_i , C_e , W , and V represent the initial concentration of the pollutant (mg/L), the equilibrium concentration of the pollutant (mg/L), the volume of the solution (L) and the mass of the adsorbent (g), respectively.

Additionally, the adsorption could occur as a monolayer or multilayer on the surface of the adsorbent, which could be investigated using a suitable adsorption isotherm. Langmuir and Freundlich isotherms are the most commonly used to investigate whether the adsorption took place as a monolayer or multilayer on the surface of the adsorbent [38]. Langmuir isotherm refers to monolayer adsorption on homogeneous sites, while the Freundlich isotherm indicates the occurrence of multilayer adsorption on heterogeneous sites [39]. The following equations represent Langmuir and Freundlich isotherms [40]:

A Langmuir isotherm

$$\frac{1}{q_e} = \frac{1}{K_L \times q_{max}} \times \frac{1}{C_e} + \frac{1}{q_{max}} \quad 8$$

B Freundlich isotherm

$$\text{Log}(q_e) = \text{Log}(K_f) + \frac{1}{n} \times \text{Log}(C_e) \quad 9$$

Where K_L , q_{max} , n and K_f are Langmuir constant (L/mg), maximum adsorption capacity (mg/g), Freundlich isotherm exponent (dimensionless), and Freundlich isotherm constant (dimensionless), respectively.

3.6. Removal experiments

The experimental work was initiated by investigating the effect of water pH level on the adsorption of F^- on the new adsorbent. The experiments were commenced in batch flow patterns using three 50 mL samples of F^- solution (15 mg/L). 15 mg of the new adsorbent was added to each sample, and then the pH value of the samples was adjusted to 3, 7 and 10 using a proper amount of HCl or NaOH. The samples were then shaken for 60 minutes at 200 rpm. By the end of the mixing period, 2 mL of each sample was collected and filtered on Whatman No.1 filters to separate solids, and then the residual concentration of F^- was measured using Hach Lang F^- cuvettes (LCK323) and spectrophotometer (DR2800). The removal efficiency was calculated using the following equation:

$$\text{Removal of } F^- = \frac{(C_i - C_e)}{C_i} \times 100\% \quad 10$$

The results of the pH level experiments were used to carry out the contact time effect, where the pH of three 50 mL samples of solution (having 15 mg/L of F^- and 15 mg of the adsorbent) was adjusted to the obtained best pH value and then shaken for 240 minutes. 2 mL samples were collected from each sample at intervals of 15, 30, 45, 60, 120, 180 and 240 minutes, filtered on Whatman No.1 filters, and then the residual

concentration of F^- was measured. The effect of the adsorbent dose was investigated using three different doses (10, 15 and 20 mg) of the adsorbent, and the samples were treated at the best pH and contact time.

For isotherm experiments, five different concentrations of F^- (7.5, 15, 22.5, 30 and 37.5 mg/L) were treated in batch flow, and results were applied to equations (8) and (9) to calculate the parameters of Langmuir and Freundlich isotherms. All experiments were carried out at room temperature (25 °C).

4. Results

4.1. Characterisation of the new adsorbent

The new adsorbent was subjected to EDX analysis to confirm the precipitation of Ca, Al and Fe ions. The EDX images depicting the surface chemicals of the particles are shown in Fig. 1A and B, and the corresponding data are summarised in Table 1. Fig. 1A illustrates that the raw sand, before coating, primarily comprises oxygen (O) and silicon (Si). In contrast, the coated sample, representing the new adsorbent, exhibits significant concentrations of Ca, Al and Fe, in addition to O and Si. The presence of Ca, Al and Fe is very important for the removal of F^- from water because they have an affinity for reacting with F^- , forming

Table 1
Chemical compositions of raw sand and the new adsorbent.

Element	Weight%	
	Raw sand	New adsorbent (coated sand)
O K	60.21	61.84
Si K	39.79	18.11
Al K	0.0	0.66
Cl K	0.0	0.45
Ca K	0.0	9.52
Fe K	0.0	9.42
Total	100	100

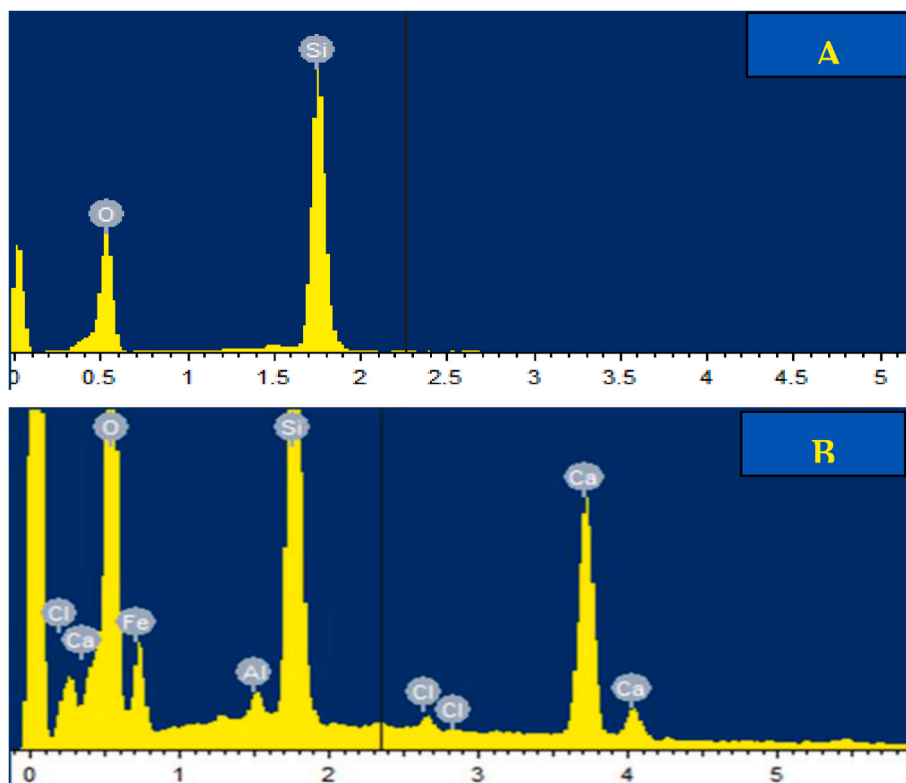


Fig. 1. EDX analysis of A) Raw sand and B) The new adsorbent.

insoluble compounds in water [41,42]. For example, Ca removes F^- from water through precipitation or co-precipitation, which relies on the fact that Ca^{2+} reacts with F^- forming a relatively insoluble compound called calcium fluoride (CaF_2) according to Eq. (11). The latter tends to precipitate, allowing the F^- to be removed.



Also, Al can remove F^- from water through chemical precipitation. Adding Al to the water leads to the formation of aluminium fluoride (AlF_3), according to Eq. (12), which is insoluble and can be easily removed from the water.



Similarly, Fe ions have the ability to remove F^- from water through adsorption F^- ions onto the surfaces of Fe-containing materials forming iron fluoride (FeF_3) compounds, according to Eq. (13). The latter can be easily removed from water.



In summary, the results of Table 1 and Fig. 1 confirm the presence of Ca, Al, Fe, and Mg, which have very good affinity for adsorbing capacity for F^- , in the structure of the new adsorbent [30,31]. Therefore, the new adsorbent can potentially remove F^- from water.

4.2. Effects of operative parameters

The effect of the initial pH of the solution on the removal of F^- was studied at 3, 7, and 10. The results indicated that the alkaline pH levels benefit the adsorption of F^- on the new adsorbent. For instance, the removal efficiency increased from 46% to the vicinity of 77% as the pH value increased from 3 to 10, as shown in Fig. 2. To understand the effect of pH on the removability of F^- by the new adsorbent, the zeta potential of the new adsorbent was studied by measuring ΔpH at a pH range of 3–10, as shown in Fig. 3. The latter clearly shows that the surface charge of the new adsorbent changes from negative (in the acidic environment) to positive (in the basic environment). Therefore, the increase in the removal of F^- with the increase of the pH value could be attributed mainly to the fact that the adsorbent surface becomes positively charged in the alkaline environment, resulting in a strong electrostatic interaction force between the negatively charged F^- and the positive surface of the adsorbent [34].

Therefore, the initial pH of the solution of 10 will be used to complete the experimental work.

The second set of experiments was devoted to investigate the effects of contact time on the removal of F^- ; the experiments were carried out using 15 mg of the adsorbent mixed with 50 mL of F^- solution at a pH of 10, and the solution was shaken for 240 minutes to identify the required time to reach the equilibrium status. Samples were collected during the course of experiments at 5, 15, 30, 45, 60, 120, 180 and 240 minutes to

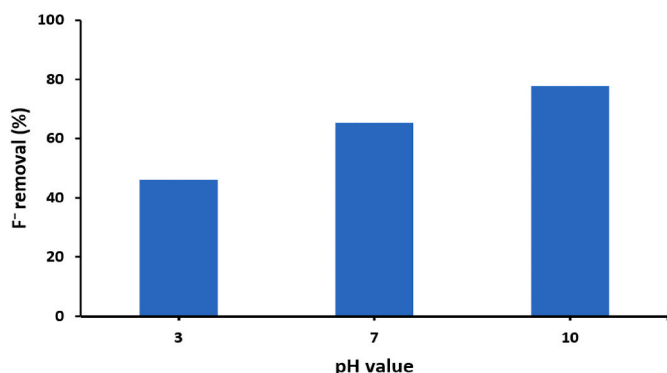


Fig. 2. Effect of the pH of water on the removal of F^- by the new adsorbent.

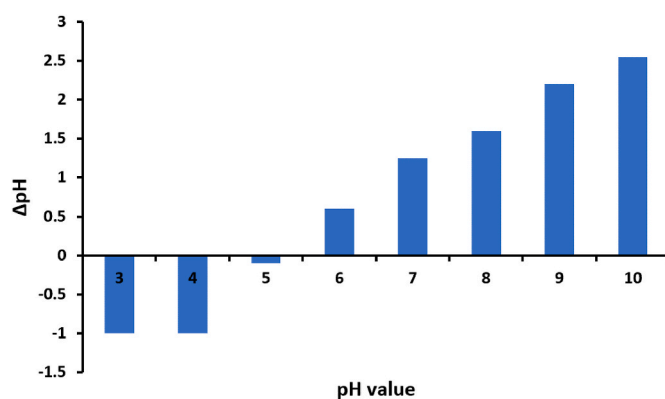


Fig. 3. The zero charge point of the new adsorbent.

measure the remaining concentration of F^- in the solution. The obtained results in Fig. 4, show that the removal of F^- increased dramatically during the first 60 minutes of the treatment, and then it showed slight progress until it reached a relatively stable status after 180 minutes. The explanation for this behaviour is attributed to the availability of the active sites on the surface of the adsorbent; during the first 60 minutes of treatment, there was an abundant number of active sites on the surface of the adsorbent, which resulted in high removal efficiency. However, most of the active sites are occupied with time, leading to a slow adsorption pace [43]. According to the obtained results, the best treatment is 180 minutes, as no significant changes can be noticed in the removal efficiency after this time.

The effect of F^- concentration on the efficiency of the adsorbent was investigated using three different concentrations of F^- (7.5, 15 and 30 mg/L), keeping the contact time and the pH value at 180 minutes and 10, respectively. The obtained results, shown in Fig. 5, indicate that the removal efficiency improved with the decrease of the F^- concentration, which is attributed to the availability of the active sites; more active sites are needed to accommodate the high concentrations of F^- [44].

It can be concluded from studying the effects of the operative parameters that the best removal efficiency was 86%, achieved at initial pH, contact time and initial F^- concentration of 10, 180 minutes and 7.5 mg/L, respectively.

Additionally, the preliminary cost of the new adsorbent was estimated based on the current prices of energy and materials in the UK market (electricity: £0.34/kWh, sand: £0.11/kg, hydrochloric acid: £5.0/L, ferric chloride: £3.63/kg and Ethylene glycol: £0.7/kg). The cost of producing 1.0 kg of the new adsorbent was found to be £6.378, which is close to the cost of some adsorbents in the literature, such as the cost of activated carbon that is produced using pyrolysis method (4–10 USD/kg, currently approximately equals £3.25–8.12/kg) [45].

Regeneration experiments were conducted to assess the reduction in adsorption capacity. It was observed that the adsorption capacity decreased from 86% to 77% after one regeneration cycle and then

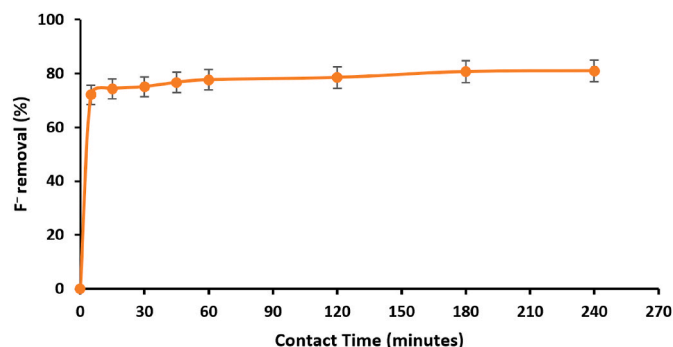


Fig. 4. Effect of contact time on the removal of F^- by the new adsorbent.

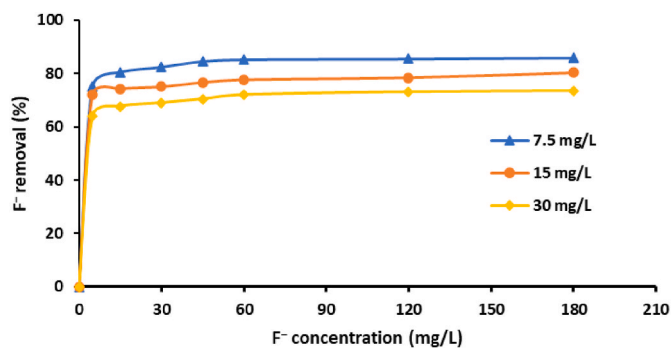


Fig. 5. Effect of F^- concentration on the removal efficiency.

significantly dropped to approximately 53% after the second regeneration cycle. Therefore, it is recommended not to use the new adsorbent for more than two cycles (one regeneration cycle). Since the new adsorbent primarily consists of sand, the depleted adsorbent has the potential to be recycled in the construction industry, such as in concrete or bricks. However, a leaching test must be performed before recycling the depleted adsorbent.

4.3. Adsorption isotherm and kinetics

As stated above, the adsorption isotherm was studied using Langmuir and Freundlich isotherms, while the adsorption kinetics were studied using Pseudo-First-Order and Pseudo-Second-Order models.

Adsorption isotherms were experimentally studied using five different F^- concentrations, namely 7.5, 15, 22.5, 30 and 37.5 mg/L, that were treated using 15 mg of the adsorbent in a batch flow system for 180 minutes and at initial pH of 10. The obtained results, shown in Fig. 6A and B, were then used to calculate the parameters of the

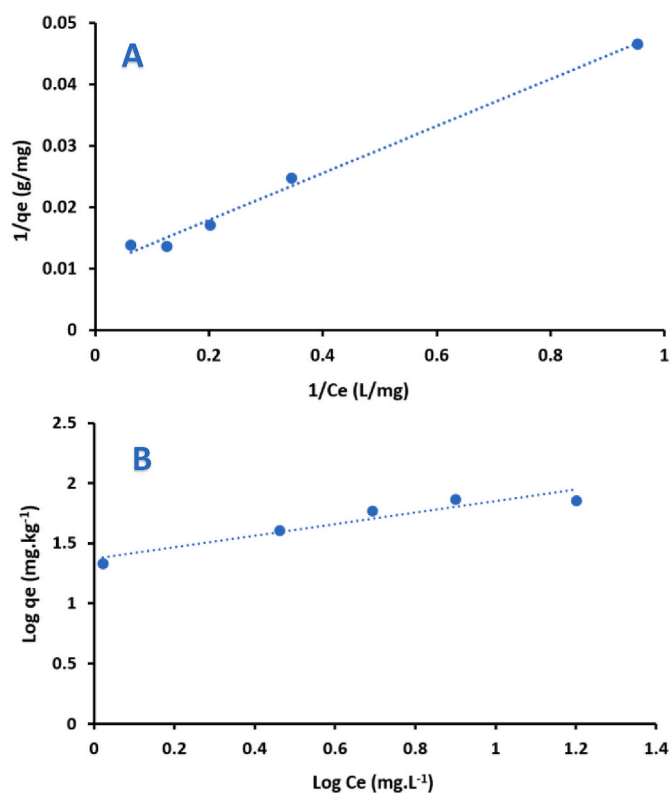


Fig. 6. A) Langmuir and B) Freundlich adsorption isotherm (pH:10, dose:15 mg, temperature = 25 °C).

Langmuir and Freundlich isotherms. Table 2 shows the calculated parameters of both Langmuir and Freundlich isotherms. It is clear that the Langmuir isotherm is more suitable for representing data than the Freundlich adsorption isotherm because the R^2 value of these models was 0.992 and 0.866, respectively. This means the adsorption of F^- occurs as monolayer adsorption on homogeneous sites on the surface of the new adsorbent [39].

Regarding adsorption kinetics, both Pseudo-First-Order and Pseudo-Second-Order models were performed using experimental for a constant concentration of F^- for different time intervals, and the obtained results are listed in Table 3. The results indicate that physisorption is more predominant than the chemisorption in the removal of F^- using the new adsorbent because the Pseudo-First-Order model has a better R^2 value than the Pseudo-Second-Order model [35,36].

Although the physisorption was predominant, the chemisorption played a role in the removal of the F^- , which has been confirmed by the XRD test (Fig. 7). The latter obviously shows the formation of peaks (marked in the figure) that confirmed the reaction between F^- and metal ions, namely Al, Fe and Ca, forming metal-fluoride phase precipitates, including AlF_3 , FeF_2 , FeF_3 and CaF_2 . These metal-fluoride phase precipitates removed a certain amount of F^- from water. A similar conclusion was noticed in the literature; for example, Xie et al. [46] attributed the removal of F^- from the solution to form metal-fluoride phase precipitates, including CaF_2 , AlF_3 , and FeF_3 .

4.4. Characterisation studies

FTIR analysis was applied to a depleted sample of the adsorbent (after using it to remove F^-). The results were compared to a fresh adsorbent sample (as a reference). The obtained results are shown in Fig. 8, which clearly shows significant changes in the transmittance for the wavenumbers between 500 and 1500 cm^{-1} .

It is well-known that fluorine is a member of the halogens group (Group 17 in the periodic table, which consists of fluorine, Cl, Br, I and At), which usually has a wavenumber ranging between 500 and 1500 cm^{-1} . The changes in the peaks within the range of halogens could be attributed to more than one bond; for example, the changes in the peaks around the wavenumber of 1100 cm^{-1} could be attributed to the formation of the Si-O bond. While the changes in the peaks at wavenumbers 690 to 705 cm^{-1} are attributed to the stretching of Al-F [47]. Additionally, the changes around the wavenumber of 774 cm^{-1} could be attributed to the presence of carbonyl- F^- [48]. In summary, the FTIR analysis again proves that F^- is removed by the new adsorbent.

Additionally, two SEM images were obtained for the new adsorbent before and after removing F^- from the water. As shown in Fig. 9 A and B, the obtained images show significant morphological differences between the two samples. For example, Fig. 9A shows the raw sample has a rough surface with relatively wide cracks (ranging from 3.045 to 5.712 μm). In contrast, Fig. 9B shows that the used sample has a smoother surface than the raw sample, and the sizes of the detected cracks are much smaller (870–900 nm) than those on the surfaces of the raw sample. These differences could be attributed to the accumulation of F^- and other chemicals on the surfaces of the new adsorbent, which resulted in a smooth surface and smaller cracks. These images could be another evidence of the removal of F^- by the new adsorbent. These

Table 2
Parameters of Langmuir and Freundlich adsorption isotherms.

Model	Parameter	Value
Langmuir isotherm	qmax (mg/g)	98.039
	K_L	0.266
	R^2	0.992
Freundlich isotherm	K_F	23.62
	n	2.096
	R^2	0.866

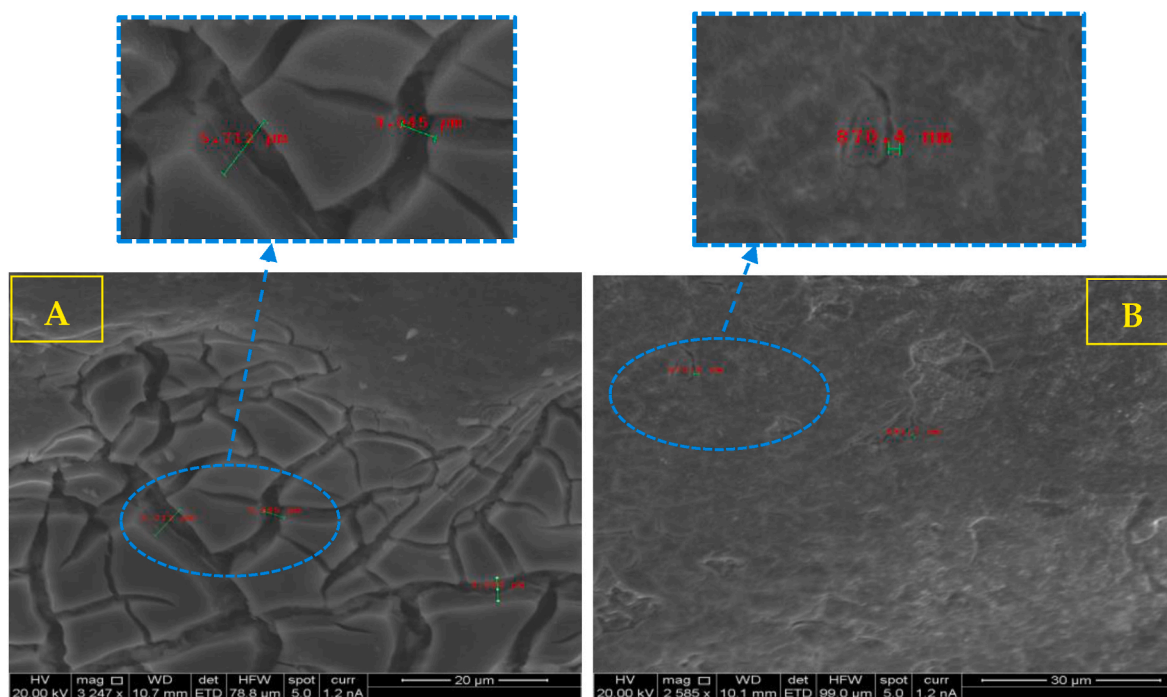


Fig. 9. SEM images of A) Raw sample and B) used sample.

V. The results of the kinetics study indicated the predominance of physisorption in the removal of F^- . In addition, the XRD results confirmed the contribution of the metal-fluoride phase precipitates to the removal of F^- .

VI. The characterisation analyses, namely FTIR, EDX and SEM, confirmed the outcomes of the experimental work.

In summary, the obtained results could be preliminary evidence of the ability of the developed new adsorbent to remediate water from F- in an eco-friendly process.

For future studies, it is recommended to investigate the ability of this new eco-friendly adsorbent to remove other pollutants, such as phosphate, heavy metals and dyes. Additionally, another study is needed to examine the effect of co-existing anions and co-existing cations. The nature of the connections between Ca, Al and Fe and the raw materials also needs to be investigated to explore the possibility of maximising the deposition of these favourable ions on the raw materials, which improves the removal efficiency. Finally, more studies should be carried out to identify the mechanism by which the green adsorbent selectively adsorbs fluoride ions from a solution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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