Removal of fluoride from aqueous solution by porous Vaterite calcium carbonate nanoparticles

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Abstract
This study is based on a simple, low-cost and a novel approach towards the removal of excess fluoride ions from aqueous solution by absorbing fluoride on porous vaterite calcium carbonate nanoparticles (PVCCNPs) synthesised using ethylene glycol-water soft template method. SEM images clearly show the porous nature of aggregated nanoparticles present in the dry powder. Physicochemical properties of synthesised PVCCNP and fluoride on PVCCNP was characterised further by FTIR, XRD, XRF, EDX, and TGA-DTG. Fluoride removal by PVCCNPs from 100.00 ml of 10.0 mg l⁻¹ NaF solution with 0.500 g of PVCCNPs, determined using a fluoride ion-selective electrode, indicates that around 90% removal is achieved within 1 h thus reducing the level to desired 1 ppm. The pseudo-second order kinetic model has a better fit to describe the adsorption of fluoride on PVCCNP than pseudo-first order model. The Langmuir isotherm model is more appropriate to describe the equilibrium behaviour of the adsorption process, than the Freundlich model. Given that the value of n (Freundlich constant) is greater than 1 (3.07) and R² value is in the range of 0 < R² < 1 (0.014–0.024) implies that the adsorption process is spontaneous and fluoride ions are favourably adsorbed on PVCCNPs. Langmuir model shows that the maximum adsorption capacity of fluoride is 1.956 mg g⁻¹. Excess fluoride in drinking waters causes several severe ill-health effects and filter media based on these nanoparticles can be used to remove fluoride down to safe and required levels to tackle these health problems. As such, PVCCNPs-based filter can be designed to remove fluoride in drinking waters. This may be a way for controlling fluorosis and many other diseases associated with excess fluoride present in drinking waters.

1. Introduction

Fluorine is one of the most reactive, lightest and the most electronegative halogen on the Earth. Fluorine occurs in nature as fluoride (F⁻) ions and is found in air (as gases or particulates), in water (present in the form of hydrated F⁻ ions), in soils and in living organisms [1]. Fluorine compounds are used in the metallurgical industry, mainly in the production of aluminium and manufacturing of glass [2], ceramics [3] and phosphate fertilizers [4]. Fluorine is present in 32 minerals as fluorides with or without carbonate, silicate, and phosphate and hydroxyl anions of alkali, alkaline earth, aluminium, bismuth, manganese or rare-earth cations [5]. Exchange of OH⁻ for F⁻ and vice versa in minerals is quite possible due to their similarities in size and charge and hence weathering of fluoride containing minerals add fluoride ions to water resources particularly under alkaline conditions [3].

Main sources of fluoride are drinking waters and a relatively small amount of fluoride comes from food items such as sea fish and tea [6]. Once absorbed, fluoride is quickly distributed throughout the body via the blood circulation [6]. In general, the level of fluoride content in the plasma is affected by the rates of bone
accretion and dissolution, and by the renal clearance rate of fluoride ions. Renal excretion is the major pathway of fluoride removal from the human body. There is no tubular secretion of fluoride. Generally, fluoride ions are filtered from the plasma by the glomerulus and then partially reabsorbed. There are several factors which can influence urinary fluoride excretion including urinary pH, urinary flow, and glomerular filtration rate [7]. Fluoride ions are not accumulated in soft tissues depending upon the concentration of fluoride present in drinking waters [10]. According to the WHO standards, the recommended desirable fluoride limit in drinking water is 1.0 ppm and maximum permissible limit is 1.5 ppm, though this value may vary slightly depending upon temperature and climate [11]. Recently, the recommended level of fluoride present in drinking water has been brought down to 0.7 ppm [12–14].

As such, removal of fluoride to the desired levels from drinking waters is an important precaution to be taken to prevent many diseases related to excess fluoride. There are several methods used for the removal of fluoride from contaminated waters, which include coagulation–precipitation, adsorption [15, 16], ion–exchange [17], electrocoagulation, membrane filtration, membrane separation [18], electrolysis, and so on. Among these methods, adsorption is the cheapest and easiest way to remove fluoride. Some of the adsorbents used to remove fluoride in water include activated alumina [19], activated carbon [20], activated alumina coated silica gel [21], calcite [22], activated saw dust [23], activated coconut shell powder [24], coffee husk [25], rice husk [26], tricalcium phosphate [27], bone charcoal [28], activated soil sorbent [29], defluoron and so on. So far, up to 90% of fluoride removal has been achieved from the adsorption technique, and the adsorbent can be regenerated by flushing with a hydroxide solution. When the nanoparticles are used the sludge generated is minimal since nanoparticles are expected to have very large specific adsorption capacity. Calcium ions have good affinity to fluoride ions and some calcium-based nanoparticles have been investigated for the removal fluoride ions from water [30].

As such, we report, in this paper, the synthesis of highly porous nanoparticles of calcium carbonate predominantly in its spherical vaterite form with some calcite nanoparticles [31] and their application in defluoridation of drinking water.

2. Materials and methods

All the chemicals were purchased from Sigma Aldrich and they were of analytical grade and used without further purification.

2.1. Synthesis of porous vaterite calcium carbonate nanoparticles (PVCCNPs)

A solution of Ca(CH3COO)2 (25.00 ml, 0.50 M), H2O (10.00 ml) and ethylene glycol (EG) (25.00 ml) labelled as solution A and a solution of NaHCO3 (25.00 ml, 0.50 M), H2O (10.00 ml) and EG (25.00 ml) labelled as solution B were prepared. The solution A was added to solution B in drop-wise manner using a dropping funnel and mixed slowly under constant stirring. After 24 h, the resultant precipitate was filtered and washed first with ethanol and then with distilled water. Product obtained was dried, at 100 °C, for 4 h, in a vacuum oven. Nanoparticles and other end products obtained were characterized by Laser Light Scattering based Particle Size Analysis (CILAS Particle Size Analyser NANO DS), XRD (Siemens D5000 x-ray powder diffractometer), XRF, FT-IR (Shimadzu IR-Prestige 21 Instrument with the KBr pellet method, SEM (Environmental SEM with EXAS Facilities) studies, TGA analysis (TA Instruments SDTQ600 Thermo-Gravimetric Analyser) The surface area of the PVCCNPs was determined by the novel BET instrument constructed in our research group.

2.2. Preparation of total ionic strength adjustment buffer II (TISAB II)

500.00 ml of distilled water, 57.00 ml of glacial acetic acid and 58.000 g of sodium chloride were mixed in a beaker, at 28 °C. The mixture was stirred to dissolve and allowed to cool down to room temperature. The pH of the solution was adjusted between 5.0 and 5.5 with 5 N sodium hydroxide solution. The pH-adjusted solution was transferred to a 1000.0 ml volumetric flask and diluted to the mark with distilled water.

2.3. Preparation of fluoride standard solutions

2.210 g of NaF solid was dissolved in 1.001 deionized water in a volumetric flask to prepare a solution of 1000ppm stock fluoride solution. This stock solution was diluted ten-fold to prepare 100.0 ppm F (aq) bulk solution. This bulk solution was diluted in respective factors to prepare 10.00, 12.00, 14.00, 15.00, 16.00, 18.00 and 20.00 ppm F−(aq) standard solutions. 4.00 ml of TISAB II prepared was added to 4.00 ml standard sample each and mixed well. 5.00 ml of each of these samples were pipetted out and filtered. Then 4.00 ml of filtrate of each sample was pipetted out, separately, and 4.00 ml of TISAB II was added to each of these samples. The
Fluoride concentrations of these samples were measured using Ion Selective Electrode which was calibrated using 1.00, 2.00 and 10.00 ppm F\(^-\)(aq) standard samples.

2.4. Fluoride removal by PVCCNP

1000.00 ml of 10.00 ppm fluoride solution was prepared by appropriately diluting 1000 ppm solution. Then 0.500 g of PVCCNPs was added to 100.00 ml of the above solution while stirring and stirring was continued for several hours. At each 1 h intervals, 5.00 ml of the sample was withdrawn and its fluoride concentration was determined by the calibrated fluoride ion-selective electrode. The removal process of Fluoride by PVCCNPs depends on several experimental parameters. These parameters are the initial pH of the aqueous Fluoride solution, PVCCNP dosage, shaking time, settling time and temperature. The optimum values determined separately by changing one parameter and others are kept constant. The all experiments are carried out at normal room temperature (298 K).

2.5. Studies on the effect of shaking time

1000.00 ml of 10.00 ppm Fluoride standard solution was prepared. 0.050 g of PVCCNPs was added to 20.00 ml of Fluoride standard sample and shaken the sample for 10 min After 1 h settling time 5.00 ml pipetted out for Fluoride analysis. The procedure was repeated for 20, 30, 40, 50, 60, 70, 80- and 90-minute time intervals by keeping other factors are constant.

2.6. Studies on the effect of settling time

In this study, 10.00 ppm Fluoride standard solution was used. As above procedure 0.050 g of PVCCNPs was added to 20.00 ml Fluoride sample and shaken for 1 h. After 30 min settling time, 5.00 ml pipetted out for Fluoride analysis. The procedure was repeated for 60, 90, 120, 150, 180, 240 and 300 min time intervals by keeping other factors constant.

2.7. Studies on the effect of PVCCNPs dosage

In this study 10.00 ppm Fluoride standard solution was used. 9 samples of 20.00 ml were separated from this standard solution and 0.050, 0.060, 0.070, 0.080, 0.090, 0.100, 0.125, 0.150 and 0.200 g of PVCCNPs were added to above samples respectively. After 1 h shaking and 2.5 h settling time 5.00 ml from each sample were pipetted out for Fluoride analysis.

2.8. Isotherm and kinetics studies

A concentration series of Fluoride from 10.00 ppm to 20.00 ppm was prepared using 100.00 ppm standard Fluoride solution. 0.110 g of PVCCNPs was added in to 20.00 ml to each sample and shake for 1 h. After 2.5 h settling time 5.00 ml from each sample were pipetted out for Fluoride analysis. In this study the Fluoride concentrations of samples were measured by 1:1 dilution with distilled water and resulted measurement was multiplied by 2. The Langmuir and Freundlich, isotherm equations were used to model the equilibrium behaviour of the Fluoride adsorption process. The pseudo-first order kinetic model and pseudo-second order kinetic model were used to analyse the kinetics of the absorption.

3. Results and discussion

3.1. Characterization of synthesized PVCCNPs

Figure 1 (a) shows a photograph of the prepared. PVCCNPs after vacuum drying. As shown, the sample consists of a fine powder which was dispersed in water using poly(ethylene glycol) (PEG) as the stabilizer. Laser light scattering based particle size analysis reveals that these particles are in a fairly narrow size range in the nanoscale between 5 nm and 50 nm with an average particle size of 11.5 nm. (Figure 1 (b)).

XRF analysis detects only Ca in this sample (figure 2). Since the XRF measures elements with atomic number > 13, it is incapable of detecting C and O. The fact that it does not detect any other element it clearly shows that the sample is free of impurity atoms with at least atomic number > 13.

Figure 3 shows EDAX mapping and elemental analysis of PVCCNPs that were used to remove fluoride from water. As seen in these figures, the sample consists of Ca, C, O and F whose elemental mapping is shown in this order in figure 3 (top). Shown in bottom of the figure are the EDAX spectrum and the part of the SEM image used to get these data. It is interesting to note that Ca, C, O, F atomic percentages are 38.6, 22.6, 28.3 and 10.5, respectively, suggesting considerable conversion of CaCO\(_3\) to CaF\(_2\) possibly on the surface of particles.

FT-IR Spectrum, given in figure 4(a), clearly shows major bands centred at 746, 874, 1088 and 1413 cm\(^{-1}\) wavenumbers. The first three IR-bands correspond to those of vaterite polymorph of calcium carbonate since standard IR bands of vaterite should appear at 745.8, 877 and 1084 cm\(^{-1}\) [32]. As can be seen from XRD in
Figure 4(b), the sample contains essentially vaterite as the major phase. The main characteristic peaks of vaterite at $2\theta$ of 20.88°, 24.94°, 26.99°, 32.78°, 38.73°, 40.56°, 41.66°, 42.57°, 43.74°, 48.95°, 49.92°, 50.93°, 52.19°, 55.65° correspond to the $(004)$, $(110)$, $(112)$, $(114)$, $(211)$, $(205)$, $(116)$, $(213)$, $(008)$, $(300)$, $(304)$, $(118)$, $(220)$, $(208)$ and $(224)$ crystallographic planes, respectively, can be clearly observed. Except for some other peaks such as 29.47°, 47.92° corresponding to calcite polymorph can also be seen due to vaterite to calcite conversion [33]. Application of the Debye–Scherrer equation (equation (1)) gives the average crystallite size to be 23.0 nm which is in the range of that obtained from solution phase particle size analysis.

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

Where, $\tau$ is the average crystallite size. $K$ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. $\lambda$ is the X-Ray wavelength, $\beta$ is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. $\theta$ is the Bragg angle.

Morphological studies of the PVCCNPs were done by SEM analysis and an image is shown in figure 5(a) which shows that large number of vacuum dried individual PVCCNPs are aggregated to highly porous spherical large micrometer-sized particles. The fact that particles in suspension contain discrete particles in the size range between 5–50 nm with 11.5 nm average particle size, it is possible that these aggregated particles can be broken down to essentially discrete single particles and they can be stabilized using EG. The SEM image shown in
figure 5(b) is the filtered air-dried sample after fluoride adsorption where nearly spherical particles in the right nano-range between 5 nm and 50 nm are apparent.

TGA (shown in figure 6) was carried out on fluoride incorporated PVCCNP samples from room temperature to 1000 °C. TGA thermogram shows that a mass loss of ∼15% was observed in the temperature range from 50 °C to 150 °C, which is due to the removal of moisture physically absorbed in the sample. A mass-loss of around 20% in the temperature range 200 °C–300 °C can be attributed to release of structurally bound
Combustion of any ethylene glycol molecules trapped within the nanoparticles or adsorbed onto nanoparticles is observed in the temperature range $300^\circ C$ to $600^\circ C$\cite{34}. Weight loss beyond $840^\circ C$ is due to the decomposition of CaCO$_3$ releasing CO$_2$ gas\cite{35}.

3.2. Use of PVCCNPs for fluoride removal from water

In this study, known amount of PVCCNPs was shaken in a fixed volume of fluoride ion solution of known concentration at a constant temperature (usually $25^\circ C$). There are several factors that could affect the fluoride removal in this process. These include the shaking time, time allowed to settle the particles after shaking for a fixed period of time (settling time), pH value of the solution, and initial fluoride concentration or the amount of PVCCNPs used for a fixed volume of fluoride solution with exactly the same initial concentration. Figure 7 shows the percentage removal $F^-$ from 20.00 ml of 10.03 ppm concentrated fluoride ion solution by 0.050 g of PVCCNPs at $25^\circ C$ for shaking times as 10, 20, 30, 40, 50, 60, 70, 80 and 90 min each followed by 1 h settling time.

Percentage of fluoride removal increases rapidly during first 40 min which reaches a maximum around 35% after about 60 min and levels off at this equilibrium value. Since in this system, the equilibrium has been reached after 60 min of shaking time, the effect of settling time on fluoride removal was studied by keeping shaking time at 1 h, and the results are depicted in figure 8. It shows that the settling time has no drastic effect on fluoride removal. These results indicate that more PVCCNPs are required for further removal of fluoride under these conditions. Shown in figure 9 is the percentage removal of fluoride from 20.00 ml of 9.92 ppm fluoride ion solutions as a function of amount of PVCCNPs. As shown, fluoride removal increase as the amount of PVCCNP is increased at the fixed initial amount of fluoride reaching equilibrium at 95% when 0.100 g or more of...
PVCCNPs is used. The maximum fluoride removal capacity can then be calculated to be around 1.96 mg fluoride ions per 1 g of PVCCNPs.

3.3. Adsorption Isotherm studies
In this study, all parameters were kept constant by considering results described above. Shaking and settling time were alarmed to 1 h and 2.5 h, respectively, and 0.110 g PVCCNPs were treated with each sample containing 12.20, 14.10, 15.00, 16.10, 18.14 and 20.02 ppm of F\(^-\) (aq). These concentrations were measured by 1:1 dilution with distilled water to be the linear dynamic calibrated range of the ISE. Data pertinent to initial F\(^-\) concentration, \(C_0\) in ppm, equilibrium F\(^-\) concentration, \(C_e\) in ppm, and specific adsorption by PVCCNPs, \(q_e\) in mg/g, and the calculated data required to fit to Langmuir and Freundlich Adsorption Isotherm.

Langmuir adsorption isotherm plot was constructed by plotting \(C_e/q_e\) in g/L versus \(C_e\) in mg l\(^{-1}\) since the linearized form of the Langmuir Adsorption Isotherm is as shown in equation (2) where \(K\) and \(q_{ml}\) are Langmuir constant in L mg\(^{-1}\) and maximum saturated adsorption capacity in mg g\(^{-1}\).
As shown in figure 10(a), The Langmuir Adsorption Isotherm is obeyed satisfactorily in the F⁻ concentration range from 1 ppm to 10 ppm indicating that there is monolayer coverage of fluoride ions on the active sites of the surfaces of PVCCNPs. The values of $q_m$ and $K_L$ obtained are 1.956 mg g⁻¹ and 3.419 L mg⁻¹, respectively, at 25 °C (table 1).

Langmuir isotherm model can be used to predict whether the adsorption is favourable or not [36]. The separation factor $R_L$ which is defined by equation (3) is a key factor determining the favourability of the adsorption. If $R_L > 1$, it is an unfavorable adsorption, when $0 < R_L < 1$ adsorption is favourable, if $R_L < 0$ adsorption is irreversible and when $R_L = 1$ it is then called linear adsorption.

$$R_L = \frac{1}{1 + K_L C_0}$$

(3)

Within the $C_0$ range investigated, $R_L$ values lie in the range from 0.014 to 0.024 indicating that fluoride ions are favourably adsorbed on PVCCNPs.

Linearized form of the Freundlich adsorption isotherm takes the form shown in equation (4) where $K_F$ is the Freundlich constant and $n$ is a constant which explains the relationship between adsorption capacity and adsorption intensity, respectively.
the R2 values to 1, indicates that the pseudo-second order kinetic model is more suitable than the pseudo-first-order model for describing the data. Considering the fact that the reaction is following pseudo-second order against t based on equation 10

\[ \frac{dq}{dt} = k_1(q_e - q_t) \]  

The integrated pseudo-first-order rate equation is written as

\[ \log(q_e - q_t) = \log q_e - k_1 t \]  

Basic equation for Pseudo-second order adsorption:

\[ \frac{dq}{dt} = k_2(q_e - q_t)^2 \]  

By integrating the equation at boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) gives

\[ \frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \]  

Where \( q_e \) and \( q_t \) are the amount of adsorbed fluoride at equilibrium and any time \( t \) (mg fluoride/g solid material), \( k_1 \) (min \(^{-1}\)) and \( k_2 \) (mg/g min \(^{-1}\)) are the equilibrium rate constant of first- and second-order sorption respectively, and \( t \) is the shaken time (min).

The value of \( n \) signifies the interactions between the adsorbent (PVCCNP) and the ion (F\(^-\)). Interactions between the adsorbent and pollutant is high if \( n \) value is high. If \( n = 1 \), it indicates the linear adsorption for all active sites of the adsorbent [37]. The ‘\( n \)’ for the fluoride adsorption to PVCCNP is 3.07 confirming the adsorption process desirable and physical process. Figure 10(b) shows the Freundlich adsorption isotherm plot and table 1 presents the both Langmuir and Freundlich isotherm results. The plot is not very linear \((R^2 = 0.9988)\) though there is some linearity can be seen. Thus Langmuir model has a better ability to describe the adsorbent isotherm behaviour than Freundlich isotherm. However it indicates the possibility for physisorption on the chemisorbed monolayer of fluoride ions that are already on the active sites of the PVCCNP surfaces. It may also be due to some precipitated CaF\(_2\) on PVCCNPs [38].

| Isotherm       | Parameter            | Fluoride ions on PVCCNP (at 25°C) |
|---------------|----------------------|-----------------------------------|
| Langmuir      | \( Q_m \) (mg g\(^{-1}\)) | 1.956                             |
| \((y = 0.5224x + 0.5337)\) | \( K_L \) (L mg\(^{-1}\)) | 3.419                             |
|               | \( R_i \) Range within C\(_0\) | 0.014–0.024                      |
|               | \( R^2 \)             | 0.9988                            |
| Freundlich    | \( n \)               | 3.07                              |
| \((y = 0.0905x + 0.1914)\) | \( K_F \) (mg g\(^{-1}\)) | 2.40                              |
|               | \( R^2 \)             | 0.9211                            |

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

3.4. Kinetic studies

The kinetic models can be used to determine the mechanisms of adsorption processes. In this study, pseudo-first and pseudo-second order models were used to study the mechanism of fluoride on PVCCNP [39].

Basic equation for Pseudo-first order adsorption:

\[ \frac{d_q}{dt} = k_1(q_e - q_t) \]  

The larger the \( k_2 \) value, the slower the adsorption rate [39]. The correlation coefficient \((R^2)\) of the pseudo-first order kinetic model for adsorption of fluoride with initial concentrations of 10 ppm is 0.2488 and that for pseudo-second order kinetic model is 0.9882. The closeness of the R2 values to 1, indicates that the pseudo-second order kinetic model is more suitable than the pseudo-first order model for describing the data. Considering the fact that the reaction is following pseudo-second order
kinetic model, $k_2$ value calculated from the gradient is $3.84 \times 10^7 \text{ g m}^{-1} \text{ min}^{-1}$. Compared with the literature values obtained for different materials $k_2$ value obtained is considerably small which highlights the high adsorption rate of our material \cite{38}.

Important point to realize here is that by taking appropriate amount of PVCCNPs (0.01 g) the fluoride concentration can be reduced to 1 ppm, to the required fluoride levels in drinking waters, from 20.0 ml of 10 ppm solution. As such, the mass of nanoparticles required to remove fluoride in 10 l water sample that is commonly used per day in household requirements is only 10 g even if this water is contaminated with 10 ppm of fluoride ions. In environmental samples, the contamination does not usually exceed 2–3 ppm and occasionally ~7 ppm has been detected in just one tube well waters. Fluoride concentrations in drinking waters of selected 30 dug and tube wells of Moneragala District of Sri Lanka are shown in figure 12(a). Analysis of show that only 10% of these samples have less than 0.5 ppm of $F^-$ which means 90% have over 0.5 ppm, 73% have over 1 ppm, 37% have over 2 ppm, 20% have over 3 ppm, 6.7% have over 4 ppm and 3.3% have over 5 ppm of $F^-$. Notably, people drinking water from these wells over a long period have caught the chronic kidney disease on unknown aetiology (CKDU). This shows that there is some correlation between fluoride in drinking waters and the occurrence of CKDU. However, there are no evidence to confirm that fluoride alone is causing CKDU except that two reports showing excess fluoride and calcium together damaging kidneys of laboratory mice \cite{40}.

To get an idea about the possible effect of excess fluoride in drinking water on the prevalence of CKDU, we have selected 30 reference drinking water resources. This was done by carefully selecting wells by taking into

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{(a) Pseudo-first order plot of fluoride adsorption kinetics on PVCCNP (b) Pseudo-second order plot of fluoride adsorption kinetics on PVCCNP.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Fluoride levels in drinking waters from 30 selected (a) sample and (b) control/reference dug and tube wells in the Moneragala District of Sri Lanka.}
\end{figure}
account of the fact that there were no recorded CKDU patients who drink water from these water sources. Data are shown in figure 12 (b). Interestingly, statistical analysis indicates that 13% > 0.5 ppm, 87% < 0.5 ppm, 10% between 0.5 ppm and 1.0 ppm, and just one reference point had 2.86 ppm which means almost all have F⁻ concentration below recommended maximum concentration of 1.5 ppm except just one [41, 42].

Therefore, on average even if 5 ppm is the level of contamination, mass of PVCCNPs required to reduce that to 1 ppm level would be only 5 g. Calcium ions required for the synthesis of PVCCCNPs can be obtained from commonly available, cheap and mundane minerals such as calcite and dolomite. We have already developed methods to separate calcium and magnesium components and silica impurities from local dolomite and developed methods to prepare various polymorphs of calcium carbonate nanoparticles and their polymer nanocomposites [33]. As such, simple and low-cost filters can be designed and developed to remove excess fluoride from drinking waters in household scale to prevent the occurrence of various chronic diseases due to exposure to excess fluoride. This is perhaps the way forward for preventing dental and skeletal fluorosis and even effects of fluoride to other organs such as heart and kidneys.

4. Conclusions

This paper describes a soft-templated approach to the synthesis of spherical nanoparticles of vaterite, their characterization and application in the removal of excess fluoride in contaminated waters. Even if the contamination level is 5 ppm the mass of vaterite form of the precipitated calcium carbonate required to reduce level down to 1 ppm is only 5 g. Physicochemical properties of synthesised PVCCNP and fluoride on PVCCNP was determined using FTIR, SEM, XRD, XRF, EDX, and TGA-DTG characterization techniques. The pseudo-second order kinetic model was better able to describe the adsorption of fluoride on PVCCNP than pseudo-first order model. The Langmuir isotherm model, in contrast to the Freundlich model, is more able to describe the equilibrium behaviour of the adsorption process. Given that the value of n (Freundlich constant) obtained is greater than 1 (3.07) and \( R_L \) value is in the range 0 < \( R_L \) < 1 (0.014–0.024) imply that the adsorption process is spontaneous and fluoride ions are favourably adsorbed on PVCCNPs. Langmuir model shows that the maximum adsorption capacity of fluoride is 1.956 mg g⁻¹. Excess fluoride in drinking waters causes several severe ill-health effects and filter media based on these nanoparticles can be used to remove fluoride down to safe and required levels to tackle these health problems.

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Conflict of interest

‘The authors declare that there is no conflict of interest regarding the publication of this paper.’

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References

[1] Evans DJ, Rugg-Gunn A J, Tabari E D and Butler T 1996 The effect of fluoridation and social class on caries experience in 5-year-old Newcastle children in 1994 compared with results over the previous 18 years Community Dent. Health 13 5–10
[2] Chen K J, Gao S S, Duangthip D, Lo E C M and Chu C H 2018 Managing early childhood caries for Young Children in China Healthcare 6 11
[3] Lagow R J and Margrave J L 1979 Direct fluorination: a ‘new’ approach to fluorine chemistry Prog. Inorg. Chem. ed S J Lippard Volume 26 (Hoboken, NJ, USA: John Wiley & Sons, Inc) (https://doi.org/10.1002/9780470166277.ch3)
[4] Ramteke L et al 2018 Study of fluoride content in some commercial phosphate fertilizers J. Fluorine Chem. 210 149–55
[5] Anthony J W, Bideaux R A B, Kenneth W and Nichols M C 2011 ‘Fluorite’. Handbook of Mineralogy III (Halides, Hydroxides, Oxides). (Chantilly, VA, US: Mineralogical Society of America)
[6] Palache C, Berman H and Frondel C 1951 Dana’s system of mineralogy Halides, Nitrates, Borates, Carbonates, Sulfates, Phosphates, Arsenates, Tungstates, Molybdates, etc 02 7th edn (New York: John Wiley and Sons, Inc)
[7] Elrashidi M A and Lindsay W L 1986 Chemical equilibria of fluorine in soils: a theoretical development Soil Science: An Interdisciplinary Approach to Soil Research 141 274–80
[8] Whitford G M 1996 The metabolism and toxicity of fluoride Monogr Oral Sci. vol 16 2nd (revised) (Basel: Karger) pp 1–9
[9] Iha S K, Mishra V K, Sharma D K and Damodaran T 2011 Fluoride in the environment and its metabolism in humans Reviews of Environmental Contamination and Toxicology (Continuation of Residue Reviews) ed D Whitacre vol 211 (New York, NY: Springer) 121–42

[10] Denissen H, De Nieuport H, Kalk W, Schaken H and Van Den Hooff A 1992 Fluorapatite and hydroxyapatite heat-treated coats for dental implants Bioceramics and the Human Body pp 130–40

[11] Chino N, Talimbo A S, Vyas H A and Mangla P 1994 Transient and reversible fluoride toxicity in some soft tissues of female mice Fluoride 27 205–214 (https://pdfs.semanticscholar.org/662a/1c0757f0a166dcd2ac0a80838193e070857.pdf)

[12] Lamberg M, Hausen H and Vartiainen T 1997 Symptoms experienced during periods of actual and supposed water fluoridation Community Dent Oral Epidemiol. 25 291–5

[13] Dunwoody S P, Rajapakse R M G, Shimomura M, Priyankarage V J, Jayasingha P and Wimalawansa S J 2017 Chronic kidney disease of multifunctional origin (CKDMFO) prevailing in srilanka reevaluated World Journal of Pharmaceutical Research, 63–66 ISSN 2277–7105 (https://wjrpr.net/admin/assets/article_issue/1512018988.pdf)

[14] Lee K and Thiesen K M 2014 A critique of recent economic evaluations of community water fluoridation International Journal of Occupational and Environmental Health. 21 91–120

[15] John Y, David V and Mrerriki D 2018 A comparative study on removal of hazardous ions from water by Adsorption: A Review. International Journal of Chemical Engineering 2018 1–21

[16] Kumpulainen J and Koivistoinen P 1977 Fluorine in foods Residues of Pesticides and Other Contaminants in the Total Environment. Residue Reviews, ed F A Gunther vol 68 (New York, NY: Springer) (https://doi.org/10.1007/978–1-4612-6355-5_2)

[17] Ekanayake I. and van der Hoek W 2002 Dental caries and developmental defects of enamel in relation to fluoride levels in drinking water in an arid area of Sri Lanka Caries Res. 36 398–404

[18] Dissanyake C B 1996 Water quality and dental health in the Dry Zone of Sri Lanka Geol. Soc. London, Spec. Publ. 113 131–40

[19] Rafique A, Awan M, Wasti A, Qazi I and Arshad M 2013 Removal of Fluoride from Drinking Water Using Modified Immobilized Activated Alumina Journal of Chemistry 2013 1–7

[20] Wu P, Xia L, Dai M, Lin L and Song S 2016 Electro sorption of fluoride on TiO2–loaded activated carbon in water Colloids Surf., A 502 66–73

[21] Nicholson J W and Czarneska B 2008 Fluoride in dentistry and restoratives Fluorine and Health. (Molecular Imaging, Biomedical Materials and Pharmaceuticals) (Ed.) ed A Tressaud and G Haufe (Amsterdam: Elsevier) pp 533–78

[22] Turner B D, Binning P and Stipp S L S 2005 Environmental Science & Technology 39 9561–8

[23] McIvor F J 1943 Ingestion of Fluoride and dental caries Quantitative Relations based on Food and Water requirements of Children one to twelve years old Am J Dis Child. 66 362–9

[24] Nemade P, Vasudeva Rao A and Alappat B 2002 Removal of fluorides from water using low cost adsorbents Water Science And Technology: Water Supply 2311–7

[25] Getachew T, Hausen A and Rao V 2014 Defluoridation of water by activated carbon prepared from banana (Musa paradisiaca) peel and coffee (Coffea arabica) husk Int. J. Environ. Sci. Technol. 12 1857–66

[26] Ganvir V and Das K 2011 Removal of fluoride from drinking water using aluminium hydride coated rice husk ash J. Hazard. Mater. 185 1287–94

[27] Mourabet M, El Rhilassi A, Bennani–Ziatni M, El Hamri R and Taitai A 2012 Removal of fluoride from aqueous solution by adsorption on Apatic tricalcium phosphate using Box–Behnken design and desirability function Appl. Surf. Sci. 258 4402–10

[28] Kawasaki N, Ogata F, Tominaga H and Yamaguchi I 2009 Removal of fluoride ion by bone char produced from animal biomass Journal Of Oeko Science 58 529–35

[29] Wang Y and Reardon E 2001 Activation and regeneration of a soil sorbent for defluoridation of drinking water Appl. Geochem. 16 531–9

[30] Tchomg从事 Kama E, Nganemi E and Darchen A 2010 Evaluation of removal efficiency of fluor trope solution using new charcoals that contain calcium compounds J. Collid Interface Sci. 346 494–9

[31] Dunwoody S P and Rajapakse R M G 2017 Synthesis of unstable vaterite polymorph of porous calcium carbonate nanoparticles, encapsulation of anticancer drug cisplatin, studying release kinetics for safe, targeted delivery and slow release Journal of Nanomedicine & Biotherapeutic Discovery 07 150

[32] Weir C E and Lippincott E R 1961 Infrared studies of aragonite, calcite, and vaterite type structures in the borates, carbonates, and nitrates Journal of Research of the National Bureau of Standards–A, Physics and Chemistry 65A 173–183A

[33] Dunwoody S P and Rajapakse R M G 2017 Encapsulation of anticancer drug cisplatin in vaterite polymorph of calcium carbonate nanoparticles for targeted delivery and slow release Biomed. Phys. Eng. Express 04 015017

[34] Sarkar A and Mahapatra S 2014 Novel hydrophobic vaterite particles for oil removal and recovery Journal of Materials Chemistry A 2 3808

[35] Galan I, Andrade C, Mora P and Sanjuan M A 2010 Sequestration of CO2 by Concrete Carbonation Environmental Science & Technology 44 3181–6

[36] Ghiori S and Pant K K 2005 Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina Sep. Purif. Technol. 42 265–71

[37] Esvandi Z, Foroutan R, Mirjalili M, Sorial G and Ramavandi B 2018 Physicochemical Behavior of Penaeseum semilatconum Chitin for Pb and Cd Removal from Aqueous Environment J. Polyom. Environ. 27 263–74

[38] Fan X, Parker DJ and Smith M D 2003 Adsorption kinetics of fluoride on low cost materials Water Res. 37 4929–37

[39] Foroutan R, Mohammadi R, Ramavandi B and Bastanian M 2018 Removal characteristics of chromium by activated carbon/CoFe2O4 magnetic composite and Phoenix dactylifera stone carbon Korean J. Chem.Eng. 35 2207–19

[40] Wasana H, Aluthpatabendi D, Kulapatne W, Wijskoon P, Weerarootiyar R and Bandara J 2015 Drinking water quality and chronic kidney disease of unknown etiology (CKD): synergistic effects of fluoride, cadmium and hardness of water Environ. Geochm. Health 38 157–68

[41] Wasana H, Perera G, De Gunawarden P and Bandara J 2015 The impact of aluminum, fluoride, and aluminum–fluoride complexes in drinking water on chronic kidney disease Environmental Science and Pollution Research 22 11001–9

[42] Dissanyake C B and Chandrajith R 2017 Groundwater fluoride as a geochemical marker in the etiology of chronic kidney disease of unknown origin in Sri Lanka Ceylon Journal of Science 463–12

[43] Danissen H W, De Nieupoort H M, Kalk W, Skaehek H G and Van Den Hooff A 1992 Fluorapatite and Hydroxyapatite Heat–Treated Coatings for Dental Implants ed A Ravaglioli and A Krajewski Bioceramics and the Human Body (New York: Springer, Dordrecht) (https://doi.org/10.1007/978–94–011–2896–4_17)