Experimental and modeling study of water defluoridation using waste granular brick in a continuous up-flow fixed bed

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Abstract
Contamination of surface and groundwater with excessive concentrations of fluoride is of significant health hazard. Adsorption of fluoride onto waste materials of no economic value could be a potential approach for the treatment of fluoride-bearing water. This experimental and modeling study was devoted to investigate for the first the fluoride removal using unmodified waste granular brick (WGB) in a fixed bed running in continuous mode. Characterization of WGB was carried out by FT-IR, SEM, and EDX analysis. The batch mode experiments showed that they were affected by several parameters including contact time, initial pH, and sorbent dosage. The best values of these parameters that provided maximum removal percent (82%) with the initial concentration of $F^-$ ions (10 mg/L) and agitation speed (200 rpm) were 90 min, 8, and 3 g/100 mL, respectively. The experimental data were found to fit the Freundlich isotherm model. The maximum adsorption capacity of fluoride on WGB was 1.1 mg/g. The continuous mode experiments clearly confirmed the important role of WGB bed in hindering and confining the propagation of the fluoride-loaded plume as well as there was a very good matching (RMSE ≤ 0.0398) with the predicted results obtained by the simulated mathematical model using COMSOL Multiphysics 3.5a software.

Keywords: Defluoridation, Fluoride adsorption, Recycling Waste granular brick, Water treatment
1. Introduction

Fluoride is the 13th most abundant naturally occurring element which is reactive and electronegative. In drinking water fluoride has a beneficial effect on teeth in low concentration. Exposure to excessive fluoride concentration can cause irreversible demineralization of tooth and bone tissues, a condition known as fluorosis, and long-term damage to liver, brain, thyroid, and kidney [1-4]. According to WHO, the acceptable level of fluoride in safe drinking water is ranged from 0.5 to 1.0 mg/L [5-7]. Many defluoridation techniques were adapted by several nations in 1930’s to investigate the negative effect of excess fluoride in drinking water and work on methods to remove excess fluoride [8-10]. The surface adsorption maintains a great place in the research and practice of defluoridation because of its general approachability and feasibility.

A wide range of materials were utilized for fluoride adsorption including lime followed by zirconium as a polishing step [11], red mud [12], amended clay [13] activated alumina, alum, and brick powder [14-16], hydrous iron III0-tin (IV) bimetal mixed oxide [5], modified bentonite clay [17], polymer/biopolymer composites [6], acidic alumina [18, 19], wheat dust, sawdust, and activated bagasse carbon of sugarcane [20], bone char [21], alum impregnated brick powder [22], citrus limonum leaf [23], raw unmodified bones [24], calcite nanoparticles [25], bio-adsorbent [26-27], laterite soil based adsorbents [28], neem oil-phenolic resin treated plant bio-sorbent [29], calcium carbonate [30-31], layered ZSM-5 zeolite [32], Ni and Zn modified LD slag based geopolymer [33]. In general, the majority of these adsorbent materials were used in batch mode experiments, while its column run was seldom studied. Waste brick material is one of these materials in which its performance and efficiency for fluoride and some other inorganic species
uptake was widely investigated in batch mode assays. Kumar et al. [34] studied the
defluoridation of groundwater using brick powder in batch experiments.

The elimination of fluoride was found to be 48.73 and 56.4% from groundwater samples
having 3.14 and 1.21 mg F⁻/l, respectively, under the optimized conditions of pH, effect of dose,
and contact time. Wijesundara et al.[35] used broken bricks as defluoridating agent for
development of a low cost domestic defluoridator for rural area. The removal rate of fluoride was
far better in small pieces than large pieces of broken bricks. Singh et al. [36] used suggested 29.8%
to 54.4% removal efficiency of fluoride from aqueous solution and ground water, respectively
using brick powder at pH of 6-8 and adsorbent dose of 0.6-1.0 g/L when the contact time was
increased from 15 to 120 min. Rani et al. [15] suggested the use of brick powder for fluoride
removal from aqueous solution and ground water. Jain and Singh [22] used alum impregnated
brick powder (AIBP) for defluoridation of water. The removal of fluoride by AIBP was 4.0 -5.0%
higher than that of brick powder (BP). Bibi [37] used hydrated cement, brick powder, and arble
powder wastes for fluoride and arsenic removal from water. Kumar et al. [38] assessed in batch
experiments the suitability of commercially available bricks powder used in fluoride-
contaminated water. Maximum removal of fluoride was observed to be 94% at optimum
conditions. Rafique et al. [39] evaluated the fluoride adsorption onto the red brick paving blocks
which is available as a cost effective potential adsorbent for defluoridation. The highest
percentage removal of fluoride in batch mode experiments was 62% achieved at pH range of 6-7.
The previously reported studies suggested using waste brick powder rather than granular waste
brick. However, to the authors’ knowledge no previous studies were reported concerned of
assessing the experimental and predicted performance of waste granular brick in a column test for fluoride removal.

This study aimed to investigate the potential of waste granular brick (WGB) for water defluoridation in a fixed bed column. A modeling study was performed using COMSOL Multiphysics 3.5a software to predict the behavior of the suggested system comparatively to experimental findings.

2. Material and Methods

2.1. Adsorbent

Raw waste granular brick (WGB) was used for fluoride adsorption from aqueous solution as inexpensive unused substance. WGB was obtained by collecting waste bricks from different local demolition locations. The collected waste bricks were crushed into smaller size granules using manual hammer, sieved, repeatedly washed with distilled water, Then dried in oven at 105°C for 24 h. Particles size ranged from 1 to 2 mm with an average of 1.414 mm was utilized for the adsorption assays.

2.2. Fluoride-loaded Aqueous Solution

Fluoride-loaded aqueous solution having concentration of 10 mg/L was prepared by dissolving the desired quantity of sodium fluoride (NaF) in distilled water. The residual concentration of fluoride ions (F⁻) in the treated solutions was determined by using a combined ion selective electrode (Ion lab pH/Ion/Cond 750, WTW). Additional cross checking was carried out using different type of separate Ion Selective Electrode (Model Orion). For, more accuracy, triple-
checking of fluoride concentrations were achieved by means of ion chromatography (Model: Metnohm Swiss 881 compact IC 2008).

2.3. Batch Experiments for Fluoride Sorption

The batch experiments for fluoride uptake were conducted at room temperature (28 ± 2°C). These experiments were carried out by agitation of 100 ml- fluoride solutions at initial concentration of 10 mg/L in 250 ml-plastic Erlenmeyer flasks using different amounts of WGB including 0.2, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 g. Several contact times of 5, 10, 15, 30, 60, 90, 120, and 180 min was carefully considered in this study. After proper predetermined time intervals, supernatant samples were filtered and analyzed to determine the remaining concentration of fluoride ions. Also, the pH adjustment was performed for various values at a range from 3 to 10 by the addition of 1 M NaOH or 1 M HCl. All experiments were carried out in duplicate. The quantity of adsorbed fluoride \( q_e \) was calculated as in Eq. (1) [40].

\[
q_e = (C_0 - C_e) \frac{V}{m}
\]  

Where, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of fluoride in the solution (mg/L), \( V \) is the volume of solution (L), and \( m \) is the mass of the adsorbent WGB (g).

2.4. Column Test Assays

The schematic diagram of the experimental system used in this study is given in Fig. 1. The cylindrical adsorption column was made of Perspex material of dimensions 85 and 10 cm for the height and diameter, respectively. The column was packed with WGB, and supplied with seven nozzles to take samples at a distance of 5, 10, 20, 30, 45, 60, and 75 cm for nozzles 1, 2, 3, 4, 5,
6, and 7, respectively from the bottom of the column. Samples were withdrawn from the column bed by inserting a needle into the center of the column at specific time intervals. First of all, to ensure that air was expelled from the column, distilled water was injected into the bottom of the adsorption column upward through the WGB bed. Then after, the fluoride-loaded solution was introduced into the column using an elevated feed tank. The flow of fluoride-loaded solution from the feed tank to the adsorption column was controlled using two valves (valves 1 and 2) and a flow meter as given in Fig. 1. The flow rate values of the fluoride-bearing solution were 15 and 25 ml/min. Monitoring of the fluoride concentration along the column throughout the sampling ports was carried out along a period of 15 days. Samples were analyzed for residual fluoride at different time intervals including 1, 5, 10, and 15 days.

Fig. 1. Schematic diagram of the lab-scale adsorption column

2.5. Characterization of WGB and Chemical Analysis

Fourier transform infrared spectroscopy (FT-IR) was carried out to characterize the presence of functional groups on the surface of fresh and spent WGB using FT-IR spectrometer (Type: EQUINOX FT-IR 55).

Scanning Electron Microscope (TESCAN Vega III) V was used for the surface studies of WGB material. The fluoride-loaded residue was filtered, washed, dried at 105°C for 30 min, and then cooled to room temperature. Fluoride-free residue was also subjected to the same conditions and both types of residues was analyzed by SEM to determine the variations on the mass surface after and before loading by the fluoride species. The micrographs were at resolution of 10000x.
SEM of virgin and fluoride-loaded WGB samples were useful to assess their surface characteristics after determining the optimal conditions for adsorption. An Energy Dispersive X-Ray Analyzer (EDX) is a potential tool for investigating the distribution of minerals and also the effect of the elements on this distribution. In this study EDX analysis was carried out for providing the desired elemental identification and quantitative compositional information.

2.6. Adsorption Isotherms
In this study, two isotherm models Freundlich and Langmuir as given by Eqs. (2) and (3) were used to fit the experimental data. The Langmuir model assumes monolayer adsorption while the Freundlich model is empirical in nature which assumes the adsorption is heterogeneous on the surface.

\[
q_e = K_F C_e^{1/N} \quad (2)
\]

\[
q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)
\]

Where:

- \(C_e\) is the remaining concentration of fluoride in the aqueous solution at equilibrium (mg F/L), \(q_e\) (mg F/g) is the mass adsorbed per unit mass of WGB at equilibrium, \(q_m\) is the amount of fluoride adsorbed per unit of adsorbent for a monolayer surface and \(b\) is the constant related to the free energy of adsorption. \(K_F\) (mg/g) (l/mg) \(1/N\) is the Freundlich sorption coefficient and \(N\) is an empirical coefficient indicative of the intensity of the adsorption.

3. Modeling Study
3.1. Transport of Contaminant through the Model Adsorption Column

In this study, a one-dimensional (ID) system model was considered. Hence, the migration and transport of fluoride ions in the porous WGB is due to the advection-dispersion processes can be represented by Eq. (4) as cited by Faisal and Abd Ali [26]:

\[
D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\rho_b \partial (q)}{\theta \partial t}
\]  

(4)

Where:

- \(D_x\) is the hydrodynamic dispersion coefficient in the x-direction (m²/s),
- \(V_x\) is the seepage velocity in the x-direction (m/s),
- \(x\) represents the distance in the x-direction (m),
- \(C\) is the fluoride concentration in water,
- \(q\) is the fluoride concentration sorbed on the adsorbent (mg/kg),
- \(\theta\) is the porosity of the media (WGB), and
- \(\rho_b\) is the dry adsorbent bulk density (kg/m³).

Under equilibrium isothermal conditions, the term \((q)\) on the right side of Eq.4 can be substituted by Eq. (2), since the experimental results of the batch test fitted very well with Freundlich isotherm, accordingly Eq. (2) can be combined with Eq. (4) as follows:

\[
D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\rho_b \theta K_F C^{1/N}}{N} \frac{\partial C}{\partial t}
\]  

(5)

This equation can be simplified as:

\[
D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \left(1 + \frac{\rho_b K_F}{\theta N} C^{1-N} \right) \frac{\partial C}{\partial t}
\]  

(6)

The effect of hindering or delaying the transport of \(F^-\) ions in relation to the advection front can be defined by the retardation factor \((R_F)\) as in Eq. (7):

\[
R_F = 1 + \frac{\rho_b K_F}{\theta N} C^{1-N}
\]  

(7)
Accordingly, the one-dimensional advection-dispersion equation that consider sorption into account for the equilibrium state of contaminant transport in the saturated zone can be written as follows:

\[ D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = R_F \frac{\partial C}{\partial t} \]  

(8)

The initial liquid and F⁻ concentrations are assumed to be zero throughout the entire flow domain, and the boundary conditions used are reported as follows:

- Lower boundary (x = 0): C = 10 mg/L
- Upper boundary (x = 75 cm): advective flux (i.e. \( \frac{\partial C}{\partial x} = 0 \))

(9)

To present a numerical solution, Eq. (8) in combination with initial and boundary conditions can be solved using COMSOL Multiphysics 3.5a software.

3.2. Longitudinal Dispersion Coefficient and Tortuosity

The effect of hydrodynamic dispersion is to cause a plume of contamination to extend in the direction of advection as well as to create a gradient of declining concentration from the center to the boundaries of the plume. However, the values of longitudinal dispersivity (\( \alpha_L \)) used in the present study for WGB adsorbent was calculated using the Eq. (10) [41]:

\[ \alpha_L = 0.83 (log L)^{2.414} \]  

(10)

where: L is the length of the flow path (cm).

Tortuosity is a measure of the influence of water molecules flow path in porous media. It is calculated depending on the porosity of the medium (\( \Theta \)) as follows [42]:

\[ \tau = (\Theta)^{m-1} \]  

(11)
As cited by Holzbecher [42], Archie in 1942 reported the values of $m$ in the range of 1.8 - 2 for consolidated sandstones, 1.3 for unconsolidated sand in a laboratory experiment, and 1.3 - 2 for partly consolidated sand. For theoretical or conceptual work the value $m = 2$ was considered, which could be justified if there is no further information available.

4. Results and Discussion

4.1. Results of WGB Characterization

4.1.1. FT-IR analysis

The results were considered by comparing the FT-IR spectra of fresh WGB with the fluoride-bearing WGB (spent WGB). The difference between FT-IR spectrum of GWB before and after fluoride adsorption demonstrated the decrease of transmittance percentage in the range of 850 – 4,000 cm$^{-1}$ and shifting of the peaks in the post sorption spectrum (Fig. 2). The FTIR spectrum before fluoride removal indicates the presence of a broad and strong band of phosphate, PO$_4^{3-}$ group (1,100-900 cm$^{-1}$), carbonate of CO$_3^{2-}$ (720 cm$^{-1}$), and a broad and strong band of calcium of Ca$^{2+}$ (550-610 cm$^{-1}$). The main functional groups, phosphate and calcium groups after fluoride uptake, the peak Ca$^{2+}$ (550-610 cm$^{-1}$) changed, was not strong and broad or was substantially lower than that before removal, suggesting some participation of Ca$^{2+}$ in the binding of fluoride by the bones and some dissolving in the solution, also phosphate peak, PO$_4^{3-}$ (1,100-900 cm$^{-1}$), changed was strongest than calcium due to elution in to solution as it the main exchangeable ions in bone structure with fluoride.
Additionally, the new peaks are emerged at few wavelengths (450 and 600 cm$^{-1}$) after fluoride adsorption. The fresh WGB showed peaks at 2,360, 1,635.64 and 1,064.71 cm$^{-1}$ due to O-H bending vibration [19].

Fig. 2. FT-IR of brick waste before and after fluoride loading.

After F$^-$ ions sorption those peaks shifted to 2365, 1634, and 1050, respectively, indicating that F$^-$ ions interaction with WGB is due to the contribution of ion exchange process. The shifting of the peaks at 929.69, 906.54, and 748.38 cm$^{-1}$ to 940.50, 900.10, and 750.55 cm$^{-1}$, respectively, is probably due to the interaction of WGB and F$^-$ ion by electrostatic attraction. The shift of peak at 651.99 cm$^{-1}$ to 655 cm$^{-1}$ could be due to the lattice vibration mode [43, 44].

4.1.2. SEM and EDX analysis

The Scanning Electron Microscopy (SEM) analysis was used to study the surface morphology of the adsorbents. Fig. S1 showed fluoride-loaded and fresh mass of WGB. Fig. S1(a) demonstrated that WGB had disparate surfaces with significant pores spaces, which could offer extended sites for physical or chemical adsorption of F$^-$ ions. Fig. S1(b) indicated that the pores were completely wrapped due to the assumption that adsorption and accumulation of fluoride from layers which settled on the irregular jagged surfaces. The data which is generated by EDX analysis consists of spectra with peaks corresponding to the different elements in the WGB sample. EDX spectra of WGB given in Fig.S2 shows the elemental composition of WGB which indicates the presence of O, Ca, Si, Al, Fe, Mg, Na, K, and S.
4.2. Fluoride Removal

So as to investigate the optimum favorable conditions for maximum fluoride removal using WGB as a sorbent material, the effect of contact time, pH, and WGB dose were carefully considered in this study as the key parameters. However, a set of preliminary batch experiments were carried out to investigate the effect of agitation rate on fluoride uptake by WGB. The results (data not shown) demonstrated that no tangible effect was observed and the percentages removal of fluoride was comparable using four different agitation rates including 100, 150, 200, and 250 rpm. Accordingly, 200 rpm was applied in all batch experiments because at this speed, the removal efficiency was relatively the highest, then, it remained stable in spite of increasing the speed, under the experimental conditions.

4.2.1. Effect of contact time

The times of equilibration in the range of 5-180 min were carried out as a set of batch experiments to estimate the time duration required to achieve equilibrium. The results demonstrated that the process of fluoride removal by WGB was relatively a rapid process. The biphasic profile of the fluoride removal involved two sections; a rapid removal rate within 30 min followed by slow removal rate until achieving equilibrium at 90 min as given in Fig. 3(a). The effect of contact time on the fluoride removal by WGB was determined using initial concentration of 10 mg F/L, pH 6, and 0.5 g/100 mL of WGB.

4.2.2. Effect of pH
The pH of the aqueous solution is a vital essential parameter that effects the sorption of ions at the solid-liquid interfaces. The effect of pH on fluoride adsorption onto WGB surface was determined via sets of experiments that used initial fluoride concentration of 10 mg F/L and maintaining pH at values of 3, 4, 5, 6, 7, 8, 9, and 10. Fig. 3(b) presents the effect of pH on the fluoride adsorption onto the WGB. The results demonstrated that the uptake of fluoride species increased with increasing the pH. However, at pH values higher than 8, the removal efficiency of fluoride ions decreased. This could be assigned to the fact that the sorbent surface sites at higher pH will take more negative charges symbolized by OH- ions which would meaningfully reject the negatively charged F- ions in the solution.

4.2.3. Effect of WGB dose
One of the important factors that affect the sorption equilibrium is the sorbent dose. As mentioned earlier in section 2.3, several doses of WGB were applied in this study to determine the optimum dose for best removal of fluoride. The results revealed that 3 g of WGB was the optimum value for a highest removal efficiency of fluoride up to 82% at pH 8 and 90 min contact time as shown in Fig. 3(c). Increasing the WGB dose will lead to increase of fluoride uptake capacity. This could be assigned to the fact that more sorbent surfaces or more active sites were available for the fluoride uptake by increasing the WGB dose. These results demonstrated a pretty agreement with the profile of fluoride sorption onto natural clay as reported by Ramdani et al. [44]. However, when the dose of the adsorbent exceeds 3g/100 mL, the fluoride removal efficiency didn’t exhibit an obvious increase. This observation could be due to the mass transfer resistance of fluoride species from the bulk of the solution to the WGB surfaces. This could
explain that once equilibrium was achieved, a constant pattern of the fluoride percentage uptake will be clearly observed. It seems that increasing the WGB amounts will cause them to lay up over one another and reduce the active site for sorption [32, 45].

**Fig. 3.** Profile of fluoride removal percent at different (a) contact times, (b) pH, and (c) dosage

### 4.3. Sorption Isotherms

As mentioned earlier, the experimental adsorption data were fitted with Freundlich and Langmuir isotherm models. Table 1 illustrates the constants values estimated using the linear form of the isotherm models. It has been noticed that values of the coefficient of determination \( R^2 \) were potentially higher for Freundlich model compared with the same for Langmuir model suggesting applicability of Freundlich isotherm model as shown in Fig. 4.

The constant \( N \) provides an indication of how favorable the adsorption processes were. According to Valko et al. [46], the slope \( I/N \) is the measure of adsorption intensity or surface heterogeneity which represents the deviation from linearity of adsorption as follows: if the value of \( I/N =1 \), the adsorption is linear, \( I/N < 1 \), it is a chemical adsorption process, if \( I/N > 1 \), the adsorption is a favorable physical process and it is cooperative. Hence, in this study the value of \( I/N \) was found to be 0.8335, indicating that the fluoride adsorption onto WGB was chemical and based on the fact that the Freundlich isotherm model describes the physicochemical adsorption onto the heterogeneous surfaces as reported by Chassapis et al. [47].

**Fig.4.** Plots of the adsorption isotherms.
4.4. Column Test

The effect of bed thickness varied from 0.05 to 0.75 m in the down gradient of the bed for at a flow rate of 20 ml/min is showed in Fig. 5. It is obvious that WGB bed exhibits better F⁻ uptake with increasing its thickness. This is due to the fact that F⁻-loaded solution has a higher retention time which permits a best adsorption process. However, it seems that this WGB bed started saturation with increasing the travel time. This indicated that the F⁻ retardation factor ($R_F$) was reduced, and a decrease in the WGB functionality towards F⁻ ions removal was occurred. The performance of WGB bed could be defined as the required duration to keep the concentration of pollutant down gradient of the bed as less than the maximum fluoride level (MFL) that could be present in drinking water (0.001 kg/m³) [7]. The performance of WGB bed increased with increasing its thickness, for example, the bed of thickness 0.75m had a higher operation time up to 13 days in comparison with 0.3m bed thickness which had an operation time of 4 days, since the outflow of F⁻ ions concentration from the 0.3m-thickness bed achieved maximum fluoride level faster than the bed of thickness 0.75m as illustrated in Fig.5.

Fig. 5. Relationship of fluoride concentration and time within the thickness of the WGB bed.

The profiles of fluoride concentration predicted by COMSOL software along the WGB fixed bed column ($x = 0.75m$) at flow rate values of 5, 10, and 20 mL/min are given in Fig. 6 at several time intervals. This figure demonstrates the importance role of WGB bed in hindering and confining the propagation of the fluoride-loaded plume. Moreover, it seems that the propagation of the contaminant front will increase with increasing the flow rate.
Fig. 6 Calculated concentration of F- along with the length of the column at different flow rates

4.5. Experimental and Predicted Results

The predicted and experimental results for the adsorption of fluoride were compared during the migration of the contaminant plume at different time periods and flow rates 15 and 25 mL/min along the adsorption column as depicted in Fig. 7. It is obvious that there is a good matching between the predicted and experimental results. Additionally, the root mean squared error (RMSE) was used in this study as a statistical tool to find the degree of agreement between these values [48]. Values of RMSE were ≤ 0.0398 confirming a very good agreement between predicted and measured values.

Fig. 7. Comparison between the predicted and experimental results.

4.6. The Prospects for Recycling Brick Waste Material

The application of available cost effective or no cost materials for the removal of numerous pollutants including fluoride removal from wastewater has been widely studied during recent years. All over the world, especially in the developing countries, brick waste are available in excessive amounts as abundant demolition wastes materials. These waste products can be recycled in a wholly practical and ecological manner, thus reducing pollution and benefiting the environment and the economy by reducing waste as well. Results obtained in this study indicate that the granular brick waste materials could be successfully applied for fluoride removal from water. A comparison between the removal efficiency of fluoride by the granular brick waste and
different adsorbents reported in previous studies are presented in Table S1.

5. Conclusions

This study investigated the ability of new application of waste granular brick (WGB) for fluoride uptake from aqueous solutions in fixed bed running in a continuous mode. The approach was reliable, easy to be applied with a significant potential for fluoride removal. Results revealed that unmodified WGB can be used effectively for fluoride removal from aqueous solution. Batch test results demonstrated that maximum removal efficiency of fluoride was found to be 82% using 10 mg/L initial concentration of F⁻, WGB dose of 3 g/100 mL at pH 8 and contact time 90 min. The adsorption followed the Freundlich adsorption isotherm model with a coefficient of determination 0.9565. Results of the column test demonstrated that the performance of WGB fixed bed for fluoride removal increased with increasing the bed thickness. A very good agreement between predicted and measured values was observed. This study is extended to investigate: (1) the potential approach for regeneration of the exhausted fluoride-bearing adsorbent, (2) the application of the suggested adsorbent for fluoride removal from real samples of groundwater and wastewater.

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Author Contributions

Z.T.A-A (Associate professor) conducted part of the experimental work, carried out the simulation work using the COMSOL software, and participated in writing the manuscript. Z.Z.I (Professor) suggested the research technical plan, carried out part of the experimental work, wrote the manuscript and revised it.

References


**Fig. 1.** Schematic diagram of the lab-scale adsorption column.
Fig. 2. FT-IR of brick waste before and after fluoride loading.

- Contact time
- \( Co = 10 \text{mg/l}, \text{Dose}= 0.5g/100\text{ml}, \text{pH}=6, \)
Fig. 3. Profile of fluoride removal percent at different (a) Contact times, (b) pH, and (c) Dosage.

Figures:
- **b- pH**: pH profile with removal percentage. Conditions: Co=10mg/l, Dose=0.5g/100ml, t=90min.
- **c- Dosage**: Dosage profile with removal percentage. Conditions: Co=10mg/l, t=90min, pH=8.
**Fig. 4.** Plots of the adsorption isotherms.

**Fig. 5.** Relationship of fluoride concentration and time within the thickness of the WGB bed.
Fig. 6. Calculated concentration of F- along with the length of the column at different flow rates.

Fig. 7. Comparison between the predicted and experimental results.
Table 1. Estimated Parameters for Freundlich and Langmuir Sorption Isotherms

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