



Use of Eggshell as a Low-Cost Alternative Adsorbent for Elimination of Fluoride from Groundwater

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Article Info	ABSTRACT
Article type: Research Article	This paper aims to study the possibility of providing a low-cost alternative for the adsorbents used in the fluoride adsorption from water by using eggshells. Indeed, eggshells were used as an adsorbent for fluoride adsorption from a drinking groundwater sample containing (2.14 mg/l) of fluoride. The eggshells were crushed and sieved into three particle sizes (0.2, 0.5, and 1mm) and then heated at different temperatures ranging from 100 to 250°C. XRD, FT-IR, pHpzc, and TG/DTA analysis were used for the characterization of the adsorbents. Adsorption batch experiments were carried out to determine the adsorption capacity of eggshell powder such as, particle size, preparation temperature, contact time, and adsorbent dose. A spectrophotometer UV-VIS was used to assess fluoride removal efficiency. The eggshell powder heated at 250°C with 0.2mm of particle size was found to be the most efficient adsorbent, with a maximum fluoride removal efficiency of 51.4%, a maximum adsorption capacity of 0.052mg/g, and a residual fluoride concentration of 1.1mg/l within 150 minutes. The data of the adsorption kinetic on ES250°0.2 were successfully fitted with the pseudo-second-order model with a satisfying coefficient of determination ($R^2=0.993$). The results of the intra-particle diffusion model showed a multi-linearity, revealing that the diffusion of fluoride into the adsorbent was by two stages with diffusion rate constants of $K_i = 0.007$ (mg /g/min ^{1/2}) and $K_i = 0.001$ (mg /g/min ^{1/2}) for the first and second stage respectively. An adsorbent dose of 1.5g and 1 hour of contact time were sufficient to decrease fluoride concentration from 2.14 to 1.1mg/l.
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INTRODUCTION

Groundwater is vital source for the water supply of cities in Algeria. The continental intercalary CI and the complex terminal CT are two aquifer systems located in the Algerian Septentrional Sahara. These latter are holding a large volume of groundwater (50 billion m³) which represents the main water resource of Algeria. However, it is characterized by excessive mineralization, usually associated with hardness and high fluoride concentrations (Aissa and Boutoutaou, 2017) as a result of leaching minerals from rocks.

Fluoride is a hazardous inorganic pollutant that exists in nature and poses serious health risks to humans (Chouhan and Flora, 2010). Fluoride in drinking water is widely prevalent, and its excessive consumption (>1.5mg/l) (World Health Organization, 2022) causes the tooth and

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bone structure to lose calcium, making cavities deteriorate for the rest of one's life (Whitford, 1996). Thus, we are witnessing silent fluorosis among Algerian citizens due to the excessive intake of fluoride-laden waters.

In order to provide safe drinking water that meet WHO standards, several researchers attempted to remove fluoride from drinking water by numerous engineering processes such as ion exchange (Viswanathan et al., 2013), coagulation (He et al., 2016), electrocoagulation, reverse osmosis (Owusu-Agyeman et al., 2019), nano-filtration (Shen et al., 2016), and électrodialyses (Aliaskari and Schäfer, 2021). Besides this, several novel materials were used for fluoride removals such as activated alumina (Samrat et al., 2020), hydroxyapatite (Mourabet et al., 2015), and bentonite (Annan et al., 2021). However, these techniques and materials have application limitations especially in underdeveloped countries due to their high cost, complexity, high installation and maintenance costs, and sludge generation. Furthermore, Several fluoride adsorbents are subjected to chemical activation and doping during their preparation. It is worth noting that the chemically modified adsorbents can alter the final parameters of the treated water, such as changing the concentration of co-ions, modification of the final pH, as well as leaving traces of the activating agents in the water after treatment. Therefore, additional treatment is necessary to adjust these parameters and remove the trace elements. Hence, it is imperative to use processes and materials that have an acceptable cost and a high fluoride removal capacity.

Eggshell is an eco-friendly material, which had been a subject of interest for many studies due to its constituent and its availability in abundant quantities. Eggshell is a bio-ceramic composite that is high in mineral salts. It is mostly composed of calcium carbonate (CaCO_3) (94%), calcium phosphate (1%), magnesium carbonate (1%), and organic components (4%) (Murakami et al., 2007). Thus, Eggshell can be a raw material to replace not only CaCO_3 extracted from non-renewable sources such as limestone (Spelta and Galdino, 2018; Tizo et al., 2018), but it can also be a precursor for calcium oxide (CaO) when it is subjected to heat treatment (Khatibi et al., 2021) (Fan et al., 2016) (Tangboriboon et al., 2012). The obtained CaO was used as a bio-sorbent for F⁻ removal in many studies (Saini et al., 2021) (Lee et al., 2021). Using fluoride synthetic solutions, Bhaumik et al. investigated the fluoride adsorption on eggshell powder. Fluoride adsorption on eggshell powder was shown to be pH-dependent, with an optimal removal efficiency at pH 6.0. The data from the adsorption equilibrium were successfully fitted to the Langmuir isotherm model (Bhaumik et al., 2012). For the adsorption of fluoride, Lunge et al. used an aluminum/eggshell composite. The results showed that aluminum/eggshell composite, with an adsorption capacity of 37 mg/g, was an effective fluoride adsorbent. Additionally, the experimental results showed that the Langmuir isotherm model more accurately predicted fluoride adsorption in a monolayer (Lunge et al., 2012). Lee et al. conducted a similar investigation. Eggshells that had undergone thermal treatment were utilized to absorb fluoride. The ideal treatment temperature was determined to be 800°C, and fluoride adsorption on ES-800°C reached 70% of adsorption equilibrium in 15 minutes (Lee et al., 2021).

Despite the significance of the fluorosis issue in the area and the study well's contribution to the region's drinking water supply, neither the studied well nor fluoride adsorption using eggshell powder as an adsorbent have been the subject of any scientific research to date at the same study area level. Thus, In this work, we opted for eggshell powder as a possible low-cost alternative for the adsorption of fluoride from the groundwater of Ain Ben Noui, with an undemanding preparation at low temperature and without chemical activation, as well as a straightforward application of the adsorbent on a domestic scale and this to make a small contribution to reducing the risks of fluorosis in the study region. Eggshells were sieved in three different particle sizes and heated at four different heating temperatures. XRD, FTIR, pHpzc characterization studies were carried out for the eggshell powder before and after it was heated at 250°C. A comparative essay of the fluoride adsorption on eggshell powder was conducted to evaluate the impact of the particles' size and heating temperature on the fluoride adsorption

capacity of the adsorbent. The essay also aimed to determine the most efficient adsorbent. Furthermore, the effect of contact time and adsorbent dosage studies were performed with the most efficient adsorbent. Three adsorption kinetic models (pseudo-first-order, pseudo-second-order, and intra-particle diffusion) were of use in the analysis of the adsorption kinetic and characteristics.

MATERIALS AND METHODS

The region of Biskra is located in the South-east of Algeria, and it extends from the Chott Melghir area in the South-East to the Eastern Erg in the South-West (latitude 34° 52' N, longitude 5° 38' E), its altitude is 125 meters above sea level. The region of Biskra is a semi-arid region that is characterized by a low amount of precipitation.

Geological and hydrogeological studies have made it possible to highlight the existence of several aquifer reservoirs. These aquifers belong to the Quaternary, Mio-Pliocene, Lower Eocene, Upper Senonian (Maastrichtian), and Albian. The Albian aquifer also called the intercalary continental aquifer (IC), is by far the most important reservoir in the region since it covers most of the northern Saharan territory (600,000 Km²), with a water capacity of about 50,000 billion cubic meters (Bouziane and Labadi, 2009).

The drinking groundwater sample was collected from a borehole located in the municipality of Ain Ben Noui, and from which the drinking water is distributed to the eastern neighborhoods of the city of Biskra.

The fluoride concentration of the groundwater sample before and after treatment was determined by SPADNS Spectrophotometric method using a spectrophotometer UV-VIS (Hach, model DR 6000) and SPADNS reagent for fluoride. Measurements were taken at a wavelength of 580 nm.

The Dosage of bicarbonate (HCO³⁻), calcium (Ca⁺²), carbonate (CO₃⁻²), magnesium (Mg⁺²), and chloride (Cl) in the groundwater sample was by the standard method of Rodier (Rodier et al., 2009). The pH, temperature, and electrical conductivity (EC) were monitored on a multi-parameter (WTW, model Multi 350i).

The agitation and the vacuum filtration of the adsorption experiment's samples was conducted by magnetic stirrers (Ika, model RCT basic) and a diaphragm vacuum pump (GM-0.50) equipped with a filtration flask and a cellulose membrane filter (0.45 μm).

Eggshells were collected from local butcher shops, and in order to remove contaminants, they were rinsed numerous times with boiling and distilled water. The raw materials were separately dried for 24h at 50°C. After that, they were crushed and grounded by a mortar grinder (RETSCH., Model RM200), then sieved into three different particles sizes (0.2mm, 0.5mm, 1mm). The sieved material was separated into three samples with a defined particles size. Each sample was then divided into five other samples, one sample was kept as raw material, and the four other samples were placed in a muffle furnace and subjected separately to a different heating temperature (100° C, 150° C, 200°C, 250°C) with a heating rate of 10°C/minute. Heating at the preset temperature was kept up for an hour. The resulted adsorbents were rinsed again with distilled water until pH=7, none of the chemical agents were added. The resulted materials were named according to their precursor (ES for Eggshell), the heating temperature that they were subjected to (ES100°), and their particles size (ES100°0.2). Concerning the raw sample, it was simply named as follows: RE for Raw Eggshell.

X-ray diffraction (XRD) analysis was performed to examine the crystalline species contained in the biosorbents, by using Bruker model D8 Advance X-ray diffractometer. Diffractograms were obtained with a step of 0.1° per minute in the range of 10° ≤ 2θ ≤ 70°.

By using an Infrared Spectrometer (Shimadzu., model IRSpirit), the functional groups on the surface of the adsorbent were identified. The crushed particles were scanned in transmittance

mode at room temperature over a wavenumber range of 4000 to 400 cm^{-1} .

The thermal stability (TG/DTA) of the material was investigated using a thermal analysis system (Setaram. model LABSYS evo) under N_2 gas flow ($100 \text{ cm}^3\text{min}^{-1}$) at a heating rate of 10°C per minute.

The point of zero charge (pHPZC) was identified using the salt addition method. The experiment was carried out as follows: A solution of 0.01 N of NaCl was prepared. Eleven 100 mL capped Erlenmeyer flasks were used for this study, and each flask contained 50 ml of NaCl solution. A variation of the initial pH (from 2 to 10) was made respectively for each flask with NaOH (0.1 N) and HCl (0.1 N) solutions. Further, A dose of 1 g of the adsorbent was introduced to each flask then subjected to agitation for 1 hour under a constant orbit (120 rpm at 25°C), after that a vacuum filtration was made to each flask.

Adsorption batch experiments were carried out as a preliminary essay to assess the fluoride adsorption capacity of the adsorbents and their potential of usability in fluoride-affected regions, as well as the effect of the particles size and thermal treatment temperature of the adsorbents on the fluoride removal ability. The efficiency of the prepared sorbents was investigated by using 100 mL capped Erlenmeyer flasks. A dose of 1g of each adsorbent was separately mixed with 50ml of Ain Ben Noui's groundwater containing 2.14 mg/L of fluoride. The initial pH solution was $\text{pH}=7.35$. The Erlenmeyer flasks were agitated for 1hour under a constant orbit 120 rpm at 25°C after that they were collected then subjected to a vacuum filtration.

It is noteworthy that the main objective of this essay was to determine the most efficient adsorbent to be used in further adsorption experiments.

Kinetic sorption experiments were performed on 100 mL capped Erlenmeyer flasks. Each flask contained a dose of 1g of the adsorbent and 50 mL of groundwater with an initial fluoride concentration and a pH solution of 2.14 mg/L and 7.35, respectively. The samples were mixed using Magnetic stirrers (Ika., model RCT basic) 120 rpm at 25°C , and the steering time was different from a sample to another, varying from 5 to 180 min. The samples were collected and subjected to vacuum filtration.

Many kinetic models are available to describe the adsorption kinetic's parameters, such as the rate constant of kinetic and the characteristic of the adsorption mechanism (physisorption or chemisorption). The data of the adsorption kinetic were fitted to the following kinetic models: pseudo-first-order (Eq.1) (Lagergren, S, 1898), pseudo-second-order (Eq.3) (Ho and McKay, 1998), and intra-particle diffusion model (Eq.4) (Weber and Morris, 1963).

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

Where q_e and q_t are the mass of sorbet fluoride per unit mass of the adsorbent (mg/g) at equilibrium and at any time t , respectively and k_1 is the pseudo-first-order rate constant(1/h).

$$q_e = \frac{(c_e - c_0) \cdot v}{m} \quad (2)$$

Where C_e is the fluoride concentration at equilibrium (mg/l), C_0 is the initial fluoride concentration (mg/l), v is the solution volume (l), and m is the masse of the adsorbent (g). Pseudo-second-order kinetic equation is given by (Ho and McKay, 1998) as follow:

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot t} \quad (3)$$

Where k_2 is the pseudo-second-order rate constant(1/h).

Intraparticle diffusion is applied to determine the nature of the rate-controlling step. The intraparticle diffusion model is represented by the following Weber and Morris equation (Weber and Morris, 1963).

$$q_t = k_i \cdot t^{0.5} + c \quad (4)$$

Where, C is the intercept, related to the thickness of the boundary layer and K_i is the intraparticle diffusion rate constant. According to this model, to this model, if the adsorption of the adsorbate is controlled by the intraparticle diffusion process, a plot of $qt = f(t^{1/2})$ show a straight line (Weber and Morris, 1963). However, if the data show a multi-linearity, it implies that intraparticle diffusion is not only the rate-controlling step (Weber and Morris, 1963).

The effect of the adsorbent dose was studied on 100 mL capped Erlenmeyer flasks in which the adsorbent's dose was varied from a flask to another (from 1 to 5 g). 50 mL of Ain Ben Noui's groundwater containing 2.14 mg/L of fluoride (initial pH 7.35) was added to each flask and then placed on a magnetic stirrer for 1h under a constant agitation (120 rpm at 25 °C). The samples were collected then subjected to a vacuum filtration.

RESULTS AND DISCUSSION

Table 1 shows the results of fluoride dosage of the Ain Ben Noui groundwater sample; according to these results, the groundwater sample is characterized by a fluoride tenor above (1.5mg/l) WHO standard for fluoride.

Figure 1 shows XRD patterns of raw eggshell powder and ES250°0.2, respectively. The XRD patterns and diffraction peaks were analyzed and identified using High Score plus software.

X-ray diffraction patterns of both samples show peaks that are characteristics of calcite (CaCO_3) and correspond to JCPD card for calcite (5-0586). The results confirm that calcium carbonate is the major component of eggshell powder (Choudhary et al., 2015).

The diffraction peaks of the raw eggshell powder observed at $2\theta = 23.1, 29.6, 31.5, 36.1, 39.6, 43.3, 47.3, 47.70, 48.7, 56.6, 57.6, 60.8, 63.22, 64.8, 65.7, 69.4, 70.4, 73.0$ and 77.3 correspond to the calcite Rhombohedral crystal planes of (0 1 2), (1 0 4), (0 0 6), (1 1 0), (1 1 3), (2 0 2), (0 2 4), (0 1 8), (1 1 6), (2 1 1), (1 2 2), (2 0 8), (1 1 9), (1 2 5), (3 0 0), (0 0 12), (2 1 7), (0 2 10), and (1 1 12), respectively. A small modification in the structure of XRD patterns had occurred while increasing temperature to 250°C. It was observed that the intensity of XRD peaks of eggshell powder had decreased, and two X-ray reflections peaks appeared at $2\theta = 61.7$, and 76.4 which they correspond respectively to (1 1 9) and (2 2 0) Rhombohedral crystal planes of calcite. On the other hand, an increase in the intensity of the new reflection peaks was observed while the reflection peaks of raw eggshell powder were decreasing. The same observations were seen in a previous work of Engin et al. (Engin et al., 2006).

FTIR spectra of both raw eggshells (RE) and ES 250°0.2 are presented in Figure 2. It is worth noting that the FTIR spectrum of both samples have the characteristic bands as natural calcites (CaCO_3), and they do not show many dissimilarities as the heating temperature increases.. The observation of the FTIR spectrum of both samples shows a strong peak at 1418cm^{-1} and a peak

Table 1. Fluoride concentration of the drinking groundwater sample.

Region	Water table	Drill	T°	pH	CE	TH(F°)	Ca ⁺² mg/l	Mg ⁺² mg/l	HCO ₃ ⁻ mg/l	Cl ⁻ mg/l	F ⁻ mg/l
Biskra	Phreatic	Ain Ben Noui AEP	18.3	7.35	7.2	182.54	416	187	234	953	2.14

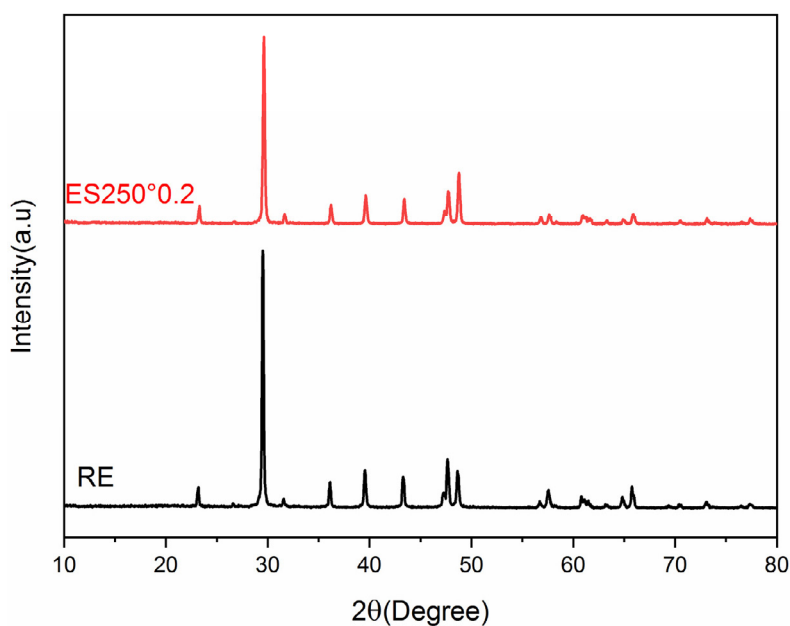


Fig. 1. XRD pattern of RE 0.2 and ES250°0.2.

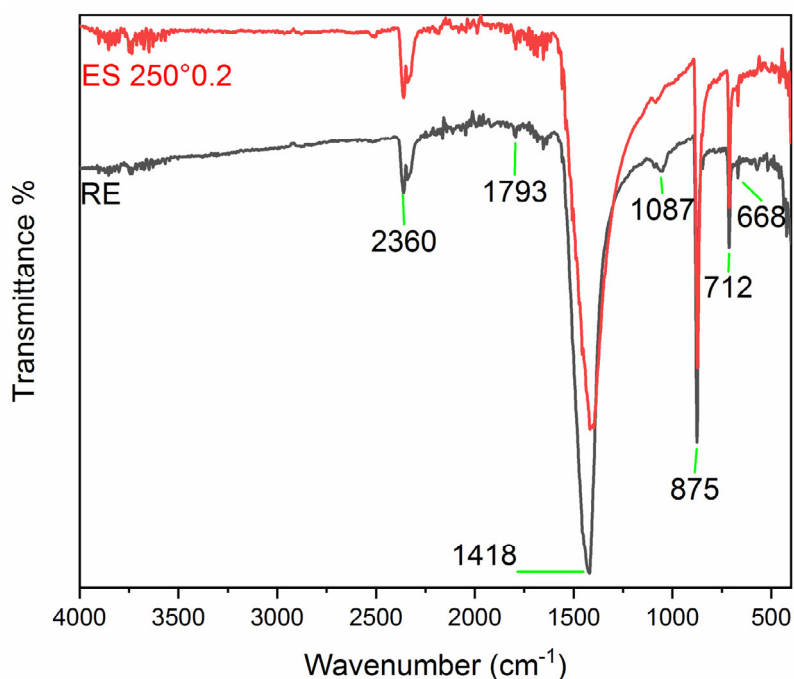


Fig. 2. FTIR spectrum of RE 0.2 and ES250°0.2.

at 712 cm^{-1} attributed to the vibration of CO_3^{2-} molecules (Berzina-Cimдина and Borodajenko, 2012; Goli and Sahu, 2018; Tsai et al., 2006). There are also two other peaks at 1087 cm^{-1} , and 875 cm^{-1} which referred to the presence of CO_3^{2-} molecules probably associated with calcium (calcite, CaCO_3) (Goli and Sahu, 2018; Pereira et al., 2017). On the other hand, the presence of amides and amines in both samples were represented by peaks at 1793 cm^{-1} , and 668 cm^{-1} respectively (Torres-Mansilla and Delgado-Me, 2017). The peak observed at 2360 cm^{-1} was attributed to the carbon dioxide stretching vibration group ($\text{O}=\text{C}=\text{O}$) (Hamidi et al., 2017).

Figure 3 shows the TG and DTA curves of the thermal degradation of eggshell in a range of temperatures from 21°C to 500°C. The obtained thermogram has been divided into two stages. The first stage shows a progressive weight loss, which occurred from room temperature up to 250°C. The mass loss observed at this stage was around (1.05mg), which was due to the removal of moisture and the evaporation of the adsorbed water molecules on the surface of the eggshell particles (Ait Taleb et al., 2017; Lee et al., 2021; Ooi et al., 2007). The second stage shows a significant increase in weight loss around (4mg), which occurred from 250°C to 500°C due to the degradation of organic matters (collagen, proteins, and carbohydrates) present in membranes (Castro et al., 2019; Ooi et al., 2007).

The DTA curve shows four endothermic peaks at 120°C, 233°C, 400°C, and 490°C, as well as two exothermic peaks at 345°C and 420°C. The endothermic peaks at 125°C and 240°C are due to the removal of moisture and adsorbed water, respectively. The endothermic peaks at 400°C and 490°C correspond to the degradation of organic matter. The exothermic peak at 420°C was probably due to the beginning of the decomposition of carbonate.

The pH_{PZC} is a pH point at which the charges on the adsorbent surface are equal. The surface charge is a significant factor; it helps to understand the mechanism of adsorption. Adsorption of anions and cations depends on the pH of the solution. It is well known that at a lower pH, the presence of H^+ ions on the adsorbent's surface favors the adsorption of anions. Whereas, at a higher pH, the presence of OH^- ions favors the adsorption of cations (Bhaumik et al., 2012). Therefore, when $\text{pH} < \text{pH}_{\text{PZC}}$, the adsorbent's surface will be positively charged due to the protonation of the functional groups of calcite. Otherwise, when $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of the adsorbent will be negatively charged due to the deprotonation of the functional groups of calcite (Nigri et al., 2017), (Medellin-Castillo et al., 2007).

The pH of point zero charge of ES 250°C is illustrated in Figure 4. The pH_{PZC} of the ES 250°C was 6.5. According to the pH of the groundwater sample ($\text{pH}=7.35$), the surface charges of ES 250°C is negatively charged, improving the electrostatic attraction of cations.

The results of the preliminary essay are summarized in Table 2 as well as in Figure 5. According to the results, we noticed that the residual fluoride concentration of the samples treated with

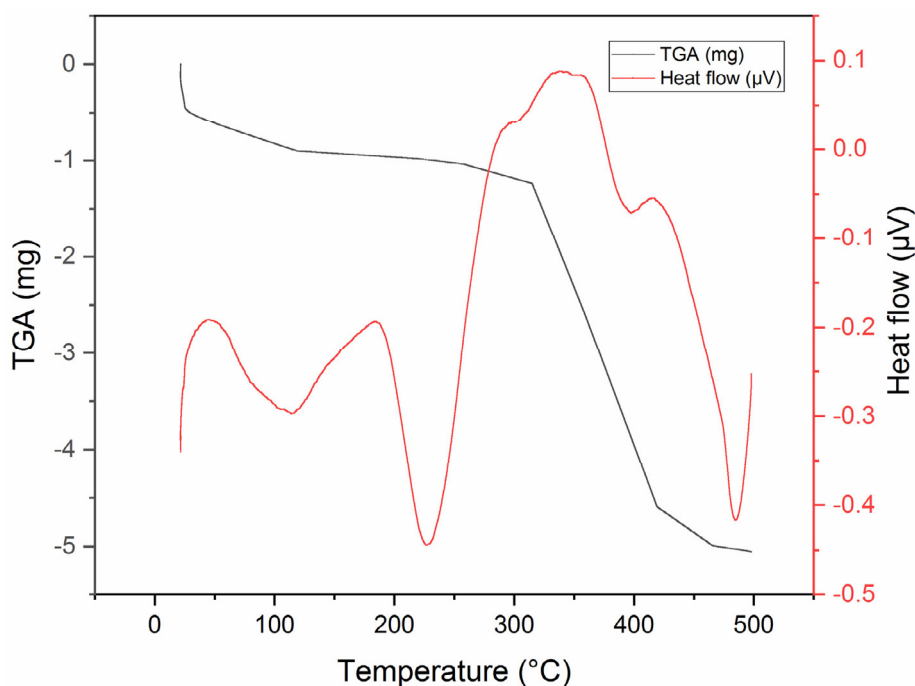


Fig. 3. TGA/DTA analysis of eggshell powder.

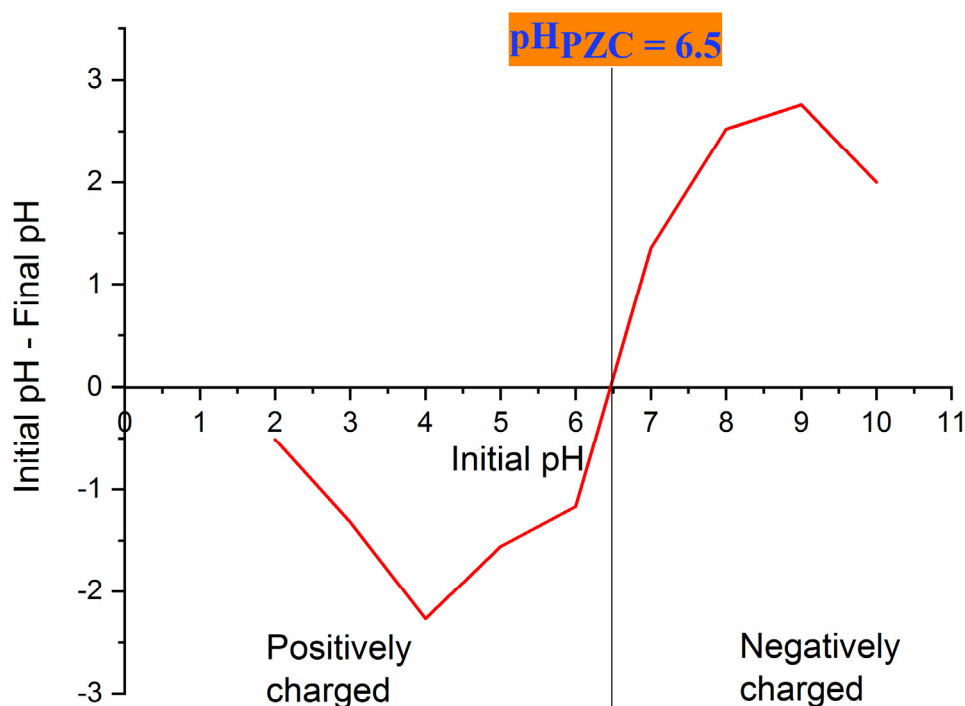


Fig. 4. Point zero charge of ES 250°0.2.

Table 2. Summary of the fluoride adsorption onto eggshell adsorbents.

Adsorbent	Final pH	qt(mg/l)
0	7.35	0
RE 0.2	8.16	0.68
ES100°0.2	8.18	0.73
ES150°0.2	8.2	0.74
ES200°0.2	8.28	0.78
ES250°0.2	8.3	0.85
RE 0.5	7.66	0.49
ES100°0.5	7.74	0.61
ES150°0.5	7.83	0.66
ES200°0.5	7.85	0.7
ES250°0.5	7.97	0.71
RE 1	7.62	0.35
ES100°1	7.7	0.41
ES150°1	7.73	0.42
ES200°1	7.78	0.47
ES250°1	7.83	0.56

ES250° meets WHO standards for fluoride concentration in drinking water. However, particles size impacted slightly, the adsorption of fluoride, which reflects the different nature of results. Thus, the smallest the particles are, the higher the adsorption capacity is. Therefore, depending on the adsorbent's particle size, the fluoride adsorption capacities were classified as follows, $q_{0.2\text{mm}} > q_{0.5\text{mm}} > q_{1\text{mm}}$. These results agree with the results of several previous studies (Chatterjee

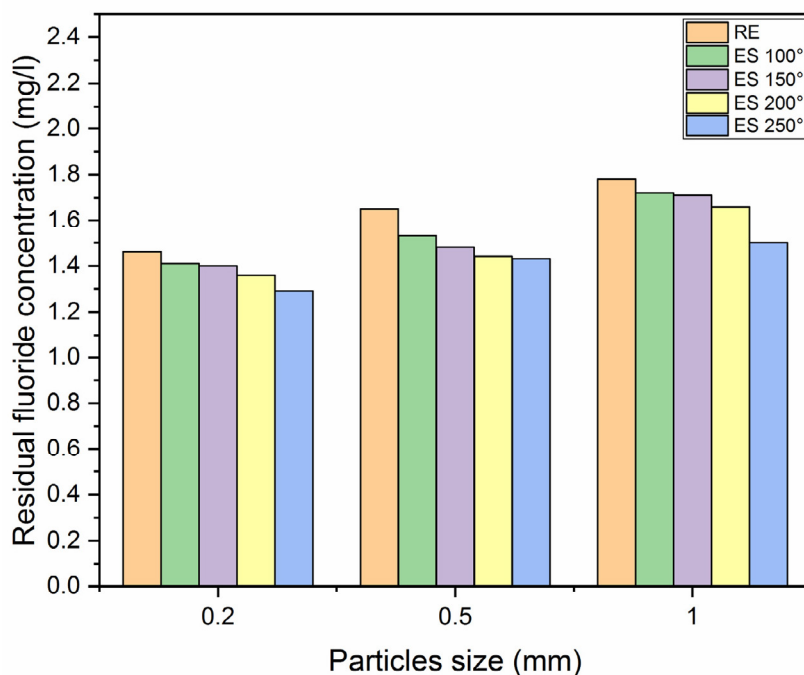


Fig. 5. Effect of the thermal treatment and particles size of the adsorbents on the residual fluoride concentration ($[F^-]_0 = 2.14 \text{ mg/l}$, $M_{\text{ADSORBENT}} = 1 \text{ g}$, $\text{Vol} = 50 \text{ ml}$, $\text{pH} \approx 7.35$, $\text{Contact time} = 1\text{h}$)

et al., 2018; Kaseva, 2006; Mutchimadilok et al., 2014; Srimurali et al., 1998), that concluded that fine adsorbent particles lead to a rapid adsorption rate at an earlier time, as well as a raise in the adsorption capacity.

Concerning the impact of heating temperatures, organic matters can also be responsible for the different nature of results. As it was observed in the essay's results, the adsorbent prepared at 250°C had a better fluoride adsorption capacity than the others, due to its low tenor of organic matter compared to the raw material. These results also agree with a previous study of Shahid et al. (Shahid et al., 2020), who reported that the presence of organic matter on the adsorbents or an inadequate elimination of organic matter can be a major reason for low adsorption efficiency.

The low sorption capacity of eggshell powder was due to its main component CaCO_3 that is known for its low affinity toward fluoride. It is well known that Hydroxides generally display a high affinity toward fluoride and that Ca(OH)_2 improves the elimination of fluoride through ions exchange and precipitation of calcium fluoride (Sternitzke et al., 2012).

Several studies (Bhaumik et al., 2012; Pérez et al., 2021) concluded that to increase fluoride removal by Eggshell powder, a thermal treatment over 800°C is needed, and that is due to the low fluoride adsorption capacity of eggshell powder specifically, samples prepared without any treatment conditions and carbonized at temperatures lower than 500°C (Bhaumik et al., 2012). We also note that fluoride adsorption capacity of eggshells increases as the calcinations temperature increases, and that is due to the transformation of CaCO_3 contained in eggshells into Ca(OH)_2 by calcinations process at high temperatures (over 800°C) (Pérez et al., 2021). Aside from that, the surface charges of the adsorbent and the fluoride adsorption capacity were controlled by the solution pH and the pH at the point of zero charge (pH_{PZC}) of the adsorbent. As it was shown in Figure 4, the pH_{PZC} of the raw eggshell powder and ES250°C was about 6.5. Thus, the pH solution ($\text{pH} = 7.35$) was higher than the pH_{PZC} . Therefore, the surface of the adsorbents has a greater number of deprotonated negative charges decreasing the fluoride adsorption capacity of the adsorbents and calcium fluoride formation and precipitation due to

competition between OH⁻ and fluoride ions F⁻, as well as repulsive forces between fluoride ions and negatively charged surfaces (Nigri et al., 2017).

Although the results consolidate the feasibility of applicability of ES250°C as an adsorbent for fluoride removal from groundwater and it is worth noting that the addition of the adsorbent did not affect the smell and taste of water, meaning that the adsorption of fluoride onto ES250°C can provide safe and reliable drinking water.

Finally, since that the ES250°0.2 appeared to be the most effective adsorbent, displaying the greatest fluoride adsorption capacity. Therefore, additional adsorption studies were performed with ES250°0.2.

From the results presented in Figure 6, a rapid decrease in the fluoride concentration from 2.14 mg/l to 1.29 mg/l was observed within 60 min. After that, the elimination of fluoride became slower, attaining equilibrium at 150 min with a minimum fluoride concentration of 1.1 mg/l. The optimum results of the essay are presented in Table 3.

Pseudo-first-order and pseudo-second-order kinetic models, as well as intra-particle diffusion model, were used to analyze the experimental data and describe the fluoride adsorption mechanism on ES250°0.2. The graphical representation and the calculated parameters of the pseudo-first-order, pseudo-second-order, and the intra-particle diffusion model are presented in Figure 7, Figure 8, and Figure 9, respectively. The calculated parameters of the three models are represented in Table 4 and Table 5.

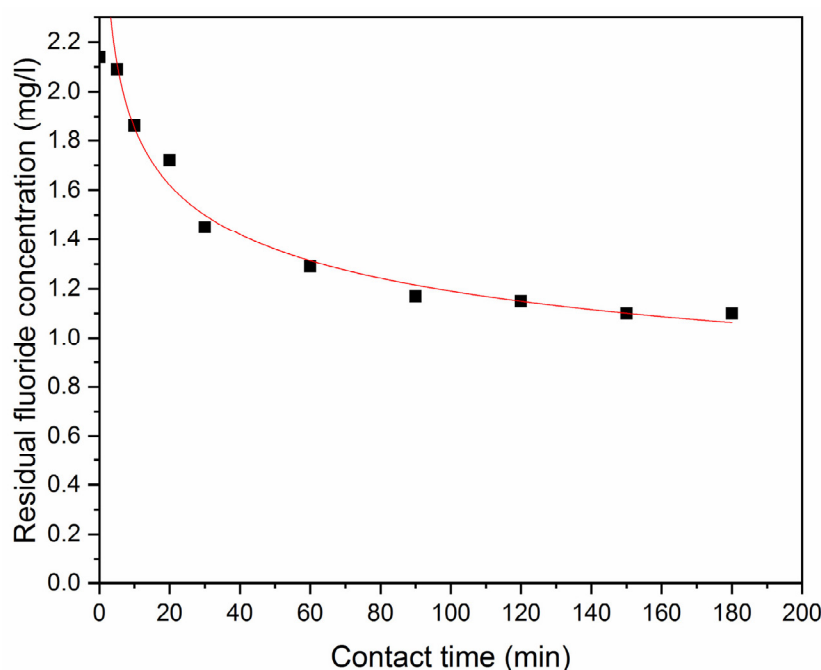


Fig. 6. Effect of contact time on the fluoride concentration ($[F^-]_0 = 2.14 \text{ mg/l}$, $M_{\text{ES } 250^\circ 0.2} = 1 \text{ g}$, $\text{Vol} = 50 \text{ ml}$, $\text{pH} \approx 7,35$)

Table 3. Effect of contact time on the fluoride adsorption by ES250°0.2

Contact time (minute)	5	10	20	30	60	90	120	150	180
Qt (mg/g)	0.002	0.014	0.021	0.034	0.042	0.048	0.049	0.052	0.052
[F]equilibrium								1.1	
Qe (mg/g)							0.052		
T _{EQUILIBRIUM}							150		

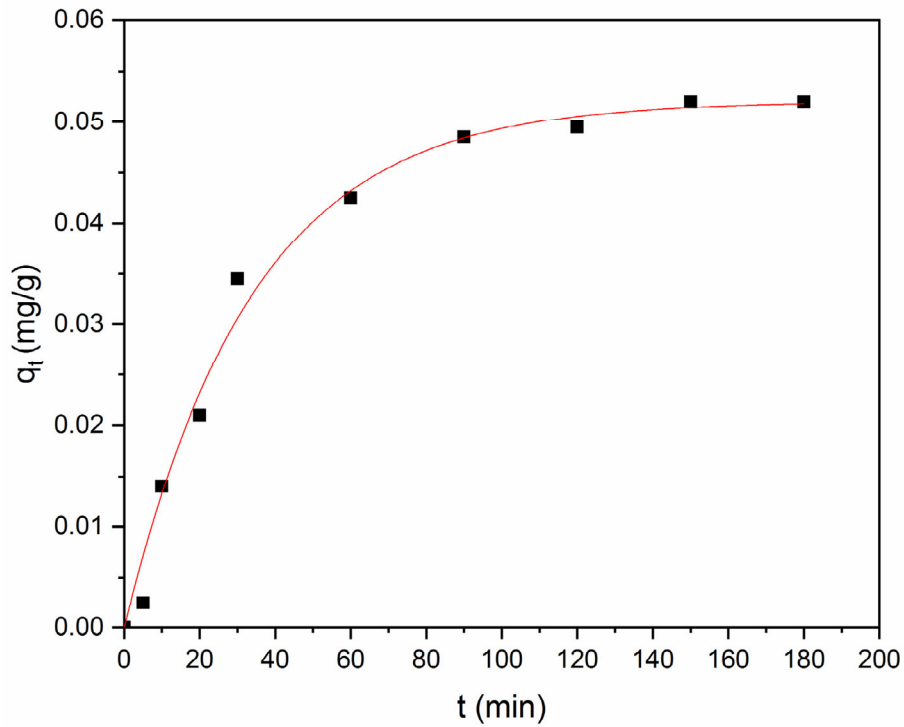


Fig. 7. Pseudo-first-order model of the fluoride adsorption kinetics on ES 250°0.2 mm ($[F^-]_0 = 2.14 \text{ mg/l}$, $M_{\text{ES} 250^\circ 0.2} = 1 \text{ g}$, Vol = 50 ml, pH $\approx 7,35$)

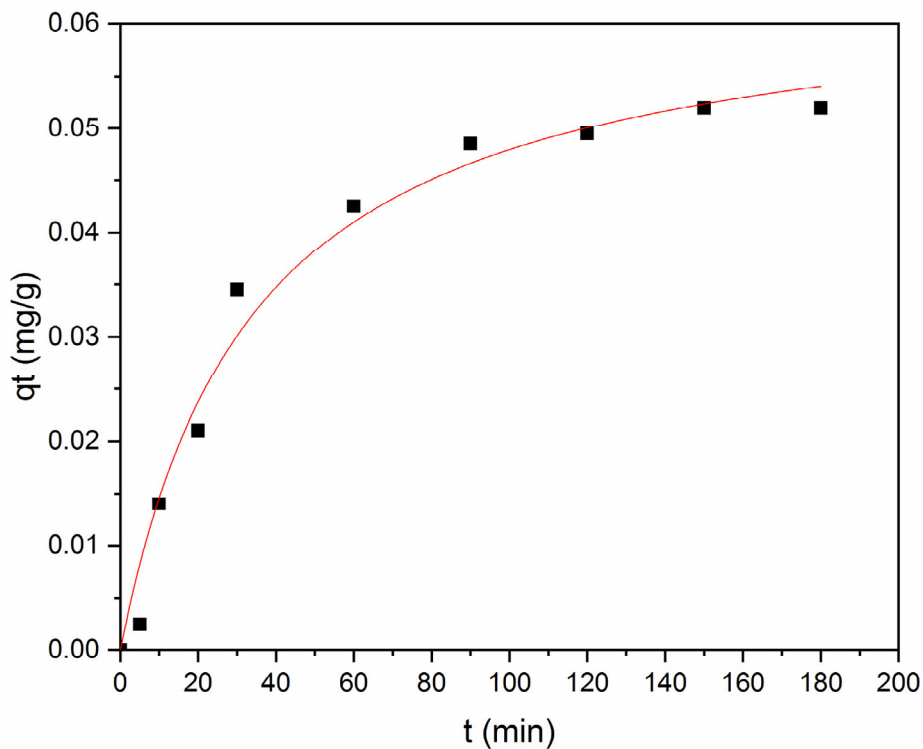


Fig. 8. Pseudo-second-order model of the fluoride adsorption kinetics on ES 250°0.2 mm ($[F^-]_0 = 2.14 \text{ mg/l}$, $M_{\text{ES} 250^\circ 0.2} = 1 \text{ g}$, Vol = 50 ml, pH $\approx 7,35$)

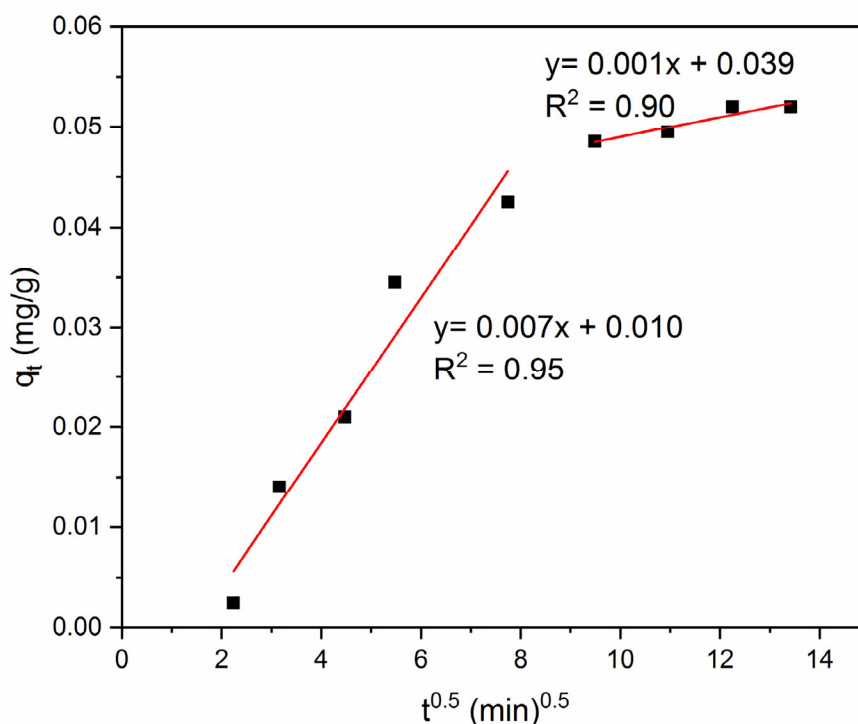


Fig. 9. Graphical representation of the intra-particle diffusion model of the fluoride adsorption kinetics on ES 250°0.2.

Table 4. Summary of the calculated parameters of the Pseudo-first-order and Pseudo-second-order models

Pseudo-first-order model				Pseudo-second-order model			
Qe exp (mg/g)	K ₁ (l/min)	Qe cal (mg/g)	R ²	Qe exp (mg/g)	K ₁ (l/min)	Qe cal (mg/g)	R ²
0.052	0.025	0.064	0.973	0.052	0.516	0.052	0.993

Table 5. The calculated parameters of the intra-particle diffusion model.

Stages	K _{INT} (mg /g/min ^{1/2})	Ci (mg/g)	R ²
First stage	0.007	0.010	0.95
Second stage	0.001	0.039	0.90

The graphical results of both models showed that the coefficient of determination of both models was satisfying, ($R^2=0.977$), for the pseudo-first-order model and ($R^2=0.993$) for the pseudo-second-order model. However, there is a difference between the experimental adsorption capacity and the calculated adsorption capacity of the pseudo-first-order model compared to the pseudo-second-order, which showed that there is a concordance between the calculated adsorption capacity and the experimental adsorption capacity ($q_{cal}=q_{exp}=0.052$), that indicates that the pseudo-second-order model is the best fitting model for the adsorption of fluoride onto ES250°0.2. These findings are consistent with previous studies (Bhaumik et al., 2012; Lee

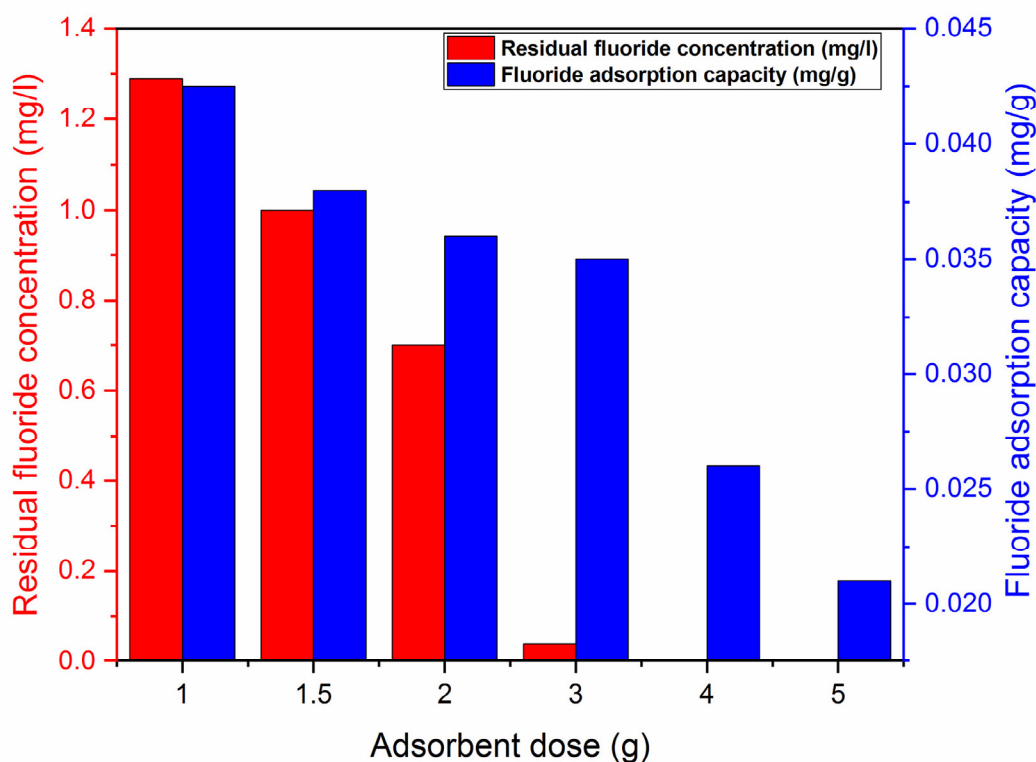


Fig. 10. Effect of the adsorbent dose on the adsorption capacity and residual fluoride concentration ($[F^-]_0 = 2.14$ mg/l, Contact time = 1h, Vol = 50 ml, pH ≈ 7.35)

et al., 2021; Xia et al., 2019), that concluded that the experimental data of fluoride adsorption on eggshell are satisfactorily fitted with the pseudo-second-order model. This suggests that the fluoride removal onto ES250 $^{\circ}$ 0.2 was by chemical adsorption (Ho and McKay, 1999) (Zhang et al., 2009), which implies the valence forces leading to the formation of a new compound which is calcium fluoride (CaF₂) (Lalley et al., 2016; Pérez et al., 2021).

The graphical representation of the intra-particle diffusion model (Figure 9) showed double linearity that reflects the existence of two stages of diffusion (Weber and Morris, 1963). The first stage is a rapid diffusion of the adsorbate from the solution to the external adsorbent surfaces causing, a rapid fluoride adsorption. The second stage is a diffusion of fluoride ions into the pores of the inner adsorbent surfaces inducing a slower adsorption rate (Weber and Morris, 1963). The values of the coefficient of determination (R^2) indicate that this model can satisfactorily describe the experimental points of kinetics, and according to the obtained diffusion rate constants, K_1 (Table 5), we can confirm that external diffusion is faster than internal diffusion.

The effect of the adsorbent dose on the fluoride adsorption is shown in Figure 10. As the dosing amount increases from 0 to 5g, the residual fluoride concentration decreases from 2.14mg/l to 0.04 mg/l at a dose of 3g, reaching 0.0 mg/l at 4 g. This result can be explained by the availability of a large number of exchange sites, which favors the fixation of a large number of fluoride ions. In contrast, a decrease in the fluoride adsorption capacity by a unit mass of adsorbent was observed, which was also due to the availability of a larger number of exchange sites compared to the fluoride tenor present in the mixture, which induced that many of these sites remained free.

Finally yet importantly, This study has a potential limitation. The removal efficiencies resulting from a small-scale application may differ from those issued out of a large-scale application.

Therefore, a fluoride adsorption essay within a water treatment plant using a column bed filter can be carried out in future studies to assess the applicability of the adsorbent and its real potential during the treatment of a large volume of water, as well as the rate and time of its saturation and its regeneration capacity.

CONCLUSION

The results of this work proved that, despite the low removal efficiency of eggshell powder as a fluoride adsorbent (51.4%), it is still applicable as a low-cost alternative for the adsorption of fluoride from the groundwater of the study region. The XRD and FT-IR patterns revealed that the main component of eggshells was calcite (CaCO_3). The adsorption batch experiments confirmed that heating temperature, particle size, and pH_{pzc} were responsible for the different nature of the results due to their impact on the tenor of organic matters present on the adsorbent surface, the adsorption rate, and the adsorbent surface charges. The pH_{pzc} of ES250°0.2 was 6.5, which is inferior to the water pH (7.35). Hence, the surface of the adsorbent was negatively charged which favors the electrostatic attraction of cations and repulsion of fluoride ions. Furthermore, a higher heating temperature was needed for the transformation of CaCO_3 contained in eggshells into $\text{Ca}(\text{OH})_2$, which has a higher affinity toward fluoride ions. However, the treated water showed a residual fluoride concentration of (1.1mg/l) that meets WHO standards for fluoride (<1.5mg/l), proving the reliability of ES250°0.2 as a fluoride adsorbent to provide reliable and safe drinking water for the population living in the study area. In addition, it is worth noting that to generate safe drinking water that meets WHO standards for fluoride, a dose of 1.5g of ES250°0.2 and a 1 hour of contact time are sufficient. Although, the adsorption of fluoride onto eggshell powder remains to be further enhanced by subjecting the eggshell to a thermal treatment at higher carbonization temperatures (800°C).

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCES

- Aissa, R.B. and Boutoutaou, D. (2017). Characterization of groundwater in arid zones (case of Ouargla basin). *Energy Procedia, International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES17*, 21-24 April 2017, Beirut Lebanon 119, 556–564. <https://doi.org/10.1016/j.egypro.2017.07.077>
- Ait Taleb, M., Rachid, M., Benomar, M., Bakka, A., Mouna, A., Taha, M., Abdeljalil, B., Bakiz, B. and Villain, S. (2017). Chemically treated eggshell wastes as a heterogeneous and eco-friendly catalyst for oximes preparation. *Journal of Environmental Chemical Engineering*, 5. <https://doi.org/10.1016/j.jece.2017.02.009>

- Aliaskari, M. and Schäfer, A. I. (2021). Nitrate, arsenic and fluoride removal by electrodialysis from brackish groundwater. *Water Research*, 190, 116683. <https://doi.org/10.1016/j.watres.2020.116683>
- Annan, E., Nyankson, E., Agyei-Tuffour, B., Armah, S. K., Nkrumah-Buandoh, G., Hodasi, J. A. M. and Oteng-Peprah, M. (2021). Synthesis and Characterization of Modified Kaolin-Bentonite Composites for Enhanced Fluoride Removal from Drinking Water. *Advances in Materials Science and Engineering*, 2021, e6679422. <https://doi.org/10.1155/2021/6679422>
- Bhaumik, R., Mondal, N. K., Das, B., Roy, P., Pal, K. C., Das, C., Banerjee, A. and Datta, J. kumar. (2012). Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies. *E-Journal of Chemistry*, 9(3), 1457–1480. <https://doi.org/10.1155/2012/790401>
- Bouziane, M. T. and Abdallah Seddik, L. (2009). Les Eaux Profondes de la Région de Biskra (Algérie). *European Journal of Scientific Research*, 25 (4), 526-537.
- Castro, L. da S., Barañano, A. G., Pinheiro, C. J. G., Menini, L. and Pinheiro, P. F. (2019). Biodiesel production from cotton oil using heterogeneous CaO catalysts from eggshells prepared at different calcination temperatures. *Green Processing and Synthesis*, 8(1), 235–244. <https://doi.org/10.1515/gps-2018-0076>
- Chatterjee, S., Mukherjee, M. and De, S. (2018). Defluoridation using novel chemically treated carbonized bone meal: Batch and dynamic performance with scale-up studies. *Environmental Science and Pollution Research*, 25(18), 18161–18178. <https://doi.org/10.1007/s11356-018-2025-z>
- Choudhary, R., Koppala, S. and Swamiappan, S. (2015). Bioactivity studies of calcium magnesium silicate prepared from eggshell waste by sol-gel combustion synthesis. *Journal of Asian Ceramic Societies*, 3(2), 173–177. <https://doi.org/10.1016/j.jascer.2015.01.002>
- Chouhan, S. and Flora, S. J. S. (2010). Arsenic and fluoride: Two major ground water pollutants. *Indian Journal of Experimental Biology*, 48(7), 666–678.
- Engin, B., Demirtaş, H. and Eken, M. (2006). Temperature effects on egg shells investigated by XRD, IR and ESR techniques. *Radiation Physics and Chemistry*, 75(2), 268–277. <https://doi.org/10.1016/j.radphyschem.2005.09.013>
- Fan, S., Yuan, X., Zhao, L., Xu, L.-H., Kang, T.-J. and Kim, H.-T. (2016). Experimental and kinetic study of catalytic steam gasification of low rank coal with an environmentally friendly, inexpensive composite K₂CO₃-eggshell derived CaO catalyst. *Fuel*, 165, 397–404. <https://doi.org/10.1016/j.fuel.2015.10.084>
- Goli, J. and Sahu, O. (2018). Development of heterogeneous alkali catalyst from waste chicken eggshell for biodiesel production. *Renewable Energy*, 128, 142–154. <https://doi.org/10.1016/j.renene.2018.05.048>
- Hamidi, A. A., Salimi, M. N. and Yusoff, A. H. M. (2017). Synthesis and characterization of eggshell-derived hydroxyapatite via mechanochemical method: A comparative study. *AIP Conference Proceedings*, 1835(1), 020045. <https://doi.org/10.1063/1.4981867>
- He, Z., Lan, H., Gong, W., Liu, R., Gao, Y., Liu, H. and Qu, J. (2016). Coagulation behaviors of aluminum salts towards fluoride: Significance of aluminum speciation and transformation. *Separation and Purification Technology*, 165, 137–144. <https://doi.org/10.1016/j.seppur.2016.01.017>
- Ho, Y. S. and McKay, G. (1998). Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal*, 70(2), 115–124. [https://doi.org/10.1016/S0923-0467\(98\)00076-1](https://doi.org/10.1016/S0923-0467(98)00076-1)
- Ho, Y. S. and McKay, G. (1999). The sorption of lead(II) ions on peat. *Water Research*, 33(2), 578–584. [https://doi.org/10.1016/S0043-1354\(98\)00207-3](https://doi.org/10.1016/S0043-1354(98)00207-3)
- Kaseva, M. E. (2006). Optimization of regenerated bone char for fluoride removal in drinking water: A case study in Tanzania. *Journal of Water and Health*, 4(1), 139–147. <https://doi.org/10.2166/wh.2006.0011>
- Khatibi, M., Khorasheh, F. and Larimi, A. (2021). Biodiesel production via transesterification of canola oil in the presence of Na–K doped CaO derived from calcined eggshell. *Renewable Energy*, 163, 1626–1636. <https://doi.org/10.1016/j.renene.2020.10.039>
- Lagergren, S. (1898). About the Theory of So-Called Adsorption of Soluble Substances. In *Kungliga Svenska Vetenskapsakademiens Handlingar* (Vol. 24, pp. 1–39).
- Lalley, J., Han, C., Li, X., Dionysiou, D. D. and Nadagouda, M. N. (2016). Phosphate adsorption using modified iron oxide-based sorbents in lake water: Kinetics, equilibrium, and column tests. *Chemical Engineering Journal*, 284, 1386–1396. <https://doi.org/10.1016/j.cej.2015.08.114>
- Lee, J.-I., Hong, S.-H., Lee, C.-G. and Park, S.-J. (2021). Fluoride removal by thermally treated egg shells with high adsorption capacity, low cost, and easy acquisition. *Environmental Science and Pollution*

- Research*, 28(27), 35887–35901. <https://doi.org/10.1007/s11356-021-13284-z>
- Lunge, S., Thakre, D., Kamble, S., Labhsetwar, N. and Rayalu, S. (2012). Alumina supported carbon composite material with exceptionally high defluoridation property from eggshell waste. *Journal of Hazardous Materials*, 237–238, 161–169. <https://doi.org/10.1016/j.jhazmat.2012.08.023>
- Medellin-Castillo, N. A., Leyva-Ramos, R., Ocampo-Perez, R., Garcia de la Cruz, R. F., Aragon-Piña, A., Martinez-Rosales, J. M., Guerrero-Coronado, R. M. and Fuentes-Rubio, L. (2007). Adsorption of Fluoride from Water Solution on Bone Char. *Industrial and Engineering Chemistry Research*, 46(26), 9205–9212. <https://doi.org/10.1021/ie070023n>
- Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M., El Hamri, R. and Taitai, A. (2015). Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology. *Journal of Saudi Chemical Society*, 19(6), 603–615. <https://doi.org/10.1016/j.jscs.2012.03.003>
- Murakami, F. S., Rodrigues, P. O., Campos, C. M. T. de, and Silva, M. A. S. (2007). Physicochemical study of CaCO₃ from egg shells. *Food Science and Technology*, 27, 658–662. <https://doi.org/10.1590/S0101-20612007000300035>
- Mutchimadilok, Y., Smittakorn, S., Mongkolnchai-arunya, S. and Durnford, D. (2014). Defluoridation with Locally Produced Thai Bone Char. *Advances in Environmental Chemistry*, 2014, e483609. <https://doi.org/10.1155/2014/483609>
- Nigri, E. M., Cechinel, M. Alice. P., Mayer, D. A., Mazur, Luciana. P., Loureiro, J. M., Rocha, S. D. F. and Vilar, V. J. P. (2017). Cow bones char as a green sorbent for fluorides removal from aqueous solutions: Batch and fixed-bed studies. *Environmental Science and Pollution Research*, 24(3), 2364–2380. <https://doi.org/10.1007/s11356-016-7816-5>
- Ooi, C. Y., Hamdi, M. and Ramesh, S. (2007). Properties of hydroxyapatite produced by annealing of bovine bone. *Ceramics International*, 33(7), 1171–1177. <https://doi.org/10.1016/j.ceramint.2006.04.001>
- Owusu-Agyeman, I., Reinwald, M., Jeihanipour, A. and Schäfer, A. I. (2019). Removal of fluoride and natural organic matter from natural tropical brackish waters by nanofiltration/reverse osmosis with varying water chemistry. *Chemosphere*, 217, 47–58. <https://doi.org/10.1016/j.chemosphere.2018.10.135>
- Pereira, A. P., Silva, M., Jr, É., Paula, A. and Tommasini, F. (2017). Processing and Characterization of PET Composites Reinforced With Geopolymer Concrete Waste. *Materials Research*. <https://doi.org/10.1590/1980-5373-mr-2017-0734>
- Pérez, S., Muñoz-Saldaña, J., Acelas, N. and Flórez, E. (2021). Phosphate removal from aqueous solutions by heat treatment of eggshell and palm fiber. *Journal of Environmental Chemical Engineering*, 9(1), 104684. <https://doi.org/10.1016/j.jece.2020.104684>
- Rodier, J. (2009). *L'Analyse de l'Eau: Eaux Naturelles, Eaux Résiduaires, Eau de Mer* (9e éd., pp. 100–110). Paris: Dunod.
- Saini, A., Maheshwari, P. H., Tripathy, S. S., Waseem, S., Gupta, A. and Dhakate, S. R. (2021). A novel alum impregnated CaO/ carbon composite for de-fluoridation of water. *Groundwater for Sustainable Development*, 14, 100622. <https://doi.org/10.1016/j.gsd.2021.100622>
- Samrat, M. V. V. N., Gandhi, K. S. and Rao, K. K. (2020). Modelling the adsorption of fluoride onto activated alumina in the presence of other ions. *Journal of Environmental Chemical Engineering*, 8(5), 103934. <https://doi.org/10.1016/j.jece.2020.103934>
- Shahid, M. K., Kim, J. Y., Shin, G. and Choi, Y. (2020). Effect of pyrolysis conditions on characteristics and fluoride adsorptive performance of bone char derived from bone residue. *Journal of Water Process Engineering*, 37, 101499. <https://doi.org/10.1016/j.jwpe.2020.101499>
- Shen, J., Richards, B. S. and Schäfer, A. I. (2016). Renewable energy powered membrane technology: Case study of St. Dorcas borehole in Tanzania demonstrating fluoride removal via nanofiltration/reverse osmosis. *Separation and Purification Technology*, 170, 445–452. <https://doi.org/10.1016/j.seppur.2016.06.042>
- Spelta, J. and Galdino, A. (2018). BIOCERAMIC COMPOSITE: HEN'S EGG SHELL CHARACTERIZATION AND MAIN APPLICATIONS. *Revista Ifes Ciência*, 4, 12. <https://doi.org/10.36524/ric.v4i1.323>
- Srimurali, M., Pragathi, A. and Karthikeyan, J. (1998). A study on removal of fluorides from drinking water by adsorption onto low-cost materials. *Environmental Pollution*, 99(2), 285–289. [https://doi.org/10.1016/S0269-7491\(97\)00129-2](https://doi.org/10.1016/S0269-7491(97)00129-2)
- Sternitzke, V., Kaegi, R., Audinot, J.-N., Lewin, E., Hering, J. G. and Johnson, C. A. (2012). Uptake of

- fluoride from aqueous solution on nano-sized hydroxyapatite: Examination of a fluoridated surface layer. *Environmental Science and Technology*, 802–809. <https://doi.org/10.1021/es202750t>
- Tangboriboon, N., Kunanuruksapong, R. and Sirivat, A. (2012). Preparation and properties of calcium oxide from eggshells via calcination. *Materials Science-Poland*, 30(4), 313–322. <https://doi.org/10.2478/s13536-012-0055-7>
- Tizo, M. S., Blanco, L. A. V., Cagas, A. C. Q., Dela Cruz, B. R. B., Encoy, J. C., Gunting, J. V., Arazo, R. O. and Mabayo, V. I. F. (2018). Efficiency of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution. *Sustainable Environment Research*, 28(6), 326–332. <https://doi.org/10.1016/j.serj.2018.09.002>
- Torres-Mansilla, A. and Delgado-Me, E. (2017). Influence of Separation Techniques with Acid Solutions on the Composition of Eggshell Membrane. *International Journal of Poultry Science*, 16, 451–456. <https://doi.org/10.3923/ijps.2017.451.456>
- Viswanathan, N., Prabhu, S. M. and Meenakshi, S. (2013). Development of amine functionalized copolymeric resins for selective fluoride sorption. *Journal of Fluorine Chemistry*, 153, 143–150. <https://doi.org/10.1016/j.jfluchem.2013.04.002>
- Weber, W. J. and Morris, J. C. (1963). Kinetics of Adsorption on Carbon from Solution. *Journal of the Sanitary Engineering Division*, 89(2), 31–59. <https://doi.org/10.1061/JSEDAI.0000430>
- Whitford, G. M. (1996). The metabolism and toxicity of fluoride. *Monographs in Oral Science*, 16 Rev 2, 1–153.
- World Health Organization. (2022). *Guidelines for drinking-water quality: Fourth edition incorporating the first and second addenda* (4th ed + 1st add + 2nd add). World Health Organization. <https://apps.who.int/iris/handle/10665/352532>
- Xia, Y., Huang, X., Li, W., Zhang, Y. and Li, Z. (2019). Facile defluoridation of drinking water by forming shell@fluorapatite nanoarray during boiling egg shell. *Journal of Hazardous Materials*, 361, 321–328. <https://doi.org/10.1016/j.jhazmat.2018.09.007>