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Adsorption of Fluoride from Aqueous Solution using Eggshell Pretreated with Plasma Technology

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Abstract

Fluoride is a toxic substance that can cause adverse effects on human health such as dental and skeletal fluorosis. Therefore, the objective of this study was to investigate the adsorption potential of fluoride from aqueous solution using eggshell pretreated with plasma technology and compare to untreated eggshell. The batch adsorption experiments of fluoride from aqueous solution using pretreated eggshell and untreated eggshell were carried out to compare their performances on fluoride removal efficiency, adsorption capacity and isotherm. The effects of adsorption factors of contact time (5 - 360 min), adsorbent dosage (10 - 35 g/L) and particle size of adsorbent (mesh sieve no.12 - 20 or 0.85 - 1.70 mm sieve opening) were studied. The results showed that with the initial fluoride concentration of 10 mg/L, the optimum condition for the adsorption of fluoride from aqueous solution was obtained with pretreated eggshell at contact time of 180 min, adsorbent dosage of 25 g/L and adsorbent size of Sieve no.16 (≤1.18 mm in diameter). With this optimum condition, the maximum fluoride removal efficiency increased from 59.88 % with untreated eggshell to 90.34 %, which was due to an increase in adsorption sites after surface modification process of eggshell. Moreover, the results clearly showed that adsorption isotherm was fitted by Langmuir model, which indicate a monolayered adsorption. The maximum adsorption capacity was 0.341 mg/g for pretreated eggshell, while this was 0.202 mg/g for untreated eggshell. This study showed that eggshell pretreated with plasma technology has potential for the application of the adsorption of fluoride from aqueous solution in the future and needs further investigation on the continuous adsorption column.

Keywords: Batch adsorption, Eggshell, Fluoride, Modified adsorbent, Plasma technology, Pretreated eggshell, Water treatment

Introduction

Clean and safe water is considered as the essential fundamental needs for human, including fluoride in water. Although fluoride has beneficial effects on human health, an excessive fluoride in drinking water has become one of the most prominent public health concerns worldwide [1]. An intake of fluoride with the concentration of 1.5 - 3.0 mg/L causes dental fluorosis that results in white spots on the surface of the teeth. While an intake of fluoride ranged from 3.0 to 10.0 mg/L causes skeletal fluorosis and above 20.0 mg/L is toxic which leads to pathological changes in the bones [2]. Therefore, according to the World Health Organization (WHO), the maximum permissible limit of fluoride in drinking water is 1.5 mg/L [3]. However, until the present time, many countries worldwide are still facing severe challenges of defluoridation of water particularly with the groundwater resources, as the fluoride levels are higher than the maximum value of 1.5 mg/L recommended by the WHO, for example, in Argentina, China, Ethiopia, Ghana, India, Iran, Pakistan, Sweden, Tanzania and Thailand [1].

Several methods have been already implemented for defluoridation and more are recently developing, such as coagulation-precipitation, ion exchange, electrocoagulation, reverse osmosis, nanofiltration membrane process, electrodialysis and adsorption process [4,5]. Each of these methods has their own advantages, limitations and different effective operational parameters. However, among the different defluoridation methods, the adsorption process is considered as a promising alternative and most popularly used for defluoridation due to its effectiveness, ease of operation, simplicity of design and economic viability [1,5]. Generally, the adsorption process can be described as a surface phenomenon in which the molecules (adsorbate) from bulk solution bind to the outside surface of a solid (adsorbent) by physical or chemical forces [4]. Moreover, it is apparent from a literature study that the most widely utilized adsorbents for water defluoridation are activated alumina and activated carbon, besides, other adsorbents such as bone charcoal, zeolite and calcite can also be used. Although these mentioned adsorbents considered as an efficient adsorbent for the removal of fluoride from aqueous solution are generally expensive and not readily available in most developing countries [4,6]. Thus, the main challenges in the future for defluoridation of water has changed to the development of high removal efficiency, sustainable operation and maximum utilization of the available wastes for the removal of fluoride from aqueous solution [5], which could have the potential for local production and the developing countries. Recently, the natural substance such as an eggshell has started to be considered as a potential local and low-cost adsorbent for the removal of fluoride from aqueous solution as well as other inorganic pollutants [7-11]. Additionally, the surface modification techniques have been investigated for improving surface properties of adsorbents with a consequent increase in adsorption efficiency like atmospheric plasma methods [7]. This is due to the advantages provided by the atmospheric plasma methods, which are the ability for selectively enhancing surface properties while remaining the bulk properties, and the reduction in usage of hazardous chemicals which resulted in reducing the operational costs and safe adsorbents used for drinking water treatment [12,13]. However, information about the application of a novel pretreated eggshell by using the atmospheric plasma for the adsorption of fluoride from aqueous solution is still limited and needs to be further investigated.

Therefore, the objective of this study was to investigate the adsorption potential of fluoride from aqueous solution using eggshell pretreated with plasma technology and compare to untreated eggshell. In this study, batch adsorption experiments were conducted under different adsorption factors, including contact time (5 - 360 min), adsorbent dosage (10 - 35 g/L) and particle size of adsorbent (mesh sieve no.12 - 20 or 0.85 - 1.70 mm sieve opening). Moreover, adsorption isotherm models were also analyzed to understand the relationship between the adsorbed molecules and adsorbent surface.

Materials and methods

Adsorbent preparation

In this study, chicken eggshell was used as an adsorbent collected from household wastes. The collected eggshell was first washed in distilled water several times to remove impurities and let it dry out with sunlight. The dried eggshell was further ground in mortar and sieved to pass through different mesh sieve sizes (Endecotts Ltd., England). Three mesh sieves were used with a pore diameter of 1.70 mm (Sieve no.12), 1.18 mm (Sieve no.16) and 0.85 mm (Sieve no.20). Consequently, the sieved eggshells used in this study had the particle size of ≤1.70, ≤1.18 and ≤0.85 mm diameter, respectively. After that, the sieved eggshells were dried in the hot air oven and pretreated with plasma technology, following the steps in the study of [7]. To prepare the untreated eggshell adsorbent, the sieved eggshells of different particle sizes were dried in the hot air oven under the temperature of 105 °C for 24 h and put in the desiccator for 6 h before packing in a plastic bag for further use. In addition, to prepare the eggshell pretreated with plasma technology, an atmospheric pressure plasma in a dielectric barrier discharge (DBD) reactor (Department of Electrical Engineering, RMUTL, Thailand) was used to improve the surface property of eggshell for enhancing the adsorption efficiency. The sieved eggshells of different particle sizes were also dried in the hot air oven under the temperature of 105 °C for 24 h and put in the desiccator for 6 h, thereafter placed on the ground electrode of DBD reactor with voltage of 13 kV for 4 min. Then, the pretreated eggshell was packed in a plastic bag for later use as the pretreated eggshell adsorbent.

Moreover, the surface morphology of eggshell pretreated with plasma technology and untreated eggshell before and after the adsorption of fluoride from aqueous solution (adsorbent size of Sieve no.16 as an example) was determined using scanning electron microscope (SEM) (Prisma E, Thermo Scientific, USA).

Standard solutions preparation

A 1000 mg/L fluoride stock solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride (NaF) in 1 L of distilled water, the same as described in [14]. After that, the fluoride standard with the concentration of 10 mg/L was prepared from 1000 mg/L fluoride stock solution and used as an initial fluoride solution throughout the batch adsorption experiments in this study.

Batch adsorption experiments

Sets of batch adsorption experiments were conducted to investigate the adsorption potential of fluoride from aqueous solution using eggshell pretreated with plasma technology and untreated eggshell under various experimental conditions. In all sets of experiments, the initial fluoride concentration of 10 mg/L and the desired adsorbent dosage (10 - 35 g/L) was mixed to a working volume of 50 mL in the 250 mL of Erlenmeyer flask. After that, the flasks were agitated at 150 rpm in an orbital shaker (Labortechnik, Germany) with the desired contact time (5 - 360 min). All experiments were carried out in triplicates at room temperature (25 - 30 °C) and the average results were reported.

The effect of contact time was explored to obtain the optimum time required for adsorption of fluoride from aqueous solution with the initial fluoride concentration of 10 mg/L at a fixed adsorbent dosage of 10 g/L which was the minimum dosage used in this study, while varying the contact time from 5 to 360 min. Besides, the effects of adsorbent dosage and particle size of adsorbent were explored by varying the adsorbent dosage from 10 to 35 g/L of pretreated eggshell and varying the adsorbent size (Sieve no.12, 16 and 20), while maintaining the other experimental conditions which were at the initial fluoride concentration of 10 mg/L and fixed optimum contact time of 180 min. As a control, the same batch adsorption experiments were repeated with replacing the pretreated eggshell with untreated eggshell. After each experiment, the samples were filtered and the residual fluoride concentration was measured according to Zirconyl-SPADNS method by using UV visible at a wavelength of 570 nm with the detection range of 0.1 to 1.4 mg Fluoride/L [14]. Then, the percentage of fluoride removal efficiency and the adsorption capacity of fluoride adsorbed per unit mass of the adsorbent at any time were determined using Eqs. (1) and (2), respectively [15].

$$Removal\ (\%) = \left(\frac{C_{in} - C_{residual}}{C_{in}} \right) * 100 \quad (1)$$

$$q_t = \left(\frac{C_{in} - C_{residual,t}}{m} \right) * V \quad (2)$$

where C_{in} is the initial fluoride concentration (mg/L), $C_{residual}$ is the residual fluoride concentration after adsorption (mg/L), q_t is the fluoride adsorption capacity at any contact time (mg/g), $C_{residual,\ t}$ is the residual fluoride concentration after adsorption at any contact time (mg/L), m is the mass of adsorbent (g) and V is the volume of the aqueous solution (L).

Adsorption isotherm

In this study, the adsorption isotherms were evaluated by varying the adsorbent dosage from 10 to 35 g/L and the adsorbent size of Sieve no.12, 16 and 20 at the initial fluoride concentration of 10 mg/L and fixed optimum contact time of 180 min. The commonly applied adsorption isotherms of Langmuir and Freundlich models were used for validity of adsorption phenomenon, which are expressed by Eqs. (3) and (4), respectively [16,17].

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where C_e is the fluoride concentration in solution at equilibrium (mg/L), q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (mg/g), q_m is the maximum adsorption capacity of the adsorbent (mg/g), b is the Langmuir constant (L/mg), K_F is the Freundlich constant ((mg/g)/(mg/L)^n) and n is the adsorption intensity.

Results and discussion

Morphological analysis

The morphology of outside surface of eggshell pretreated with plasma technology and untreated eggshell using adsorbent size of Sieve no.16 before and after the adsorption of fluoride from aqueous solution is depleted in **Figures 1** and **2**, respectively.

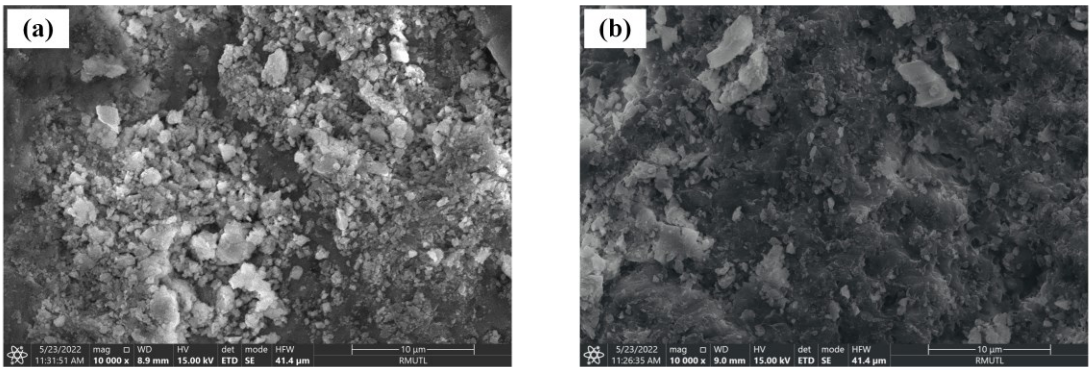

Figure 1 Scanning electron microscope (SEM) pictures of the eggshell surface before the adsorption: (a) Eggshell pretreated with plasma technology and (b) Untreated eggshell.

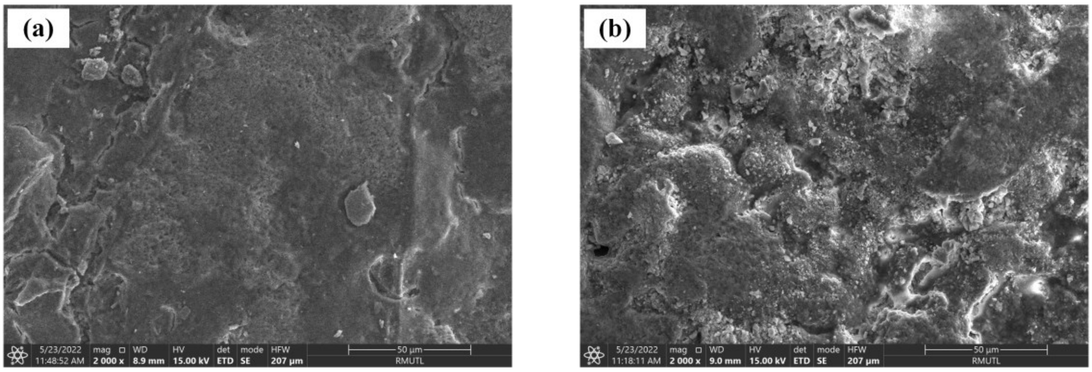

Figure 2 Scanning electron microscope (SEM) pictures of the eggshell surface after the adsorption of fluoride from aqueous solution: (a) Eggshell pretreated with plasma technology and (b) Untreated eggshell.

As expected, before the adsorption (**Figure 1**), the surface of both pretreated egg-shell with plasma technology and untreated eggshell clearly indicated that these were porous material, which therefore can be used as effective adsorbents for the removal of fluoride. However, as shown in **Figure 1(a)**, a magnified picture of the surface of pretreated eggshell showed more open pore volumes than untreated eggshell (**Figure 1(b)**), which thereby could lead to a higher adsorption efficiency [18,19]. Moreover, **Figure 2** revealed that after the adsorption of fluoride from aqueous solution, the structure of the adsorbent surface was significantly altered before the adsorption. The surface of both pretreated and untreated eggshells after the adsorption of fluoride from aqueous solution appeared smoother than before the adsorption. These results indicated that the material adsorbents were more saturated with fluoride molecules after the adsorption of fluoride from aqueous solution, as the fluoride molecules were diffused onto the internal layers of the adsorbent.

Effect of contact time

Figure 3 shows the results of average fluoride removal efficiency and adsorption capacity of eggshell pretreated with plasma technology and untreated eggshell with respect to different contact times that ranged from 5 to 360 min.

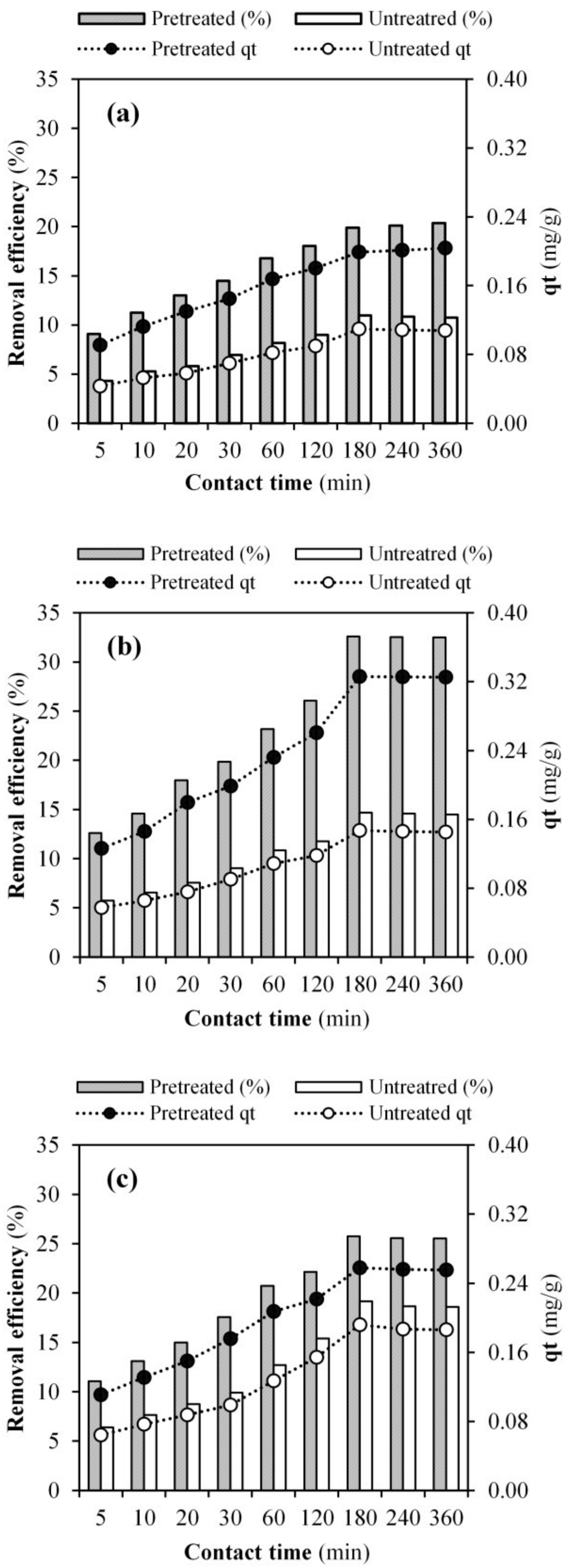

Figure 3 Effect of contact time on average fluoride removal efficiency and adsorption capacity of eggshell pretreated with plasma technology and untreated eggshell for different sizes of adsorbent used: (a) Sieve no.12, (b) Sieve no.16 and (c) Sieve no.20. (Experimental conditions: initial fluoride concentration of 10 mg/L and adsorbent dosage of 10 g/L).

As can be seen from **Figure 3**, the fluoride removal efficiency and adsorption capacity of both pretreated and untreated eggshells for all the 3 adsorbent sizes increased gradually with the contact time increase from 5 to 180 min. However, the trends of fluoride removal efficiency and adsorption capacity remained constant or slightly decreased as the contact time increased from 180 to 360 min. This is due to abundant fluoride molecules and available adsorption sites resulting in the increase of adsorption until reaching the adsorption equilibrium where the rate of adsorption equals the rate of desorption [5]. After equilibrium, the adsorption sites that were saturated by fluoride molecules may begin to release the fluoride molecules back into the aqueous solution, leading to the decrease of adsorption efficiency [20,21]. Therefore, the contact time of 180 min was chosen to be the optimum contact time of fluoride adsorption from aqueous solution for the subsequent experiments in this study. At the optimum contact time of 180 min, the average fluoride removal efficiencies achieved by pretreated eggshell with adsorbent sizes of Sieve no.12, 16 and 16 were 19.89, 32.60 and 25.76 %, respectively; while the corresponding adsorption capacities were 0.20, 0.33 and 0.26 mg/g. Whereas, the untreated eggshell achieved 10.96, 14.69 and 19.17 % average fluoride removal efficiencies with corresponding adsorption capacities of 0.11, 0.15 and 0.19 mg/g.

Effects of adsorbent dosage and size

Figure 4 shows the results on the effects of adsorbent dosage (10 - 35 g/L) and particle size of adsorbent (mesh sieve no.12 - 20) on the average fluoride removal efficiency by eggshell pretreated with plasma technology and untreated eggshell.

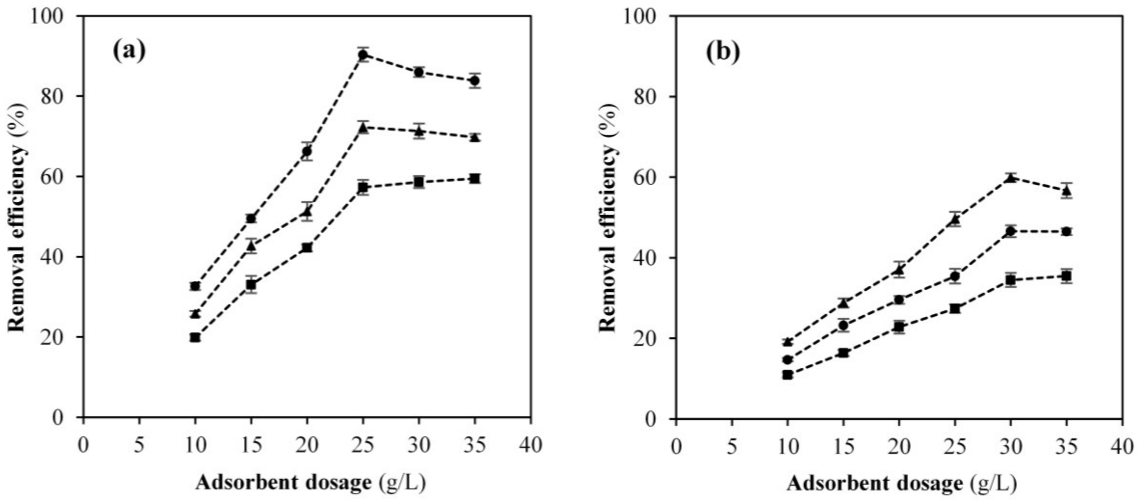

Figure 4 Effects of adsorbent dosage and size on average fluoride removal efficiency by (a) Eggshell pretreated with plasma technology and (b) Untreated eggshell for different sizes of adsorbent used: (■) Sieve no.12, (●) Sieve no.16 and (▲) Sieve no.20. (Experimental conditions: Initial fluoride concentration of 10 mg/L and contact time of 180 min).

As shown in **Figure 4**, 6 different adsorbent dosages from 10 to 35 g/L and 3 adsorbent sizes of Sieve no.12, 16 and 20 of both pretreated and untreated eggshells were studied at fixed optimum contact time of 180 min. The results showed that with increasing the dosage of pretreated eggshell from 10 to 25 g/L, there was a significant increase in removal efficiency of fluoride from aqueous solution (**Figure 4(a)**). In particular, the maximum average removal efficiency of fluoride was obtained with size Sieve no.16, which was found to be 32.60, 49.50, 66.22 and 90.34 % for the adsorbent dosage of 10, 15, 20 and 25 mg/L, respectively. Whereas with the untreated eggshell, the removal efficiency increased with increasing the adsorbent dosage from 10 to 30 mg/L and reached the maximum average removal efficiency of fluoride with size Sieve no.20, which was found to be 19.17, 28.77, 37.07, 49.60 and 59.88 % for the adsorbent dosage of 10, 15, 20, 25 and 30 mg/L, respectively (**Figure 4(b)**). Meanwhile, for the adsorbent dosage of more than 25 g/L of pretreated eggshell and more than 30 g/L of untreated eggshell, the average fluoride removal efficiency kept relatively stable or slowly decreased. Similar results have been reported by other studies [6,15,20,22], for example, the study of [15] showed that the fluoride removal efficiency by natural grade diatomite at the initial fluoride concentration of 10 mg/L, pH of 5 and optimum contact time of 60 min increased gradually with increasing the adsorbent dosage from 10 to 60 g/L and then was relatively stable from 60 to 100 g/L. These results can be explained by the higher adsorbent sites for fluoride adsorption from aqueous solution at higher dosage, which resulted in a higher adsorption efficiency. However, the adsorption equilibrium between the adsorbent sites and fluoride molecules would be achieved after the amount of adsorbent increased to a certain extent [22]. Thus, a decrease in the fluoride removal efficiency after the equilibrium can be caused by the desorption of fluoride molecules or by the partial aggregation of eggshell particles at higher adsorbent dosage which resulted in the reduction of available surface area for adsorption [23]. Besides, the higher optimum dosage required for untreated eggshell was possibly due to the lower active adsorption sites of untreated eggshell compared to pretreated eggshell, which consequently required more adsorbent dosage to reach the equilibrium.

In addition, the particle size of adsorbent is also one of the important factors that influences the adsorption process [23]. As presented in **Figure 4(b)**, the fluoride removal efficiency by untreated eggshell increased with decreasing the particle size of eggshell. At the optimum dosage of 30 g/L of untreated eggshell, the average fluoride removal efficiencies were 34.50, 46.61 and 59.88 % for the size Sieve no.12 (≤1.70 mm diameter), Sieve no.16 (≤1.18 mm diameter) and Sieve no.20 (≤0.85 mm diameter), respectively. This is because the smaller adsorbent size offered comparatively higher available adsorption sites [23], which is consistent with the previous studies of Bhaumik *et al.* [24] and Chandraker *et al.* [25]. However, at the optimum dosage of 25 g/L of pretreated eggshell, the maximum average removal efficiency was obtained with size Sieve no.16 (90.34 %), followed by Sieve no.20 (72.25 %) and Sieve no.12 (57.25 %) (**Figure 4(a)**). This might be caused by the non-homogeneity of the treated surface eggshell especially in very small particle size and thereby leading to insufficient surface modification with plasma technology [26].

All these results showed that the optimum condition for adsorption of fluoride from aqueous solution was obtained with pretreated eggshell at contact time of 180 min, adsorbent dosage of 25 g/L and adsorbent size of Sieve no.16, which resulted in the maximum average fluoride removal efficiency of 90.34 %.

Adsorption isotherm

The adsorption isotherm was studied to understand the interactive behavior between the adsorbate (fluoride molecules) and the adsorbent (eggshell). The calculated Langmuir parameters (q_m, b and R_L) and Freundlich parameters (K_F and n) as well as the correlation coefficient (r^2) are given in **Table 1**.

Table 1 Parameters of the Langmuir and Freundlich isotherms for the adsorption of fluoride from aqueous solution by eggshell pretreated with plasma technology and untreated eggshell. (Experimental conditions: Initial fluoride concentration of 10 mg/L, contact time of 180 min and adsorbent dosage of 10 to 35 g/L).

Isotherm	Parameters		Eggshell pretreated with plasma technology*			Untreated eggshell*		
			Sieve no.12	Sieve no.16	Sieve no.20	Sieve no.12	Sieve no.16	Sieve no.20
Langmuir	q_m	(mg/g)	0.220	0.341	0.287	0.117	0.164	0.202
	b	(L/mg)	2.216	4.056	1.788	1.970	1.281	2.340
	R_L	-	0.043	0.024	0.053	0.048	0.072	0.041
	r^2	-	0.907	0.988	0.934	0.905	0.925	0.950
Freundlich	K_F	$((mg/g)/(mg/L)^n)$	0.169	0.298	0.216	0.095	0.121	0.170
	n	-	9.064	23.785	9.097	13.551	9.802	17.121
	r^2	-	0.089	0.050	0.113	0.045	0.109	0.045

Note: *Referring to the particle size of diameter ≤1.70 mm (Sieve no.12), ≤1.18 mm (Sieve no.16) and ≤0.85 mm (Sieve no.20).

As demonstrated by the data in **Table 1**, the Langmuir isotherm model best fitted the adsorption data as shown by the correlation coefficient ($r^2 > 0.900$) for both pretreated and untreated eggshells. The results clearly suggest that the monolayer adsorption of fluoride molecules occurred on the outside surface of the adsorbent (eggshell). This is consistent with the review study done by Yadav *et al.* [5] which indicated that most of the adsorption data on the removal of fluoride appeared to fit well with the Langmuir model than the Freundlich model and others such as Temkin model and Dubinin-Radushkevich model. Moreover, from the Langmuir isotherm model, the maximum adsorption capacity was found to be 0.220, 0.341 and 0.287 mg/g for pretreated eggshell with size Sieve no.12, 16 and 20, respectively, while this was 0.117, 0.164 and 0.202 mg/g for untreated eggshell with size Sieve no.12, 16 and 20, respectively.

Based on the results obtained, it is evident that the eggshell pretreated with plasma technology can be considered as a promising adsorbent for removing the fluoride from the aqueous solution. With the highest maximum adsorption capacity obtained as 0.341 mg/g under the initial fluoride concentration of 10 mg/L and the optimum condition of contact time of 180 min and adsorbent dosage of 25 g/L, the pretreated eggshell used in this study shows a higher adsorption capacity than other reported materials for a similar initial fluoride concentration. These were, for example, activated carbon (*Morringa Indica*) (0.231 mg/g under the initial fluoride concentration range of 2 - 10 mg/L, contact time of 5 - 40 min and temperature of 30 - 50 °C) [27], granular acid-treated bentonite (0.278 mg/g under the initial fluoride concentration range of 0 - 20 mg/L, contact time of 0 - 120 min and temperature of 25 °C) [28] and pumice (0.310 mg/g under the initial fluoride concentration range of 2 - 7 mg/L, contact time of 0 - 180 min and ambient temperature) [29]. In addition, the separation factor or equilibrium parameter (R_L) which is known as a dimensionless constant was further computed using the relation of $R_L = 1/(1 + bC_{in})$. This R_L was used to predict the essential characteristics of the Langmuir isotherm, as linear if $R_L = 1$, unfavorable if $R_L > 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$ [30]. In this study, the obtained values of R_L were found between 0 and 1 (**Table 1**), indicating the favorable equilibrium adsorption of fluoride by both pretreated and untreated eggshells.

Conclusions

This study explored the adsorption potential of fluoride from aqueous solution using eggshell pretreated with plasma technology as a novel and low-cost adsorbent. The effects of adsorption factors of contact time, adsorbent dosage and particle size of adsorbent on the fluoride removal efficiency and adsorption capacity by pretreated eggshell were investigated using batch adsorption experiments and compared that to untreated eggshell. According to the findings of this study, it can be concluded that the plasma technology could be efficiently used for modifying eggshell to enhance the adsorption potential of fluoride from aqueous solution. The SEM pictures showed that there was a significant change in the surface morphology of pretreated eggshell, as more open pore volumes were found on the surface area of pretreated eggshell than untreated eggshell. The optimum condition for the adsorption of fluoride from aqueous solution was obtained with pretreated eggshell at contact time of 180 min, adsorbent dosage of 25 g/L and adsorbent size of Sieve no.16 (≤1.18 mm diameter). With this optimum condition, the maximum fluoride removal efficiency could reach up to 90.34 %, whereas the maximum fluoride removal efficiency with untreated eggshell was 59.88 %. Moreover, the adsorption isotherm was fitted by Langmuir model, which indicated a monolayered adsorption, with the maximum adsorption capacity of 0.341 and 0.202 mg/g for pretreated eggshell and untreated eggshell, respectively. This study not only offers the opportunity to enhance the adsorption potential and sustainability of water treatment, but also develop sustainable utilization of available household wastes as the low-cost adsorbent for the removal of fluoride from aqueous solution.

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