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Removal of fluoride from urban drinking water by eggshell powder

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The aim of this applied-analytical study was to investigate the feasibility of fluoride (F) removal from drinking water using a batch reactor by using eggshell powder. The variables under study involved are the pH, contact time, adsorbent doses, initial F concentration, reaction kinetics and eggshell powder characteristics. A sample of urban drinking water was prepared containing 3-12 mg/L of F. Eggshell powder was prepared in a laboratory oven at 105˚C for 12 h. The F-containing water was introduced into a batch reactor and the F removal efficiency was studied in different cases for pH (4-10), contact time (0-80 min) and adsorbent doses (1-2.5 gr/dl). The characteristics of the eggshell powder showed that the average diameter in size of the eggshell powder particles is 2 μm. The main component of the eggshell powder was calcium carbonate ($CaCO_3$). The best conditions for F removal attained were at pH 6, contact time 60 min., an adsorbent dose of 3 gr. and an F concentration of 3 mg/L. The adsorption of F in eggshell powder was obtained from the Langmuir isotherm.

Keywords: Adsorbent, Calcium carbonate, Eggshell, Langmuir, Urban drinking water.

INTRODUCTION

Chemically, fluoride (F) is the most reactive and electronegative of all the elements due to its small radius/charge ratio. Low concentrations of F in the drinking water were proposed as necessary to prevent against dental caries and as an indispensable element to help build the dental enamel in humans [1]. The high concentrations of F (>1.5 mg/L) in drinking water results in serious diseases, such as dental fluorosis, skeletal fluorosis and non-skeletal fluorosis (including neurological, allergic, gastro-intestinal, bone cancer and urinary tract conditions) [2]. The maximum permissible level for F in potable water is 1.5 mg/L, according to the World Health Organization (WHO) [3]. The increase of F levels in the groundwater is mainly attributed to anthropogenic factors (rapid urbanization and the growth of modern industries) and natural phenomena (geochemical dissolution of F bearing minerals) [4]. The water interaction and volcanic rock activity were considered as the most effective factors for increasing the F concentration of groundwater and surface water [5]. It was estimated that there are at least 25 countries which are affected by fluorosis world-wide including Algeria, Argentina, Australia, China, Ethiopia, India, Iran, Japan, Kenya, Mexico, Morocco, New Zealand, Senegal, Sri Lanka, Tanzania, Thailand, Turkey and the USA [6]. The defluoridation methods usually applied include adsorption, chemical precipitation, ion exchange, reverse osmosis, and electrodialysis [7-9]. The selection of the method was related to variables such as the area, concentration and availability of the resources. The most important disadvantage of the coagulation method was the high concentration of residual toxic chemicals such as aluminium and sulphate in the water after treatment. The main disadvantage of the ion exchange technique was the low selectivity of anions. The most important disadvantage of reverse osmosis was clogging, scaling and the fouling problem. The main disadvantage of the electrodialysis technique was the high capital and operational cost [10]. The advantages of the adsorption technology were applicable in batch and continuous arrangements, easier accessibility, economical and retain effectiveness at a low fluoride concentration [11]. Experiments have been done with many natural adsorbents such as defluoridation agents including Cynodon dactylon-activated carbon [12], Typha angustata-activated carbon [13], Pine wood and Pine bark chars [14]. The aim of this applied-analytical study was to investigate the feasibility of F removal from drinking water using a batch reactor by using eggshell powder. The variables under study involve the pH, contact time, adsorbent

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doses, initial F concentration, reaction kinetics and eggshell powder characteristics.

EXPERIMENTAL

Preparation of a water sample

F-contaminated water samples used for adsorption experiments were obtained from urban distribution systems situated at the site of a laboratory of the Islamic Azad University Tehran Medical Sciences Branch, in the city of Tehran. The samples were tested for the main physicochemical characteristics. The mean values of these water characteristics were presented in Table 1. All the reagents used were of an analytical grade. A solution of 3, 6, 9 and 12 mg/L of F was prepared by dissolving an appropriate amount of sodium fluoride (Merck, Germany) in deionized water.

Table 1. The main physicochemical characteristics of nitrate-contaminated urban water

Parameter	Unit	Value
Calcium	mg/L as $CaCO_3$	162
Dissolved oxygen	mg/L	8.05
Nitrate	mg/L	9.5
ORP	mV	272
pH	-	7.19
Sulfate	mg/L	93.8
Temperature	˚C	20
Total Alkalinity	mg/L as $CaCO_3$	122

Preparation of eggshell powder

After collecting chicken eggshells from local markets in Tehran city, removing the waste matter such as colour and fat, boiling in deionized water for 30 minutes and washing with deionized water, eggshell powder was prepared by heating the collected eggshells in a hot air oven (Dena, Iran) at 105˚C for 12 h, maybe, a temperature higher than 105˚C led to a decrease in defluoridation due to damaging the calcium carbonate structure, while temperatures below 105˚C led to developing a bad taste and odour in the treated water. Heat pretreatment removed the organic matter, the cause of taste and colour problems in the water. After heating, the eggshells were crushed by a laboratory electrical crusher (AIKA, Germany) for 20-30 second and were sieved several times to get a uniform fraction of eggshell of a specific size (60-100 mesh/0.25-0.104 mm), according to the ASTM standard [15]. The eggshell powder was stored in a desiccator after pretreatment containing a solution of sodium hypo chloride (NaOCl) (Merck, Germany), to eliminate the dust particles [16].

Determination of the eggshell powder characteristics

A Scanning Electron Microscopy **(**SEM) image (Philips, XL 30, Holland) was prepared from the eggshell powder. X-ray diffraction patterns were measured using RINT 2000 (Rigaku Instrument Corp.) with Cu Kα radiation to confirm the structure and mineral composition of the eggshells powder (Philips, Xpert, Holland). An eggshell powder composition was obtained by energy dispersive X-ray (EDX) analysis. The surface area of the eggshell powder was analyzed through nitrogen adsorption measurements at 77 K using Micromeritics Gemini 2370 equipment. The zeta potential was analyzed with a Nano Zetasizer (Philips, Holland).

Experimental set up

The batch reactor was a 250 ml plastic container (10×6×6 cm). To evaluate the effect of adsorption, on the F removal process, samples underwent treatment with different pH (ca. 4-10), different times (0-80 min), different concentrations of F (3-12 mg/L) and adsorbent dosages (1-2.5 gr/dl). The number of samples obtained was 256. A magnetic stirrer (AIKA, Germany) was used for the homogeneous mixing of water samples (120 rpm). For each test, 200 ml of sample water was poured into the reactor. All tests were performed at a laboratory temperature (20˚C). Chloric acid and sodium hydroxide solutions (0.1 N) (Merck, Germany) were used for pH adjustment.

Analytical methods

All tests were performed in triplicate and the mean data values were reported. The water samples were tested for F after the adsorption process by using a spectrophotometer (Hach DR5000, America) at a wavelength of 580 nm. F was determined by a standard method 4500D [17]. The percentage of F removal was calculated in accordance with the following equation:

$$\text{Removal (\%)} = \left(1 - \frac{C_t}{C_{t0}}\right) \times 100 \quad (1)$$

Where the percentage of F removal (*R*, percentage) and the F value before and after treatment (C_0 and C, mg/L) are expressed.

The defluoridation capacity of the regenerated eggshell powder was calculated according to the following equation:

$$DC_{FC} = \left(\frac{S_0 - S_t}{X_{FC}}\right) \quad , (2)$$

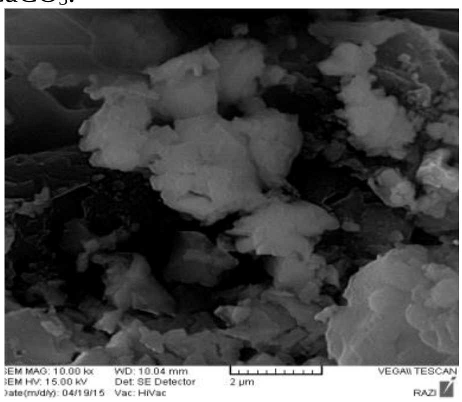
Where the defluoridation capacity of the regenerated eggshell powder (DC_{FC}, mg/g) and the F concentration before and after treatment (S_0 and S_t, mg/L) are expressed.

RESULTS AND DISCUSION

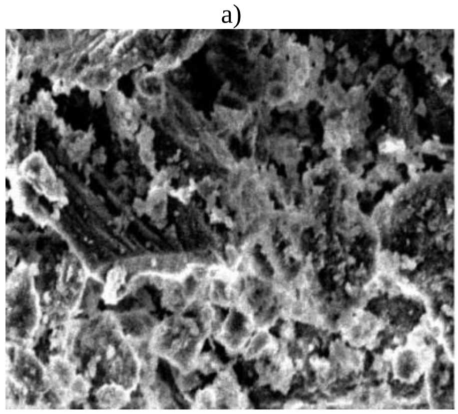
The reduction of F in urban drinking water was investigated in an adsorption reactor with filler particles made of charred chicken eggshells in a batch mode. Several operational variables were examined for the effects on process reduction efficiency. The following results were obtained from the experiments.

The characterization of eggshell powder

Figure 1 illustrates SEM images of the eggshell powder. As observed, the average diameter in size of the eggshell powder particles was 2 µm. Figure 2 illustrated X-ray dispersive (XRD) analysis of the eggshell powder. As found in Figure 2, the analyzed eggshell powder was composed of the elements calcium (Ca) and phosphor (P) as the main elements, respectively. Figure 3 illustrates the EDX analysis of the eggshell powder. As shown in Figure 3, the analyzed eggshell powder was composed of the elements calcium (Ca), oxygen (O), magnesium (Mg), carbon (C) and others. The spectrum of the analysed eggshell powder was adapted to the 2370 standard. The peaks confirmed that the main component of the eggshell powder was calcium carbonate ($CaCO_3$). The calcium to carbon (Ca/C) ratio of eggshell powder was 2.9. The SEM analysis was helpful to determine the surface morphology of an adsorbent. The agglomerate, non-adhesive, porous and irregular surface structure of the adsorbent is distinctly observed in the SEM image as indicated in Figure 1a. Furthermore, the pores of the adsorbent surface are regular, adhere to each other, but are heterogeneous as can be observed in Figure 1b. The heterogeneous pores represent a lager exposed surface area for the adsorption of fluoride. The diameters of the pores are symptomatic of the anticipated adsorption of fluoride molecules onto the surface of the adsorbent. It distinctly indicated the formation of a porous surface that supports the adsorbent with a large surface area and enhanced adsorption capacity. The SEM analysis showed that the removal of fluoride affects the orientation of the eggshell powder particles. The treated sample illustrates a regular, adhesive appearance leading to a higher adsorption. F. Bhaumik et al. [18] reported that the particle size of the eggshell powder was 150-350 µm. The characteristics of the eggshell powder are shown in Table 2. Specific surface area, BET measurements were performed and the highest BET was obtained for an eggshell powder 7.43 m^2/g. Zulfikar et al. [19] reported the BET of eggshell powder to be 3.23 m^2/g. Tsai et al. [20] reported that the composition of eggshell powder consisted of calcium carbonate (94%); magnesium carbonate (1%); calcium phosphate (1%); and organic matter (4%). Agarwal and Gupta [21] reported that the compound in the eggshell powder with the highest content was calcium carbonate. Functional groups of eggshells were diagnosed by infrared analysis. The peaks at about 710, 875, 1420, 1807 and 2520 cm^{-1} coincide with those of pure $CaCO_3$.



a)



b)

Fig. 1. SEM images of eggshell powder a) before treatment, b) after treatment.

Table 2. Characterization of BC_S particles

Particle	pH_{ZPC}	Density (g/cm^3)	Specific Surface Area, BET (m^2/g)	Diameter (µm)
Eggshell	8.2	1.148	7.43	2

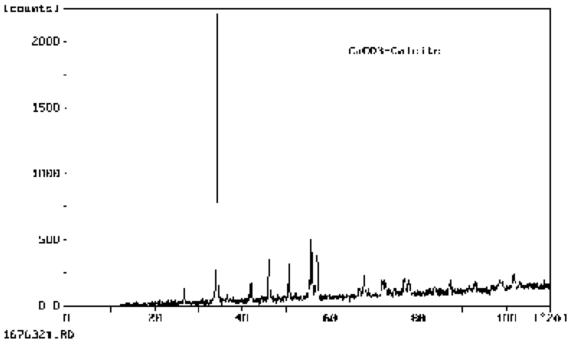


Fig. 2. XRD analysis of eggshell powder.

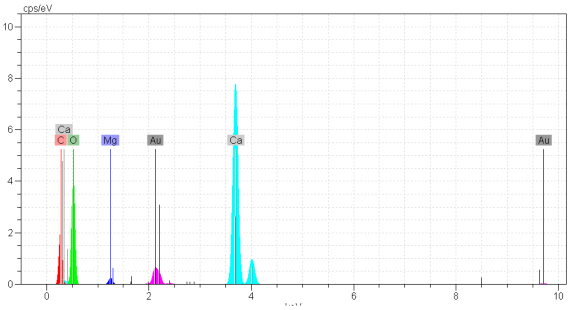


Fig. 3. EDX analysis of eggshell powder.

Effect of water pH

Adsorption experiments were carried out for pH values in the range of 4 to 10 and experimental conditions such as contact time (60 min), F concentration (6 mg/L) and amount of eggshell powder adsorbent (2 g). The mean F removal increased from 90% to 100% when the pH increased from 4 to 6 (Figure 4). F removal in the adsorption reactor was mainly influenced by the water pH. The pH had a significant effect on F reduction due to the surface charge of the absorbent, with the highest reduction obtained at pH 6. It was connected by a competing potential of [H^+] with the adsorbate ions and active sites on the adsorbent surface. The lower adsorption at acidic pH could be due to the formation of a weak hydrofluoric acid and a composition effect of the chemical and electrostatic interaction between the surface and the F ions. The removal of F ions in the alkaline condition is diminished and this can be due to strong competition from hydroxide ions at the active sites due to the prevailing OH^- and CO_3^{-2}. This was in agreement with Chowdhury et al. [22], who reported that the fastest removal rate occurred at a pH equal to 6.5. The pH at the point of zero charge (pH_{ZPC}) is an important parameter in F sorption, for it is the pH at which the sorbent has a neutral charge. When the pH is increased above the pH_{ZPC}, F sorption decreases due to electrostatic repulsion between the surface and the F anions, also, as a result of competition with the hydroxides in solution. When pH_{ZPC} is increased above the pH, the F sorption is increased.

Effect of eggshell powder adsorbent dosage

Adsorption experiments were carried out with an initial adsorbent dosage in the range of 1 to 2.5 g at the experimental conditions such as contact time (60 min), F concentrations (6 mg/L) and a pH value (6). The mean F removal increased from 60% to 100% when the adsorbent dosage increased from 1 to 2 (Figure 5). Enhancing the adsorbent dosage increased the percentage of F that was attributed to enhancing of sportive surface area, since more active adsorption sites and a proper porosity were available. The optimum dosage of eggshell powder adsorbent was 2 g. It was seen that 2 g was a better adsorbent dosage than 1 g. This phenomenon can be due to the exposure of the active sites of the adsorbent which allowed the F ions of water to be in direct contact with the eggshell powder, therefor increasing adsorption capacity. Increasing the adsorbent dosage also led to decreasing the surface area between the eggshell powder adsorbent and the F adsorbate due to the formation of aggregates. Increasing the adsorbent dosage resulted in increasing the pH. Suneetha et al. [23] reported that the optimum dosage of active carbon derived from the barks of the *Vitex negundo* plant was 4.0 g/L. At a constant pH, the activity of F^- was directly proportional to the concentration of HCO_3^-. CaF_2 precipitated when the concentration of Ca^{+2} and F^- in water exceeded the solubility product of F^-. If Ca was present in the raw water, it precipitated out the F.

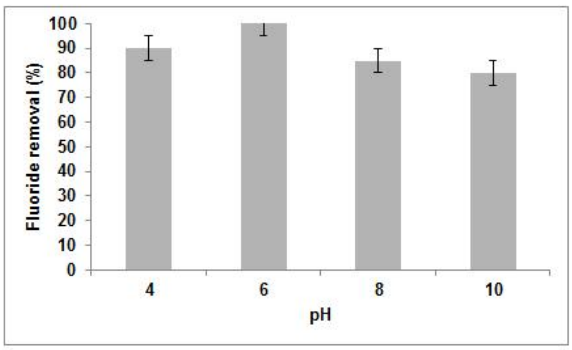


Fig. 4. The effect of water pH on fluoride removal in the batch adsorption reactor.

Effect of contact time

Adsorption experiments were carried out as a function of the time in the range of 0 to 80 min at the experimental conditions such as amount of eggshell powder adsorbent (2 g/dL), F concentration (6 mg/L) and pH value (6). The efficiency of F removal increased as the contact time increased. The mean F removal increased from

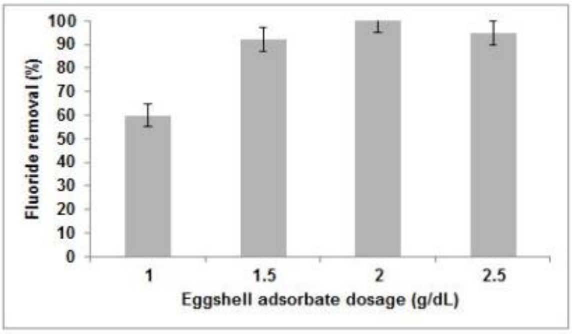


Fig. 5. The effect of eggshell powder adsorbent dosage on fluoride removal in the batch adsorption reactor.

82% to 100% when the contact time increased from 20 to 60 min (Figure 6). The efficiency of F removal initially increased as the contact time increased, but then gradually approached a more or less constant value, indicating a point of equilibrium. As there was no enhanced F removal efficiency between the 65th and 80th minute, an equilibrium time of 60 minutes was selected for the eggshell powder adsorbents. These variations could be due to the fact that initially, all the absorbent sites were empty and active, the solute concentration gradient was high and the opportunity for adsorption reactions was high. Then, the F adsorption rate on an eggshell powder adsorbent noticeably diminished due to a decrease of the absorbent sites. This phenomenon indicated a monolayer of F ions on the external surface and pores of eggshell powder and pore diffusion on to the internal surface of the eggshell powder. During this period the residual F fluctuated from a maximum value of 1.07 mg/L at 20 min. contact time to a minimum value of 0.0 mg/L for a contact time of 60 min. The highest removal capacity of eggshell powder (3 mg/g) was obtained for 60 min. An equilibrium time of 120 minutes was selected for the lemon leaves treated with a Ca^{+2} solution extracted from the eggshell adsorbent by Bhaumik et al [24].

Effect of initial F concentration

Adsorption experiments were carried out with an initial F concentration in the range of 3 to 12 mg/L at the experimental conditions such as contact time (20-80), amount of eggshell powder adsorbent (2 g/dL) and pH value (6). The mean F removal decreased from 100% to 84% when the initial F concentration increased from 3 to 12 mg/L for the duration of 60 minute (Figure 7). If the F ions were more than the absorbent sites, adsorption decreased due to saturation of the absorbent sites at a constant concentration. The F removal as a function of contact time was proportional to the F ions found in the water. Due to enhancing the concentration gradient, as a driving force, the predominant mass transfer resistances of the fluoride between the solution and solid phase, resulted in enhancing the sorption equilibrium, until sorbent saturation was obtained. This was in agreement with Bahatti et al. [25], who reported that the defluoridation efficiency decreased when the initial F concentration was increased. In other hands, increasing the concentration of F led to shifting the pH_{ZPC} to a lower value and decreasing the electrostatic attraction between the sorbent surfaces and the F anions.

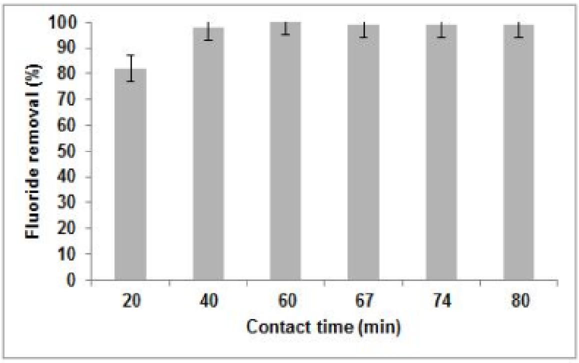


Fig. 6. The effect of contact time on fluoride removal in the batch adsorption reactor.

The proposed mechanism of the F uptake rate onto the eggshell powder surface involved the replacement (ion exchange adsorption) of the carbonate radicals of the eggshell powder, by F ions to form an insoluble fluorite. This compound could

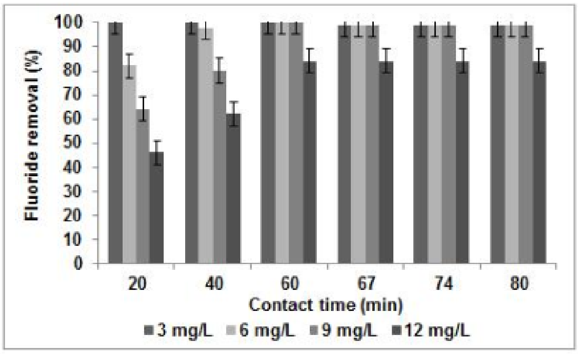


Fig. 7. The effect of initial fluoride concentration on fluoride removal in the batch adsorption reactor.

be returned to a form suitable for repetitive F adsorption with a caustic solution such as sodium hydroxide. This resulted in the formation of calcite ($CaCO_3$), with the F removed as sodium fluoride. This reaction could be represented by the following equations:

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^-, \quad (3)$$

$$2F^- + Ca^{+2} \rightarrow CaF_2, \quad (4)$$

$$CaF_2 + 2Na^+ \rightarrow NaF + Ca^{+2}, \quad (5)$$

The application of 1% solution of sodium hydroxide for regeneration had been reported by Piddennavar and krishnappa [26]. F reduction followed a Langmuir isotherm model (R^2>0.99). Therefore, the eggshell powder adsorption reactor, in batch mode, was shown to be efficient and viable for meeting a high degree of F reduction from drinking water and was considered as a promising technology for treating F-polluted drinking water in developing countries. Water treated by eggshell powder gave allowable residual F, which was recommended by the WHO[3] and Iranian National Standards [27].

CONCLUSIONS

The experimental results suggest that the batch chicken eggshell powdered reactor is a practical and promising method for the treatment of F-contaminated water. F removal was affected by pH, the concentration of F, the concentration of adsorbent and the reaction time. This reactor is capable of F removal at the pH value (6) investigated, with a reaction time of 60 min. It is proposed that the process can be successfully applied to study other materials.

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