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Adsortive defluoridation from aqueous solution using a novel blend of eggshell powder and chitosan nanofibers

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**Abstract**

Groundwater mostly contains many impurities thus can not be consumed as drinking water directly. The acceptable limit of fluoride in drinking water is 0.5–1.5 mg l\(^{-1}\) recommended by World Health Organization (WHO). In this research, a novel nanofiber hybrid; based on Chitosan (CTS) and Eggshell (EGG) was prepared via electrospinning technique and investigated for defluoridation from aqueous solution. SEM images reveal bead-free, smooth morphology and the FTIR confirmed the presence of chitosan and egg within the novel nanofiber blend. The defluoridation efficiency was assessed by varying the different parameters like pH, mass of nanofibers, contact time and initial concentration for adsorption. Studies revealed that CTS/EGG nanofibers hybrid shows incredible adsorption efficiency of 86%. Furthermore, isotherm studies show that the Langmuir isotherm model was well fitted for both CTS and CTS/EGG nanofibers.

**1. Introduction**

Water is considered as one of the root resources for not the living beings only but also for the overall environment. For the last few years, inappropriate usage of water by industries and urbanization has drastically contaminated the water quality and made water unsuitable for drinking [1]. There is a huge list of these impurities contaminating the water such as fluoride, arsenic, nitrate, sulphate, pesticides, metallic species and dyes [2]. Fluoride is one of the basic minerals found in nature in abundance, but human body requires its small amount in water for drinking. It is reported that the huge intake of fluoride may cause serious health issues [3] for the human’s bones and skeleton. It may also lead to fluorosis and countries on the globe are facing the problem of fluorosis such as Iraq, India, Iran, China, Morocco, Pakistan and Libya [4]. The suitable amount of fluoride in water used for drinking ranges from 0.5 to 1.5 mg l\(^{-1}\) as per recommendation of WHO [5]. The probability of its risk towards human health varies with the concentration of fluoride in drinking water [6]. Fluoride ranging from 1.0 to 3.0 mg l\(^{-1}\) is considered as low risk causing dental fluorosis. If the concentration of fluoride in water is in the range of 3.0 to 5.0 mg l\(^{-1}\) then it may cause both dental and mild skeletal fluorosis and can be considered as elevated risk, however the concentration of fluoride in water greater than (5.0 mg l\(^{-1}\)) is considered as higher risk towards the human health [7].

Some of the initiatives have been reported to overcome this hazardous risk of fluorosis by treating fluoride contaminated water [8]. These methods include precipitation, ion exchange, membrane separation and
adsorption. Each technique has its own limitations and advantages. Some of these methods are semi quantitative and requires longer reaction times. Precipitation process is carried out in 18–48 h for efficient results whereas in membrane separation process, membrane fouling effects which lead to decreases in permeate flux. Expensive cleaning and regeneration schemes are necessary for ion exchange method that demands relatively a high capital cost and also the product recovery possibly requires a special, expensive distillation or extraction [9]. Some of the processes like adsorption require higher time for the preparation of adsorbents at lower pH values. Some fluoride removal techniques have the problem of sludge formation which causes water to taste bitter [10, 11]. Among these techniques the adsorption technique via nanofiber is a most versatile and efficient one because of its higher efficiency and maximum capacity of fluoride removal from water [12].

Recent reports reveal that defluoridation is done using different materials such as alumina, sweet lemon peel, chitosan beads, CaO, Chromium, Magnesium oxide coated with alumina, CaCO3 and Ce-Zn metal oxide. Some of the biopolymers are introduced in last few years which have higher potential for defluoridation from the water. Amongst them; CTS has showed higher efficiency for the fluoride removal as one of the biopolymers and has been also considered as non-degradable and non-toxic polymer [13]. CTS is a polymer which is easily available at low cost [14, 15]. CTS has a remarkable potential that eliminates the fluoride from water [16, 17]. The structure of CTS polymer consists of amino and hydroxyl groups; which is why, the adsorption can be effectively done to remove fluoride [18]. In addition, it is reported that an eggshell contains 94.06% calcium and it also contains calcite and calcareous soil [19], and it has greater affinity to fluoride ions [20].

Therefore, in the current research, removal of fluoride via adsorption technique using a novel nanofiber hybrid prepared from Eggshell powder (EGG) incorporated Chitosan (CTS) nanofibers was proposed. The bead free CTS/EGG nanofibers were prepared using electrospinning with smooth morphology. The resultant CTS/EGG nanofibers hybrid was characterised and investigated by its efficiency to remove the fluoride from the aqueous solution.

2. Materials and methods

2.1. Materials

CTS having molecular weight (Mw = 90,000) was purchased from Sigma Aldrich, USA. Chicken eggshell powder as a removal material was obtained by grinding eggshells purchased from local market. Trifluoro acetic acid (CF3COOH) and Glutaraldehyde used for preparing nanofibers and Potassium Fluoride for preparing fluoride solution; all were obtained from Sigma-Aldrich USA. In this study, CTS was taken as 3.5% of total weight of solution. The remaining 96.5% weight of total solution was consisting of Trifluoro Acetic acid. The solution was prepared at room temperature with continuous magnetic stirring for 18 to 24 h.

2.2. Preparation of CTS/EGG nanofibers

Eggs were obtained after boiling the eggs purchased locally. The shells were peeled off, washed several times with deionised water and dried till constant weight was achieved. The eggshells were then washed with the help of pastel and mortar to achieve fine powder. For the preparation solution, CTS (3.5%) was dissolved in Trifluoro Acetic Acid at room temperature for 18 to 24 h. Eggshell powder (10% of CTS weight) was then added in solution to obtain a composite solution. The solution was then poured into plastic syringe and the electrode was inserted into the syringe. This electrode was coupled with a wire connected to power supply. Another wire from the power supply was connected to the ground collector for the collection of nanofibers on its surface. The applied voltage on CTS and CTS/EGG was 25 and 26 KV respectively. The distance between the syringe and collector was 17 cm with an angle of 15°. The ground collector was wrapped with an aluminium foil. After the completion of electrospinning process, the electrospun nanofibers were collected and dried overnight.

2.3. Cross linking of CTS and CTS/EGG nanofibers

The nanofibers sheet collected after electrospinning was crosslinked following the reported method [21]. The nanofibers were placed in a desiccator for 24 h for fuming under few drops of glutaraldehyde. This increases the stability of the prepared nanofibers and resists to get dissolved in water. After fuming process, the nanofibers sheet was dried for 24 h more and later preserved to be used for defluoridation.

2.4. Characterizations

2.4.1. Scanning electron microscopy

Scanning electron microscope helps to examine the surface morphology of nanofibers. Both CTS and CTS/EGG nanofibers were examined under the Scanning electron microscope (JEOL JSM 6010LA). The given voltage was 30 kV with highest magnification of 500,000×. Both samples were sputtered with Pd-Pt before SEM assessment.
2.4.2. Fourier transform infrared spectroscopy
Chemical structural changes were determined in neat CTS and CTS/EGG nano fiber hybrid. The samples were analysed using Fourier transform infrared spectroscopy (FTIR) on IR prestige - 21 by Shimadzu Japan.

2.4.3. Adsorption studies
The adsorption study of fluoride ion from water was studied at room temperature by using batch-wise process. In this study an automatic gallenkamp shaker was used for shaking. The fluoride concentration before and after adsorption from the aqueous solutions was measured by Lambda 35 UV–vis spectrophotometer from Perkin Elmer USA. The absorbance values were taken at \( \lambda_{\text{max}} = 590 \) nm. Different mass studies were carried out ranging 10 mg-60 mg of nano fibers in 10 ml of water at different standard concentration of fluoride until the equilibrium condition was achieved. In order to analyse the removal efficiency and removal percentage of fluoride, different adsorption parameters were studied such as pH study (2–12), contact time (20–120 min), adsorbent dosage (10–60 mg) and fluoride concentration (2–8 mg l\(^{-1}\)). The pH of the solution was adjusted by adding 0.01 M of HCl or 0.01 M of NaOH. After adsorption, nano fibers were removed manually. The adsorption efficiency of CTS/EGG nano fibers was calculated by equation (1).

\[
\text{Adsorption efficiency} = \frac{(C_i - C_f)}{C_i} \times 100
\]

(1)

Where, \( C_i \) is the initial concentration and \( C_f \) denotes the concentration after fluoride adsorption.

3. Results and discussions

3.1. Morphology of CTS and CTS/EGG nanofiber
Figure 1(a) shows the SEM image of CTS nanofibers with a smooth and bead free morphology and the figure 1(c) shows the average diameter of CTS nanofiber as 100 ± 80 nm. On the other hand, the figure 1(b) reveals the bead free and smooth morphology of CTS/EGG nanofibers, and the average diameter was found as 100 ± 50 nm as shown in figure 1(d). The results revealed that there is not any significant influence on CTS nanofibers after incorporation of EGG. EGG incorporation proved to be better for morphology to reduce the number of diameter distributions which confirms a greater number of similar average diameter value of nanofiber can be achieved.
3.2. Adsorption studies

3.2.1. Effect of mass of nano fibers

The adsorption experiment was carried out with an initial adsorbent mass, ranging from 10 mg to 70 mg for both CTS and CTS/EGG nano fibers respectively. The efficiency of defluoridation using CTS nano fibers observed as

**Figure 2.** Adsorption study (a) mass of nano fiber (b) pH (c) contact time (d) initial concentration.

**Figure 3.** Langmuir and Freundlich Isotherms of CTS and CTS/EGG nano fiber.

3.2. Adsorption studies

3.2.1. Effect of mass of nano fibers

The adsorption experiment was carried out with an initial adsorbent mass, ranging from 10 mg to 70 mg for both CTS and CTS/EGG nano fibers respectively. The efficiency of defluoridation using CTS nano fibers observed as
lower than the CTS/EGG nanofibers. The removal of fluoride from water was increased with the increase of mass of an adsorbent from 10 mg to 60 mg. Increasing the number of nanofiber was the reason of increase in removal percentage providing more active sites available on surface of CTS/EGG nanofibers as per previous report [22]. The optimum results were found at 60 mg of nanofibers. At this level, the equilibrium condition was attained, and no further removal was observed afterwards.

3.2.2. Effect of pH
The parameter of pH plays a vital role in the removal of fluoride. The adsorption experiments were carried out for pH values ranging from 2 to 12 for CTS and CTS/EGG nanofibers. The removal percentage for CTS was 23% at pH 7 and the maximum removal percentage for CTS/EGG was 86% at pH6 as shown in figure 3(b), keeping all the conditions constant. The removal of fluoride in this adsorption process is highly based upon pH of water. The efficiency of removal of fluoride by CTS nanofibers was very low as compared to the CTS/EGG nanofibers. The highest removal of fluoride for CTS/EGG was around 86% at pH6. The adsorption capacity was low in acidic pH because of formation of weak hydrofluoric acid which may inhibit the availability of free fluoride ion [23]. In alkaline pH the lower adsorption was noticed, and this may be because of greater competition of hydroxyl ions at active sites [24].

3.2.3. Effect of contact time
In order to attain maximum removal efficiency of CTS/EGG nanofibers, the impact of time was investigated. The efficiency of removal of fluoride by CTS nanofibers was very low as compared to the CTS/EGG nanofibers. As shown in figure 3(c). The adsorption efficiency of both CTS and CTS/EGG nanofibers increased with increase in contact time. Compared to CTS, CTS/EGG nanofibers showed enhanced removal performance (i.e. 82% to 86% in 120 min). Initially, there was increase in removal efficiency with increase in contact time but after some time equilibrium condition was achieved at 120 min The removal percentage was almost constant with further increase in contact time. The minimum removal within initial contact time was just 21% whereas the maximum removal value was 86%. This indicates that CTS/EGG shows good removal of fluoride because egg is a calcium rich material having CaCO3, which along with OH and NH2 groups from chitosan may be responsible for defluoridation [25–27].
3.2.4. Effect of initial concentration

The adsorption experiments were carried out with an initial concentration of fluoride in range of 2 to 8 mg l\(^{-1}\) for both CTS and CTS/EGG nanofibers. The optimum results for CTS and CTS/EGG found 23% and 86% of fluoride removal respectively, when the initial concentration was 2 mg l\(^{-1}\).

In figure 3(d) it is noted that with an increase in initial concentration of fluoride, the removal efficiency decreases, and this may be because of limited number of the active sites of adsorbent \[25\]. Some reports also showed the similar studies for fluoride removal with Fe(III) loaded carboxylated chitosan bead and La(III) incorporated carboxylated chitosan beads respectively \[26, 27\].

3.3. Adsorption isotherm studies

Adsorption isotherm studies have been used in this study to examine the data for fluoride concentrated water and treated water. Langmuir and Freundlich isotherms (equations (2) and (3) as shown below) were applied in this study to examine the adsorption characteristics of CTS and CTS/EGG nanofibers.

\[
\frac{C_e}{q_e} = \frac{1}{b \times q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \\
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]

(2) (3)

Where, \(C_e\) expresses the equilibrium concentration of Fluoride (F) in the solution. The \(q_{\text{max}}\) is used to mention maximum capacity of adsorption (mg/g), and \(b\) belongs to adsorption energy expressing the affinity of nanofibers, \(k_f\) denotes the Freundlich adsorption capacity and \(1/n\) is relative distribution of active sites. In Freundlich isotherm, the higher value of \(1/n\) shows the less availability of heterogeneous active sites and the smaller value of \(1/n\) shows the maximum availability of heterogeneous active sites and adsorption \[28\]. The Langmuir and Freundlich isotherm parameter of this study for CTS and CTS/EGG are as shown below in table 1.

Furthermore, isotherms studies found that the Langmuir isotherm model was well fitted for both CTS nanofibers and CTS/EGG nanofibers due to high value of \(R^2\) in Langmuir isotherm for both materials as shown in figures 4(a) and (c) respectively. The maximum adsorption capacity of CTS nanofibers and CTS/EGG nanofibers were found to be 0.1017 mg g\(^{-1}\) and 0.6265 mg g\(^{-1}\) respectively.

3.4. Chemical Structure of CTS and CTS/EGG nanofiber

Figure 2 shows the FTIR spectrum of CTS and CTS/EGG nanofibers before and after adsorption of fluoride respectively. It can be observed that many chemical groups were found at different peaks in CTS and CTS/EGG. In CTS, C-O observed at the spectrum from 1020 to 1186 cm\(^{-1}\), the CH also observed at 1374 cm\(^{-1}\), the peaks at 1650 cm\(^{-1}\) showed presence of amide groups, a long stretching band of –OH group also found at 3424 cm\(^{-1}\).

Whereas, in CTS/EGG nanofibers, no any significant difference in absorption bands was observed as EGG also
contains similar groups and the CaCO\(_3\) of EGG also reported at the same spectrum in previous reports. The peaks observed in CTS/EGG nanofibers are intensive compared to CTS nanofibers which may be due the presence of same functional groups from EGG incorporation within the CTS nanofibers [29]. The peak positions were also changed significantly suggesting interactions of these groups with eggshells. The high peak observed for C–O stretching at 1194 cm\(^{-1}\), the CH group was observed at 1431 cm\(^{-1}\), an amide group can be seen at 1668 cm\(^{-1}\) and a long stretching band of –OH group can be seen at 3428 cm\(^{-1}\) [30]. The FTIR spectrum of both CTS and CTS/EGG after fluoride adsorption reveals that the reduced intensities of functional spectrum effectively participated in removal of Fluoride. –OH group effectively participated and disappeared from FTIR spectrum whereas NH\(_2\), CO and CH also effectively participated. The more defluoridation percentage in CTS/EGG nanofiber may also be justified by reduction of more intensive spectrum to the same level as CTS nanofibers defluoridation. The results revealed that the CTS/EGG contains more participating groups on the surface for effective removal of Fluoride.

3.5. Comparison to previous studies on defluoridation

Compared with the previous reports on defluoridation, the existing study of CTS/EGG nanofiber hybrid showed a significant defluoridation of 86% at pH 6 within a remarkable minimum time. Though the natural chitosan has a good adsorption capacity, yet the removal percentage is comparatively low i.e. 60%. Quartz can also be effectively used as an adsorbent for defluoridation but it requires more contact time with less adsorption capacity. Sweet lemon peel is also the natural material and easy to obtain, but the removal of fluoride is achieved in acidic pH, which is practically not suitable particularly for drinking water. Granular Red Mud is also reported as an adsorbent for fluoride removal with contact time of 360 min Another reported adsorbent; montmorillonite does not show enough removal percentage and adsorption capacity even at 180 min of contact time. Laterite shows very low adsorption capacity with more contact time when compared with the current research. Similarly, the adsorption capacity of alumina is lower and contact time is higher as compared with present study of CTS/EGG nanofiber hybrid. Therefore, this discussion proves that CTS/EGG nanofibers have good adsorption capacity with maximum removal percentage for fluoride from aqueous solution at minimum contact time.

4. Conclusion

The CTS/EGG nanofibers hybrid was successfully prepared via electrospinning and showed the significant adsorption results for the removal of fluoride from aqueous solution. Defluoridation efficiency of 86% within 120 min at pH 6 was successfully achieved. The optimum initial concentration of fluoride as adsorbate was 2 mg l\(^{-1}\) and mass of CTS/EGG nanofibers was 60 mg. The study also revealed CTS/EGG nanofiber adsorbent can be replaced to other conventional adsorbents due to its exceptional advantages like easy fabrication, no sludge formation and minimum cost. The SEM analysis showed smooth and bead free morphology of this novel hybrid nanofiber. FTIR spectroscopy determined the presence of some added functional groups on the surface of CTS/EGG nanofiber contributing in defluoridation. The Langmuir isotherm model was well fitted for both CTS nanofibers and CTS/EGG nanofibers blend because of high value of \(R^2\) i.e. 0.93 and 0.99 respectively. The maximum adsorption capacity for CTS nanofibers and CTS/EGG nanofibers were noted to be 0.1017 mg g\(^{-1}\) and 0.6265 mg g\(^{-1}\) respectively at room temperature. The adsorbent showed good removal performance and can be further evaluated for using commercial filters in treating ground water loaded with Fluoride.

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