

DEVELOPMENT OF AN ADSORBENT MATERIAL TO REMOVE FLUORIDE FROM WATER

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Abstract: Groundwater is a scarce commodity in Sri Lanka where it fulfills more than 80% of rural drinking water supply-demand. Dental fluorosis, skeletal fluorosis, and kidney diseases are commonly observed in most parts of rural areas due to the presence of fluoride in groundwater at harmful levels ($>1\text{mg/L}$). The conventional water treatment process has failed to ensure safety level of fluoride in water before consumption. Adsorption is one of the widely used methods of removing fluoride due to its effectiveness, low cost, and availability of a wide range of adsorbents. Chitosan is a low-cost biopolymer used as a biosorbent for fluoride removal. In this study, Chitosan - biochar composite beads were prepared to compare its effectiveness against raw chitosan in removal of fluoride from synthetic fluoride solution. Chitosan and sawdust-biochar were converted into bead form and they were chemically modified via crosslinking followed by protonation. The effect of adsorbent dosage, initial fluoride concentration, and contact time were investigated by conducting batch experiments in neutral pH at room temperature. Fluoride sorption equilibrium was reached after 1 hour for modified chitosan with excellent removal efficiency more than 90% whereas raw chitosan indicated a very low removal efficiency of 16% after 2 hours of reaching the equilibrium. At 90% removal, the final fluoride content was recorded at 0.5 mg/L and it is well below 1mg/L which is required as per Sri Lankan Standards for Potable Water (SLS 614:2013). Therefore, the developed sorbent material gives promising results in removing fluoride from water.

Keywords: Adsorption; Chitosan; Composite; Crosslinking; Fluoride; Sawdust.

1. Introduction

With limited access to safe water, most people living in rural communities in developing countries depend on groundwater for drinking water purposes. Fluoride is a major contaminant in groundwater and fluoride may enter into groundwater due to weathering of fluoride bearing minerals and various anthropogenic activities (Dharmagunawardhane, 2009). The presence of fluoride beyond tolerance limit could bring detrimental health issues such as dental fluorosis, skeletal fluorosis and kidney diseases (Dissanayake, 2010). WHO standard states that the safe level of fluoride in drinking water must be below 1.5 mg/L (WHO, 2018). Hence, it is vital to ensure safe levels of fluoride in drinking water prior to consumption. Out of numerous techniques available for defluoridation, the process of adsorption has gained the spotlight over the past years due to its simplicity of operation, cost effectiveness and efficiency (Wang, 2007). Adsorption has provided promising results on removal of fluoride with several adsorbents such as oxides and hydroxides, biosorbents, geomaterials, carbonaceous materials and industrial products and by products (Stanic et al., 2014).

The use of biosorbents in the process of adsorption in fluoride removal has been widely studied by many researchers since it offers several advantages such as biodegradability, biocompatibility and low cost over other conventional adsorbents. As a biosorbent, biochar is found to be effective in removing various organic and inorganic pollutants from water. Biochar could be characterized by high surface area and high porosity similar to activated carbon (Dai et al., 2019). Saw dust is one of the sources of biochar produced in large quantities at saw mills. Saw dust biochar could be prepared by pyrolyzing saw dust at elevated temperatures in an oxygen depleted environment (Mohan et al., 2014). Recent studies show the potential of sawdust biochar in removal of various pollutants in drinking water including fluoride (Guan et al., 2015; Zhou et al., 2017).

Chitosan is a naturally occurring biopolymer and has been extensively studied as an adsorbent material in removing dyes, heavy metals, organic pollutants, fluoride etc (Vishwanathan & Meenakshi, 2008; Ngah et al., 2011). Chitosan is normally processed from alkaline deacetylation of chitin, present in shellfish and available in flakes or powder form. Presence of functional groups such as amino and hydroxyl groups enhances its capacity to interact physically and chemically with a variety of molecules (Zhou et al., 2013; Ngah et al., 2011). Thus several modifications such as cross linking, grafting, chelating

with metal ions, have been applied on chitosan polymer to enhance its defluoridation capacity (Agarwal & Vaishali, 2017). Even though, the defluoridation capacity of unmodified chitosan is negligible, modified chitosan has proven to be effective in fluoride removal.

Since no previous study has been conducted to explore the combined effect of chitosan and biochar on fluoride removal, this study aims to develop a novel chitosan sawdust biochar composite bead to investigate its capacity on removal of fluoride from water. Chitosan-biochar composite beads were suitably modified via cross linking followed by protonation to further enhance its defluoridation capacity. A comparative study on raw chitosan and modified chitosan-biochar composite beads were made using batch experiments. The effect of various influencing parameters such as contact time, initial fluoride concentration and adsorbent dosage was evaluated.

2. Materials and methods.

2.1 Materials

Chitosan powder was obtained from Norwegian University of Life Sciences and was used as the raw material without any modification. Physical modification of chitosan was carried out using glacial acetic acid (CH_3COOH), sodium hydroxide (NaOH) procured from Sisco Re-search Laboratories Pvt. Ltd, India and Pyrolyzed Sawdust Prepared from softwood Sawdust ($550\text{ }^\circ\text{C}$ - $660\text{ }^\circ\text{C}$).

2.2 Preparation of Sawdust-biochar.

Saw-dust biochar was prepared by pyrolyzing softwood sawdust collected from a saw mill. Pyrolyzing temperature range of the sawdust was $550\text{ }^\circ\text{C}$ – $660\text{ }^\circ\text{C}$ with a resident time of 40 min inside the reactor. The resulting biochar was washed several times with distilled water to remove any adhered impurities and oven dried for 24 h at $37\text{ }^\circ\text{C}$. The dried biochar was then grounded and sieved through a 75 micron sieve and used for adsorption studies without further modification.

2.3 Preparation of chitosan-biochar composite beads.

Initially, Chitosan powder (1g) was dissolved in 100 ml of 1% acetic acid (v/v) solution followed by addition of 0.5 g of sawdust biochar. The mixture was stirred at room temperature for 2 h. Chitosan-biochar composite beads were prepared by drop wise addition of this solution into a 1M NaOH solution. The formed beads were kept in NaOH solution for 24 h.

Thereafter, chitosan-biochar composite beads were washed several times with distilled water to remove excess NaOH .

2.4 Preparation of protonated chitosan-biochar composite beads.

The wet beads were cross linked with 2.5 wt. % glutaraldehyde solution. The mixture was kept in a refrigerator at 25 °C for 48 h to facilitate cross linking reaction. The cross linked beads were washed with distilled water to remove any free glutaraldehyde. Thereafter the beads were treated with concentrated HCl for about 30 min for protonation of ammine groups in chitosan. The resulting Protonated Chitosan Biochar Composite Beads (PCBCB) were then washed with distilled water to a constant pH and used for adsorption studies.

2.5 Sorption experiments

A stock solution (100 mg/L) of fluoride was prepared by dissolving 221 mg of anhydrous sodium fluoride in one litre of deionized water and diluted to obtain the desired concentration of fluoride for adsorption experiments. Batch experiments were conducted to study the effect of various influencing parameters like contact time, adsorbent dosage and initial fluoride concentration. All experiments were conducted at room temperature (25 °C) and neutral pH was maintained throughout the experiments since the groundwater is considered to be at neutral pH. Samples were shaken in a mechanical shaker at 200 rpm in each experiment. Sorption experiments conducted with raw chitosan were filtered using Whatman No. 42 filter paper and filtrate was analysed for fluoride concentration by SPANDS method using a potable colorimeter.

3. Results and discussion

3.1 Characterization

Raw chitosan adsorbent and the protonated chitosan-biochar adsorbent were characterized using pH of zero point charge (pHzpc) method. pHzpc was determined using pH drift method. pHzpc for raw chitosan was found to be at pH 7 whereas, pHzpc of protonated chitosan-biochar adsorbent was shifted to pH 2.2. This indicates occurrence of structural changes in the composite (Sundaram et al., 2009).

3.2 Effect of contact time.

Figure 1 shows the results of the contact time test carried out for both raw and modified chitosan using initial fluoride concentration of 5 mg/L with neutral pH at room temperature (25 °C). A rapid fluoride adsorption was observed initially for modified adsorbent and thereafter gradually reaching the equilibrium. It is interesting to note that the equilibrium time of modified chitosan was around 60 minutes while

raw chitosan reached equilibrium at around 120 minutes. This equilibrium time was fixed as contact time for both raw and modified chitosan in further experiments. Excellent removal efficiency was recorded for modified chitosan which was more than 90% at equilibrium, whereas only 16% of maximum removal efficiency was observed for raw chitosan at the time of equilibrium. Moreover, since chitosan has been modified both physically and chemically a mixed mechanism of adsorption is observed in the modified chitosan unlike the raw chitosan. This explains the desorption that happens from time to time with modified chitosan.

The rapid uptake of fluoride observed initially for modified adsorbent could be due to the adsorption on the outer surface, and subsequently, adsorption taking place slowly inside the pores (Geethamani, et al., 2014). As time elapses, the fluoride concentration in the solution gets reduced, thus reducing the concentration gradient between the bulk solution and the adsorbent surface and thereby reducing the net driving force to overcome the resistance between bulk solution and adsorbent surface (Anbia & Salehi, 2012). Hence the rate of adsorption gradually declines with attainment of saturation of active sites and functional groups.

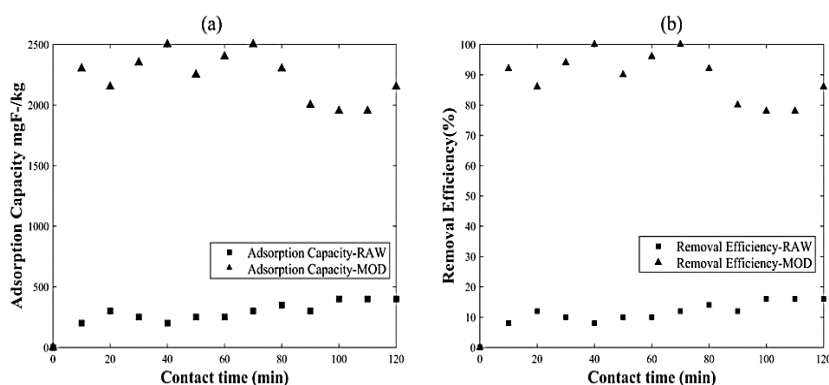


Figure 1: (a) Adsorption capacity as a function of contact time
 (b) Removal efficiency as a function of contact time
 (Temperature = 25 °C; Initial fluoride concentration = 5 mg/L; Adsorbent dosage = 2 g/l; pH = 7)

3.3 Effect of adsorbent dosage

The effect of adsorbent dosage was investigated for both raw and modified chitosan and the results are illustrated in Figure 2. Study was conducted with initial fluoride concentration of 10 mg/L for a dosage

ranging from 0.5 g/L to 5 g/L at initial pH of 7 in room temperature (25 °C). The fluoride adsorption capacity of both raw and modified chitosan decreases with the increase in adsorbent dosage while fluoride removal efficiency increases in modified adsorbent. The increase in removal efficiency can be attributed to the availability of active sites and increased surface area when dosage increases from 0.5 g/L to 5 g/L, whereas the decrease in adsorption capacity could be due to the presence of unsaturated sites during the adsorption process as the initial fluoride concentration is kept constant. (Anbia & Salehi, 2012).

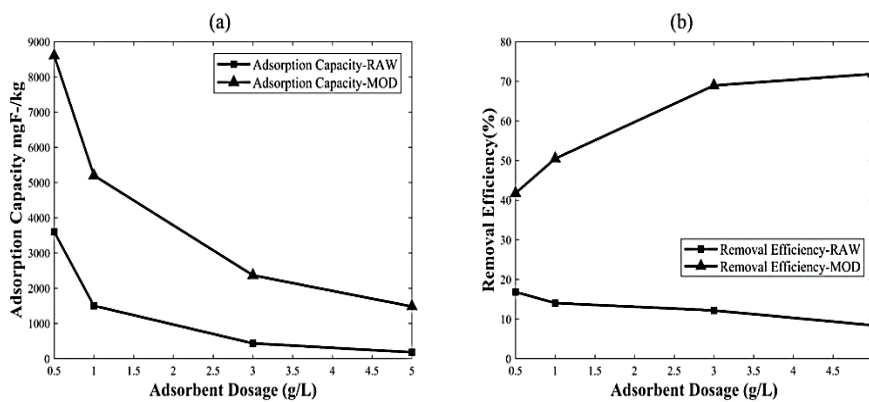


Figure 2: (a) Adsorption capacity as a function of adsorbent dosage
 (b) Removal efficiency as a function of adsorbent dosage
 (Temperature = 25 °C; Contact time = 60 min for Mod. Adsorbent and 120 min for Raw adsorbent; Initial fluoride concentration = 10 mg/l; pH = 7)

3.4 Effect of initial fluoride concentration

The adsorption of fluoride onto raw and modified chitosan was carried out for initial concentrations 2, 3, 5, 6, 7, 8, 10 and 15mg/L for a fixed contact time and the result obtained are illustrated in Figure 3. It was observed that the adsorption capacity of both raw and modified chitosan increased when initial fluoride concentration increased. Similar observations were made by Viswanathan and Meenakshi (2008) on their modified adsorbent in fluoride removal study. The reason behind this observation is that at higher fluoride concentrations there is high concentration gradient acting as a driving force to overcome mass transfer resistance between bulk solution and adsorbent surface. The decrease in fluoride removal efficiency was observed in both cases since there is limited number of active sites to accommodate fluoride ions for a certain amount of adsorbent dosage (Patnaik et al., 2016;

Yadav et al., 2013). As for raw chitosan the adsorption capacity decreased with increase in initial fluoride concentration. This could be a result of fluoride ions not being able to come in contact with active sites of the adsorbent.

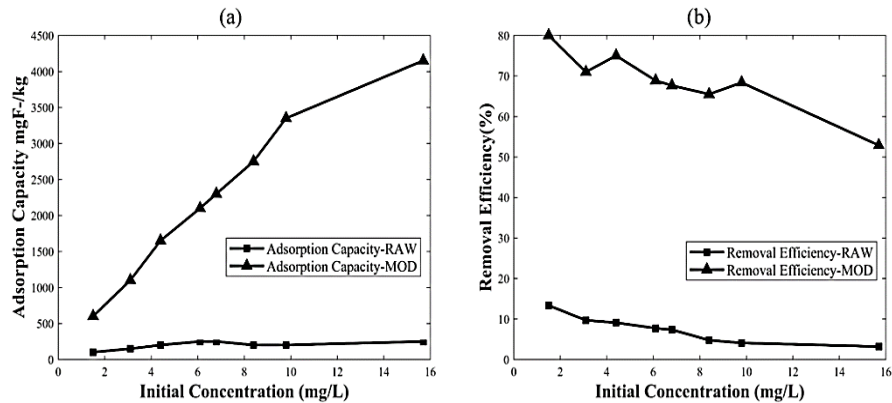


Figure 3: (a) Adsorption capacity as a function of initial fluoride concentration (b) Removal efficiency as a function of initial fluoride concentration (Temperature = 25 °C; Contact time = 60 min for Mod. Adsorbent and 120 min for Raw adsorbent; Adsorbent dosage = 2 g/l; pH = 7)

4. Conclusion

In this study the fluoride removal using raw chitosan powder and Protonated Chitosan Biochar Composite Beads (PCBCB) was investigated. The experiments were conducted at pH 7 owing to the fact that groundwater is at neutral pH. It is evident that modified chitosan possesses an excellent defluoridation capacity when compared to raw chitosan. The optimum contact time for modified chitosan is 60 minutes with excellent removal efficiency more than 90% while, raw chitosan powder indicated a very low removal efficiency of 16% after 120 minutes of equilibrium time. The zero-point charge of PCBCB was found to be 2.2 and it suggests the occurrence of structural changes on the surface of the adsorbent. Considering all the above facts, it could be said that Protonated Chitosan Biochar Composite beads can be used effectively for removal of fluoride from water.

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