Utilization of coal fly ash in the adsorptive removal of fluoride from contaminated groundwater

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Abstract. 75% of the global production of fly ash (FA) totalling 562 million metric tonnes becomes solid waste causing major environmental and economic havoc. In this research, a comparative study was conducted on the utilization of raw and chemically modified FA adsorbents in the removal of fluoride (F\(^-\)) from contaminated water. The modification was done by using hydrochloric acid (HCl) and magnesium chloride (MgCl\(_2\)). Characterization of the adsorbents was done by using SEM-EDX analysis, specific surface area (S\(_S\)) and pH of zero point charge (pH\(_{zpc}\)). The characterisation confirmed that the modification process removed the impurities in FA and improved the S\(_S\). However, the shift of pH\(_{zpc}\) from 10.71 to 4.94 was unfavourable for the F\(^-\) removal due to the reduction in the pH range in which the adsorbents surface charge is positive. Adsorption studies indicated that raw adsorbent is more effective than the modified adsorbent. The maximum adsorption capacity obtained at the optimum conditions (pH = 2; contact time = 120 minutes; dosage =2.0 g/L) was 3.64 mg/g and at neutral pH it was 1.0 mg/g. In conclusion, raw FA adsorbent can be used as a low-cost adsorbent material to remove F\(^-\) from contaminated water.

1. Introduction

Fluoride is an essential ion for humans as it prevents tooth decay but excess fluoride levels can cause adverse health effects like; dental fluorosis, skeletal fluorosis and crippling fluorosis [1]. The World Health Organisation (WHO) guideline indicates that the fluoride level in drinking water should not exceed 1.5 mg/l. In Sri Lanka, SLS 614: 2013 indicates an upper limit of 1.0 mg/L in drinking water. In Sri Lanka, the presence of high concentrations of fluoride especially in the groundwater sources in the dry zone has become a serious problem [1]. This is highlighted by the study conducted by [1] which reports that high fluoride levels are present in many of the groundwater sources in the dry zone which affects over 8 million people. The study conducted by [2] also highlights this fact by presenting that the overall prevalence of dental fluorosis of 43.2% was indicated in a study conducted in the South of Sri Lanka by examining 518 children of 14 years of age.

Through the conventional treatment processes of coagulation and precipitation, only 18 - 33% of fluoride present in raw water can be removed as a precipitate. The remainder (67 - 82%) will form a soluble aluminium fluoride complex ion which is toxic [3]. Therefore, it is necessary to employ an effective treatment process to lower the fluoride level up to a level which is safer for consumption. Therefore, to achieve the required drinking water standards different advanced methods have been employed in the treatment process. These methods include membrane, ion exchange and
adsorption processes. Despite the high removal efficiencies in membrane and ion exchange processes, the usage is discouraged due to the high costs involved. As a result, National Water Supply and Drainage Board which is the main supplier of potable water in Sri Lanka, is reluctant to use both these methods in water treatment.

Comparatively, adsorption process is a cost-effective method having the potential to remove fluoride from contaminated water. Additionally, [4] states that “adsorption is regarded as one of the most suitable techniques for the defluoridation because it is economical, robust, environmentally benign and efficient”. As reported in [3] commonly used adsorbent materials for the removal of fluoride are activated alumina and activated carbon. When using activated carbon the pH values should be below 3.0 for efficient removal of fluoride [3]. This requirement of pH adjustment makes it a costly process. Studies have found out that in place of these costly adsorbent materials like activated alumina and activated carbon, a solid waste material like fly ash can be used.

Fly ash is a by-product of coal combustion and it mainly consists of SiO₂ and Al₂O₃. Globally the annual production of fly ash is approximately 750 million tonnes and out of that only 25% of it is utilized while the remaining amount ends up in a landfill [5]. When considering Sri Lanka annually 150 metric tonnes of it is produced in the Norochcholai coal-fired power plant but of that only 20% is utilized which is lower than the global average utilized while the rest of it becomes solid waste [6].

Fly ash has a good potential of being used as a low-cost adsorbent material in water treatment because of its chemical composition and good adsorbent characteristics like porosity, large surface area and particle size distribution [7]. In literature, there exist several studies where raw and modified fly ash adsorbents have been used for defluoridation. The research conducted by [8] using synthetic wastewater to investigate the ability of raw fly ash in defluoridation indicates that fly ash can be used for defluoridation. This also agrees with the findings of [9].

Modifications on fly ash can be done through physical means or chemical treatments. Through literature, it can be observed that these modifications help to increase the effective surface area and porosity of the raw fly ash which helps to increase its adsorption capacity. From the batch experiments done by [4] and [8], it can be observed that modified fly ash has a greater adsorption capacity than raw fly ash. However, comparative studies between the raw and modified fly ash adsorbents are rather limited. In this research, a comparative study was conducted on the utilization of raw and chemically modified FA adsorbents in the removal of F⁻ from synthetic wastewater.

2. Materials and methods

2.1 Materials

The adsorbent material used in this study was fly ash obtained from the Norochcholai coal power plant. For the adsorbent modification process, HCl and MgCl₂ were used. For the determination of the specific surface area of the adsorbents methylene blue dye was used. In the adsorption studies, the stock solution of fluoride was prepared by using sodium fluoride. SPADNS reagent was used in the process of measuring the fluoride concentrations. The adjustments for pH were done using HCl and NaOH. All chemical reagents used were of analytical grade.

2.2 Methods

2.2.1 Preparation of the Adsorbents. The raw adsorbent was prepared by washing the acquired fly ash with distilled water until the wash water pH and electrical conductivity became stable. Then it was oven dried for 24 hours at 104°C after which, the sample was sieved using a 75 µm sieve and stored in an air tight container. The first stage of the modification process involved mixing prepared raw adsorbent with 12 mol/dm³ HCl solution with a solution to sample ratio of 5 ml: 1 g of fly ash for 8h at 80°C. Then it was washed with distilled water until the wash water pH and electrical conductivity became stable and then oven dried for 24 hours at 104°C. Next, the dried sample was mixed with a 0.6 mol/dm³ MgCl₂ solution with a solution to sample ratio of 10 ml: 3 g of HCl modified fly ash and the
mixture was incubated at 25°C for 48 hours. After that, the excess solution was removed and the modified adsorbent was washed with distilled water until the wash water pH and electrical conductivity became stable and was oven dried at 104°C for 24 hours. Then, the particles passing through a 75 µm sieve were stored in an air tight container.

2.2.2 Characterisation of the Adsorbents. The characterizations of the raw and modified adsorbents were done by using SEM-EDX analysis, the pH of zero-point charge (pH_{zpc}) and the specific surface area. The Scanning Electron Microscopy with Energy Dispersive X-Ray analysis was done by using Scanning Electron microscope (EVO LS 15). The surface chemical compositions of the adsorbent materials were analyzed through the EDX analysis. The pH_{zpc} of the adsorbents was investigated by adding 0.05 g of raw and modified fly ash adsorbent to 25 ml samples of the prepared pH solution series. Then, they were shaken for 24 hours at 200 rpm after which the final pH was recorded. The pH measurements were taken by using HACH sensION+ PH1 portable pH meter. The specific surface areas of the adsorbents were investigated by using the methylene blue (MB) dye method. After approximating the complete cation replacement point by the spot test, titration method was carried out to exactly identify the complete cation replacement point. Then, the specific surface area was calculated using Eq (1).

\[ S_S = \frac{m_{MB}}{319.87} \cdot A_v \cdot A_{MB} \cdot \left( \frac{1}{m_f} \right) \]  

where \( S_S \) is the specific surface area, \( m_{MB} \) is the mass of the absorbed MB at the point of complete cation replacement, \( m_f \) is the mass of the sample, \( A_v \) is the Avogadros number (6.022 \times 10^{23} \text{ mol}) and \( A_{MB} \) is the area covered by one MB molecule assumed to be 130Å².

2.2.3 Adsorption Studies. The effect of pH, contact time and the adsorbent dosage in the removal of fluoride were analyzed based on the adsorption capacities. The pH value at which the maximum adsorption capacity is observed was selected as the optimum pH value. The optimum contact time was selected as the time in which the adsorption equilibrium was reached.

The adsorption capacities were calculated by comparing the initial and final pollutant concentrations in the synthetic waste water samples as shown in Eq. (2)

\[ q_e = \frac{(C_0 - C_f)V}{W} \]  

where \( q_e \) is the adsorption capacity, \( C_0 \) is the initial pollutant concentration, \( C_f \) is the final pollutant concentration, \( V \) is the volume of the sample and \( W \) is the weight of the adsorbent added into the sample.

In all the experiments, the initial concentrations of fluoride were maintained at 10 mg/L. The fluoride concentration was measured by using HACH DR900 Multi parameter Portable. Before measuring the final concentrations the samples were filtered by using 11 µm filter papers.

3. Results and discussion

3.1 Characterisation of the Adsorbents

3.1.1 SEM EDX Analysis. Figure 1 illustrates the SEM images obtained for the raw, HCl modified and MgCl₂ modified adsorbent samples. Even though in literature a uniform smooth surface has been observed in raw fly ash cenospheres (Xu, et al., 2011), the SEM images obtained for the raw fly ash cenospheres as shown in figure 1(d) had a rough surface. This could be due to the presence of FeO that was identified from the EDX analysis.

Based on Figure 1(a), (b) and (c) a change in the microstructure of the adsorbents can be observed with each modification step. Table 1 which shows the chemical composition of adsorbents after each modification step indicates that after the HCl modification a significant amount of impurities contained in the raw adsorbent has been removed. The removal of impurities highlighted in
table 1 can be observed through figure 1(d) and 1(e). Further, table 1 indicates that during the MgCl$_2$ modification magnesium (Mg) had not been successfully loaded on the surface of the modified adsorbent cenospheres.

![Figure 1](image)

**Figure 1.** SEM images of (a) Raw FA under low magnification, (b) HCl modified FA under low magnification, (c) MgCl$_2$ modified FA under low magnification, (d) Raw FA cenospheres and (e) MgCl$_2$ modified FA cenospheres.

**Table 1.** Chemical Composition of Adsorbents obtained through EDX Analysis.

| Compound | SiO$_2$ | Al$_2$O$_3$ | CaO | FeO | MgO | TiO$_2$ | K$_2$O | Na$_2$O | Nb$_2$O$_5$ |
|----------|--------|------------|-----|-----|-----|--------|-------|--------|-----------|
| Raw      | 50.10  | 32.05      | 5.15| 5.92| 1.68| 1.43   | 0.41  | 0.11   | 3.15      |
| HCl Modified | 58.53 | 35.42      | 1.32| 1.23| 0.35| 2.09   | 0.48  | 0.59   | 0.00      |
| MgCl$_2$ Modified | 59.59 | 34.47      | 0.92| 1.74| 0.63| 2.07   | 0.59  | 0.00   | 0.00      |

3.1.2 pH of Zero Point Charge ($pH_{zpc}$). The $pH_{zpc}$ studies were conducted at 30°C for both raw and modified adsorbents. The $pH_{zpc}$ of the raw and modified adsorbents were found to be 10.71 and 4.94 respectively. Based on the obtained $pH_{zpc}$ values it can be seen that at neutral pH the surface charge on the raw adsorbent is positive and that on the modified adsorbent is negative. Thus, the raw adsorbent can be used to remove negatively charged pollutants at neutral pH effectively, when compared with the modified adsorbed.

3.1.3 Specific Surface Area ($S_b$). The specific surface area of the adsorbents was determined by using the MB method. The complete cation replacement point of the raw and modified adsorbents was identified to occur at the ratio of the weight of added MB to the weight of adsorbent $1.8\times10^{-4}$ and $9.0\times10^{-4}$ respectively. The specific surface area obtained for the raw adsorbent was 0.44 m$^2$/g. The obtained
value falls within the range mentioned in [5], which states that the specific surface area of coal fly ash is between 0.3 m$^2$/g - 0.5 m$^2$/g. The specific surface area of the modified fly ash adsorbent determined through the MB method was 2.20 m$^2$/g. It can be seen that after the modification the specific surface area of the adsorbent increased by 5 times. The increment factor in the specific surface area corresponds to the increment factor found in literature for HCl modification of fly ash [10]. Since adsorption is a surface process the increment in the surface area of the material will favour better removal of pollutants.

3.2 Adsorption studies

3.2.1 Effect of Initial pH. Figure 2 presents the fluoride adsorption by using Raw Fly ash Adsorbent (RFA) and Modified Fly ash Adsorbent (MFA) over the pH range of 2 - 12. The shape of the obtained curves was similar to that found in literature [4]. For both adsorbents, adsorption capacity increased with the decrease in the initial pH of the solution. The maximum absorption capacity achieved by the raw and modified adsorbents as shown in figure 2 at pH 2 was 3.64 mg/g and 1.60 mg/g respectively. At lower pH values raw adsorbent showed a higher adsorption capacity than the modified adsorbent. Since fluoride is a negative ion, removal by adsorption was favoured when the surface charge of the adsorbent was positive, which occurred at pH values lower than the pH$_{ZPC}$ of the adsorbent.

3.2.2 Effect of Contact Time. Results of adsorption studies conducted to study the effect of contact time for both raw and modified adsorbents are shown in figure 3. The initial pollutant concentration of fluoride was 10 mg/L. The optimum contact time of 2 hours was observed for both raw adsorbent and the modified adsorbent. The adsorption capacities achieved by the raw and modified adsorbents after reaching the adsorption equilibrium were 3.62 mg/g and 1.67 mg/g respectively. Similar results have been observed in previous researches [8]. The maximum adsorption capacity achieved by the modified adsorbent was similar to that found in literature where a similar magnesium loading has been done successfully [4].

![Figure 2. Effect of the initial pH on the adsorption of fluoride on the raw and modified adsorbents (Temperature = 30°C; Contact Time = 24 hours; Adsorbent dosage = 2 g/L; Initial fluoride concentration = 10 mg/L).](image1)

![Figure 3. Effect of the contact time on the adsorption of fluoride on raw and modified adsorbents (Temperature = 30°C; pH = 2.0; Adsorbent dosage = 2 g/L; Initial fluoride concentration = 10 mg/L).](image2)
3.2.3 Effect of Adsorbent Dosage. Studies were done only for raw adsorbent as it showed higher removal efficiency than the modified adsorbent. The results obtained are shown in figure 4. As mentioned in [4], the removal efficiency increased with the dosage because of more active sites from an increase in the amount of the adsorbent. But the adsorption capacity reached a maximum at the adsorbent dosage 2.0 g/L and then it reduced as shown in figure 4. The reduction occurred because even though the dosage was increased, the fluoride concentration of the initial samples remained constant. As a result, the decrease of the fluoride adsorption capacity could be observed. The same observation has been made in available literature where the adsorption capacity reached a maximum and then it reduced [4].

4. Conclusion
The fluoride adsorption studies were conducted by varying the pH of the initial solution, contact time and adsorbent dosage. From the experiments conducted to study the effect of pH, it was found that raw adsorbent had higher adsorption capacity than the modified adsorbent. The optimum initial pH value of the solution, contact time and the adsorbent dosage for the raw adsorbent in the removal of fluoride were 2, 120 minutes and 2.0 g/L respectively. The maximum adsorption capacity achieved by using the raw adsorbent was 3.64 mg/g. Even at the neutral pH, the raw adsorbent showed considerable adsorption capacity (1 mg/g), therefore it is possible to use the raw adsorbent in pretreatment of groundwater.

Acknowledgments
The authors acknowledge the WaSo - Asia Project and TOKYO Cement grant for providing financial assistance in carrying out this research project

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