

Research Paper

Efficacy of Quaternary Ammonium Functionalized Waste Paper Bio-Coagulant for Removal of Fluoride Ions from Aqueous Solution

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Abstract— Fluorides are one of the many pollutants found in water. At low concentration, fluorides are essential for improving the density and hardness of bones and teeth enamel during their growth. A concentration greater than 1.5 mg/L in drinking water has several detrimental effects on human health, including dental and skeletal fluorosis. There are several methods employed to rid water of fluorides. These include, reverse osmosis, adsorption, ion exchange, coagulation and flocculation. This study focuses on removal of fluorides from aqueous solutions by coagulation using quaternary ammonium functionalized waste paper bio-coagulant. Quaternary ammonium compounds were synthesized from waste paper by first nitrating cellulose present in waste paper. The attached nitro groups, were reduced to amine groups and quaternization was done using methyl iodide. The prepared bio-coagulant was characterized using FTIR and TGA. The coagulant was used to remove fluorides from model solutions and real water samples from Gilgil area in Nakuru county, Kenya. A fluoride ISE was used to determine fluoride ion concentration in each model solution and in the real water samples. Optimized parameters included pH, initial fluoride ion concentration, contact time and bio-coagulant dosage. Characterization data confirmed successful quaternization was achieved. Thermal stability of the material was up to a temperature of 563.15 K. The optimum pH value was 4.0 while the contact time was 15 minutes. Fluoride removal increased with increase in initial concentration up to an optimum 20 mg/L. Fluoride removal was also observed to increase with increase in coagulant dosage. Obtained data fitted well on Langmuir adsorption isotherm with R^2 value of 0.9707, confirming chemisorption as the predominant intermediate process. An adsorption capacity of 3.6311 mg/g was obtained. Fluoride ion removal percentage in the model solution was 81% and 66.25% in the real water sample.

Keywords— Coagulation, Bio-coagulation, Fluoride, Quaternary ammonium, Water, Adsorption

1. Introduction

Fluorides are a major water pollutant that contributes greatly to the scarcity of drinking water in the world [1], [2]. There are many methods used to rid water of contaminants, among them fluorides, depending on the degree of pollution, the quality of untreated water and regulations imposed by public health in the specified region. [3]. Some of these methods include reverse osmosis, ultra-filtration, precipitation, ion exchange, adsorption and coagulation/flocculation [4], [5]. Coagulation/flocculation was employed in this study as it is one of the most preferred water treatment methods, due to its low cost, effectiveness, reliability, simplicity and low-energy consuming nature [6].

Inorganic coagulants may pose detrimental effects on living organisms and human health [6]–[8]. Such health effects include Alzheimer's disease, neurotoxic and carcinogenic effects [6], [7]. Bio-coagulants are usually non-toxic alternatives to inorganic coagulants [9]. They are also cheaper

than inorganic coagulants, biodegradable, have high performance in the removal of pollutants and are highly available [10].

Bio-coagulants and/or bio-flocculants are usually obtained from living organisms. [11], [10]. Plant-based bio-coagulants are the most widely used bio-coagulants due to their high abundance as compared to animal or microorganism-based coagulants [10].

Bio-coagulants, just like other coagulants, work by several mechanisms including double layer compression, polymer bridging, charge neutralization, and sweep coagulation [8], [12]. Polysaccharides, proteins, carbonyl, carboxyl and hydroxyl groups are responsible for the bridging mechanism in bio-coagulants and bio-flocculants [13], [10]. Amides, amines, carbonyl, methylene and hydroxyl groups work as charge neutralization groups in organic coagulants and flocculants [10]. Amines and hydroxyl groups that exist on the surface of the bio coagulant are important for adsorption, which is an intermediate process in bio-coagulation [14], [15].

At low to neutral pH, amine groups show a high positive zeta potential, which helps facilitate coagulation by charge neutralization [16]. Adsorption is also involved in bio coagulation, but is considered an intermediate mechanism especially for sweep and polymer bridging mechanisms [15]. The effectiveness of a coagulant is determined by pH, coagulant dosage, ionic strength, pollutants' concentration and the nature of the pollutants [17]. In this work, used waste paper was used to formulate a bio-coagulant intended for fluorides removal from aqueous solution. Cellulose present in paper was nitrated, after which, nitro groups were reduced to amines before quaternizing the amines using methyl iodide to form quaternary ammonium salts. FTIR and TGA were used to characterize the bio-coagulant formed. The optimized parameters in this study were pH, coagulant dosage, contact time and initial fluoride ion concentration were the.

The next sections in this research paper, are organized as follows. Section 2 contains recent studies that are related to this research work. Section 3 is the experimental region. Section 4 contains results and discussion while conclusions and future scope are laid down in the last section.

2. Related Work

Numerous studies on the treatment of water to remove pollutants using coagulation/flocculation have been undertaken [17]–[19]. For the fluoride ion removal from water, several methods have been employed among them, adsorption, complexation, and coagulation [15], [20]–[26]. Some unconventional materials used in treatment of water containing fluorides by coagulation include chitosan, diatomite, mushroom biomass and maize plant remains [16], [20], [22], [25]. Instrumental methods among them electrocoagulation and ultrafiltration have also been employed to treat water containing fluorides [21], [27].

3. Materials and Methods

3.1. Chemicals and Reagents

Analytical grade reagents and chemicals were obtained from Kobian Kenya Limited, which is a Sigma Aldrich's outlet in Kenya. Distilled water was used to prepare reagents and for dilution.

3.2. Preparation of Fluoride Stock Solution

A fluoride standard stock solution of 1000 mg/L was prepared by weighing 2.21 g of sodium fluoride and dissolving it in distilled water. Topping up to a 1000 mL mark in a volumetric flask was then done. The prepared solution was used to prepare subsequent dilute working solutions. A solution of 0.1 M NaOH and 0.1 M HNO₃ was used to adjust the working solutions' pH to the values dictated by each experiment [28].

3.3. Sample Collection and Pre-Treatment

One kilogram of used waste paper was randomly collected from Dedan Kimathi University of Technology and cut into small pieces. The pieces were soaked in distilled water for 48

hours before being dried under the sun for 48 hours. This was followed by oven drying for a further 48 hours at 353.15 K [29]. The dried paper was ground, milled and passed through a 200-micron mesh sieve. The powdered paper was stored in desiccators and labelled Raw Waste Paper (RWP) awaiting further modification and analysis.

3.4. Chemical Modification

Raw waste paper was treated as follows. A mass of 30 g of the powdered paper was weighed using a laboratory analytical balance. The sample was placed in 500 mL, 1:50 concentrated sulfuric acid - nitric acid mixture containing 14% water while stirring using a magnetic stirrer for 90 minutes. The nitrating mixture was left to stand overnight [30]–[32]. Crude cellulose nitrate obtained was then centrifuged at 400 rpm for 10 minutes to remove excess acid and then stabilized by treatment in water for 3 hours under reflux. Cellulose nitrate formed was treated in 100 mL 0.03% sodium carbonate solution at 358.15–368.15 K for 3 hours. This step was followed by soaking in distilled water at 358.15 – 368.15 K for a further 1 hour. The material was washed with water to a neutral pH to obtain Nitro Functionalized Waste Paper (NFWP) [31], [32].

Chemical reduction was done using 5 g tin metal and 250 mL of 2.5 M hydrochloric acid to form Amine Functionalized Waste Paper (AFWP). A 10 g sample of aminated cellulose was reacted with 500 mL mixture of 50 mL methyl iodide and 25 g anhydrous potassium carbonate in anhydrous dimethyl formamide (DMF). Washing using 100 mL DMF, 100 mL water and finally 100mL diethyl ether was done [33]. The formed Quaternary Ammonium Functionalized Waste Paper (QAFWP) coagulant was dried and stored in desiccators.

3.5. Instrumentation

Attached functional groups were identified using Fourier Transform Infrared spectrophotometer (JASCO FT/IR-4700) before and after each modification step. RWP, NFWP, AFWP and QAFWP were characterized using FTIR in the 4000 – 500 cm⁻¹ range. FTIR results were presented in Figure 1-4. Thermal stability of the prepared material was determined using TGA (SHIMADZU TGA-50). Fluoride ion determination was done using fluoride ion selective electrode (HACH ISEF12101), in all determinations

3.6. Batch Experiments

Contact time, pH, initial fluoride ion concentration and bio-coagulant dosage were the optimized experimental conditions in this study. A volume of 50 mL of fluoride ion solution was used to study each batch experiment. Coagulation was done by stirring at 100 rotations per minute (rpm). Each sample was allowed to settle for 5 minutes and then filtered using filter papers. Fluoride ion concentration of each sample filtrate was then determined.

3.6.1. Effects of pH

The effects of pH on fluoride removal were studied using 0.2 g of the bio-coagulant. A concentration of 20 mg/L was used for each of the pH values. The solutions were placed in

beakers and the pH buffered at different pH values ranging from pH 2.5 to pH 9.0. Stirring was done at 100 rpm for 15 minutes. The resulting graph was presented in Figure 6.

3.6.2. Effects of Contact Time

Influence of contact time on fluoride removal was studied using 0.2 g of the bio-coagulant. A fluoride concentration of 20 mg/L was used for each experiment. The solutions were placed in beakers and the pH values were buffered at pH 4.0. Coagulation time was varied for each sample from 5 to 30 minutes. The resulting graph was presented in Figure 7.

3.6.3. Effects of Initial Fluoride Ion Concentration

For each experiment, 0.2 g of the bio-coagulant was used. Various batch experiments of 5, 10, 15, 20, 25, 30, 40, 50 and 60 mg/L initial fluoride ion concentration were studied. The solutions were placed in beakers and buffered at pH 4.0. Coagulation was done on each solution by stirring at 100 rpm for 15 minutes. The results were presented in Figure 8.

3.6.4. Effects of Bio-Coagulant Dosage

The effects of bio-coagulant dosage on fluoride removal from model solutions were studied by varying the dosage as follows: 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50 and 0.60 g. For each experiment, 0.2 g of the bio-coagulant was used. The solutions were placed in beakers and buffered at pH 4.0. Coagulation was done for 15 minutes by stirring at 100 rpm. Fluoride ion concentration of the filtrate was determined.

The fluoride removal percentage was calculated using equation 1.

$$R\% = \frac{(C_i - C_e)100}{C_i} \quad (1)$$

Where, C_i is the initial fluoride ion concentration (mg/L) and C_e is the fluoride ion concentration at equilibrium (mg/L). The quantity of fluoride ions removed per unit mass of QAFWP bio-coagulant was calculated using equation 2

$$q_e = V \left(\frac{c_0 - c_e}{m} \right) \quad (2)$$

Where, V is the volume of the solution (L), C_0 is the concentration of fluoride ions (mg/L) at the beginning of the experiment, C_e is the concentration of fluoride ions (mg/L) at equilibrium and m is the mass of QAFWP bio-coagulant (g).

3.7. Removal of fluorides from real water sample

Gilgil area in Nakuru County, Kenya, a region known to have high Fluoride ion concentrations in water was randomly selected and random surface water samples obtained from three points. The samples were stored in 500 mL clean plastic bottles. The concentration of fluoride ions in the samples was determined using the ISE. A volume of 50 ml of each of the three samples was placed in a 100 mL beaker and the pH buffered to pH 4.0. The bio-coagulant 0.2 g was added to the samples and coagulated for 15 minutes under stirring at 100 rotations per minute (rpm). Settling was allowed for 5 minutes then samples filtered using filter papers. The

concentration of fluoride ions in the filtrate was determined using the fluoride ISE.

3.8. Adsorption capacity

Since adsorption is the major intermediate process used to remove fluoride ions from bulk of solution during coagulation, adsorption data was fitted onto Langmuir and Freundlich adsorption isotherms to determine the removal capacity of fluoride ions. The obtained optimum parameters of pH, contact time and coagulant dosage were used while varying initial fluoride ion concentration. A volume of 50 mL of 10, 20, 30, 40, 50 and 60 mg/L of fluoride ion solutions were measured, placed in beakers and buffered at pH 4.0. A mass of 0.2 g of the bio-coagulant was added in the beakers and the solutions coagulated by stirring at 100 rpm for 15 minutes. Settling was allowed for 5 minutes then samples filtered using filter papers. The concentration of fluoride ions in the filtrate was determined using the fluoride ISE.

3.9. Adsorption isotherms

Fluoride ions removal capacity was determined using Langmuir and Freundlich adsorption isotherms. [14], [15]. Langmuir equation can be presented in equation 3 as.

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

Where, C_e is the concentration of fluoride ions at equilibrium (mg/g). q_e is the solid phase concentration of fluoride ions at equilibrium (mg/g). b is the Langmuir constant (mg/g). q_m (mg/g) is an empirical constant, that can be determined from the gradient and intercept of the linear plot of C_e/q_e against C_e . The value of q_e is calculated using equation 2.

Freundlich equation can be presented in equation 4 as.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Where, q_e is the solid phase concentration of fluoride ions (mg/g). K_f is the Freundlich constant [(mg/g) (L/g)^{1/n}]. $1/n$ is the adsorption heterogeneity factor that can be obtained from the intercept and slope of $\ln q_e$ against $\ln C_e$. C_e is the fluoride ion concentration at equilibrium (mg/g) [34].

4. Results and Discussion

4.1. Fourier Transform Infrared Spectrophotometer (FTIR) Characterization

4.1.1. Raw Waste Paper (RWP)

Figure 1 shows the Fourier transform infrared spectrum for raw waste paper (RWP). Broad peaks are seen between 3600.45 and 3278.39 cm⁻¹, which were attributed to -OH stretching vibrations [35]. The peak at 2916.81 cm⁻¹ was assigned to C-H stretching bonds [36]. These peaks are characteristic stretching vibrations of O-H and C-H bonds in polysaccharides [35]. The strong sharp peak at 1019.19 cm⁻¹ was assigned to C-O-C stretching vibration which absorb in the 1000-1320 cm⁻¹ region [36]-[38].

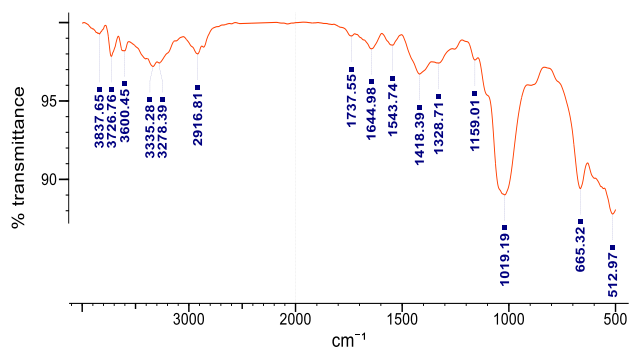


Figure 1. Fourier transform infrared spectrum for raw waste paper (RWP).

Similar results were reported by Xue and co-authors. [36]. Joshi and co-authors also reported similar results when they synthesised and characterized carboxymethyl cellulose using waste paper [39]. This confirmed presence of cellulose in the used waste paper that was necessary for the subsequent steps.

4.1.2. Nitro-Functionalized Waste Paper (NFWP)

Figure 2. shows Fourier transform infrared spectrum for nitro-functionalized waste paper (NFWP).

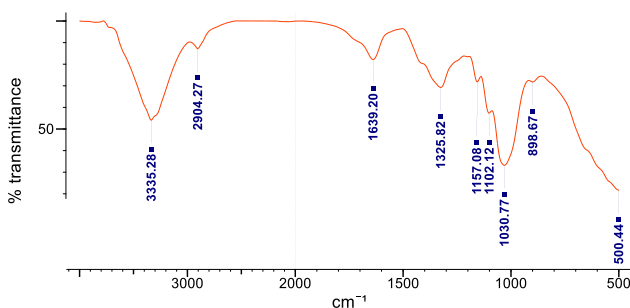


Figure 2. Fourier transform infrared spectrum for nitro-functionalized waste paper (NFWP).

The spectrum showed strong peaks at around 3335, 2904, 1639, 1325 and 1030 cm^{-1} . The broadness of the peak assigned to hydroxyl groups at around 3335 cm^{-1} was reduced as some of the hydroxyl groups were used up during nitro group attachment [40]. New peaks were observed around 1325.26 and 1639.20 cm^{-1} which were attributed to symmetric and asymmetric $-\text{NO}_2$ stretching vibrations respectively [40], [41]. Gumel and Dambata reported similar results [37]. This was an indication of cellulose nitrate formed because of nitration of the raw waste paper (RWP).

4.1.3. Amine-Functionalized Waste Paper (AFWP)

Figure 3. below shows the Fourier transform infrared spectrum for amine-functionalized waste paper (AFWP).

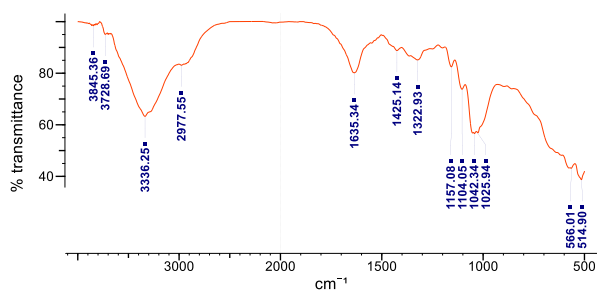


Figure 3. Fourier transform infrared spectrum for amine-functionalized waste paper (AFWP).

The peak around 3336.25 cm^{-1} broadened due to overlapping of O-H and N-H stressing vibrations [38]. The peak at 1635.34 cm^{-1} also broadened and was attributed to N-H stressing vibrations that overlapped with $-\text{NO}_2$ stretching vibrations [36], [42]. Xue and co-authors reported similar results. [36]. This confirmed the reduction of some of the nitro groups to form amine groups.

4.1.4. Quaternary Ammonium Functionalized Waste Paper (QAFWP) Bio – Coagulant

Figure 4. below shows Fourier transform infrared spectrum for quaternary ammonium functionalized waste paper (QAFWP) bio – coagulant.

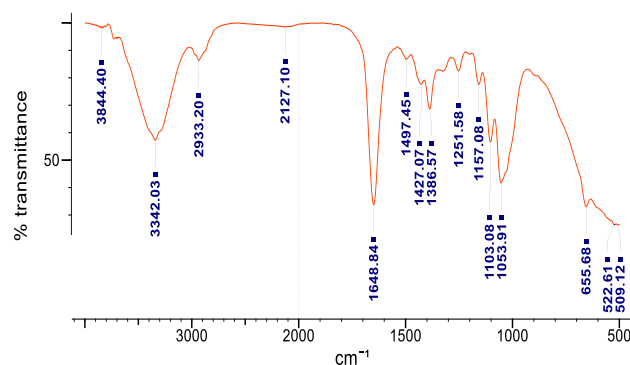


Figure 4 Fourier transform infrared spectrum for quaternary ammonium functionalized waste paper (QAFWP) bio – coagulant

The peak at around 3342 cm^{-1} narrowed due to the fact that N-H bonds were broken to form C-N bonds during quaternization, to form ($^+\text{NR}_4$). A new sharp peak appeared around 1648.84 cm^{-1} and was attributed to C-N stressing vibrations as a result of quaternization. The peak at around 2933.20 cm^{-1} shifted from 2977.55 cm^{-1} and its intensity increased due to increase of $-\text{C}-\text{H}$ stressing vibrations as a result of the methyl groups attached to nitrogen during quaternization [24], [43]–[45]. Mwangi and co-authors observed similar cases in their research. [25]. This was an indication of methyl groups being attached to nitrogen during quaternization to form characteristic charged quaternary ammonium salts ($^+\text{NR}_4$) [46], [47].

4.2. Thermogravimetric Analysis (TGA) Characterization

4.2.1. TGA Curve of Quaternary Ammonium Functionalized Waste Paper (QAFWP) Bio – Coagulant

Figure 5. shows the Thermogravimetric analysis curve of QAFWP bio – coagulant. The TGA curve showed a distinct weight loss of about 29.93% from room temperature to about 125 $^{\circ}\text{C}$. This was due to the loss of water that may have been absorbed by the material before the analysis [45], [48], [49]. The quaternary ammonium functionalized waste paper (QAFWP) bio – coagulant formed was stable up to a temperature of about 290 $^{\circ}\text{C}$ before decomposition [50].

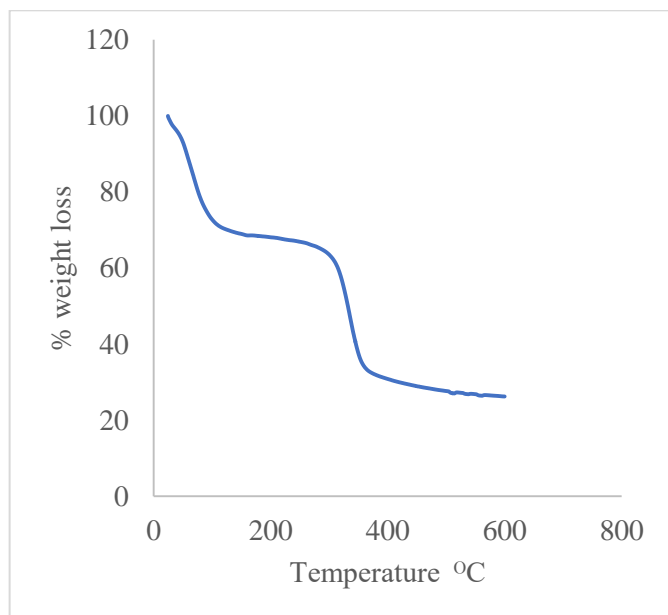


Figure 5. Thermogravimetric analysis (TGA) for quaternary ammonium functionalized waste paper bio-coagulant

The decomposition was expressed in the section that starts from 290 to 375 °C, which agrees with thermal decomposition of quaternary ammonium salts [45], [50]. In this section, a total weight loss of about 50.30% was observed.

The thermal stability of up to 290 °C, would make it possible to use the bio-coagulant at high temperatures to remove fluorides from aqueous solutions. The thermal stability of the material may have been caused by the tetrahedral structure of ammonium cations [50].

4.3. Optimization of Experimental Parameters on Fluoride Removal from Model Solutions

4.3.1. Effects of pH

Figure 6. shows the graph of effects of pH on coagulation of fluorides.

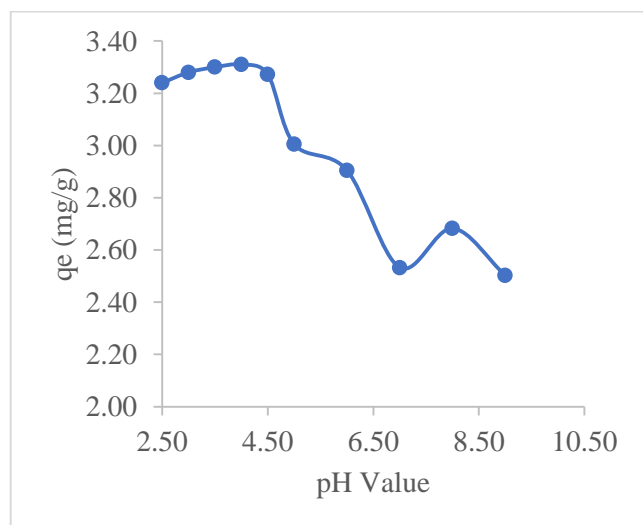


Figure 6. Effects of pH on coagulation of fluorides. (Initial fluoride ion concentration of 20 mg/L, 15 minutes contact time and 0.2 g).

Results in Figure 6. indicate that, removal of fluorides was high at low pH values and reduced gradually towards higher pH values. The optimum point was observed at pH 4.0 (q_e 3.31 mg/g). At low pH (3.0 - 4.0), hydrogen ion concentration was high, this increased positive charges on the coagulant that attracted the negatively charged fluorides [51].

There was a high hydroxyl ion concentration at high pH values which lead to repulsion and competition between hydroxyl and fluoride ions [51]. This was in agreement with similar studies done by Wambu and co-authors., which showed high fluoride uptake at pH 4.0 [52].

Removal of fluorides from the bulk of solution was achieved through adsorption and ion exchange intermediate processes of sweep and polymer bridging coagulation mechanisms [15]. The iodide counter ion to the positive ammonium ion in the coagulant, replaced the fluoride ion in the bulk of solution.

4.3.2. Effects of Contact Time

Figure 7. shows a graph depicting how contact time affects coagulation of fluorides. There is a rapid increase in fluoride removal capacity by the coagulant from 5 to 15 minutes as observed on figure 7. This is as a result of presence of a high number of active $^+NR_4$ sites and a high concentration of fluorides in the solution [53]. Fluoride removal capacity by the coagulant increased with time up to 15 minutes where the observed removal capacity was 3.25 mg/g.

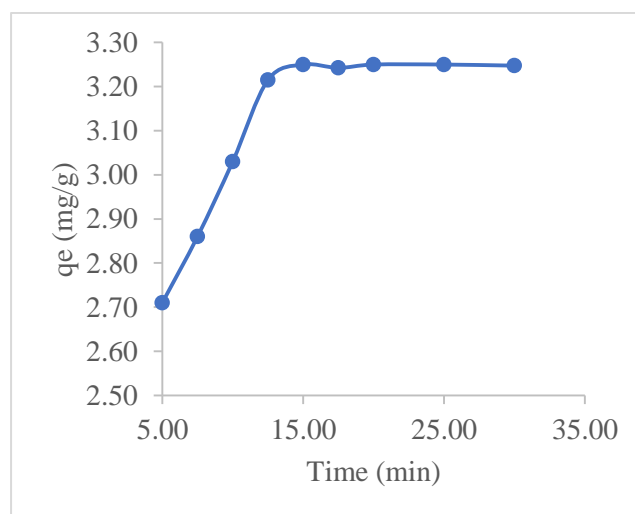


Figure 7. Effects of contact time on coagulation of fluorides. (pH was buffered at pH 4.0, Initial fluoride ion concentration, 20 mg/L and 0.2 g). At this point equilibrium was established due to exhaustion of the active sites [22]. Mbugua and co-authors reported a similar trend in their research [23].

4.3.3. Effects of Initial Fluoride ion Concentration

Figure 8. shows a graph depicting how initial fluoride concentration affects coagulation of fluorides. The fluoride ion removal capacity increased up to 20 mg/L initial fluoride ion concentration before forming a plateau. The initial high rate of fluoride removal at relatively low concentration was due to easy movement of fluoride ions to the active sites [22]. The binding sites for fluoride removal were the positively charged nitrogen present in QAFWP.

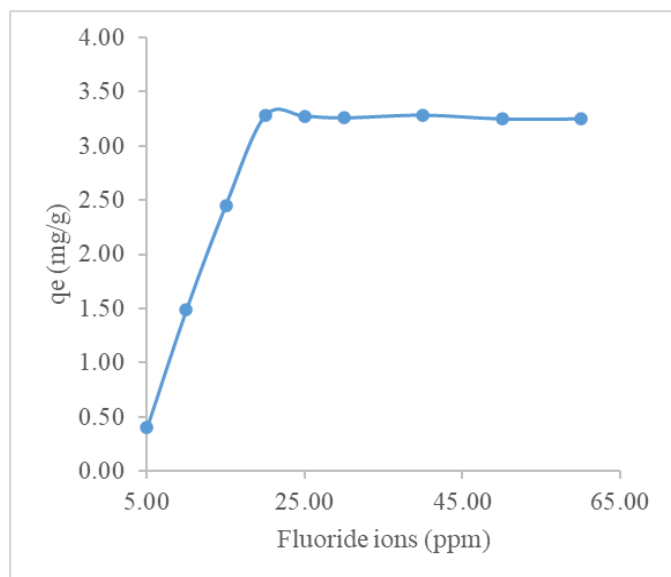


Figure 8. Effects of initial fluoride ion concentration on coagulation of fluorides. (pH was buffered at pH 4.0, contact time 15 minutes and 0.2 g).

Fluoride ions were attracted to the positively charged nitrogen in QAFWP and were replaced by iodide ions in the bulk of solution. When the active sites were saturated, a plateau was formed as observed in Figure 8. At high concentration, saturation of active sites was achieved, since there was a fixed number of active sites on the bio-coagulant [25].

4.3.4. Effects of Coagulant Dosage

Figure 9. shows a graph of percentage removal against coagulant dosage in grams to determine how coagulant dosage affects coagulation of fluorides. Generally, the fluoride removal percentage increased with increase in coagulant dosage.

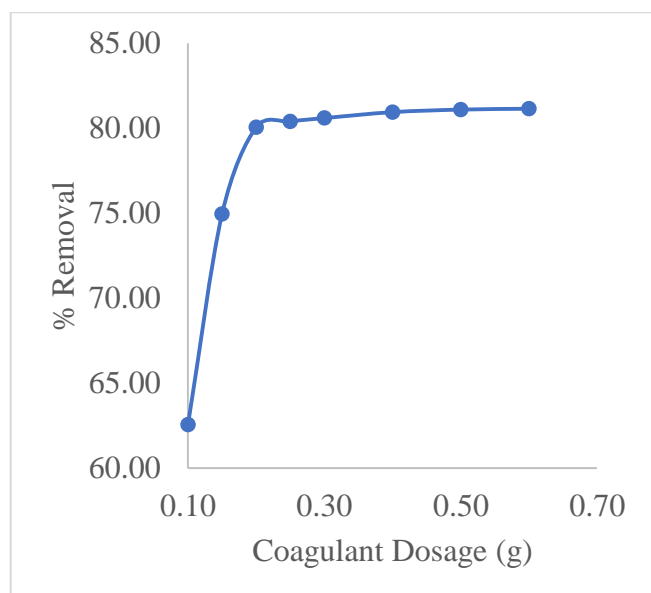


Figure 9. Effects of coagulant dosage on coagulation of fluorides. (pH 4.0, 15 minutes contact time and 20 mg/L initial fluoride concentration).

The highest fluoride removal rate was experienced from 0.1 g to 0.2 g of the coagulant dosage. Above 0.2 g of the material, there was minimal increase in removal of fluoride ions as

observed on Figure 9, which was also the case for Chen and co-authors [22]. The increase in percentage removal in every step and overall was due to the increase in the number of active sites with increase in coagulant dosage [54]–[56]. Liu and co-authors reported a similar trend. [53]. These results also agreed with those obtained by Anusha and Murugadoss on the adsorption of fluoride ions [57].

4.4. Adsorption Studies and Fluoride Removal Capacity

Adsorption data obtained was fitted on Langmuir and Freundlich adsorption isotherms.

Table 1. Langmuir and Freundlich adsorption constants for removal of fluoride ions

Langmuir		Freundlich			
Q_{max} (mg/g)	$b(dm^3/g)$	R^2	$1/n$	$Kf(mg/g)$	R^2
3.6311	0.2380	0.9707	0.2786	1.2447	0.4468

The Langmuir constants, q_m was found to be 3.6311 while b was 0.2380. The linear regression for Langmuir adsorption isotherm was 0.9707 while that of Freundlich adsorption isotherm was 0.4468. The Freundlich adsorption isotherm linear regression was clearly much lower than the Langmuir adsorption isotherm linear regression.

From this data, the predominant adsorption mechanism that took place was chemisorption, as Langmuir adsorption isotherm had a higher linear regression (0.9707) [22]. The adsorption capacity in Langmuir adsorption isotherm was 3.6311 mg/g. As observed, data fitted well on Langmuir adsorption isotherm which is an indication that the coagulation process was aided by a chemisorption monolayer adsorption intermediate process [23].

4.5. Removal of Fluorides from Real Water Samples

The average fluoride ion concentration of the water samples obtained from Gilgil area in Nakuru County was 3.2 mg/L. After treatment, fluoride ion concentration reduced to 1.08 mg/L. This value was below the WHO maximum permissible concentration standard for drinking water. A removal percentage of 66.25% was achieved. This was lower than the removal percentage of about 81% on model solutions using optimum conditions obtained. This may have been caused by competing ions in the real water samples, which were absent in the model solution.

5. Conclusion and Future scope

Quaternary ammonium functionalized waste paper bio-coagulant was successfully formulated and confirmed from characterization results. The FTIR spectrum proved the successful anchoring of quaternary ammonium compounds on used waste paper. TGA results confirmed that the material was stable up to a temperature of about 563.15 K, after which it disintegrated. This high thermal stability would allow the use of the bio-coagulant at elevated temperatures.

The optimum pH value for fluoride ions removals was pH 4.0 while the optimum contact time was 15 minutes. Fluoride

removal by the bio-coagulant increased with increase in concentration up to an optimum of 20 mg/L. Removal of fluoride ions also increased with the increase in bio-coagulant dosage.

Data obtained was observed to fit well onto Langmuir adsorption isotherm with R^2 value of 0.9707. This confirmed that chemisorption was the predominant intermediate process. The adsorption capacity from Langmuir adsorption isotherm was 3.6311 mg/g. Polymer bridging, which employs adsorption as the major intermediate process, and sweep coagulation were the identified major coagulation mechanisms involved in this study.

The average fluoride ion concentration of the real water samples was 3.2 mg/L which reduced to 1.08 mg/L after coagulation. This value was below the WHO maximum permissible fluoride ion concentration in drinking water. The percentage removal in the real water sample was 66.25%, which was lower than the 81% removal percentage in the model solution, using the obtained optimum conditions. Competing anions in the real water sample may have caused this as they competed for the active sites with fluoride ions. The study provides an important way to utilize used waste paper to formulate a bio-coagulant, which would help solve the problem of high fluoride concentrations in water. From this study, it is evident that used waste paper can be modified and used to treat water containing fluorides.

Conflict of Interest

The authors declare no conflict(s) of interest in this research.

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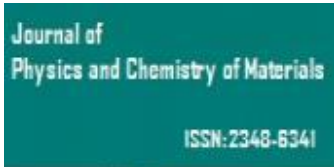


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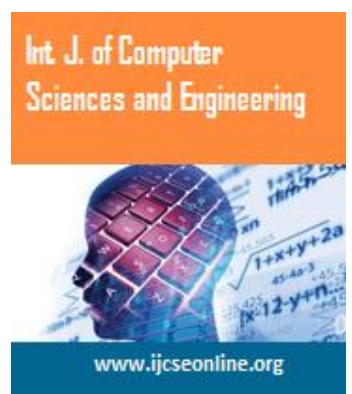
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