

Article

Preparation of Poly(vinylidene fluoride-co-hexafluoropropylene) Doped Cellulose Acetate Films for the Treatment of Calcium-Based Hardness from Aqueous Solution

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Abstract

Calcium (Ca^{2+} ions) is one of the dominant elements that contribute to water hardness, scaling in pipes, bathroom faucets, and kitchen utensils. Herein, we report on the development of poly(vinylidene fluoride-co-hexafluoropropylene) cellulose acetate (PVDF-HFP/CA) films for the treatment of Ca^{2+} ions as one of the constituents that causes water hardness. CA and PVDF-HFP polymers, and their blend consisting of 3 wt.% PVDF-HFP/CA, were effectively synthesised through the phase inversion technique. Analysis using thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) confirmed the effective incorporation of 3 wt.% PVDF-HFP into the cellulose acetate film. Parameters such as temperature, initial concentration, pH, adsorbent dosage and contact time were investigated in batch studies during the removal of Ca^{2+} ions in synthetic water samples. Under optimal conditions (pH 7, adsorbent dosage of 0.5 mg/L, and concentration of 120 mg/L), the 3 wt.% PVDF-HFP/CA film achieved a 99% adsorption efficiency for Ca^{2+} ions in 90 min. The adsorption process adhered to pseudo-second-order and Freundlich isotherm models, which suggest that the adsorption of Ca^{2+} ions is heterogeneous. The maximum adsorption efficiency achieved was 56 mg/g, indicating an endothermic physisorption process. The 3 wt.% PVDF-HFP/CA film maintained higher adsorption in the presence of counter ions and in a binary system, and it could be recycled at least three times. Thus, the findings demonstrated that the 3 wt.% PVDF-HFP/CA film could be a valuable material for Ca^{2+} ions removal to acceptable drinking water levels.

Keywords: PVDF-HFP; cellulose acetate; water hardness; calcium²⁺ ions; aqueous solution



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1. Introduction

In rural and arid regions, the majority of water supplies come from both groundwater and river sources [1]. However, these water sources have elevated levels of dissolved salts, including calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, which contribute to water hardness, particularly when concentrations exceed 120 mg/L [2,3]. Consuming water with higher levels of calcium and magnesium, particularly magnesium, lowers the risk of stroke in postmenopausal women [4]. Although magnesium and calcium present in hard water have some health benefits, calcium causes major challenges in industrial processes, which

might cause severe economic impact [5,6]. For instance, the hardness of water contributes to scale buildup in both industrial and household electrical devices, which functions as an insulator and extends the heating duration [7]. In industrial sectors, water hardness is frequently monitored to prevent expensive failures of cooling towers, scaling in boilers, and various other equipment [8]. The use of domestic water containing high levels of calcium and magnesium ions can react with soap anions which reduces cleaning efficiency and increase detergent consumption [3]. Research also indicates that the effectiveness of certain herbicides is diminished by water hardness, especially in areas where the bedrock is predominantly made up of lime and dolomite [9,10]. Although both calcium and magnesium contribute to water hardness, magnesium is mainly found in natural groundwater at low concentrations (below 100 mg/L); hence, calcium-based hardness often predominates [11].

A study conducted by Elumalai et al., 2020 showed that groundwater collected from Luvuvhu catchment area had moderate to hard water levels of calcium [12]. Most water-softening treatments available for water hardness are very costly, directly affecting the rural and low-income community [1]. Despite the preference for ion-exchange and adsorption methods due to their cost-effectiveness, the limited adsorption capacity and specific properties of ion-exchange materials present significant challenges [13].

Although substantial scientific research has been conducted on the elimination of contaminants from water [13–17], there have been limited investigations focused on reducing water hardness, especially through the use of composite films. For instance, a study carried out by Sepehr et al., 2013 using alkaline modified pumices stone achieved 96% Ca^{2+} and 73% Mg^{2+} ions adsorption within 300 min from synthetic water [18]. Werkneh et al., 2015 developed an alkali-treated sugarcane bagasse and coffee husk for the adsorption of Ca^{2+} and Mg^{2+} ions from water samples [19], achieving 78% and 73% calcium and magnesium adsorption, respectively, within 200 min. In another study, Hailu et al., 2019 reported maximum adsorption of 80% Ca^{2+} and 85% Mg^{2+} ions from water samples using natural zeolite as an adsorbent [1].

In recent years, poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) has been employed as membranes in water disinfection as a result of their excellent dielectric properties, mechanical strength, and elevated ionic conductivity [20,21]. However, this polymer has low thermal stability, swellability, water content and porosity which limit its performance in adsorption processes [22]. The PVDF-HFP polymer can be modified with a variety of materials such as other polymers or carbon nanocomposites, to improve its performance in water purification [23–26]. Incorporating cellulose acetate (CA) into PVDF-HFP polymer membranes and films has been found to notably enhance porosity, electrolyte absorption, ionic conductivity, and hydrophilicity [27,28], owing to its outstanding wettability, cost-effective processing, high porosity, and favourable mechanical attributes [29].

Therefore, this research seeks to develop a CA-modified PVDF-HFP film using phase inversion techniques to remove Ca^{2+} ions from synthetic water samples. Batch adsorption experiments were conducted to examine the impacts of pH, adsorbent dosage, concentrations of Ca^{2+} ions, counter ions, and other variables.

2. Materials and Methods

The chemicals utilised were all of analytical grade. Cellulose acetate (CA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), dimethylformamide (DMF), nitric acid, calcium sulphate, polyethylene glycol (PEG), and sodium hydroxide were all purchased from Merck Life Science (Pty) Ltd., Modderfontein, South Africa.

2.1. Preparation of PVDF-HFP Film

2.1.1. Preparation of CA Film

Cellulose acetate films were fabricated utilising a phase inversion technique as described in the existing literature [22]. A cellulose acetate (CA) polymer solution was prepared by combining CA (0.900 g) and PEG (0.2 g) in 10 mL of DMF within a round-bottom flask, followed by stirring this mixture vigorously at 80 °C for 2 h. Subsequently, the polymer solution was placed in a silica gel desiccator overnight. The next day, it was manually cast onto a glass plate using a 180 µm thick casting knife (Elcometer 3580, Elcometer Limited, Manchester, UK). The resulting films were washed with deionised water and then air-dried on plain paper at room temperature.

2.1.2. Preparation of PVDF-HFP and 3 wt.% PVDF-HFP/CA Film

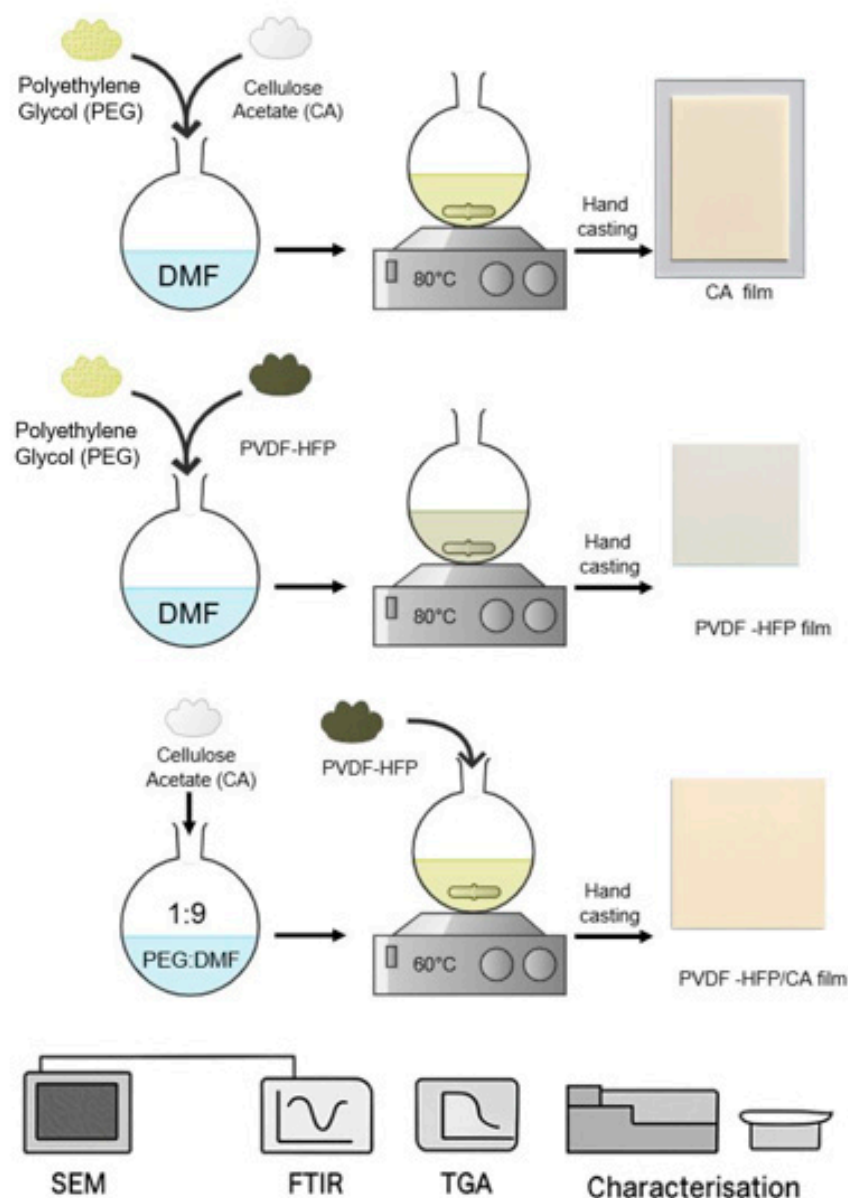
The PVDF-HFP films were synthesised utilising a phase inversion technique as documented in the prior literature [22]. In summary, PVDF-HFP (1.00 g) and PEG (0.2 g) were dissolved in DMF (10 mL) inside a round-bottom flask, and the mixture was stirred intensely at 80 °C for 2 h. Afterward, the reaction mixture was left to settle overnight in a silica gel desiccator. The solution was then hand-cast onto a glass plate using an Elcometer 3580 casting knife (Elcometer 3580, Elcometer Limited, Manchester, UK) with a 180 µm gap. Once fabricated, the films were dried in a vacuum oven at 80 °C for 30 s to partially evaporate the solvent, followed by immersion in a coagulation bath of deionized water maintained at 5 °C to trigger phase inversion. The final PVDF-HFP film was rinsed with deionized water and air-dried on plain paper towels at room temperature (see the detailed schematic process in Scheme 1).

The 3 wt.% PVDF-HFP/CA film was crafted following the previously mentioned procedure described above. Initially, 0.97 g of cellulose acetate was combined with 9 mL of DMF and 1 mL of PEG (used as a pore-forming agent) while stirring constantly at 600 rpm and maintaining a temperature of 60 °C, resulting in a cellulose acetate solution. Subsequently, 0.03 g of PVDF-HFP polymer was incorporated into the cellulose acetate solution to form a 3 wt.% PVDF-HFP/CA solution. [27]. Lastly, the solution was cast as described above.

The concentration of 3 wt.% PVDF-HFP film was selected based on preliminary trials, as this composition was found to enhance the removal efficiency of Ca^{2+} ions from water samples while maintaining good film stability and processability.

2.1.3. Characterisation Techniques

The surface morphology of the specimens was analysed by scanning electron microscopy (SEM) with a JSM 5910 model from JEOL, Tokyo, Japan. The functional groups were identified through Fourier transform infrared (FTIR) spectroscopy using a BRUKER-FTIR-ATR spectrometer. This analysis was conducted in the 650 to 4000 cm^{-1} range, with a resolution of 4 cm^{-1} , employing four scans at a temperature of 25 °C. Additionally, thermogravimetric analysis (TGA) was performed with a Perkin Elmer STA 4000 analyser to assess the mass changes in the films across various temperatures, thereby evaluating the thermal stability of the specimens.



Scheme 1. Preparation and characterisation of cellulose acetate-based thin films.

2.1.4. Adsorption Studies of Ca^{2+} Ions in Synthetic Water Samples

The study of pH was conducted by adjusting the initial pH of a 35 mg/L copper sulphate solution to values of 5, 5.5, 6, 6.5, and 7. The pH levels were modified using 0.1 M nitric acid (HNO_3) and 0.1 M sodium hydroxide (NaOH). During each experiment, 25 mg of films were immersed in 50 mL of these prepared solutions and stirred vigorously for 90 min at room temperature (25 °C) [30]. Flame-atomic absorption spectroscopy (F-AAS) was employed to analyse the concentration of Ca^{2+} ions post-adsorption. Each experiment was conducted in triplicates, with mean values presented. The same procedure was followed to investigate the influence of variables such as dosage (ranging from 0.1 to 0.9 mg/L), time (at intervals from 30 to 180 min), initial concentration (spanning 100 to 1200 mg/L), and temperature (between 25 and 35 °C).

The equation below was used to obtain the amount of the adsorbed salts:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100$$

where C_o and C_e denote the initial and final concentrations of Ca^{2+} ions, respectively, in mg/L [31,32].

The adsorption kinetics were examined by evaluating the kinetic parameters of the Lagergren pseudo-first-order and pseudo-second-order models. This process involved performing nonlinear regression analysis to align the experimental data with these empirical kinetic models [32]. The Lagergren's pseudo-first-order model and its linearised representation, as detailed in the equations below, were utilised [25,33].

$$q_t = q_e \left(1 - e^{-k_1 t}\right)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Furthermore, the Lagergren pseudo-second-order model expressed below was used:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t (mg/g) represent the concentrations of Ca^{2+} ions adsorbed at equilibrium and at time, t . The constants k_1 (min^{-1}) and k_2 (g/mg·min) correspond to the pseudo-first-order and pseudo-second-order reaction rate constants, respectively.

The experimental data collected from the results were analysed using both Langmuir and Freundlich isotherms. The theoretical adsorption capacity of the PVDF-HFP film was calculated based on the nonlinear Langmuir and Freundlich isotherm models [16,34].

The nonlinear equation for the Langmuir isotherm may be expressed as [35]:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e}$$

where q_e and $q_{\max}$ represents both the equilibrium and maximum adsorption capacity (mg/g), respectively. C_e (mg/L) is the equilibrium concentration of metal adsorbed in the solution and b (L/mg) is the Langmuir equilibrium constant.

The Langmuir adsorption isotherm model includes a significant dimensionless factor R_L , which can be determined using the following equation:

$$R_L = \frac{1}{1 + b C_o}$$

where C_o (mg/L) represents the initial concentration of the metal and b (L/mg) represent the Langmuir equilibrium constant for adsorption.

The Freundlich isotherm, another renowned adsorption model, can be represented as [33,36]:

$$q_e = K_f C_e^{1/n}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where q_e represents the adsorption at equilibrium measured in mg/g and C_e (mg/L) is the solute concentration at equilibrium. The Freundlich constants are K_f (mg/g), indicating adsorption capacity, and n (dimensionless) signifying adsorption intensity.

The equations provided below were utilised to perform a thermodynamic analysis [37,38]:

$$\Delta G^\circ = -RT \ln K_c$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$K_c = \frac{C_{ad}}{C_e}$$

where C_e (mg/L) and C_{ad} (mg/L) represent the equilibrium concentration of metal present in the solution and the concentration of the metal within the adsorbent at equilibrium. R denotes the universal gas constant (8.314 J/mol. K). ΔH° , ΔG° , and ΔS° represent changes in standard enthalpy (kJ/mol), the standard Gibbs free energy (kJ/mol), and standard entropy (J/mol/K), respectively. A plot of $\ln K$ against $1/T$ results in a straight line that has a slope of $\Delta H^\circ/R$ and an intercept $\Delta S^\circ/R$; from the slope and intercept, the values of ΔS° and ΔH° were obtained.

2.1.5. Effect of Counterions

To evaluate the performance of PVDF-HFP films under field conditions, water samples were prepared with concentrations of sulphate (325 mg/L), nitrate (25 mg/L), and chloride (450 mg/L) in the presence of 120 mg/L calcium. These mixtures were created using sodium sulphate, potassium nitrate, sodium chloride, and analytical-grade calcium sulphate. Each solution provided 12.5 mL, which was then poured into a 100 mL conical flask, culminating a total volume of 50 mL [39,40]. The same procedure was employed to investigate the impact on a binary system, involving approximately 25 mg of the PVDF-HFP film, which was introduced into a 50 mL solution comprising 25 mL of Ca^{2+} and Mg^{2+} ions (concentration: 120 mg/L) at a pH of 7 for a duration of 90 min at ambient temperature. Each experiment was conducted in triplicate, and the average results were documented.

2.1.6. Reusability Studies

The most effective polymeric film underwent recycling by monitoring the adsorption and desorption of Ca^{2+} ions over three cycles. Used PVDF-HFP films (25 mg) were submerged in a 50 mL solution containing Ca^{2+} ions at a concentration of 120 mg/L for 90 min at ambient temperature. After the 90 min period, the concentration of Ca^{2+} ions was assessed using F-AAS. The Ca^{2+} -saturated PVDF-HFP films were air-dried and then immersed in a 0.1 M NaOH solution (50 mL) for 2 h at 25 °C for Ca^{2+} ion removal (desorption process). Afterwards, the films were removed from the solution, rinsed with deionized water, and dried at 60 °C. The recycling protocol for the spent PVDF-HFP films was conducted four times to address the hardness components [32].

3. Results

3.1. Characterisation of Films

3.1.1. The FTIR Profiles of PVDF-HFP, CA, and 3 wt.% PVDF-HFP/CA Films

Figure 1 presents the FTIR spectra for the as-prepared PVDF-HFP, CA, and the PVDF-HFP/CA composite films containing 3 wt.% PVDF-HFP. The peak observed at 840 cm^{-1} confirms the amorphous phase formation of PVDF-HFP (Figure 1 (a)). Meanwhile, the IR bands at 1402 and 1279 cm^{-1} correspond to the deformation vibration of CH_2 and the stretching vibration of CF_2 , which are characteristic of the PVDF-HFP polymer, respectively [22,24]. In Figure 1 (b), the carbonyl (C=O) stretching vibration at 1738 cm^{-1} confirms the existence of cellulose, and in Figure 1 (c), it indicates that CA was successfully blended into the PVDF-HFP polymer. The cellulose addition to the PVDF-HFP strengthened the vibration at 1045 cm^{-1} , while the presence of cellulose was also confirmed by the O—H stretch with a broad peak at 3406 cm^{-1} , as observed in the literature [27,41].

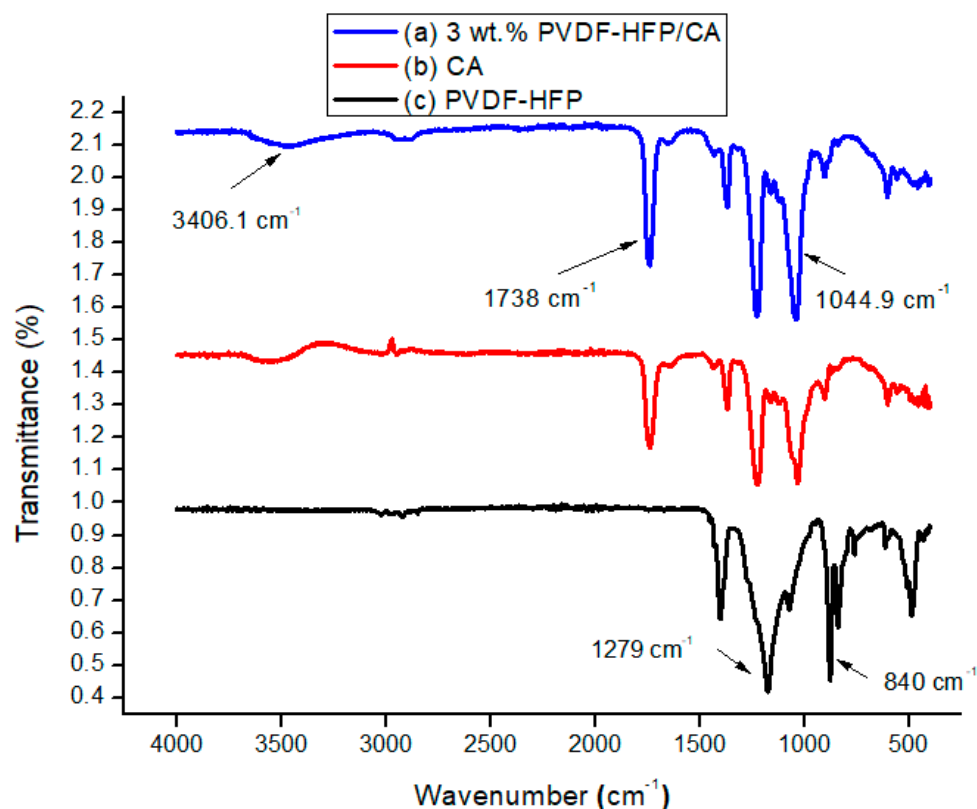


Figure 1. FTIR spectra of PVDF-HFP, CA, and 3 wt.% PVDF–HFP/CA films.

3.1.2. TGA Profiles of PVDF-HFP, CA, and 3 wt.% PVDF-HFP/CA Films

Figure 2 presents the TGA curves for PVDF-HFP, CA, and films composed of 3 wt.% PVDF-HFP/CA. The thermogram of the PVDF-HFP film alone (Figure 2 (a)) displays one significant weight loss occurring approximately between 420 and 470 °C, which can be ascribed to the breakdown of the polymeric backbone, specifically the PVDF matrix [31,42]. The TGA profile of CA (Figure 2 (b)) shows a decomposition at 200 and 350 °C, corresponding to the deacetylation and the collapse of the CA structure [27,43]. After the addition of PVDF-HFP on CA (Figure 2 (c)), the thermal stability of CA decreased. This indicates that the small percentage (3 wt.%) of PVDF-HFP introduced on CA does not improve the stability of CA; instead, it slightly weakens the structure of CA. However, the 3 wt.% PVDF-HFP/CA film has good thermal stability below 200 °C, which is within the water purification operating temperature range.

3.1.3. SEM Images of PVDF-HFP, CA, and 3 wt.% PVDF-HFP/CA Films

Figure 3 presents SEM images that were employed to examine the surface morphology of the PVDF-HFP, CA, and 3 wt.% PVDF-HFP/CA films. The SEM images confirm the dense nature of the films, indicating that Ca^{2+} ions removal arises mainly from surface interactions rather than from internal porosity. SEM images of the prepared PVDF-HFP film (Figure 3a) shows some interconnected pores distributed uniformly, and a porous honeycomb structure within the films [27]. The SEM image of CA films (Figure 3b) shows a dense surface layer, with agglomerates on the surface [41,44]. This is due to the intermolecular forces from hydrogen bonds found within the CA molecules. The morphology of 3 wt.% PVDF-HFP/CA film (Figure 3c) shows a spongy structure with visible rough surface. This morphology is noted for its extensive surface area and superior adsorption capability [25]. The results demonstrate that the preparation of all the PVDF-HFP films was successful.

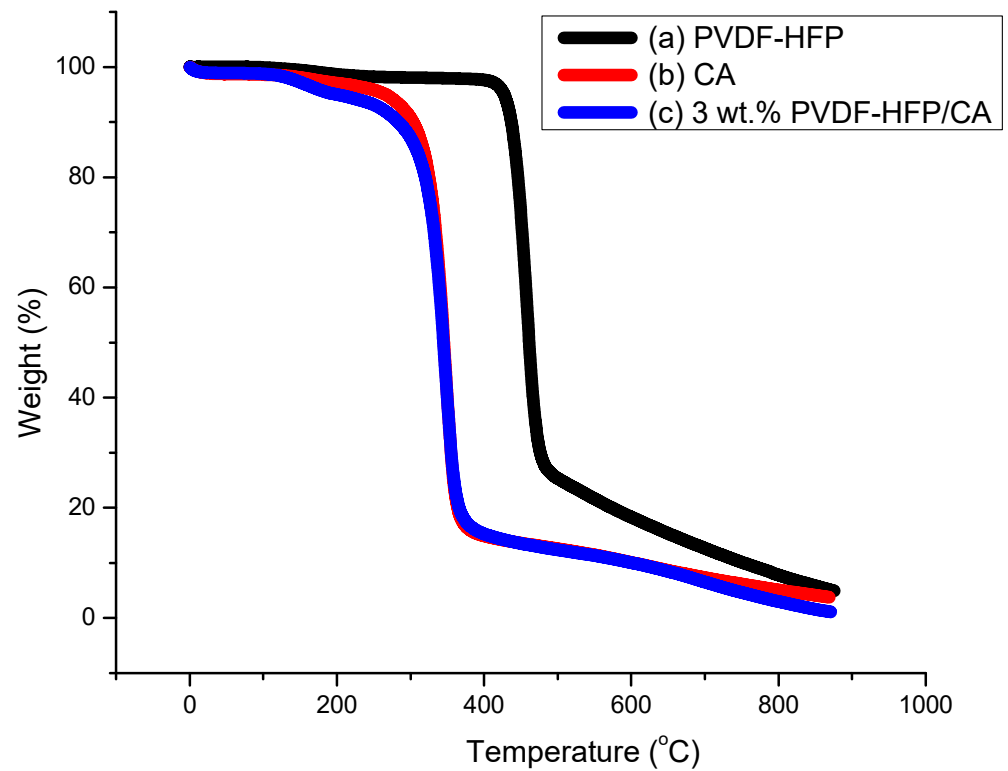


Figure 2. Thermogravimetric analysis profiles of PVDF-HFP, CA, and films containing 3 wt.% PVDF-HFP blended with CA.

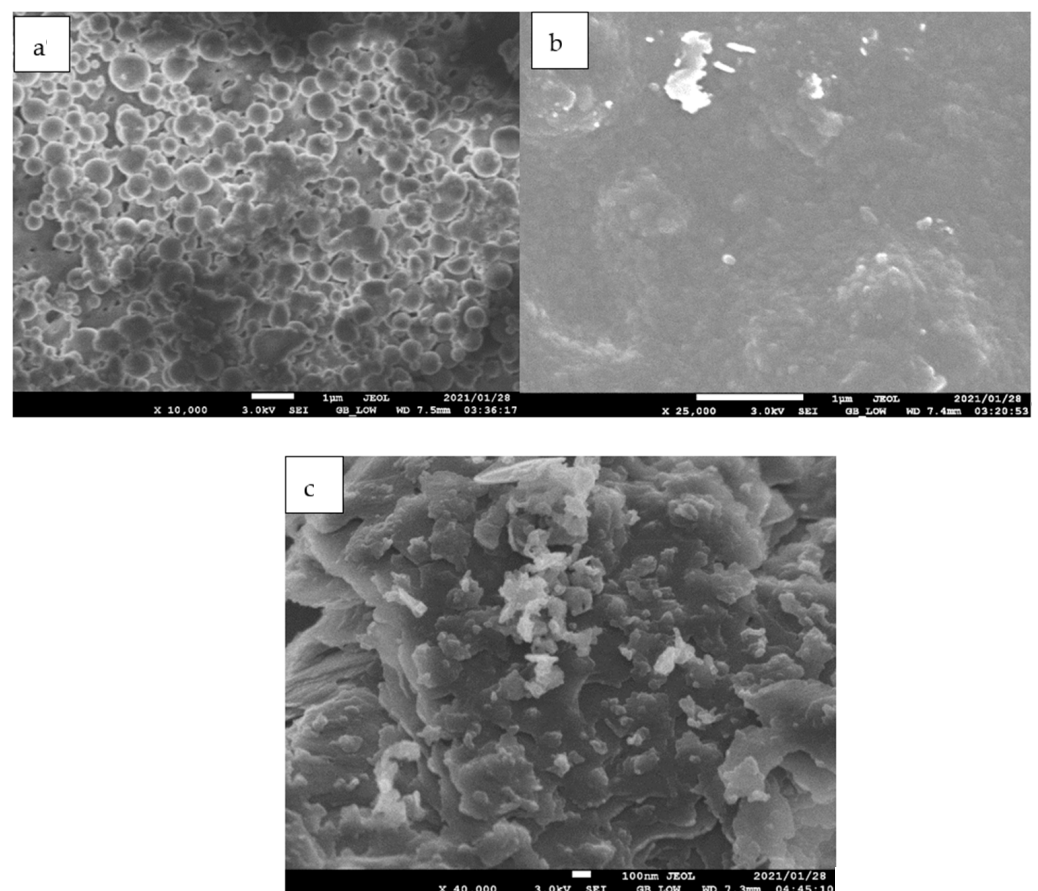


Figure 3. SEM images of (a) PVDF-HFP, (b) CA, and (c) films containing 3 wt.% PVDF-HFP blended with CA.

3.2. Adsorption Studies

3.2.1. Impact of pH on Ca^{2+} Ions Removal by PVDF-HFP Film

Figure 4 illustrates how pH influences the adsorption of Ca^{2+} ions onto a PVDF-HFP film. As depicted, the removal efficiency of Ca^{2+} ions rises from 74.5% to 79.5% when the solution's pH increases from 5 to 7. The removal efficiency increased steadily from acidic conditions toward neutral pH, with values ranging from 76.3% at pH 6.0 to 75.7% at pH 6.5 and higher at pH 7.0. The slight decrease at pH 6.5 (0.6%) is within the experimental uncertainty and does not affect the overall trend. Maximum adsorption efficiency of the PVDF-HFP film for Ca^{2+} ions is observed in the pH range of 6.8 to 7.0, compared to more acidic conditions. The lower percentage removal at the acidic pH is attributed to competition between the H^+ and Ca^{2+} ions for binding to the available active sites of the film. These reduced percentages might also be attributed to the extended protonation of the adsorbent's functional groups, caused by the introduction of 0.1 M HNO_3 during the pH adjustment process. It was also observed that when the pH exceeded 7, the adsorption of the Ca^{2+} ions diminished, likely due to the generation of OH^- ions. Consequently, this led to the creation of metal hydroxide ($\text{Ca}(\text{OH})_2$), which precipitates as white crystals, thereby resulting in a reduced percentage of ion removal. Similar results were reported at pH of 6.5 by Muqet et al., 2018 and Macevele et al., 2021 during the adsorption of Ca^{2+} ions and Cd^{2+} ions, respectively [25,30]. For the subsequent adsorption tests, a pH of 7.00 was chosen.

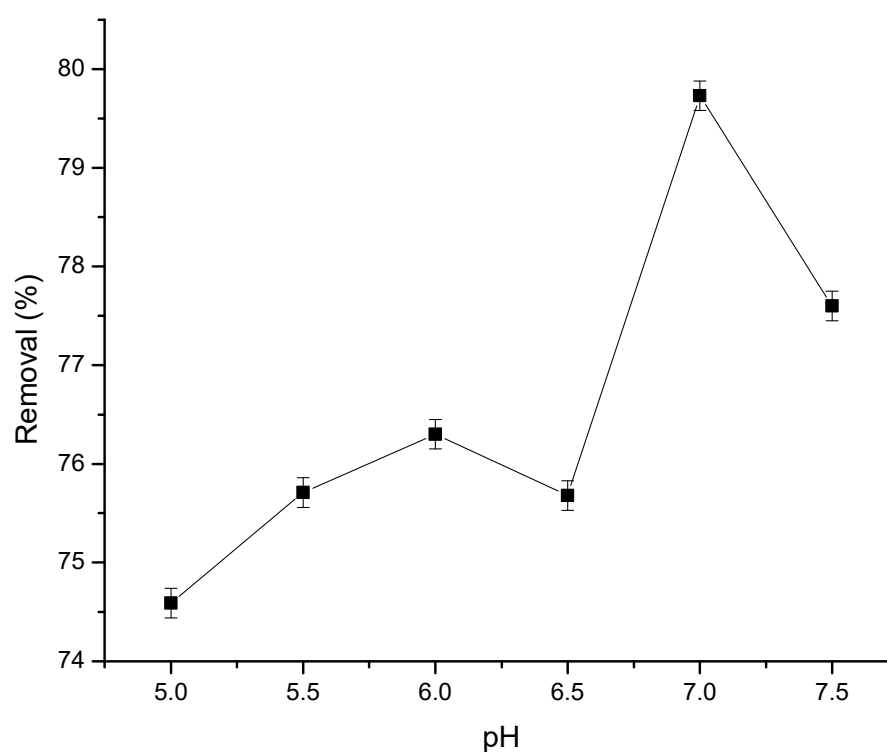


Figure 4. Impact of pH on the uptake of Ca^{2+} ions by PVDF-HFP films.

3.2.2. Effect of Film Adsorbent Dosage

Figure 5 illustrates the investigation into the influence of CA, PVDF-HFP, and a 3 wt.% PVDF-HFP/CA film adsorbent dosage on the hardness of Ca^{2+} ions. When the film dosages were varied from 0.1 to 0.9 mg/L, the removal efficiency increased. The CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA films attained their peak adsorption capacities for Ca^{2+} ions at 70%, 62%, and 80%, respectively, when an adsorbent dosage of 0.5 mg/L was employed. This rise can be attributed to a greater number of active sites available on the sorbent material. Furthermore, the enhanced Ca^{2+} removal observed for the PVDF-HFP/CA films can be

explained by a synergistic mechanism wherein the polar functional groups of CA ($-\text{OH}$ and $-\text{C}=\text{O}$) provide active binding sites for Ca^{2+} ions, while the incorporation of PVDF-HFP improves the stability and hydrophilic–hydrophobic balance of the film, thereby increasing the accessibility and effectiveness of these sites [45,46]. However, upon further increase in dosage, the films yielded a negligible Ca^{2+} ions adsorption, which is consistent with the data reported by Rolence et al., 2014 [47]. Nonetheless, this contrasted with the findings presented by Sepehr et al., 2013, who observed an increase in Ca^{2+} ions uptake as the dosage increased [18]. Interestingly, the 3 wt.% PVDF-HFP/CA film achieved much better Ca^{2+} ion adsorption (80% Ca^{2+} ions per 0.5 mg/L of adsorbent dosage) in comparison with the data reported by Sepehr et al., 2013 [18] and Werkneh et al., 2015 [19].

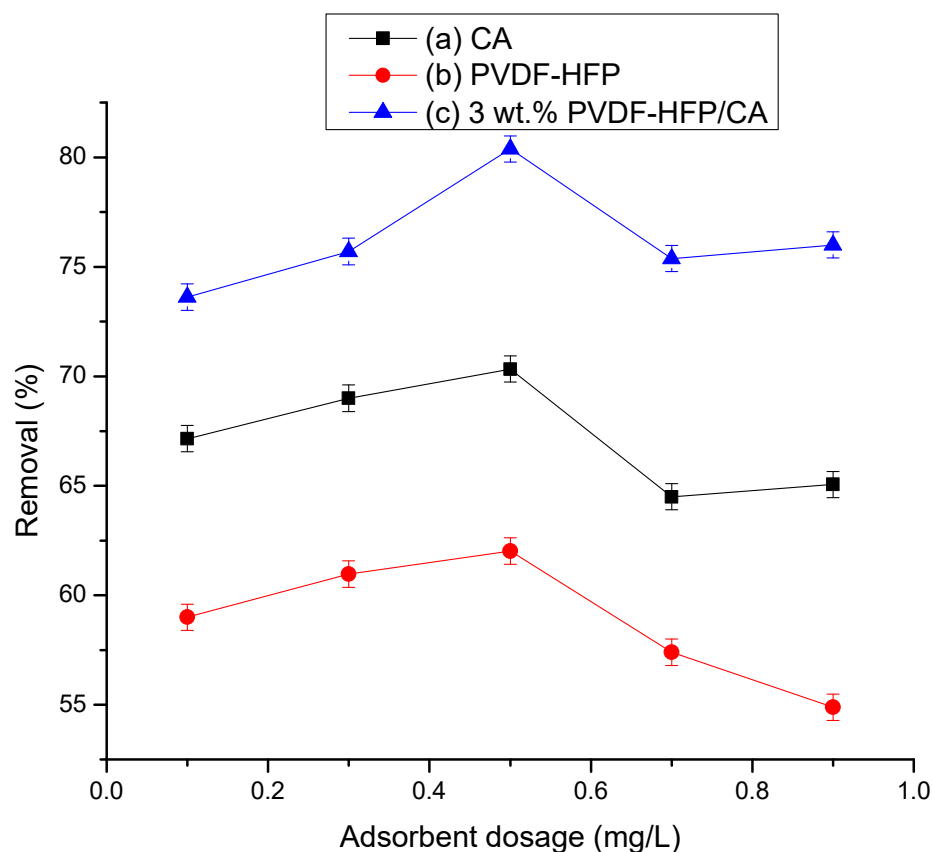


Figure 5. Impact of film adsorbent dosage on the adsorption of Ca^{2+} ions by (a) CA, (b) PVDF-HFP, and (c) 3 wt.% PVDF-HFP/CA films.

3.2.3. Influence of Contact Duration on the Adsorption of Ca^{2+} Ions onto Polymeric Films

Figure 6 illustrates the impact of time on the adsorption of Ca^{2+} ions by CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA films. The results indicate that over 90% removal was attained within the initial 30 min for all polymer films, and this level was maintained nearly stable up to 180 min. Initially, numerous vacant adsorption sites are available for Ca^{2+} ions; as these sites become saturated, the adsorption rate slowed down, nearing equilibrium [19]. These findings indicate that the PVDF-HFP film independently removed 94% of Ca^{2+} ions, with a marginal enhancement when CA was utilised. When 3 wt.% PVDF-HFP/CA film was used, roughly 99.7% of Ca^{2+} ions were removed within 30 min, and the removal rates remained stable for almost 120 min. The results surpass the previous 96% removal rate of Ca^{2+} ions, which required 120 min and a high dosage of 2 g/L, utilising alkali-modified sugarcane bagasse [19]. The optimal time chosen for the extraction of Ca^{2+} ions was 90 min. Unless otherwise specified, the adsorption studies presented here and onward were performed at pH 7 with a fixed adsorbent dosage of 0.5 mg/L.

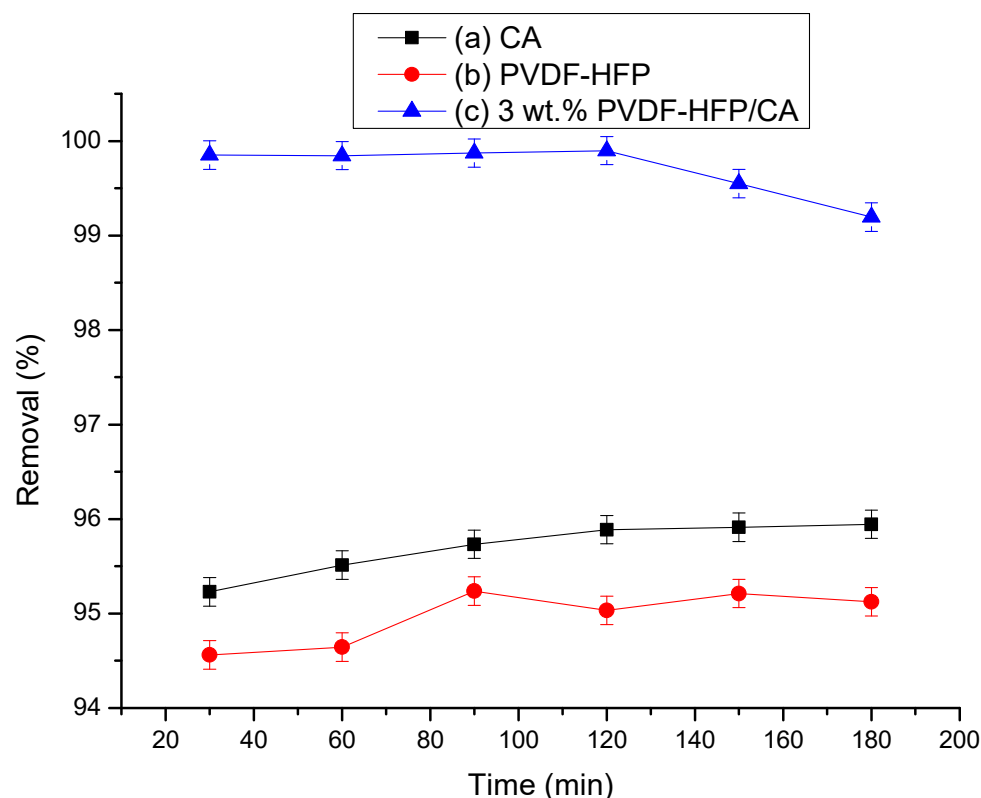


Figure 6. Influence of the impact of time on the adsorption of Ca^{2+} ions by (a) CA, (b) PVDF-HFP, and (c) 3 wt.% PVDF-HFP/CA films.

3.2.4. Influence of Ca^{2+} Ion Concentration on Their Adsorption by Different Polymeric Films

Figure 7 demonstrates how varying the concentration influences the adsorption of Ca^{2+} ions on CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA films. As the concentration rose from 100 to 120 mg/L, the adsorption of Ca^{2+} ions by the PVDF-HFP film increased from 85% to 89%, whereas the CA film exhibited a minor reduction in adsorption from 89% to 87%. The 3 wt.% PVDF-HFP/CA film showed a slight increase from 99 to 99.5% with an increase in concentration of Ca^{2+} ions, which is slightly higher than the data reported by Sepehr et al., 2013 while using alkali-modified pumice stone [18]. The 3 wt.% PVDF-HFP/CA film reached saturation just above 300 mg/L of Ca^{2+} ions.

3.2.5. Effect of Temperature

Figure 8 illustrates how temperature affects the adsorption of Ca^{2+} ions using CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA films. The findings show that as temperature rises, the efficiency of Ca^{2+} ion removal by these films also rises, achieving 92%, 96%, and 97%, respectively. The enhanced adsorption rate is attributed to the increased thermal energy of the films at higher temperatures. This rise in temperature leads to swelling of the adsorbent materials, thereby exposing more active sites for the adsorption of Ca^{2+} ions [47].

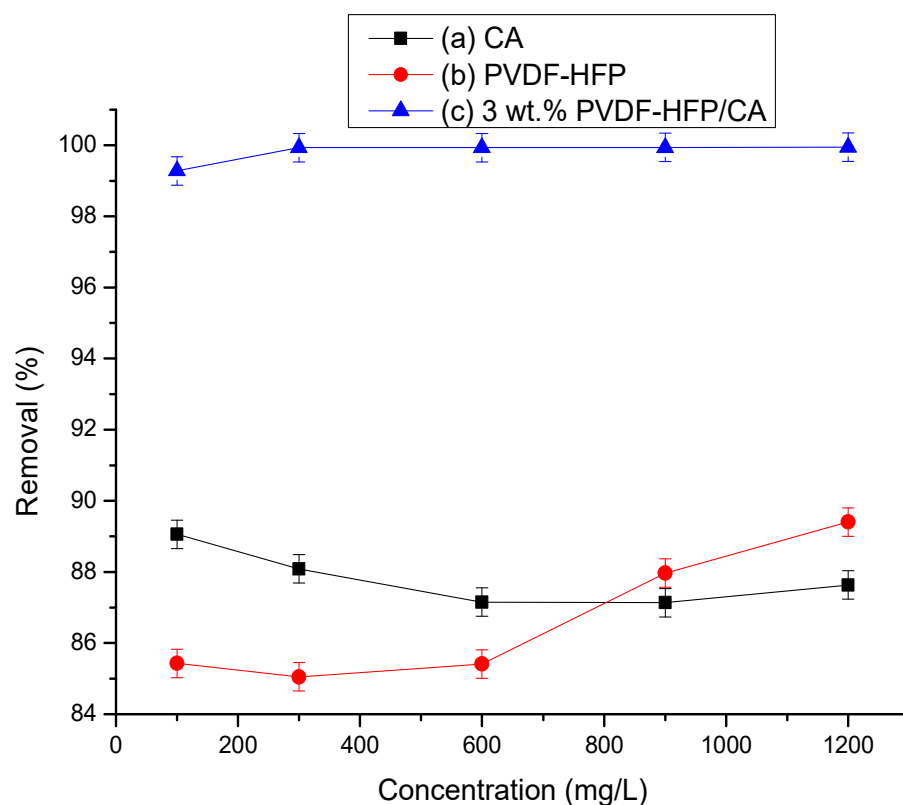


Figure 7. Impact of starting concentrations of Ca^{2+} ions on the adsorption performance of (a) CA, (b) PVDF-HFP, and (c) 3 wt.% PVDF-HFP/CA films.

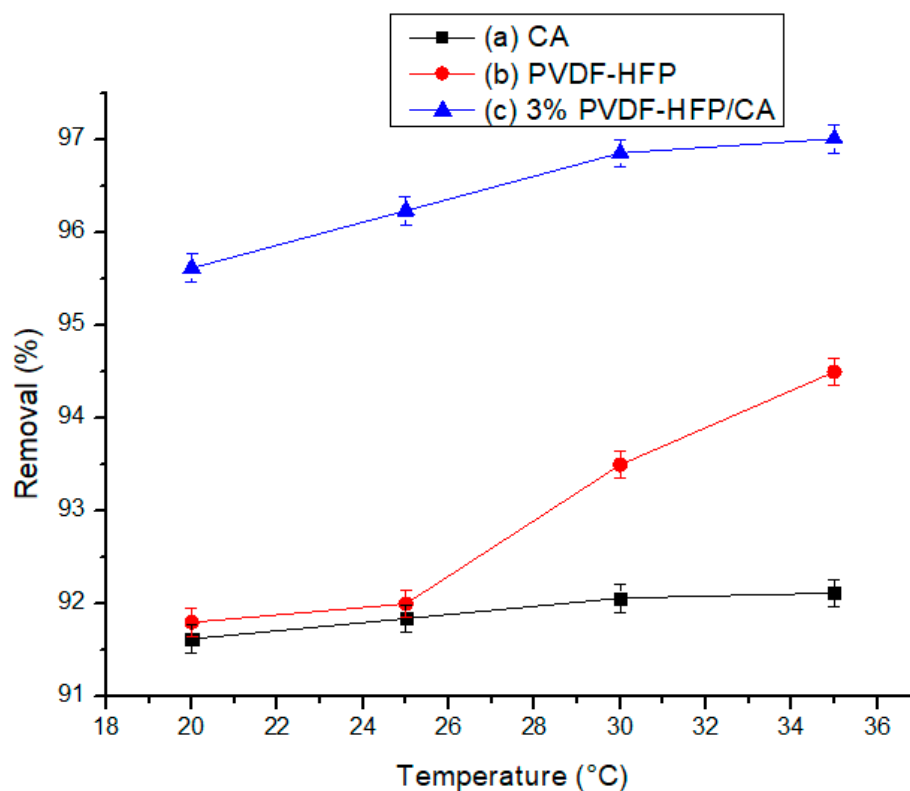
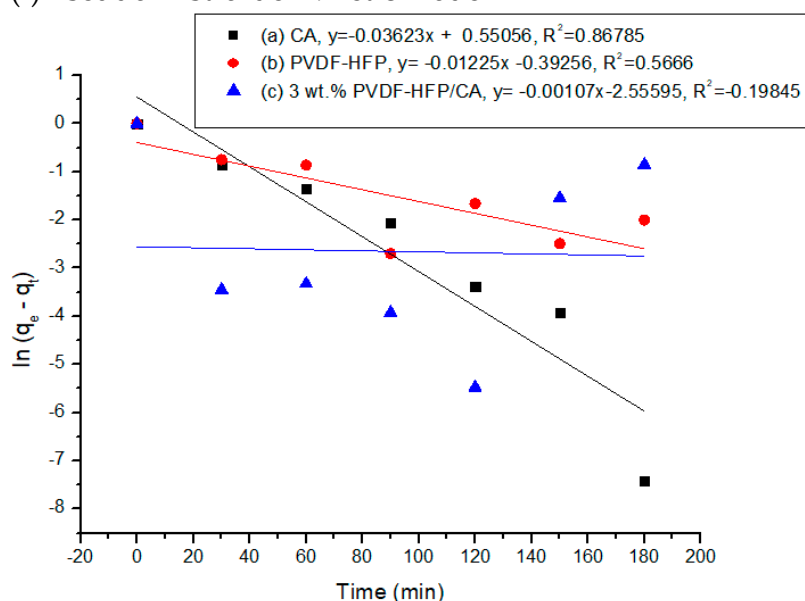


Figure 8. Influence of temperature on the adsorption of Ca^{2+} ions by (a) CA, (b) PVDF-HFP, and (c) 3 wt.% PVDF-HFP/CA films.

3.3. Adsorption Kinetics of Ca^{2+} Ions Using Polymer-Based Films

Figure 9i,ii illustrate the behaviour of the pseudo-first-order and pseudo-second-order kinetic models in the adsorption of Ca^{2+} ions across CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA films. Table 1 outlines the sorption rate parameters (K_1 , K_2 , and q_e) in addition to the coefficient of determination (R^2) values for both kinetic models. The results indicate that the pseudo-second-order kinetic model (represented in Figure 9ii) provides a superior fit compared to the pseudo-first-order model (shown in Figure 9i). According to Table 1, the experimental q_e values closely matched those predicted by the pseudo-second-order model, demonstrating that this model accurately represents the data for all film types: CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA. In addition, the high R^2 values further support that the adsorption process adheres to a pseudo-second-order mechanism, as corroborated by the existing literature [18].

(i) Pseudo-first-order kinetic model



(ii) Pseudo-second order kinetic model

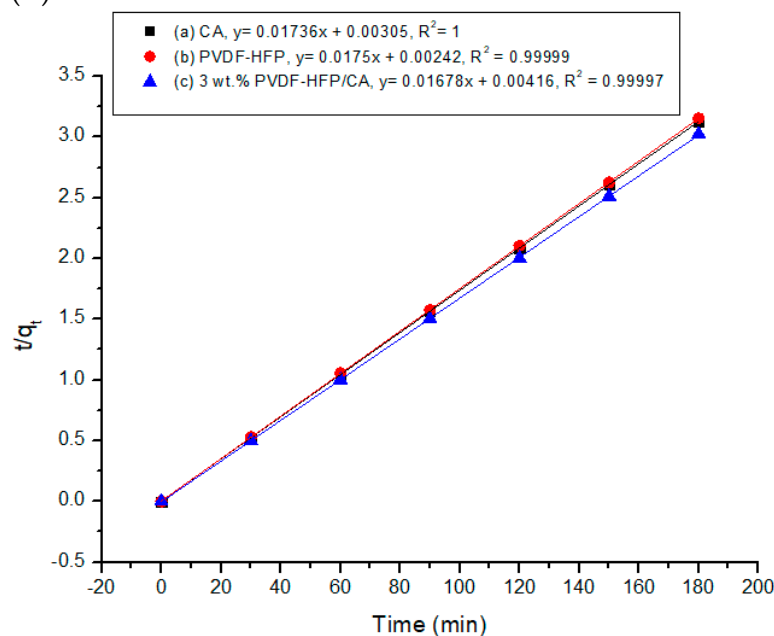


Figure 9. Pseudo-first-order (i) and pseudo-second-order (ii) kinetic models describing the adsorption of Ca^{2+} ions onto (a) CA films, (b) PVDF-HFP films, and (c) films composed of 3 wt.% PVDF-HFP/CA.

Table 1. Adsorption kinetics parameters for Ca^{2+} ions on the prepared films.

Film	Experimental q_e (mg/g)	Pseudo-First-Order Kinetic Model			Pseudo-Second-Order Kinetic Model		
		K_1 (min^{-1})	q_e ($\text{mg}\cdot\text{g}^{-1}$)	R^2	K_2 ($\text{g}/\text{mg}\cdot\text{min}$)	q_e ($\text{mg}\cdot\text{g}^{-1}$)	R^2
CA	57.57	0.04	1.73	0.87	0.10	57.60	1.00
PVDF-HFP	57.21	0.01	0.68	0.57	0.13	57.14	0.99
3 wt.% PVDF-HFP/CA	59.94	0.00	0.08	−0.20	0.07	59.60	0.99

3.4. Models for Adsorption Isotherms

The outcomes of the adsorption tests were analysed using the Langmuir and Freundlich adsorption isotherm models. As illustrated in Figure 10, the adsorption isotherms are presented, with the calculated values detailed in Table 2. When attempting to fit the equilibrium data to both the Langmuir and Freundlich models, it was evident that the Freundlich isotherm model provided a superior fit, yielding higher R^2 values ranging from 0.99633 to 0.99991, in comparison to the Langmuir R^2 values between 0.96464 and 0.99957. This suggests that the Freundlich model, which indicates a surface with nonuniform characteristics and multilayer adsorption, aligns well with observations noted in previous studies [48]. Moreover, the Freundlich isotherm is an empirical model that is highly recommended because of its precision [49]. Each film's equilibrium parameter values (specifically, R_L) are less than one, suggesting a favourable adsorption as documented in the literature [25,50]. The Langmuir isotherm model for the 3 wt.% PVDF-HFP/CA film indicated a maximum adsorption capacity (q_{max}) of 56 mg/g. This value is higher than the q_{max} values reported in the literature, although smaller than the q_{max} of modified pumice adsorbent [18], while the percentage removal by the prepared film was still higher (99%) (Table 3).

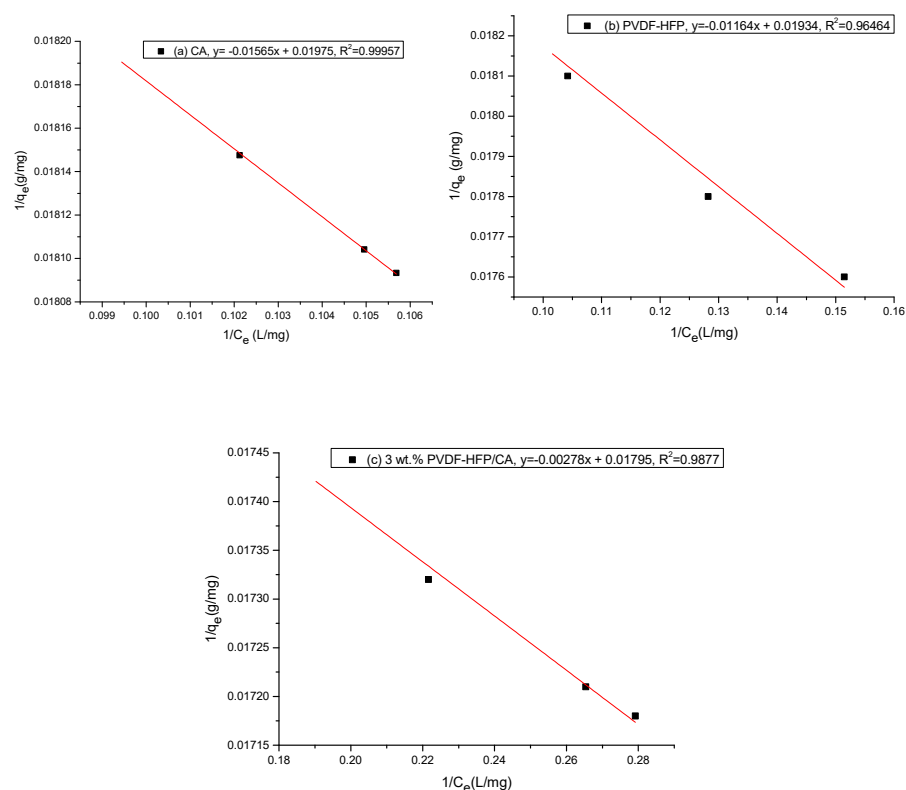
Table 2. Parameters of Langmuir and Freundlich isotherms for the adsorption of Ca^{2+} ions by films.

Film	q_{max} (mg/g)	Langmuir Model			Freundlich Model		
		b (L/mg)	R^2	R_L	K_f (mg/g)	n	R^2
CA	50.63	−1.26	0.99	−0.01	16,268.22	−11.29	0.99
PVDF-HFP	51.71	−1.66	0.96	−0.01	15,000.30	−13.70	0.99
3 wt.% PVDF-HFP/CA	55.71	−6.46	0.99	−0.001	12,944.94	−26.66	0.99

Table 3. Evaluation of the adsorption capabilities of different materials for Ca^{2+} ions.

Adsorbent	Conditions of the Experiment	Adsorption Capacity (mg/g)	% Removal	Reference(s)
3 wt.% PVDF-HFP/CA	pH = 7, Temp = 298 K, Dosage = 0.5 mg/L	56	99	This study
Modified pumice adsorbents	pH = 6, Temp = 293 K, Dosage = 10 g/L	62.34	96	[18]
Coconut shell activated carbon	pH = 6.30, Temp = 303 K, Dosage = 0.16 g/cm ³	48.50	60	[47]
Alkali-modified sugarcane bagasse	pH = 7.50, Temp = 298 K, Dosage = 2.5 g/L	52.9	78	[19]
Natural and homoionic clinoptilolite	Not specified	10.50	Not specified	[48]
Surfactant-modified bentonite adsorbent coating	Not specified	29.27	66.67	[2]
Modified Amorphophallus campanulate skin as a low-cost adsorbent	Not specified	10.85	85	[51]
Bigadic clinoptilolite	Temp = 299 K, Dosage = 20 g/L, Time = 93 min	12.30	99	[52]
Natural zeolite	pH = 6.9, Dosage = 50 g/L	−	80.2	[1]

(i) Langmuir adsorption isotherms



(ii) Freundlich adsorption isotherm

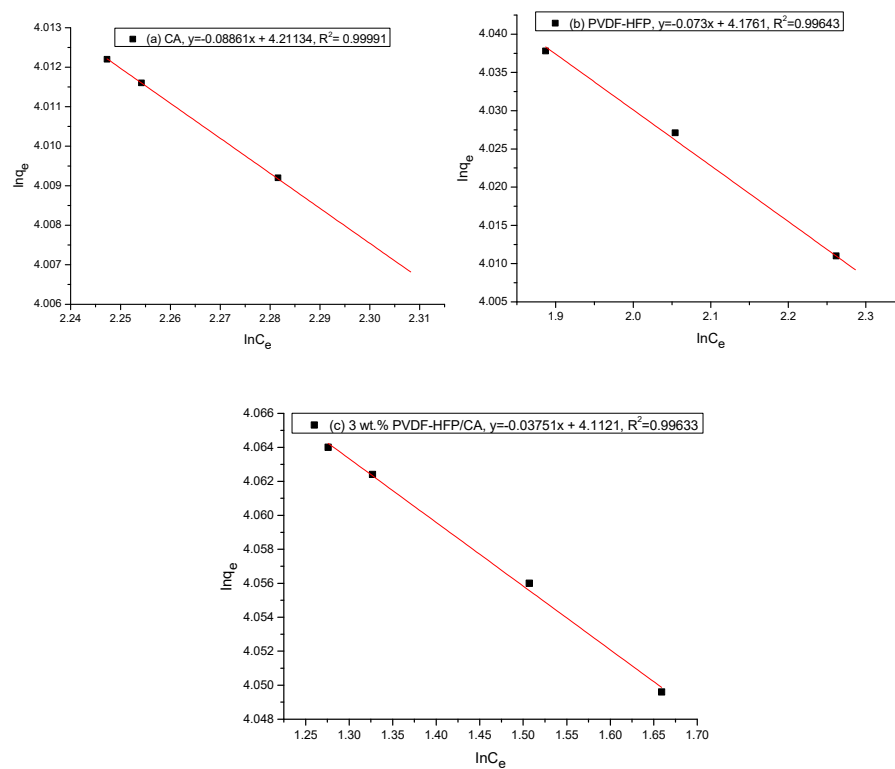


Figure 10. Adsorption of Ca^{2+} ions is described by (i) Langmuir and (ii) Freundlich isotherms for the following films: (a) CA, (b) PVDF-HFP, and (c) 3 wt.% PVDF-HFP/CA.

3.5. Thermodynamics Studies of Ca^{2+} Ions Adsorption on 3 wt.% PVDF-HFP/CA

Figure 11 illustrates the linear graph of $\ln K_o$ against $1/T$ for the adsorption of Ca^{2+} ions on 3 wt.% PVDF-HFP/CA films. Utilising the slope and intercept from the van't Hoff plots enabled the computation of the thermodynamic parameters ΔH° and ΔS° , which are detailed in Table 4. The effect of temperature (ranging from 20 to 35 °C) on the adsorption process of Ca^{2+} ions by 3 wt.% PVDF-HFP/CA films was examined, and the results are presented in Table 4. The adsorption process is endothermic, as evidenced by the positive ΔH° value of 313 KJ/mol (see Table 4). Conversely, the negative ΔG° value, that decreases with a rise in temperature, suggests that the adsorption of Ca^{2+} ions occurs spontaneously [38]. Furthermore, the sorption was accompanied by an increase in entropy, as supported by the positive value of ΔS° , which arises from the release of the structured hydration shell around Ca^{2+} ions upon adsorption [53].

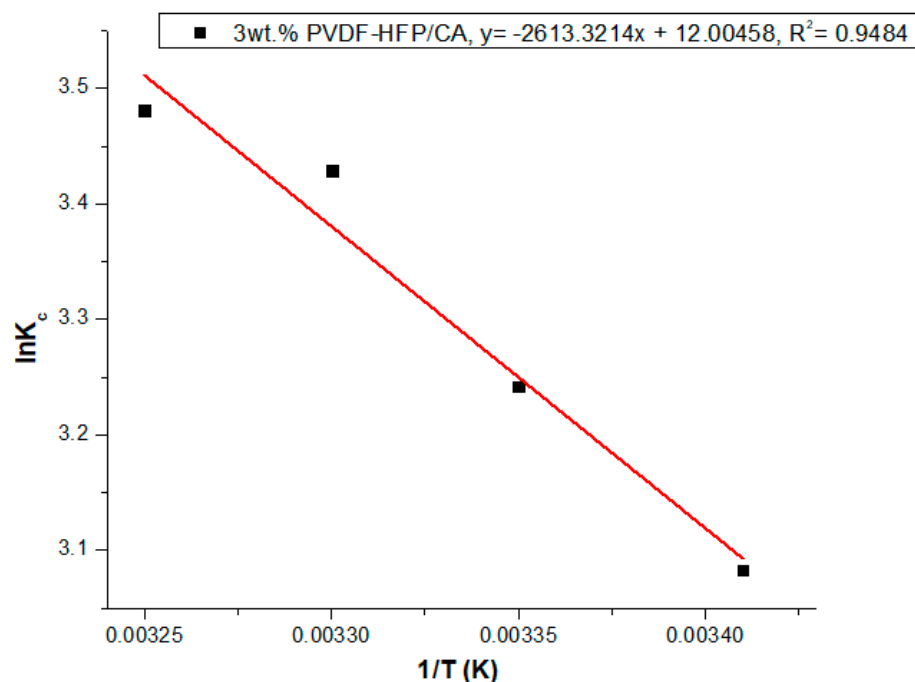


Figure 11. Thermodynamic parameters for the adsorption of Ca^{2+} ions on 3 wt.% PVDF-HFP/CA films. Conditions: 0.5 mg/L dosage, duration = 90 min, 120 mg/L concentration of Ca^{2+} ions, and pH = 7.

Table 4. Thermodynamic variables of Ca^{2+} ion adsorption using 3 wt.% PVDF-HFP/CA films.

Film	Temperature (K)	Thermodynamic Variables		
		ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J.mol/K)
3 wt.% PVDF-HFP/CA	293.15	−7514.85	314.33	1.44
	298.15	−8037.39		
	303.15	−8642.53		
	308.15	−8918.86		

Conditions: 0.5 mg/L dosage, duration = 90 min, 120 mg/L concentration of Ca^{2+} ions, and pH = 7.

3.6. Impact of Counterions

Actual water samples comprise diverse ionic species which could impact the adsorption of hardness-inducing agents. A simulation study using sodium sulphate, potassium nitrate, sodium chloride, and high-purity calcium sulphate (to simulate a real water sample) was undertaken to assess the impact of varying concentrations of metal ions. Figure 12 illustrates how the presence of counterions affects the adsorption of Ca^{2+} ions by films

composed of 3 wt.% PVDF-HFP/CA. As indicated in Figure 12 (a), without counterions, the adsorption of Ca^{2+} ions by the 3 wt.% PVDF-HFP/CA film exceeded 99%, consistent with the findings in Section 3.2.5. However, in the presence of counter ions (Figure 12 (b)), a 3% drop in Ca^{2+} ion adsorption was observed. The drop is insignificant when compared to the results reported by Sepehr et al., 2013 [18], who observed about a 33% decrease in Ca^{2+} ion uptake when exposed to counterions. This is due to competition between the counterions and hardness-causing agents for the available active sites [18].

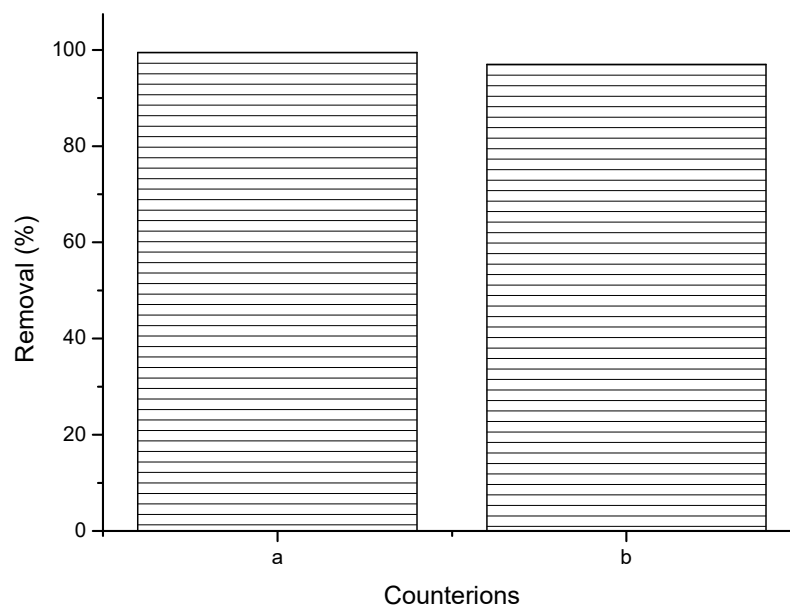


Figure 12. Impact of counterions on the adsorption of Ca^{2+} ions by 3 wt.% PVDF-HFP/CA films: (a) in the absence of counterions and (b) in the presence of counterions. Experimental conditions: 0.5 mg/L dosage, duration = 90 min, 120 mg/L concentration of Ca^{2+} ions, and pH = 7.

3.7. Influence of Binary System on the Uptake of Ca^{2+} Ions

Experiments were conducted under optimal conditions to investigate how Mg^{2+} ions interfere with the adsorption process of Ca^{2+} ions (i.e., 0.5 mg/L dosage, run time = 90 min, 120 mg/L Ca^{2+} ions, and pH = 7) (Figure 13). The 3 wt.% PVDF-HFP/CA films was able to adsorb 91% of Ca^{2+} ions, which is an 8% drop as compared to a single system. The adsorption of Ca^{2+} ions on a binary system reported by Sepehr et al., 2013 [18] had a 22% drop. These results suggest that the 3 wt.% PVDF-HFP/CA is highly selective towards Ca^{2+} ions adsorption and much better as compared to an alkali-modified pumice stone.

3.8. Reutilisation of Films

Reusability trials were performed to investigate the regeneration of used films, an essential factor for evaluating the economic viability of the method developed. A sodium hydroxide solution was utilised to conduct reusability tests on the spent 3 wt.% PVDF-HFP/CA film (refer to Figure 14). The 3 wt.% PVDF-HFP/CA film exhibited an adsorption loss of 0.34% (from 95% to 94.6%) after three adsorption cycles, as opposed to the 20% loss noted by Muqet et al., 2018 [30]. Notably, even after three consecutive cycles, the adsorption efficiency was retained above 90%, suggesting that the 3 wt.% PVDF-HFP/CA film is reusable for the adsorption of Ca^{2+} ions.

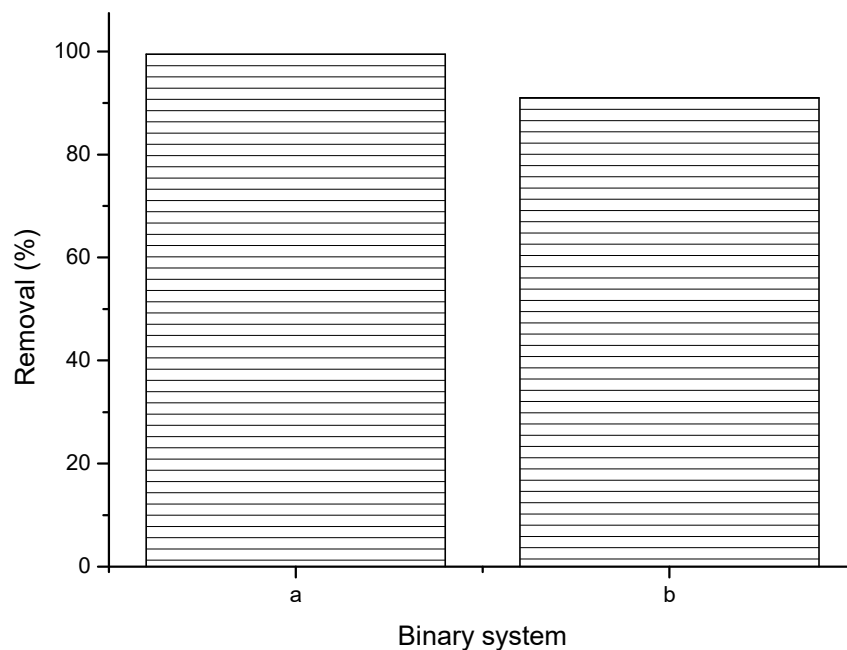


Figure 13. Impact of (a) isolated and (b) binary systems on the uptake of Ca^{2+} ions by a 3 wt.% PVDF-HFP/CA film (Conditions: 0.5 mg/L dosage, run time = 90 min, 120 mg/L Ca^{2+} ions, and pH = 7).

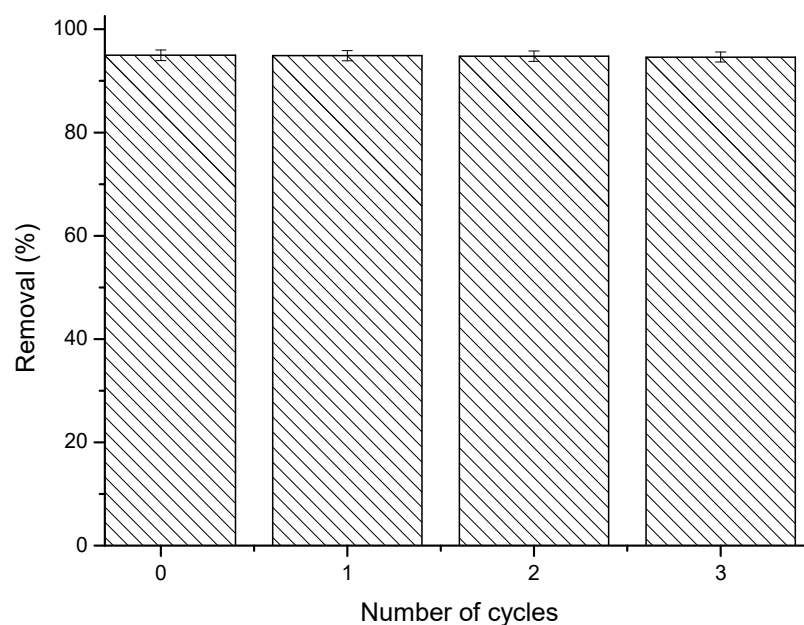


Figure 14. Impact of recycling 3 wt.% PVDF-HFP/CA films on the adsorption of Ca^{2+} ions (Conditions: 0.5 mg/L dosage, run time = 90 min, 120 mg/L Ca^{2+} ions, and pH = 7).

4. Conclusions

This research focused on the softening of hard water by eliminating Ca^{2+} ions using films made from PVDF-HFP as adsorbents. Films composed of CA, PVDF-HFP, and 3 wt.% PVDF-HFP/CA were successfully synthesised through the phase inversion method. The FTIR, TGA, and SEM analyses of the PVDF-HFP/CA films confirmed that 3 wt.% PVDF-HFP was effectively incorporated into the CA structure. Concentrations of Ca^{2+} ions in synthetic water samples were examined through batch studies, optimising parameters like pH, duration, temperature, and adsorbent dosage. The 3 wt.% PVDF-HFP/CA film exhibited around 99% adsorption of Ca^{2+} ions. Using the Langmuir isotherm, the peak

adsorption efficiency was found to be 56 mg/g at an optimal pH of 7, with an adsorbent dose of 0.5 mg/L at a 120 mg/L concentration of Ca^{2+} ions over 90 min. The adsorption kinetics and isotherm models were in line with the pseudo-second-order model. All films followed the Freundlich isotherm model, indicating that the sorption process involved heterogeneous adsorption. Additionally, the thermodynamic parameters suggested that the adsorption process was physical and endothermic. The presence of counterions and binary systems led to a minor reduction in Ca^{2+} ion adsorption on the 3 wt.% PVDF-HFP/CA film. Reusability tests showed that the 3 wt.% PVDF-HFP/CA film could be reused at least three times with only a 0.34% loss in adsorption efficiency. Consequently, this study indicates that PVDF-HFP-based films could serve as effective materials for reducing the hardness of Ca^{2+} ions to acceptable levels.

Author Contributions: K.V.R. prepared all samples, investigated all the data, and wrote the first draft of the manuscript. L.E.M. and A.A.A. co-supervised the research project, supported data analysis, and interpretation from various characterisation techniques. T.M. supervised the project, supported data interpretation, and contributed to the introduction of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that there are no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy
FTIR	Fourier transform infrared
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
CA	Cellulose acetate

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