

## Research Article

# An Investigation on Effectiveness of Grafted Potato Starch as an Adsorbent for Hard Water Treatment

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Water is essential for the life of all living organisms. But water with very high hardness ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) is harmful to health. In addition, hard water clogs the pipes in the industries. This study was conducted to investigate the effectiveness of grafted potato starch as an adsorbent for hard water treatment. Four samples of well water from Nzuguni, Ng'hong'hona, Kisasa, and Swaswa of Dodoma municipal were analyzed by the EDTA titrimetric method. The results showed the highest hardness of 547 mg/L in the water sample of Ng'hong'hona from which hardness was removed. The maximum percentage removal of 74.50% was achieved at 80 minutes of optimum contact time. The optimum adsorbent dose is 3.5 g at which 80.7% of removal was achieved. The optimum temperature was 80°C at which 75.8% of removal achieved. An increase in pH increased the percentage of removal up to a pH of 12 with 71.1%. The data obtained showed that the adsorption process fitted Langmuir type II isothermal model and pseudo-second-order kinetic model with correlation coefficients of 0.9994 and 0.9940, respectively. Grafted potato starch has shown higher efficiency in hardness removal, and hence, this adsorbent is highly recommended for the treatment of hard water.

## 1. Introduction

Hardness of the water in Tanzania is a problem, especially in the central zone of Tanzania which is Dodoma and Singida. Hard water is water that contains carbonates/bicarbonates, chlorides, sulphate of calcium, and magnesium ions. The presence of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in water can react with soap anions and lower the cleaning efficiency and leads to higher consumption of detergents due to the formation of calcium stearate which is insoluble [1, 2]. Bathing with soap in hard water leaves a film of sticky soap curd on the skin, but also skin washed with hard water can become itchy and dry [3]. Hard water produces deposits of precipitate-scaling mostly in hot water pipes, heaters, boilers, kitchen, and bathtubs [4]. Hard water can lead to the purchase and use of large volumes of soaps and other cleaning materials during domestic laundry that is capable of lathering in hard water conditions. Hard water reduces the life span of water meters, water taps, valves, and pipes due to

clogging and choking caused by accumulation of salt deposits.

According to Dodoma Urban Water and Sewerage Authority (DUWASA) analytical results, the water in Dodoma is hard. The main sources of hardness are due to dissolved polyvalent metallic ions from sedimentary rocks, seepage, and runoff from soil [5]. The physical and chemical parameters of Dodoma municipality water were analyzed in 2015, and it was reported that the calcium ions range was 105–217 mg/L which is greater than the allowed range of 50–100 mg/L. The magnesium ions range was 31–217 mg/L which is also greater than the allowed upper limit of 30 mg/L [6]. The occurrence of cardiovascular diseases has been experienced in areas with hard water [7]. However, numerous debates and disagreements prevailed over time. Some scientists had been trying to associate the cardioprotective factor of hard water while others were working on the toxic factor of soft water with this geoselective predisposition to cardiovascular events. Now the factor is

unanimously agreed upon and can be concluded as magnesium [8]. The World Health Organization states that hard water may cause cardiovascular diseases, although there are not enough studies for this finding to be conclusive [9]. 50% increase of the urinary calcium concentration in the absence of changes of oxalate excretion; the calcium-citrate index revealed an important threefold increase during the consumption of hard water as compared to soft water [10]. Hard water has an unpleasant taste and also causes toughening of skin and hair [11]. Public acceptable level of hardness varies remarkably according to local conditions in general. Water supplies with total hardness higher than 200 mg/L can be tolerated by consumers, but values higher than 500 mg/L are not acceptable for most of the domestic consumption [4].

Hardness concentration can be reduced by various methods like ion exchange, lime soda, complexation, and precipitation. Many processes have been attempted to treat hardness, but due to its cost, it has become unaffordable. Many researchers have studied various adsorbents which are relatively inexpensive with higher efficiency of reducing hardness ions. These adsorbents are *Moringa oleifera* [12], cactus (*Opuntia* spp) [2], and cashew nutshell activated carbon [11], pumice stone adsorbent [13], coalesced and uncoalesced adsorbents [14], polyacrylic acid [15], activated *Phyllanthus emblica* wood powder adsorbent [1], and modified chitosan [16]. The grafted potato starch has not yet been used for the adsorption process. Thus, in this study, adsorbents prepared from grafted potato starch (GPS) have been used for the removal of hardness ions from hard water.

## 2. Materials and Methods

**2.1. Chemicals.** Vinyl monomers, methyl methacrylate (Assay 99% CAS No: 80-62-6), oxalic acid (Assay 99.5%, AR/ACS) and potassium permanganate (Assay 99.5%), acetone (Assay AR/ACS 99.5%), EDTA (Assay > 98%), and all the other chemicals were analytical grade purchased from Nebrix company. Ethylenediamine tetraacetic acid (EDTA) disodium salt dehydrate was dried for 2 h at about 80°C in an oven before use. To prepare 0.01 mol/L of EDTA, 3.725 g of the substance was dissolved in distilled water. The solution

was then transferred quantitatively to a 1000 mL volumetric flask and filled up to the mark with distilled water, then stored in a polyethylene bottle. A solution of calcium chloride (0.01 mol/L) was prepared by drying calcium carbonate (99% purity) for 4 h at about 105°C in the oven before use, then weighed 1.0 g of dried calcium carbonate and transferred to a 500 mL conical flask. 21 mL of 1.0 mol/L hydrochloric acid solution was added slowly drop by drop and the contents of the flask were swirled until all the carbonate was dissolved. 200 mL of water was added and boiled to expel the carbon dioxide and cooled. A few drops of methyl red indicator solution was added and adjusted to intermediate orange color with a hydrochloric acid solution. The solution was transferred quantitatively to a 1000 mL volumetric flask and made up to the mark.

**2.2. Water Sample.** To get composite samples, water samples collected from the surface, middle and lower parts of the well from each of the sites Nzuguni, Ng'hong'hona, Kisasa, and Swaswa in Dodoma municipal. The collected water samples were stored in high density polyethylene (HDPE) bottles of 5000 mL which were washed thoroughly with distilled water and dried prior to use. Collected water samples were kept at room temperature in a clean place to avoid contamination. All samples were labeled in accordance to place collected, date, and time.

**2.3. Determination of Hardness of Water.** 50.0 mL of the water sample from Nzuguni, Ng'hong'hona, Kisasa, and Swaswa each was taken into a 250 mL conical flask and diluted to 100 mL, with distilled water. 4 mL of the buffer solution was added to maintain the pH of the solution and 6 drops of the EBT indicator solution was added. The solution was titrated with a standard EDTA solution until the color of the solution starts to change from violet to blue and then to a distinct blue endpoint. Then the volume of EDTA was recorded. Hardness was calculated using the following equation:

$$\text{hardness as } \frac{\text{mg}}{\text{L}} \text{CaCO}_3 = \frac{\text{mL of EDTA solution used} \times 1000}{\text{volume of water samples taken}} \quad (1)$$

**2.4. Preparation and Characterization of the Adsorbent.** The adsorbent, graft potato starch, was synthesized by following the procedure of Singh and coworkers with slight modification [17]. The starch powder was weighed (200 mg) and poured into each of the two clean and dry 250 mL conical flasks, and then the powder was dissolved by adding 50 mL of distilled water to each flask separately and heated at very low temperature to dissolve amylopectin which is

insoluble at room temperature. Vinyl monomer, methyl methacrylate (2.5 mL) was added to the two flasks. The reaction mixture was exposed to a temperature of 45°C for about 30 min in a thermostatic water bath. 50 mg of each, oxalic acid, and potassium permanganate (99.5%), was added to the reaction flasks and shaken, then again kept in a water bath at 45°C and the graft copolymerization was carried out for one hour. The reaction mixture was finally poured into 100 mL of acetone solvent to precipitate the graft copolymer. The copolymer was repeatedly washed with acetone as a solvent to remove the adhered homopolymer (if

any), and dried in an oven at 50°C and then weighed. These materials were then preserved in air tight plastic bag.

The moisture content of the obtained adsorbent was determined by using the gravimetric method [18]. The weight of the adsorbent sample was determined before and

after drying. The weight of water was obtained from the difference between the weight of the sample before and after drying which was calculated using the following equation [16]:

$$\% \text{ of moisture content} = \frac{\text{weight before drying, (g)} - \text{weight after drying, (g)}}{\text{weight before drying, (g)}} \times 100. \quad (2)$$

The values of moisture content were used to predict the equivalent amount of raw materials which will give the desired amount of dry materials.

In order to confirm the grafting of potato starch, KBr pellets were prepared with potato starch before grafting and after grafting and analyzed by using Fourier Transform Infrared Spectrophotometer (FT-IR) in the range of 4000–400  $\text{cm}^{-1}$ . The infrared spectra produced were interpreted to confirm if the materials were grafted [19]. Potato starch was also studied by X-ray diffractometer before grafting and after grafting for phase identification of materials.

**2.5. Batch Adsorption Experiments.** Batch tests were carried out in 250 mL beaker to check the influence of various parameters such as contact time, adsorbent dose, temperature, and pH in order to check the possible maximum removal of hardness. The parameters were optimized by varying each at a time by keeping the remaining parameters constant. Control experiments were also carried out. The experiments were performed at the same stirring speed and same time period for each experimental run. 100 mL of water sample of known hardness was taken in a 250 mL beaker that contained a known amount of grafted potato materials. These beakers were stirred at a constant speed for 10 minutes at room temperature (24°C), centrifuged and filtered by filtration through Whatman filter paper (Diameter 15.0 cm Cat. No. 100115) to separate solution from the adsorbent. The hardness was analyzed using EDTA titrimetric method.

The effect of various parameters on percentage of adsorption was studied by varying contact time,  $t$  (20, 40, 60, 80, 100 and 120 min), adsorbent dosage (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 g/100 mL), temperature (30, 40, 50, 60, 70, 80 and 90°C), and pH of solution (2, 5, 7, 9 and 12). The hardness of filtrates obtained was measured using EDTA titrimetric method. The percentage removal of hardness was calculated using the following equation:

$$\% \text{ removal} = \frac{C_i - C_e}{C_i} \times 100, \quad (3)$$

where  $C_i$  and  $C_e$  are the initial and final hardness of the water in mg/L, respectively.

**2.6. Adsorption Isotherms.** Adsorption experiments for isotherms were carried out at different adsorbent doses 1, 2, 3, 4, 5, and 6 g in 100 mL of the water sample, at an optimized contact time of 80 minutes, the optimized temperature of 80°C, and at optimized pH of 9. Samples were stirred at a constant speed of 320 rpm for 10 minutes by a magnetic stirrer (Labcon-Ms 20) and then filtered by Whatman filter paper and hardness determined by using EDTA titration [20]. In order to determine the mechanism of adsorption of hardness ions on the grafted potato starch, the experimental data were applied to the Langmuir and Freundlich adsorption isothermal equations. The constant parameters were calculated by regression using a linear form of the isotherm equation.

**2.7. Adsorption Kinetics.** Adsorption kinetics of hardness is obtained by the sorption experiment which was tested to fit the pseudo-first-order and pseudo-second-order mechanisms, which describe the mechanisms of adsorption and potential rate controlling steps. Adsorption kinetics was studied by using constant surface loading of 200, 250, and 300 g which are corresponding to the initial concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  of 300 and 200 mg/L, respectively. Total hardness was measured at different time intervals (20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 minutes) by taking 100 mL of water sample.

**2.8. Regeneration of Adsorbent Materials.** The used adsorbent was regenerated continuously due to exhausting of the active site or redissociation of the trapped hardness causing ions from hard water. Regeneration removes the previously adsorbed hardness causing ions from the surface of adsorbents. Regeneration tests for saturated adsorbent were carried out by adding 6g of adsorbents in 0.01 M of phosphoric acid then followed by 2 M solution of NaOH. Then washed with distilled water and dried at 55°C for 24 h. The regenerated adsorbent for an optimized dose of each adsorbent was dissolved in 100 mg/L of a water sample with an initial hardness of 547 mg/L and stirred with an optimum contact time of 80 min, then left to stand for 10 minutes. The adsorbent was filtered with Whatman filter paper. The regenerated adsorbents were retested again for hardness removal by EDTA titrimetric method [13]. The addition of phosphoric acid releases hardness causing ions on the

adsorbent surface and the use of 2 M of NaOH reactivates the surface of the adsorbent for hardness causing ions.

### 3. Results and Discussion

**3.1. Hardness of Water Samples.** The total hardness of water samples from the sites Nzuguni, Ng'hong'onha, Kisasa, and Swaswa was  $380.7 \pm 0.0125$ ,  $547.9 \pm 0.0099$ ,  $293.7 \pm 0.0112$ , and  $317.1 \pm 0.0227$  mg/L, respectively. Among all the water samples analyzed, a water sample from Ng'hong'onha had the highest hardness; therefore, this sample was used for subsequent adsorption studies for the removal of hardness.

**3.2. Characterization of Adsorbents.** The moisture content of grafted potato starch was found as 6.1%. The values of moisture content were used to predict the equivalent amount of raw materials which gave the desired amount of dried materials.

The pattern of adsorption of hardness ions by grafted potato starch was analyzed and recognized with the active groups and bonds present on them. Plant cell walls, mainly consisting of polysaccharides, proteins, and lipids, offer many functional groups such as carboxyl, carbonyl, hydroxyl, amino, aromatic nitro, silicate, sulphonate, etc., which can be involved in metal binding [21].

FT-IR spectrum of pure potato starch before grafting showed broad strong band at  $3292\text{ cm}^{-1}$  due to O-H stretching. Also, bands observed at about  $2925\text{ cm}^{-1}$  could be assigned to the aliphatic C-H stretching. The band around  $1634\text{ cm}^{-1}$  corresponds to C=O stretching vibration of amide. The bands at  $1416$  and  $1337\text{ cm}^{-1}$  correspond to carboxylate anion (C-O) stretching and the band at  $992\text{ cm}^{-1}$  corresponds to characteristic absorption of the carbohydrate [22]. A comparison of the FT-IR spectrum of grafted potato starch with potato starch without grafting showed that some of the peaks are missing and some new peaks have appeared. The intensities of some of the peaks also changed and some peaks slightly shifted. For instance, the intensity of the O-H peak at around  $3300\text{ cm}^{-1}$  decreased. A new sharp and strong peak appeared at  $1726\text{ cm}^{-1}$  which indicates the formation of a new ketonic carbonyl group in addition to amide carbonyl at  $1621\text{ cm}^{-1}$ . More number of peaks observed in the FT-IR spectrum of grafted potato starch in the range of  $1435\text{--}999\text{ cm}^{-1}$  compared to the potato starch without grafting. This result provides substantial evidence of grafting of potato starch [23–25]. The infrared spectra of potato starch before and after grafting are shown in Figure 1.

X-ray diffractograms (Figure 2) of potato starch before and after grafting showed increased crystallinity due to grafting of poly methyl methacrylate on potato starch backbone. The peaks are sharp in the diffractogram of grafted potato starch compared to the potato starch before grafting, which indicates the crystallinity during grafting of the potato starch. The XRD of the grafted potato starch supported grafting and revealed that the potato starch in their natural form amorphous in nature as their XRD showed no peaks for the crystalline areas, whereas after grafting, peaks for the crystalline areas appear near  $2\theta$ ;  $12\text{--}25^\circ$  and  $28\text{--}34^\circ$  [26].

### 3.3. Optimization of Factors Affecting Removal of Hardness from Water

**3.3.1. Effect of Contact Time.** The effect of the contact time was investigated using grafted potato starch as an adsorbent and the water with an initial hardness of 547 mg/L from Ng'hong'onha. The hardness removal ability of adsorbent increased with contact time up to 80 min and then decreased (Figure 3). The percentage of removal was increased from 44.64% at 20 min to 74.50% at 80 minutes. This might be due to the occupation of all sites on the adsorbent surface [20]. The efficiency then decreases to 70.8% and 67.3% at 80 and 100 minutes, respectively. At this point, the number of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the number of metal ions desorbed from the adsorbent [27]. Therefore, the optimum contact time for achieving the maximum percentage of removal is 80 min.

**3.3.2. Effect of Adsorbent Dose.** The effect of adsorbent dose was studied at room temperature ( $24^\circ\text{C}$ ) by varying the sorbent amounts of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 g. For all these runs, the water with initial hardness 547 mg/L from Ng'hong'hona was used. An increase in the dosage of adsorbent results in the increase of the percentage removal of hardness up to an adsorbent dose of 3.5 g with maximum percentage removal of 80.7%, and above that dose it almost remained constant (Figure 4). The observed increment in sorption yield with increasing sorbent dosage could be due to an increase in the number of available binding sites and surface area of the adsorbent [11]. Adsorption efficiency increases with increase in adsorbent dose until it reaches the equilibrium between active sites of adsorbent and the trapped hardness caused metals ions. This result shows that 3.5 g of grafted potato starch was enough to bind the hardness causing metals ions in given hard water.

**3.3.3. Effect of Temperature.** The effect of temperature on removal of hardness was performed at temperatures of 30, 40, 50, 60, 70, 80, and  $90^\circ\text{C}$  using the water with an initial hardness of 547 mg/L from Ng'hong'hona. Figure 5 shows an increase in adsorption capacity with an increase in activation temperature of adsorbent up to  $80^\circ\text{C}$  with a maximum percentage removal of 75.8% and then starts to decrease due to deactivation of the adsorbent surface or the damage of some active sites on the adsorbent surface [28]. Another possible description was that the metal ions were well hydrated. They have to lose part of the hydration sheath in order to be adsorbed. This dehydration process of metal ions required energy. At higher temperatures of more than  $80^\circ\text{C}$ , some desorption occurs due to the shrinkage of the sorbent and releases some of the sorbed ions resulting in increasing the ion concentration in the solution again [29]. This observation supports chemisorption process. The optimum temperature for achieving the maximum percentage removal of hardness is  $80^\circ\text{C}$ .

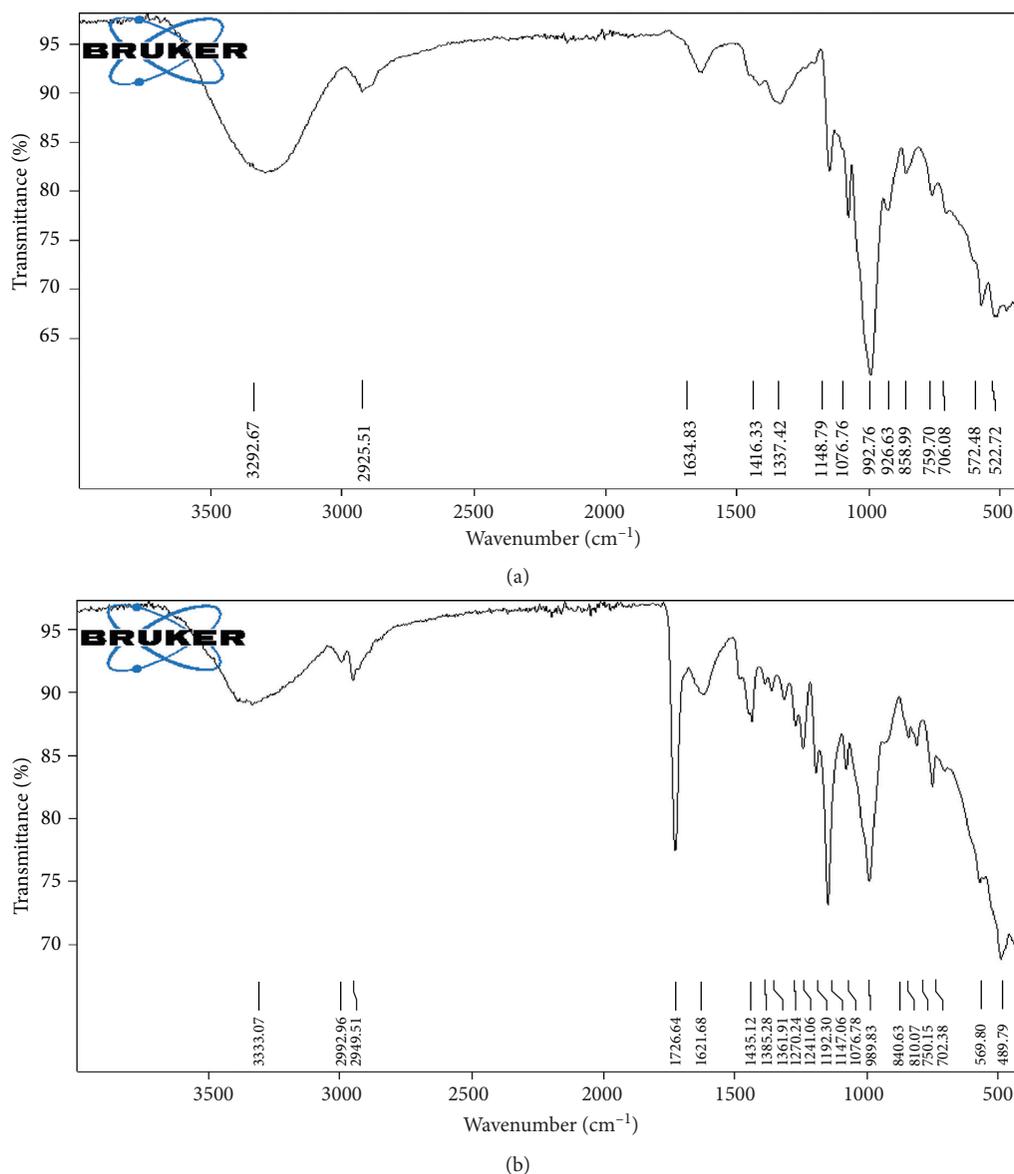


FIGURE 1: FT-IR spectra of (a) potato starch before grafting and (b) potato starch after grafting.

**3.3.4. Effect of pH.** The effect of pH was studied at the pH of 2, 5, 7, 9, and 12 on the water with an initial hardness of 547 mg/L from Ng'hong'hona. The results indicate that the removal of hardness from aqueous solution was strongly affected by the pH of the water. The removal of hardness was low in acidic medium and increased with an increase in the pH of the water (Figure 6). At low pH values, the removal of hardness was low because a large amount of protons compete with the hardness causing ions at the active site of the adsorbent surface [29]. The surface of adsorbent materials becomes negatively charged with increase in pH of the solution which leads to increase in removal of positively charged hardness causing ions through electrostatic forces of attraction [20]. At higher pH, deprotonation of the adsorbent surface takes place due to which the surface becomes negatively charged. In addition, there are no protons in the solution to compete with

hardness causing ions in order to be adsorbed on the adsorbent surface.

**3.4. Adsorption Isotherms.** The adsorption data for the removal of hardness using grafted potato starch was analyzed by a regression analysis to the five linearized expressions of the Langmuir isotherms models (Table 1). Among these five, Langmuir type II and type IV, showed the best agreement ( $R^2 = 0.9993$ ) with experimental data and are the most frequency used by several researchers because of the minimized deviations from the fitted equation resulting in the less error distribution. The Langmuir type II showed higher acceptance with the experimental data (Figure 7). This implies that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of

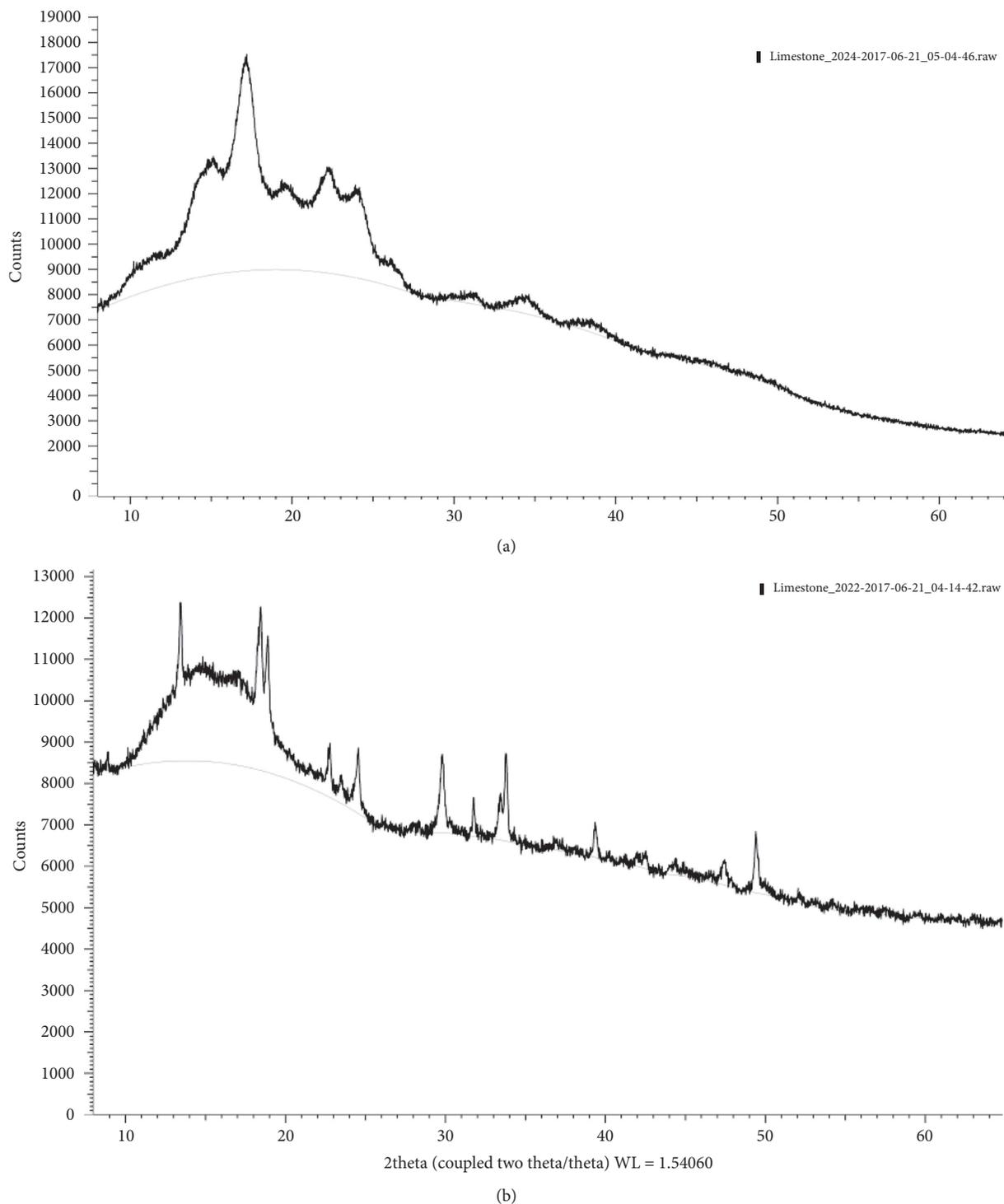


FIGURE 2: X-ray diffractograms of (a) potato starch before grafting and (b) potato starch after grafting.

molecules at an adjacent site. The maximum adsorption capacity,  $q_{\max}$  is 3.647 obtained from the slope of the type IV isotherm.

To determine if the adsorption process is favorable or unfavorable for the Langmuir type adsorption process, the isotherm can be classified by a term  $R_L$  a dimensionless

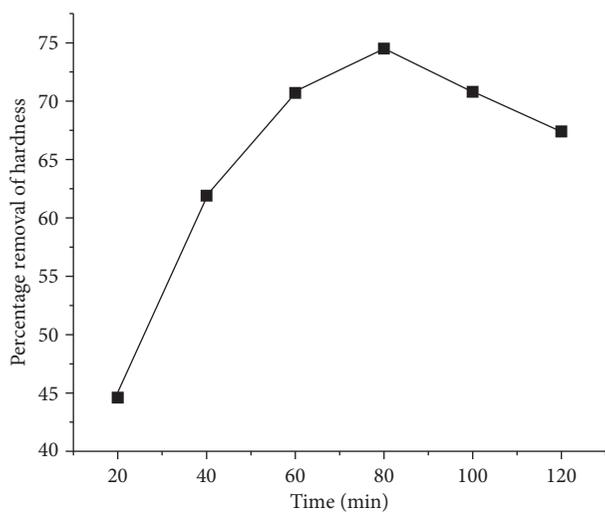


FIGURE 3: Effect of contact time on the percentage of removal of hardness of the water.

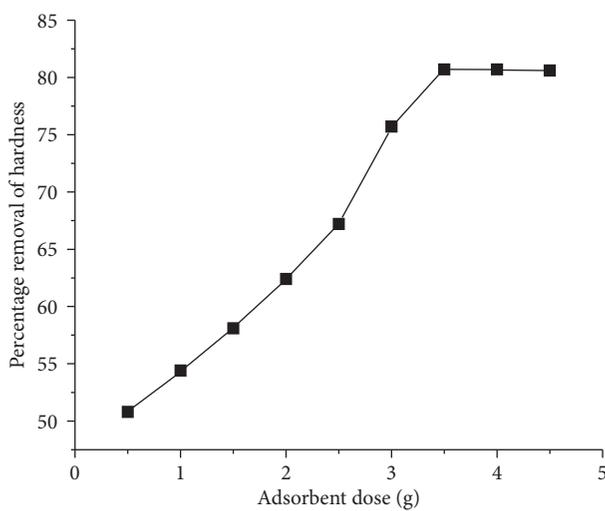


FIGURE 4: Effect of adsorbent dose on the percentage removal of hardness of the water.

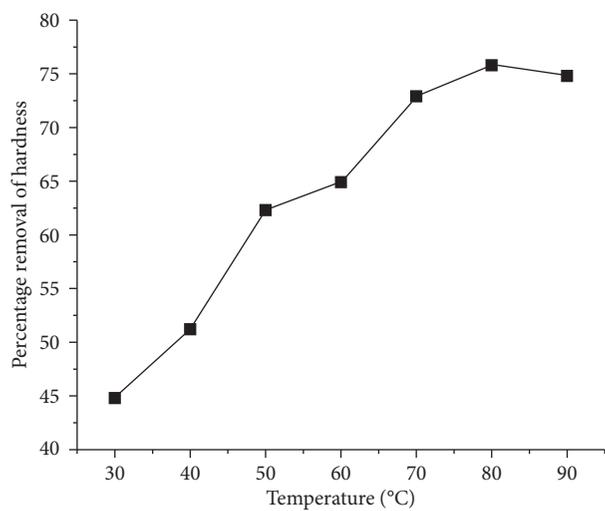


FIGURE 5: Effect of temperature on the percentage of removal of hardness of water.

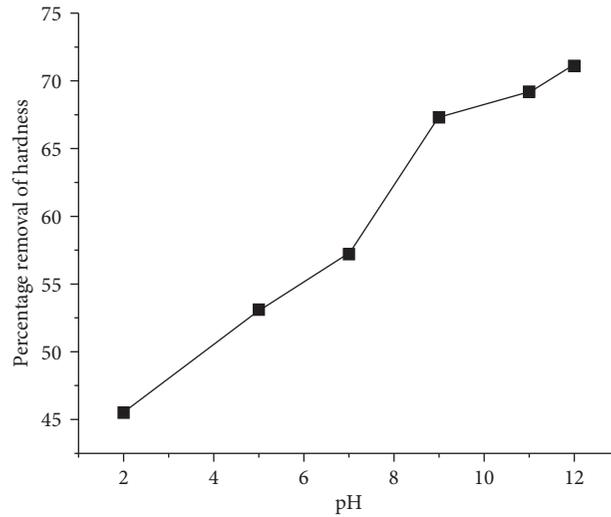


FIGURE 6: Effect of pH on the percentage removal of hardness of water.

TABLE 1: Langmuir isothermal linear models for the removal of hardness using grafted potato starch.

Type	Linear form	Plot	$q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$
I	$1/q_e = (1/K_L q_{\max} c_e) + (1/q_{\max})$	$1/q_e$ vs. $1/c_e$	2.524	$-9.14217 \times 10^{-03}$	0.9750
II	$c_e/q_e = (1/q_{\max})c_e + (1/q_{\max}K_L)$	$c_e/q_e$ vs. $c_e$	2.846	$-6.7919 \times 10^{-03}$	0.9993
III	$q_e = -(1/K_L)(q_e/c_e) + q_{\max}$	$q_e$ vs. $q_e/c_e$	2.588	$-9.30778 \times 10^{-03}$	0.9920
IV	$q_e/c_e = K_L q_e + K_L q_{\max}$	$q_e/c_e$ vs. $q_e$	3.647	$-8.2611 \times 10^{-03}$	0.9930
V	$1/c_e = K_L q_{\max} (1/q_e) - K_L$	$1/c_e$ vs. $1/q_e$	2.533	$-9.133 \times 10^{-03}$	0.9680

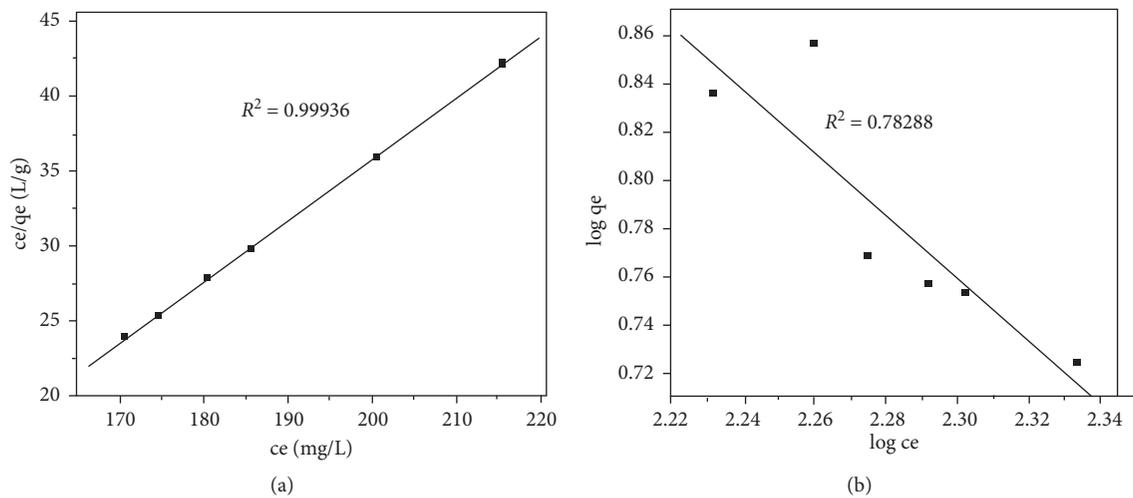


FIGURE 7: Linear Langmuir (a) and Freundlich (b) adsorption isotherms.

constant called separation factor, which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (4)$$

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial metal ion concentration (mg/L).

It has been known that for favorable adsorption  $0 < R_L < 1$ , for unfavorable adsorption  $R_L > 1$ , for the linear adsorption  $R_L = 1$  and if the adsorption process is reversible, then  $R_L = 0$  [25]. The  $R_L$  value obtained in this study is 0.04566. Since these values are between zero and one, it can be concluded that the adsorption of hardness causing ions on the adsorbents was favorable under the experimental conditions.

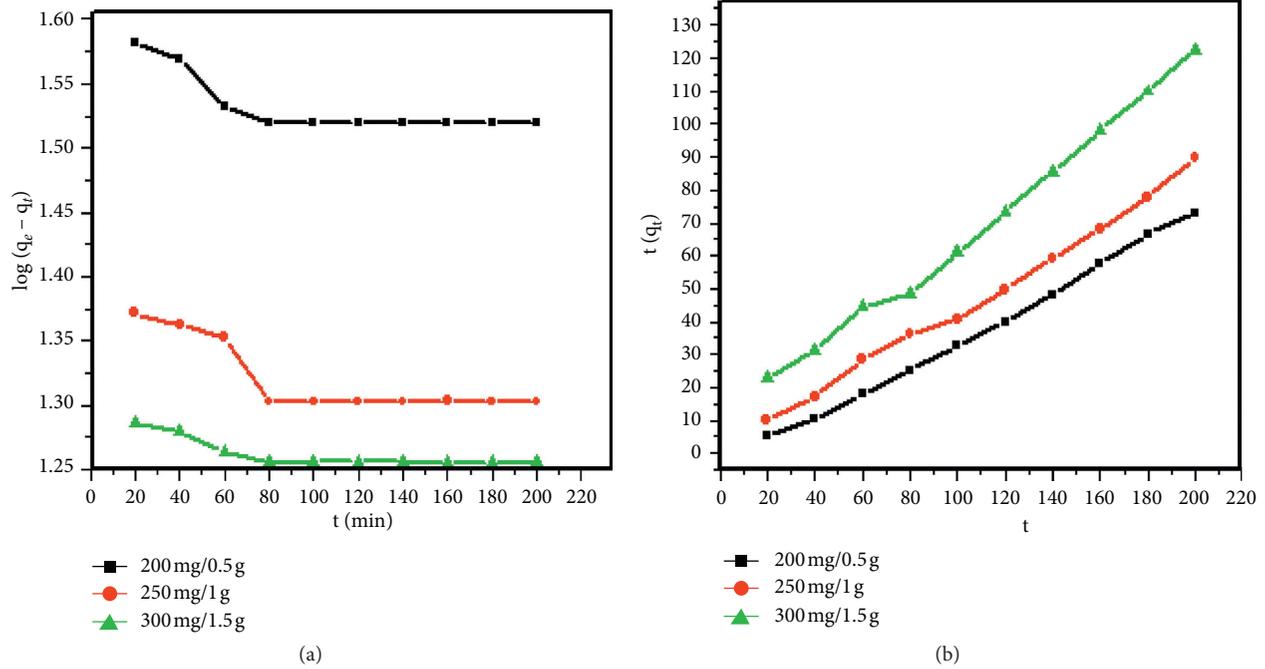


FIGURE 8: Pseudo-first-order (a) and pseudo-second-order (b) plots.

TABLE 2: Adsorption kinetic parameters for pseudo-first- and second-order kinetic models.

Hardness (mg/L)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$q_e$ , cal (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ , cal (mg/g)	$K_2$ ( $\text{g mg}^{-1}\text{min}^{-1}$ )	$R^2$
200	1.413	-8.2612	0.652	0.369	0.369	0.996
250	1.292	-7.2428	0.659	0.403	0.403	0.994
300	1.223	-4.0870	0.607	0.522	0.522	0.994

The Freundlich isotherm describes the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm does not predict any saturation of the sorbate, thus infinity surface coverage is mathematically predicted, which is indicating multilayer adsorption onto the surface of the adsorbent. Freundlich isotherm derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by Freundlich (1906):

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e, \quad (5)$$

where  $q_e$  is the equilibrium amount adsorbed (mg/g).  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $K_F$  (L/g), and  $1/n$  are Freundlich constants related to adsorption capacity and intensity of adsorbents.

The values of  $K_F$  and  $1/n$  found were 3.73491 and -1.2965, respectively. The value of  $1/n < 1$  indicate that the adsorption capacity of adsorbent for hardness causing ions is slightly suppressed at lower equilibrium concentrations and the adsorption process is not favorable. The value of  $n$  obtained was -0.7771 which represents a less beneficial adsorption. The regression coefficient  $R^2$  obtained was 0.7828 which showed that the data were unfit compared to

the Langmuir in which its regression coefficient  $R^2$  was 0.9993 (Figure 7). This shows that the Langmuir model better fitted to the experimental data compared to Freundlich model. It is indication that the surface was very homogeneous in Langmuir model comparison to the Freundlich model.

**3.5. Adsorption Kinetics.** The kinetic parameters for the adsorption process were studied from variation in contact time and analyzed using pseudo-first- and second-order kinetic models [28]. The following pseudo-first-order rate expression was used to calculate the kinetic parameters:

$$q_t = q_e - q_{e,\text{exp}}(-k_1 t), \quad (6)$$

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{k_1}{2.303} t. \quad (7)$$

The plot (Figure 8) of  $\text{log } (q_e - q_t)$  versus  $t$  gave a straight line for pseudo-first-order adsorption kinetics. The slope and intercept of this plot was used to obtain the pseudo-first-order rate constant  $k_1$  and equilibrium adsorption capacity  $q_e$ , respectively. The calculated  $q_e$ ,  $k_1$  and correlation coefficient  $R^2$  values are summarized in Table 2.

The pseudo-second-order kinetic parameters were calculated using the following equation:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t). \quad (8)$$

Integration of the equation above between the limits at  $t = 0$ ,  $q_t = 0$  and at  $t = t$ , and  $q_t = q_t$  which gives the following equations:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t, \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2}. \quad (10)$$

The plot of  $t/q_t$  versus  $t$  is shown in Figure 8. The values of pseudo-second-order rate constant  $k_2$  and equilibrium adsorption capacity  $q_e$  were calculated from the intercept and slope of the plot, respectively. The calculated  $q_e$ ,  $k_2$  and correlation coefficient  $R^2$  values are presented in Table 2.

Initially, the rates of adsorption of calcium and magnesium onto the adsorbent were very fast and then slowed down as the contact time increases. This is due to the fact that, initially, all adsorbent sites were unoccupied and the calcium and magnesium concentration gradient was high. As the contact time increases, the calcium and magnesium uptake rate by adsorbents decreases significantly due to the decrease in active sorption sites on the adsorbent [20]. The trend for the variation of residual concentration is the same for all the three concentrations with three different doses. But the residual concentrations reached to equilibrium at 100 minutes when the residual concentration was 117.8 mg/L at 200 mg/0.5 g, 179.5 mg/L at 250 mg/1g, and 239.9 mg/L at 300 mg/1.5 g. Hence, the influence of adsorbent dose is more on the trends of variation of residual concentration with respect to time. The higher values of correlation coefficient ( $R^2$ ) for pseudo-second-order kinetics than the pseudo-second-order kinetics strongly evidencing that the adsorption of hardness causing ions onto the grafted potato starch follows pseudo-second-order kinetics [30]. Moreover, there is better agreement between the calculated  $q_e$  and the experimental  $q_e$  values which suggests that the chemisorption is the rate-determining step in the adsorption of hardness causing ions by grafted potato starch [31].

**3.6. Regeneration and Reuse of Adsorbent Materials.** After all the microspores of adsorbent become saturated, the adsorbent regenerated and the results showed that the materials have ability to adsorb again the hardness. The adsorbed materials still have large number of active sites that can lead to continuation of accepting hardness causing ions for one time reusability until it reached saturation point for the first cycle at 3 g with the percentage adsorption 67.9% which might be due to all sites on the adsorbent surface being occupied [20]. But for the second cycle percentage removal was 38.2% with 2.5 g and then started to decrease. It can be understood that the amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent [32].

## 4. Conclusions

In this study, the removal of hardness of water using grafted potato starch was conducted using batch experiments; it was found that the percentage removal was dependent on contact time, adsorbent dose, temperature, and pH. The maximum percentage removal of 74.50% was achieved at 80 minutes of optimum contact time. Optimum adsorbent dose is 3.5 g at which 80.7% of removal achieved. Optimum temperature was 80°C at which 75.8% of removal achieved. Increase in pH increased the percentage removal up to a pH of 12 with 71.1%. The data obtained showed that the adsorption process fitted Langmuir type II isothermal model with correlation coefficient of 0.99936. The data fitted to pseudo-second-order kinetic model with a correlation coefficient value of 0.994. The adsorbent prepared in this study also useful for the regeneration and reuse. These results showed that the grafted potato starch can be used as an alternative adsorbent for the removal of hardness from water.

## Data Availability

All the data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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