Nanocrystalline cellulose based on chitosan hydrogel structure as a biological adsorbent for effluent of fish culture farms

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Abstract
Synthetic hydrogels have been replaced by natural hydrogels due to their properties such as being long-lasting, more capacity for water absorption, high strength, and resistance. Recently, hydrogels have been defined as two- or multi-component systems consisting of three-dimensional networks of polymer chains that fill the space between macromolecules. Their water absorption efficiency depends on both polymeric nature and the capacity of the polymer network connections. Because of climate change and frequent droughts, fresh water supply has become a limiting factor for sustainable aquaculture development in Iran. Therefore, wastewater treatment and reuse can be a reasonable solution to meet the required water for expanding the aquaculture industry. The present study assessed the efficiency of a new hydrogel prepared from sugarcane waste (bagasse) to remove nitrogen and phosphate compounds from the effluent of fish farms. First, the hydrogel was prepared during the polymerization process, and then, in order to determine the optimal absorption, it was tested in a discontinuous system by performing absorption isotherm calculations. In cellulose/chitosan nanocrystalline hydrogel nanosorbent, the removal rates for nitrate, nitrite, and phosphate were 84.3%, 86%, and 90.9%, respectively. Optimal adsorption was determined at acidity of 6, time of 30 min, temperature of 40 °C, concentration of 100 mg/L, and adsorbent dose of 0.5 g. A comparison of adsorption isotherm models showed more conformity with Freundlich and Tamkin absorption models with correlation coefficients of 0.99 and 0.97 for nitrate, 0.98 and 0.91 for nitrite, and 0.99 and 0.93 for phosphate, respectively.

Keywords Nanocrystalline cellulose · Chitosan · Freshwater deficiency · Wastewater · Agricultural waste

Introduction
Developing intensive aquaculture increases the discharge of farm effluents into ecosystems such as lakes and rivers, which contain large amounts of nitrogen and phosphate compounds, and its discharge into the aquatic environment causes degradation and adverse effects (Nora'aini et al. 2005). In aquatic ecosystems, the most common ionic forms of mineral nitrogen are ammonium (NH₄), nitrate (NO₃), and nitrite (NO₂). These ions may enter nature due to the runoff entry from flowing and groundwaters which are rich in nitrogen compounds (Spagnol et al. 2012; Hokkanen et al. 2018; Wetzel 2001). Nitrate concentration in freshwater and marine ecosystems is higher than ammonium and nitrite. Nitrogenous compounds cause eutrophication, a nutrient-rich phenomenon, in aquatic ecosystems that disrupts the balance of these ecosystems (Fernández-Nava et al. 2008). Biofloc and aquaponic systems have also been used in aquatic effluent treatment methods, but these systems have disadvantages such as increased energy for aeration and mixing, need for start-up period and alkaline supplementation, increase in pollution due to nitrate accumulation, and inconsistent and seasonal fluctuations.

Nowadays, nanotechnology is used in various fields such as medicine, agriculture, fisheries, and many other industries. In the fisheries industry, nanotechnology is acquiring several purposes, including improvement of fish growth with
the aid of nanomaterials such as vitamins C, E, and selenium within diets used in aquaculture and leads to weight gain as well as elevation of antioxidant levels in the blood (Zhou et al. 2009). They are also used in vaccine production to prevent bacterial and viral diseases in aquatic animals (Habibi et al. 2010; Rajeshkumar et al. 2009) and also in polylimide hooks that attract fish due to light absorption (Rather et al. 2011; Raissy and Ansari 2011). One of the important factors of adsorbents is adsorption capacity, adsorbent selectivity based on surface properties, reusability, compatibility with adsorbed material, and cost of its production and consumption. Criteria for selecting a good adsorbent include suitable stability along time, a wide range of temperature and acidity, high adsorption capacity, efficiency in removing contaminants, easy reabsorption of contaminants from the adsorbent, environmental characteristics such as degradability, environment friendly, and low production costs. Cellulose is the most abundant natural polymer on earth, which is structurally a linear polymer composed of a glucose bond with 1, 4 beta glycoside bonds (Sticklen 2008). Cellulose has many properties that are different and superior to polymers extracted from petroleum materials, such as degradability, bio-compatibility, thermal stability, chemical stability, and low production cost (Habibi et al. 2010; Tsioptsias et al. 2008).

Nanocelluloses have a crystalline and amorphous structure and have impressive and adjustable mechanical and chemical properties that have led to their use in a wide range of hydrophobic and hydrophilic applications (Negro et al. 2020; De France et al. 2017). Cellulose nanocrystals and nanofibers can be isolated from cellulose, but their production process and properties are different. NCC are produced by cellulose acid hydrolysis, and they are light, highly stiff, with a rod-like morphology (width 5 to 10 nm, length 50 to 500 nm) and high crystallinity. On the other hand, NFC are mostly produced by paper manufacturers using mechanical defibrillation; they are light and flexible and present high aspect ratios of 20 to 220 (length>1 µm) (Balea et al. 2021). Cellulose nanofibers in the water form hydrogels where nanofibers form a 3D structure with a high swollen capacity holding a significant volume of water without dissolving. Nanofibers suspensions are able to interact by hydrogen bonds with different nanoparticles within several matrices (Sanchez-Salvador et al. 2020; Balea et al. 2019a; Azeredo et al. 2010; Spagnol et al. 2012; De France et al. 2017).

The ability of hydrogels to absorb water is due to the action of hydrophobic groups attached to the structure of the hydrogel, while their resistance to dissolution is due to the interconnection between the chains of the polymer network. Synthetic hydrogels have been replaced by natural hydrogels for their properties such as being long-lasting, adequate potentially in water absorption, high strength, and resistance. Chitosan is a linear polysaccharide derived from chitin, the world’s second-most natural polymer (Parhizgar et al. 2017). Chitosans with polycationic properties can be chemically and electrostatically bonded with negatively charged functional groups. Chitosan has properties such as biodegradability, environmentally friendly, availability, and absorption of cationic ions (Parhizgar et al. 2017). Chitosan is an abundant and available polysaccharide, which is renewable and degradable (Vold et al. 2003; Wu et al. 2010). Substitution of the catalyzed based on the steel group allows the formation of chitosan from chitin. It also increases the electron density and increases the affinity of the amine groups in chitosan and the positive ions in water. It also shows that the pH range of chitosan absorption capacity is close to the neutral range (Chassary et al. 2004).

The combination of nanocellulose and chitosan for the removal of water contaminants such as dyes, heavy metals, and nitrates is of great interest according to green chemistry principles (Goswami et al. 2021; Balea et al. 2019b; Mahnooei et al. 2020; Azadbakht et al. 2017).

In a study conducted by Sharma et al. (2018) on the extraction of nanocellulose from beach sheath grass to remove cadmium from water, the results indicated that more than 84% of cadmium is removed from water by nanocellulose and that it was most consistent with the Langmuir model. Adherence to the principles of green chemistry is essential in biological and environmental studies, especially in aquatic ecosystems. The principles of green chemistry state that product design is done with minimal risk. This study showed that nanocellulose can be used effectively in the adsorption of heavy metals from water.

Nanocellulose can be obtained from different sources, including agricultural wastes such as bagasse. The use of this secondary raw material is of great interest in Khuzestan, Iran. So, the aim of the current study was to introduce a new and efficient adsorbent that can replace synthetic and chemical hydrogels and, due to its biological and optimal performance, can be introduced in the fields of water and wastewater treatment.

Materials and methods

Chemical compounds and preparation

Sodium hydroxide,1 sulfuric acid,2 glacial acetic acid,3 acrylic acid,4 and N, N'-methylene base acrylic amide5 were supplied from Merck, Germany. Hydrochloric acid6 was purchased from Sigma-Aldrich, USA. Chitosan with a

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1 NaOH.  
2 H₂SO₄.  
3 CH₃COOH.  
4 C₃H₅O₂.  
5 C₆H₈N₂O₂.  
6 HCl.
molecular weight of 50,000–80,000 daltons and a degree of deacetylation of 85–85% was purchased from Nano Novin Polymer Company, Iran.

**CNC production**

For the preparation of materials prior to cellulose adsorbent, painted bagasse paste was supplied from Nano Novin Polymer Company. First, a 2% w/w solution of sodium hydroxide was used for 12 h at room temperature under a magnetic stirrer to remove impurities. In order to complete the process of removing impurities, the obtained suspension was washed several times with distilled water; then, during the process of acid hydrolysis using 64% sulfuric acid at 45°C, it was continuously stirred for 1 h. The resulting suspension was washed with distilled water and centrifuged at 10,000 rpm for 15 min. Centrifugation was continued until the supernatant pH reached 4. Dialysis membranes were used to remove sulfate ions and reach a neutral pH. After reaching neutral pH, the suspension was stirred with a homogenizer at 450 rpm for 1 h.

**Cellulose nanocrystalline/chitosan hydrogel production**

In order to make nanoparticles of sugarcane waste, sugarcane pulp was supplied from Haft Tappeh Sugarcane Company, Iran. Then the waste was washed with deionized distilled water for several steps to remove the waste completely. After drying at room temperature, it was placed in a grinder with a size of 40 microns. After grinding, it was immersed in distilled water for several hours and using a fully mechanized method with a super disc grinder at 1500 rpm. In order to make a green-based hydrogel, first, a suitable amount of chitosan in 30 ml of acetic acid solution (1% by volume) was poured into a three-hole balloon and placed on a magnetic stirrer, and nitrogen gas was injected into it for 30 min to bubble out oxygen from the container. Then the temperature was increased to 70°C, and then 0.1 g of potassium persulfate was added to produce free radicals on the chitosan functional groups. After 10 min, 3.60 g of acrylic acid and a portion of -NN methylene bisacrylamide was added to the solution for crosslinking, and then, 40 g of cellulose nanocrystalline gel was added. The temperature was maintained at 70°C for 2 h; then, the resulting hydrogel was cooled to room temperature with a 1-M gain to reach pH 7 after cooling (De France et al. 2017). Finally, the hydrogel was washed with distilled water several times and dried in an oven at 70°C. Then it was ground using a mill and passed through a sieve (Fig. 1).

**Experimental design**

In order to determine the optimal absorption conditions, experiments were performed in a stable order with three replications for each parameter, in such a way that during each experiment, one of the parameters was variable and the other parameters were kept constant. Studied parameters
The amount of adsorbed nitrogen and phosphate ions was calculated according to Eq. (1) at time t, $q_t$ (mg/L) and at equilibrium $q_e$ (mg/L). In this regard, $C_0$ and $C_t$ are the initial concentration and equilibrium concentration (mg/L), respectively. $C_e$ (mg/L) is the concentration of adsorbent per unit time, and Y is the ratio of nitrogen and phosphate ion removal. $q_e$ is adsorption capacity (mg/g), V is solution volume (L), and m is adsorbent dose (g). Equation (2) was used to evaluate the adsorption capacity of nanoadsorbents. One of the isothermal models of adsorption is the Langmuir adsorption model, which is based on the assumption that adsorption takes place in a single layer at specific locations so that all adsorption sites have the same energy and between surface molecules adsorbent reactions do not take place (Eq. (3)).

In Eq. (3), $C_e$ is the equilibrium concentration (mg/L), $q_{max}$ is the adsorption capacity of the adsorbent monolayer in terms of (mg/g$^{-1}$), and b is the absorption constant of Langmuir in terms of (l/mg$^{-1}$). In the Freundlich absorption model, it is assumed that adsorption is multilayer, heterogeneous and non-uniform surface energy distribution. In this absorption model, Eq. (4) is described as reversible and multilayer.

In this equation, the coefficients $K_f$ and $n$ are the adsorption coefficients of the Freundlich isotherm, where $K_f$ and $n$ represent the adsorption capacity of the multilayer and the adsorption intensity, respectively. $C_e$ is the equilibrium concentration in terms of (mg/L), and $q_e$ is the adsorption capacity in terms of (mg/g). In the Temkin absorption model, which is based on the assumption that adsorption is the equilibrium constant of the obedience isotherm. $C_0$ is the equilibrium concentration in terms of (mg/L). In the quasi-first-order synthetic model (Lagergren model (Lagergren 1898)), it is based on the assumption that adsorption takes place in the boundary layer and in which the changes are proportional to the number of unoccupied sites at the adsorbent surface (Ofomaja 2010).

To calculate the thermodynamic parameters, the Van Hoff free energy equation, there are changes in the Gibbs free energy standard (kJ/mol), enthalpy (kJ/mol), and entropy (kJ/mol). The negative Gibbs free energy indicates the spontaneity of the reaction, and the positive enthalpy indicates that the solid-solution ratio is exothermic and the entropy increases randomly during the adsorption process (8.314 J per mole). By drawing $T_0 q_C/ C_n$ against $T$, the isoeithermic and the adsorption process.

### Characterization of cellulose nanocrystalline/chitosan hydrogel

In order to study the morphological and internal structure of nanosorbents as well as the type of porosity, FESEM was used at Razi Metallurgical Laboratory and Bim Gostar Taban Laboratory (Tehran). To perform this test, the samples were first covered with a thin gold coating and studied using the FESEM microscope model MIRA III and the device MIRA3TESCAN-XMU model (made in Czech Republic) with different magnifications of 50–150 KX. TGA test was performed in the temperature range of 0–600 °C at a rate of 10 °C/min using the device TG 209F3 NETZSCH (made in Germany). This test is to examine and discover how a substance behaves at various temperatures. XRD test was performed by the Dutch model PW1730 XRD to detect the crystal structure of the adsorbents in the angle range of 0–5.5$^{\circ}$ and 02–70 and temperature of 25 °C. This test is based on X-ray diffraction and Bragg’s law. EDS test was used to identify the constituent elements and determine their percentage in the adsorbent. This test was performed using a FESEM.
device manufactured by TESCAN (model MIRA III, Czech Republic). The FTIR test was performed to determine the functional groups in the structure of gravity with an infrared spectrometer in the wavelength range (400–4000/cm) with the FTIR Tensor II model by the German company Bruker.

**Results**

In the experiment on the effect of adsorbent dose on the removal of nitrate, nitrite, and phosphate parameters by hydrogel adsorbent synthesized under 60 min, acidity of 5, volumetric concentration of 100 mg/L of effluent, and ambient temperature, the results showed that in the range of 0.1–1 g, weight concentration of 0.1 to 0.5 g, removal rate showed an increase of 67.69%, 73.91%, and 70.9% for nitrate, nitrite, and phosphate ions to 75.38%, 78.26%, and 86.36%, respectively. In this experiment, no significant increase was observed from the adsorbent dose of 0.5 to 1 g ($P < 0.05$). The optimum weight for cellulose-chitosan nanocrystalline hydrogel adsorbent was 0.5 g (Fig. 2). In the study of the effect of pH on the removal of the desired parameters, the results showed that at pH 4 to 6, the removal of nitrate, nitrite, and phosphate ions showed a significant increase of 75.38%, 80%, and 87.27%, respectively, but with further increase in pH (6 to 8), removal efficiency decreased by 43.07%, 42.6%, and 26.36%, and the results showed that the optimal pH for effective removal of nitrate, nitrite, and phosphate ions was 6 (Fig. 2). The effect of concentration on the removal rate of the desired parameters showed that at pH 6, time of 60 min, and adsorbent dose of 0.5 g, a concentration of 100 mg/L with an increasing concentration

![Fig. 2 The effect of different adsorption parameters on the phosphate, nitrite, and nitrate compounds by cellulose nanocrystalline/chitosan hydrogel adsorbent: (a) weight, (b) pH, (c) concentration, (d) time, and (e) temperature](image-url)
of 25 mg/L, removal rate significantly increased ($P < 0.05$) from 69.86%, 65.51%, 81.48% to 75.38%, 80%, 87.27% for nitrate, nitrite, and phosphate ions, respectively. Therefore, a concentration of 100 mg/L was reported as the optimal concentration (Fig. 2). Examining the effect of time on effective removal of desired compounds using cellulose-chitosan nanocrystalline hydrogels, the results showed that in the time range of 15 to 90 min, with increasing contact time from 15 to 30 min, the rate of removal increased from 69.23%, 78.26%, 86.36% to 75.38%, 80%, 87.27% for nitrate, nitrite, and phosphate ions in 30 min, respectively, but from 30 to 90 min, no significant increase was observed in the removal of nitrate, nitrite, and phosphate ions ($P < 0.05$), and time of 30 min was selected as the optimal time for cellulose-chitosan nanocrystalline hydrogel (Fig. 2).

The effect of temperature on the removal of nitrate, nitrite, and phosphate ions using synthesized hydrogels at a concentration of 100 mg/L, time of 30 min, and pH 6 showed an increasing the temperature from 25 to 40 °C that could elevate the removal efficiency by 84.3%, 86%, and 90.9% for nitrate, nitrite and phosphate ions, respectively, and no significant increase was observed at 50 °C ($P < 0.05$). Therefore, $40\, ^\circ\mathrm{C}$ was chosen as the optimal temperature (Fig. 2). In the study of isothermal adsorption models of cellulose-chitosan nanocrystalline hydrogel, the results showed that nitrate ion is most consistent with Freundlich and Tamkin adsorption models with correlation coefficients of 0.99 and 0.97. In nitrite ion, the highest agreement was in Tamkin and Freundlich models with correlation coefficients of 0.98 and 0.91, respectively, and for phosphate ion, the highest agreement was in Freundlich, Tamkin, and Langmuir models calculated with correlation coefficients of 0.99, 0.93, and 0.91, respectively. The highest values of $q_{\text{m}}$ were measured in nitrate, nitrite, and phosphate ions with values of 250, 142.85, and 27.77, respectively. In Freundlich constants, the highest levels of $K_f$ and $n$ in phosphate ion and nitrite ions were calculated with 285.57 and 198.87 for adsorption capacity and intensity. The highest amount of $K_f$ was measured in the Tamkin adsorption model for phosphate and nitrate ions with rates of 26.31 and 14.01, respectively. In the study of quasi-first-order and quasi-second-order synthetic models, it shows more compatibility of nitrate, nitrite, and phosphate ions with the second-order synthetic model with a coefficient of 1 for nitrate, 0.99 for nitrite, and 0.99 for phosphate. In the first-order synthetic model, the maximum value calculated was 3.17 mg/g for the phosphate ion, followed by the $q_e$ for nitrate at 3 mg/g and for nitrate at 3.09 mg/g. In the second-order synthetic model, the maximum amount of $q_e$ for nitrate was estimated to be 0.49 mg/g and the amount of K2 for nitrite was 58.82 per minute. In the study of the thermodynamic model of nitrate, nitrite, and phosphate ions, the results show that with increasing temperature, the amount of Gibbs free energy increased for nitrate, nitrite, and phosphate ions.

The TGA curve of cellulose-chitosan nanocrystalline hydrogel indicates three temperature zones, in the first of which the weight loss from 25 to 200 °C is related to the initial weight loss, which is mainly due to evaporation of water from the cellulose sample. The second zone is related to severe weight loss and weight loss of 75.95%, which continues from a temperature of 200 to 400 °C. In the second zone, weight loss due to the de-polymerization of chitosan chains is based on the decomposition and separation of glycosidic bonds, water depletion, and decomposition of glycosylic units, resulting in the formation of volatiles and the subsequent formation of coal. After the second zone from 400 °C to the final test temperature of 600 °C, the last degradation is the result of oxidation and decomposition of coal and reduction of molecular weight. The highest weight loss at 300 °C was related to the thermal fluctuations of the polymer structure and the rapid evaporation of the polymer parts (Fig. 3).

The results of EDS analysis show that in the cellulose-chitosan nanocrystalline hydrogel, the amount of carbon elements was 47.94% by weight, 54.32% atomic, nitrogen amino group 11.45% by weight and 11.13% atomic, and oxygen 40.61% and 34.5% by atomic weight (Fig. 3). The scanning electron image is made of a nanocrystalline structure of cellulose and hydrogel, which indicates the porous structure and the presence of very small pores on the surface of the hydrogel produced to absorb water. The image of cellulose nanocrystals shows the presence of cellulose networks in the structure of cellulose nanocrystals. Also, the average diameter of cellulose nanocrystals is 25 nm (Fig. 3).

Water absorption in cellulose/chitosan nanocrystalline hydrogel was 375%. X-ray diffraction analysis shows hydrogel peaks at an angle 20 of 12.5 and 20.1 degrees, which is due to the natural crystal structure in chitosan. A wide peak at an angle of 20 degrees indicates the semi-amorphous nature of chitosan. Peak increase is followed by an increase in cellulose content, which results in de-crystallization. Crystallization is defined as the orientation of the crystals of a semi-crystalline matrix in the natural direction of cellulose nanocrystals. The presence of a peak at an angle of 22.5 degrees in the hydrogel structure is a characteristic of the presence of nanocellulose. The peaks observed at the angle 20 are equal to 14, 18, 22.5, and 34.5 due to the presence of crystalline structure in cellulose nanocrystals. The peak increase of 12.5 degrees is due to an increase in the chitosan yield of the hydrogel (Fig. 3). The FTIR curves before and after adsorption are shown in Fig. 3.

 Peaks 1001, 1056, and 1157 indicate the tensile strength of the C-O, O-H, and C-N bands (Khan et al., 2014). Peaks 1715 and 1533 belong to chitosan amide groups I and II in the hydrogel structure, respectively. Also, the strong band 1715 is related to the C = O tensile bond in the di-aldehyde groups of cellulose nanocrystals. Bond 799 is related to the formation of new bonds of aldehyde groups with hydroxyl cellulose groups.
The results indicate the successful oxidation of hydroxyl groups on the molecular chain of nanocrystalline cellulose to aldehyde groups. Extensive peaks 3200–3450 are related to O–H and N–H tensile bonds. The presence of peak 3342–2926 is related to the symmetric and asymmetric vibrations of C-H. Peak 1583 also indicates the reaction of ester end groups on nanocellulose surfaces with chitosan amine groups. Changes after adsorption indicate the presence of amine and aldehyde groups in the adsorption process.

Discussion

Experiment on the effect of adsorbent dose

A decrease in removal efficiency by an increase in the adsorbent dose can be due to the high specific surface area of nanoparticles that have high reactivity and with increasing adsorption weight nanoparticles stick together and become lumps which reduces the specific surface area. In a study on the effect of adsorbent dose on the removal of nitrate, nitrite, and phosphate parameters by synthesized hydrogel adsorbent under 60 min, acidity of 5, volume concentration of 100 mg/L of effluent, and ambient temperature, the results showed that in the range of 0.1 to 1 g, removal rate increased from 67.69%, 73.91%, 70.9% to 75.385, 78.26%, 86.36% for nitrate, nitrite, and phosphate, respectively; also, no significant increase was observed from the adsorbent dose of 0.5 to 1 g ($P<0.05$); 0.5 g was determined as the optimum weight for cellulose-chitosan nanocrystalline hydrogel adsorbent. One of the most important factors in choosing the weight of the adsorbent to eliminate the desired parameters is the cost-effectiveness of the adsorbent. With an increase in the weight of the adsorbent, the percentage removal increased in nanogels due to the elevation of sites and adsorption sites. The adsorption capacity decreases as the adsorbent exceeds the optimum value due to the unsaturation of some active sites due to the blockage and overlap of the sites. The decrease in removal efficiency can be due to the decrease in phosphate concentration gradient due to the increase in adsorbent dose, which is followed by a decrease in the removal driving force. The decrease in particle size efficiency at the nanoscale due to the increase in surface-to-volume ratio has a significant effect on the adsorption processes, achieving the optimal value, reducing the cost, and attaining the maximum adsorption (Norisepehr et al. 2013). One of the important parameters in adsorption processes is to determine the amount of adsorbent dose in terms of performance and economics. Choosing the right weight of adsorbent can reduce wastewater treatment costs.
Experiment on pH effect

At acidic pH, the functional groups present on the adsorbent surface due to the presence of H+ ions in the protonated solution increase the positive ion charge at the adsorbent surface and some kind of electric charge of the adsorbent surface occurs. The surface affects the functional groups involved in adsorption and causes electrostatic bonding in the adsorption phenomenon, and this type of bond between the adsorbent and the adsorbed results in an increase in the removal rate. In the study of the effect of pH on the removal of the target parameters in the acidity range of 4 to 8, the results showed that at pH 4 to 6, the removal of nitrate, nitrite, and phosphate ions showed a significant increase and the removal rates were 75.38%, 80%, and 87.27%, but with an increase in pH from 6 to 8, the removal efficiency decreased to 43.07%, 42.6%, and 26.36%, respectively, and the optimal pH was 6 for effective removal of nitrate, nitrite, and phosphate. In the pH experiment, the rate of elimination of electrostatic reactions between the adsorbent and the establishment of chemical reactions between the soluble ions and the adsorbent were monitored. In acidic conditions, the removal rate increases due to the establishment of electrostatic attraction, but in alkaline conditions, due to the presence of electrostatic repulsion forces, the removal rate decreases and causes a weak interaction between the adsorbent and absorbing forces. Nitrate removal rate at pH 6 using cellulose nanocrystals extracted from bagasse was reported to be 25%. In 2016, Yang et al. examined cellulose-chitosan nanocrystalline aerogels for removing dye. Negatively charged factors absorb cationic dye. The aerogel produced showed the ability to remove the dye in the constant pH range up to a capacity of 785 mg/g (Yang et al. 2016).

Experiment on the effect of concentration of effluent

With increasing concentration, the adsorption rate increased, which can be due to the increase of active sites against elevating the number of adsorbed ions. The initial concentration of driving force is necessary to overcome the resistance of nitrate, nitrite, and phosphate ions to the active sites on the adsorbent surface. The higher initial concentration could lead to higher efficiency and adsorption capacity. In the study on the effect of concentration on the removal of the target parameters, in terms of acidity 6, time of 60 min, adsorbent dose of 0.5 g with an increasing concentration of 25 mg/L at a concentration of 100 mg/L, the removal rate of 69.86%, 65.51%, and 81.48% increased to 75.38%, 80%, 87.27% for nitrate, nitrite, and phosphate ions, respectively, and concentration of 100 mg/L was determined as the optimal and concentrations of 1.1 mg/L, 0.23 mg/L, and 0.14 mg/L were estimated for nitrate, nitrite, and phosphate ions, respectively. Azadbakht et al. in 2017 showed that increasing the nitrate concentration from 30 to 100 mg/L increases the removal rate of nitrate removal using nanocrystalline cellulose. Increasing the effects of electrostatic force could elevate the adsorbent capacity. Vesali-Naseh et al. (2019) applied acrylic acid-based hydrogels on wheat bran and montmorillonite to remove copper; they reported that the adsorption rate increased with elevating concentration due to the driving force of mass transfer.

Experiment on the effect of contact time

With an increase in contact time, the probability of the adsorbed ions colliding with the adsorbent increases. The adsorption of nitrate, nitrite, and phosphate ions in the early hours increases rapidly due to a large number of active sites, but with increasing contact time, the amount of adsorption decreases due to clogging of adsorption sites. It could also be due to the decrease in the concentration of nitrogen and phosphate ions that were initially absorbed by the adsorbent and the decrease in the active surfaces available due to the overlap of the surface and the adhesion of the nanoparticles to each other. In examining the effect of duration on the effective removal of desired compounds using cellulose-chitosan nanocrystalline hydrogels, the results show that in the time range of 15 to 90 min, with increasing contact time from 15 to 30 min, the removal rate of nitrate, nitrite, and phosphate within 30 min increased from 69.23%, 78.26%, 86.36% to 75.38%, 80%, 87.27%, respectively, but in 30 to 90 min range, no significant increase was observed in the removal of nitrate, nitrite, and phosphate ions, and 30 min was considered as the optimal time for cellulose-chitosan nanocrystalline hydrogel.

In the study on the effect of temperature (25 to 50 °C), the rate of removal showed an increase in the amount of adsorption from 25 to 40 °C. Temperature is an important parameter in the physical and chemical processes of absorption processes. The positive effect of temperature increase on the adsorbent of cellulose-chitosan nanocrystalline hydrogel describes the adsorption process as anotherm, which can be due to factors such as rapid movement of ions and molecules due to increased heat and increase in the probability of ions colliding with the site. Also, this increase in temperature causes swelling in the internal structure of the adsorbent and bulking of the pores and porosity in the adsorbent surface, increases the adsorption sites, and reduces the viscosity of the solution and easier penetration of nitrogen and phosphate ions. It described adsorbent surfaces and increased adsorption efficiency and increased removal. The effect of temperature on the removal of nitrate, nitrite, and phosphate ions using synthesized hydrogels at a concentration of 100 mg/L, time of 30 min, pH 6, and temperature range
of 25 to 50 °C, the results showed that by increasing the temperature from 25 to 40 °C, the removal efficiency and removal rates increased by 84.3%, 95%, 86%, and 90.9% for nitrate, nitrite, and phosphate ions, respectively, and with an increase in temperature from 40 to 50 °C, there was no significant increase (P < 0.05). Therefore, the temperature of 40 °C was determined as the optimal temperature.

In the study of isothermal adsorption models of cellulose-chitosan nanocrystalline hydrogel, the results showed that nitrate ion is most consistent with Freundlich and Tamkin adsorption models with correlation coefficients of 0.99 and 0.97. In the Freundlich model, it is assumed that the adsorption is heterogeneous and non-uniform with non-uniform adsorption energy. In the Tamkin model, it is assumed that the adsorption heat of all molecules at the adsorption surface decreases linearly, indicating the adsorption-adsorption interaction. In nitrite ion, the highest match was with Tamkin and Freundlich models with correlation coefficients of 0.98 and 0.91, respectively, and also for phosphate ion, the match was calculated in Freundlich, Tamkin, and Langmuir models with correlation coefficients of 99, 0.93, and 0.91, respectively. The results of the experiments at ambient temperature showed a better match with the Tamkin model than the Langmuir and Freundlich models for nitrite ions, which can be due to the heterogeneous distribution of adsorption sites. The highest values of \( q_m \) were measured in nitrite, nitrate, and phosphate ions, respectively, with values of 250, 142.85, and 27.77, respectively. In Freundlich constants, the highest levels of \( K_f \) and \( n \) in phosphate ion and nitrite ion were calculated with 285.57 and 198.87 for adsorption capacity and intensity. \( K_f \) is an important constant used to measure the relative absorption efficiency (synthetic). In the Freundlich model, the larger the \( n \) constant, the more desirable, indicating the optimal absorption. The Freundlich absorption model describes the reversibility of adsorption. The highest amount of \( K_f \) was measured in the obedience absorption model for phosphate and nitrite ions with the rates of 26.31 and 14.01, respectively. Adsorption models can determine the affinity of the adsorbent and the surface properties of the nanosorbent. The Freundlich model expresses the non-uniformity of the adsorbent surface, and the Langmuir model expresses the uniformity of the adsorbent surface in order to absorb the desired parameters (Table 2).

In 2018, Hokkanen et al. used a hydroxyapatite composite of bentonite clay and nanocellulose to remove phosphate, nickel, and cadmium from an aqueous solution. The results showed that the maximum adsorption for nickel, cadmium, and phosphate was 29.46 mMol/g, 10.34 mMol/g, and 4.90 mMol/g, respectively. The reabsorption process was performed for metal ions with 0.1-M nitric acid, and for phosphate ions with 0.1-M gain up to 5 re-adsorption cycles, the results of which showed that the removal rate was from 97 to 74% for cadmium ion, which reduced by 98 to 80% for nickel ions and 75 to 68% for phosphate ions (Hokkanen et al. 2018). The rate of phosphate removal using cellulose-chitosan nanocrystalline hydrogel produced was 90.9%, which indicates the high adsorption capacity of the synthesized hydrogel in removing the phosphate composition. In a study conducted by Sharma et al. (2018) on the extraction of nanocellulose from beach sheath grass to remove cadmium from water, the results of this study indicate that more than 84% of cadmium is removed from water by nanocellulose and showed a high match with Langmuir model. This study showed that nanocellulose can be used effectively in the adsorption of heavy metals from water (Sharma et al. 2018).

Synthetic models are highly dependent on the physical and chemical properties and structure and constituents of nanosorbents. In the study of quasi-first-order and quasi-second-order synthetic models, it is more consistent with nitrate, nitrite, and phosphate ions with the second-order synthetic model with a coefficient of 1 for nitrate, 0.99 for nitrite, and 0.99 for phosphate. In the study of the amount of

| Table 2 | Isotherm models and kinetic and coefficients |
|---------|---------------------------------------------|
| a) Isotherm | Langmuir | Freundlich | Temkin |
| | \( K_f \) (l/mg⁻¹) | \( q_m^{exp} \) (mg/g⁻¹) | \( R^2 \) | \( K_f \) (l/mg⁻¹) | \( N \) | \( R^2 \) | \( K_f \) (l/mg⁻¹) | \( B_T \) | \( R^2 \) |
| NO₃ | 0/15 | 142/85 | 0/45 | 26/31 | 0/92 | 0/99 | 6/55 | 11/49 | 0/97 |
| NO₂ | 0/33 | 250 | 0/70 | 198/87 | 1/52 | 0/91 | 14/61 | 16/85 | 0/98 |
| PO₄ | 3/33 | 27/77 | 0/91 | 287/57 | 1/36 | 0/99 | 26/31 | 14/15 | 0/93 |
| b) Kinetic | Pseudo-first-order | Pseudo-second-order | |
| | \( K_1 \) (min⁻¹) | \( q_m \) (mg/g⁻¹) | \( R^2 \) | \( q_m \) (mg/g⁻¹) | \( K_2 \) (min⁻¹) | \( R^2 \) |
| NO₃ | 0/168 | 3/09 | 0/36 | 0/49 | 12/34 | 1 |
| NO₂ | 0/17 | 3/15 | 0/36 | 0/18 | 58/82 | 0/99 |
| PO₄ | 0/17 | 3/17 | 0/36 | 0/19 | 23/80 | 0/99 |
In the first-order synthetic model, the maximum value was calculated for phosphate ions with a rate of 3.17 mg/g, and then the amounts of $q_e$ for nitrite and nitrate were 3 mg/g and 3.09 mg/g. In the second-order synthetic model, the highest amount of $q_e$ for nitrate was 0.49 mg/g and the amount of $K_2$ for nitrite was 58.82 per minute. $K_2$ is a constant indicator of the rate of adsorption and indicates how fast the adsorption is done over time. In surface adsorption systems, in order to design the system and know the type of isotherms, the study of adsorption rate in the time interval has been determined, which determines the parameter of efficiency, removal, and adsorption capacity (Jesus et al. 2011). Manhooei et al. reported that the effect of 3-chloropropyl trimethoxy silage-modified cellulose nanocrystals had the highest nitrate adsorption agreement with the Freundlich and quasi-second-order synthetic model (Manhooei et al. 2020).

Positive entropy indicates an increase in irregularity in the adsorption process and an increase in the probability of collision of contaminant molecules with active sites at the nanosorbent surface. Also, positive entropy indicates the existence of some structural changes in the soluble and solid phases. In the study of the thermodynamic model of nitrate, nitrite, and phosphate ions, the results showed with increasing temperature, the amount of Gibbs free energy increased for nitrate, nitrite, and phosphate, which indicates the high adsorption capacity at low temperature (Table 3). Negative enthalpy indicates that the adsorption reaction is exothermic and the adsorption process is physical, and negative entropy indicates a reduction in irregularity and the placement of adsorbed ions on the adsorbent surface on a regular basis. The reaction between cellulose nanocrystals and chitosan forms a matrix polymer network, and aldehyde groups on the cellulose surface bond with free amine groups in chitosan (Figs. 2, 3, and 4). Binders in polymer hydrogels are important in creating three-dimensional networks and increasing water absorption. Hydrogels are hydrophilic polymer networks that do not dissolve in water due to crosslinking. Hydrogels with high functional groups of OH, NH$_2$, COOH, SO$_3$H, and COONa are able to absorb water at a high rate (Zohuriaan-Mehr and Kabiri 2008).

Cellulose hydrogels have received a lot of attention due to their intelligent behavior due to their cellulose derivatives and non-toxicity. The use of binders in large quantities reduces the rate of swelling and water absorption, which is due to the reduction of the elastic behavior of the hydrogel network. The hydrogel produced in this study has covalent bonds due to the presence of a networking agent in the structure of the hydrogel, which increases the strength of the hydrogel. Covalent bonds between polymer chains are formed by the reaction

$$
\Delta G (kJ/mol) \quad \Delta H (kJ/mol) \quad \Delta S (kJ/mol.K^{-1})
$$

| T (K) | $q_e$ (mg/g) | $K_2$ (mg/min) | $T (K)$ (NO$_2$) |
|-------|-------------|----------------|-----------------|
| 298   | 14/8        | 16/5           | 01/01           |
| 303   | 19/8        | *              | *               |
| 313   | 29/8        | *              | *               |
| 323   | 39/8        | *              | *               |
| T (K) (NO$_3$) |
| 298   | 54/16       | 6/7            | 01/03           |
| 303   | 69/16       | *              | *               |
| 313   | 99/16       | *              | *               |
| 323   | 29/17       | *              | *               |

![Figure 4](image)

**Fig. 4** Adsorption studies based on discontinuous adsorption system

| pH               | Contact time (min) | Temperature (°C) | Adsorbent weight (g) | Initial concentration (mg/l) |
|------------------|--------------------|------------------|-----------------------|-----------------------------|
| Equilibrium Isotherm Studies | Adsorption Kinetics Studies | Adsorption Thermodynamics Studies |
| FESEM, FTIR, TGA, XRD, EDX |
of functional groups with the reactivity of amine-carboxylic acid groups (Akhtar et al. 2016). Chitosans are cross-linked under more favorable conditions by having amino groups. The strength part of the hydrogel is a network of bonded polymer chains, a three-dimensional grid, commonly known as a mesh. As shown in Figs. 3 and 4, each mesh is filled with spaces of a liquid that is normally water. The meshes hold the fluid and provide an elastic force that can be completed by expansion and contraction and are therefore responsible for the hydrogel’s strength. The ionic phase of hydrogels usually consists of ionization groups attached to polymer chains and a number of mobile ions due to the presence of the electrolyte solvent that surrounds the hydrogel (Ullah et al. 2015).

In a system of discontinuous reactors, nanosorbents enter the system from the very beginning and are mixed vigorously by rotary agitators for a specified and optimal time, and after elapse of a specified time and the reaction processes, the contents of the reactor are removed. No material or compound enters or leaves the system during reactor operation. Temperature control in the system is very important due to the exothermic and endothermic absorption reactions. As a result, the contents of the system may continuously increase or decrease due to ambient temperature during the operation of the reactors, disrupting the adsorption reactions and reducing the adsorption capacity and efficiency. Heat exchangers can be used to regulate the temperature during the adsorption reaction, which can be done by pipes that control the temperature inside the system by passing hot and cold currents. The operation and the speed of the agitator inside the system are of great importance because if the mixing is not done well, there is no possibility of reaction and collision between the adsorbent and the adsorbent.
The shape design of stirrers depends on various factors such as the shape and volume of the tanks and the speed and intensity of the flow inside the system. The use of polymer reactors can keep the temperature constant throughout the system during the absorption reaction (Fig. 5).

Conclusions

The use of nanocrystalline cellulose/chitosan with optimal adsorption conditions can have a good performance as an adsorbent of fish farm effluent. The introduced nanoadsorbent can be used as a new adsorbent that has properties such as environmental friendliness and biodegradability. The synthesized cellulose-chitosan Nano crystallized hydrogel nanosorbent can have a removal efficiency of 84.3%, 86%, and 90.9% for nitrate, nitrite, and phosphate ions, respectively. Cellulose/chitosan crystal nano hydrogels showed the highest removal rate for phosphate ions. Nano-adsorption without sludge production has the ability to remove the desired compounds and can be easily removed from the culture system and will not pose a risk to the environment. The nano-adsorbent is easily usable and can be used for small and large farms (Fig. 6).

In this study, new methods in the manufacture and preparation of nanosorbents were used. In this study, nanosorbents in wastewater treatment bioreactors and their wash ability without deformation were used. Finally, it can be concluded that nanocrystalline cellulose based on chitosan hydrogel structure has a lower adsorbent and shorter duration compared to other adsorbents produced. Also, the simple use of herbal nanosorbents for fish farms and the high ability of nanosorbents produced in the removal of nitrogen and phosphate compounds were confirmed as biological adsorbent for the effluent of fish culture farms. Therefore, this study on the performance of adsorbent and its structures indicates the desired capability of this adsorbent. More studies are suggested regarding the present adsorbent on competitor anions generally present in water such as chloride, sulfate, and bicarbonate.

Author contribution Fatemeh Darabtabar: investigation, methodology, visualization; Vahid Yavari: project administration, supervision, resources, writing – review and editing; Aliakbar Hedayati: writing – original draft, data curation, validation; Mohammad Zakeri: conceptualization; Hossein Yousefi: formal analysis, software.

Data availability The data is available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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