



# Fabrication, characterization and statistical investigation of a new starch-based hydrogel nanocomposite for ammonium adsorption



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## ABSTRACT

This work investigates a new starch-based hydrogel nanocomposite made from starch and poly vinyl alcohol blend as polymeric matrix and fumarate–aluminum (Fum-A) and maleic anhydride (MA) as cross-linking agents, for its use in  $\text{NH}_4^+$  removal from aqueous solutions.

The adsorption performance of the hydrogel nanocomposite and also, nanocomposite's maximum adsorption capacity for ammonium adsorption via isotherm studies are examined. Box–Behnken experimental design is used to evaluate performance of hydrogel nanocomposite in the adsorption process. A mechanism was proposed for the chemisorption of ammonia. The water adsorption degree of cross-linked hydrogel nanocomposites decreased with increasing the amount of nanoparticles. The swelling degree of hydrogel nanocomposite (3.6 wt%) was improved about 1.5 units as compared with the hydrogel alone. The maximum removal efficiency ( $R\%$ ) of ammonium ion by hydrogel nanocomposite was 97.99%. The Langmuir isotherm model agrees well with the experimental data and its correlation coefficient value was close to adjust the correlation coefficient value, as compared with Temkin and Freundlich isotherm models. The maximum capacity of the model being 19.01 mg/g was improved compared with the maximum capacity of the Langmuir isotherm (7.43 mg/g).

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## 1. Introduction

Ammonia contamination contributes to widespread environmental problems such as increasing the speed of eutrophication water bodies, depletion of dissolved oxygen and toxicity to fish and aquatic lives. Some kinds of biological and physicochemical method have been presented for the removal of ammonia from wastewater. Air stripping, chemical precipitation, ion exchange and biological nitrification–denitrification are more traditional techniques for removal of ammonia [1–3]. Comparing methods of removal of ammonia from wastewater, the adsorption method has achieved much attention as cost-effective, fast-responsive, high efficiency and environmentally friendly [1]. Lately, various types of multifunctional hydrogels with ionic groups have attracted much attention as the potential adsorbents for the removal of some pollutants such as metal ions [4–6], dyes [7–9] and ammonium ion ( $\text{NH}_4^+$ ) from wastewater [10–13]. Hydrophilic gels called hydrogels are slightly cross-linked materials that are capable of holding large amount of water or biological

fluids in their three-dimensional networks without dissolving [10]. Furthermore, there has been increased concern in finding modified biopolymers as cheaper and more effective sorbents. Among various sorbents, starch and its derivatives have been shown to be biodegradable, ecofriendly, renewable and relatively inexpensive materials. Blending of polyvinyl alcohol (PVA) and starch is appropriate because both of them are polar constituent, which have many hydroxyl groups in their chemical structure. These polar hydroxyl groups tend to form intermolecular and intra molecular hydrogen bonds [14–16]. Due to limitations that pure polymeric hydrogels have, such as poor gel adhesion and strength and stability, cross-linking and modifying is necessary to enhance the structural entity of the polymer [12,17]. This work investigates a new starch-based hydrogel nanocomposite for its use in  $\text{NH}_4^+$  removal from aqueous solutions. The Box–Behnken design (BBD) method as an effective response surface methodology based on three-level is selected to evaluate and optimize the performance of hydrogel nanocomposite in the adsorption process. Initial concentration of ammonium ion, contact time, weight of adsorbent and temperature factors were considered. Adsorption performance of prepared hydrogel nanocomposite and also, nanocomposite's maximum adsorption capacity for ammonium removal are examined via isotherm studies.

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## 2. Experimental

### 2.1. Materials

PVA ( $M_w$  60,000–72,000, fully hydrolyzed), maleic anhydride, fumaric acid,  $Al(NO_3)_3 \cdot 9H_2O$ , NaOH, ammonia solution (25%) and Nessler's reagent were purchased from Merck. Starch ( $M_w$  180,000) was purchased from Ghatran Shimi.

### 2.2. Synthesis of boehmite nanoparticles

Boehmite used as the precursor material, were synthesized based on a sol-gel method published previously [18]. In brief, a solution of 6.490 g NaOH dissolved in 50 ml of deionized water and 20 g  $Al(NO_3)_3 \cdot 9H_2O$  dissolved in 30 ml deionized water were prepared. The NaOH solution was then added to the  $Al^{3+}$  solution by the rate of 2.94 ml/min under stirring for 18 min. The resulting mixture was sonicated in the ultrasonic bath for 3 h at a temperature of 25 °C. The resulted gel was kept in the oven at 220 °C for 4 h. Finally obtained powders washed with deionized water and dried in oven at 60 °C. Boehmite nanoparticles were characterized by FTIR spectroscopy and TEM.

### 2.3. Synthesis of fumarate-alumoxane (Fum-A)

Fum-A nanoparticles were synthesized with boehmite nanoparticles and fumaric acid as precursors, based on a method reported earlier [19]. In brief, 7.8 g boehmite and 5 g fumaric acid were mixed thoroughly with 200 ml distilled water in a 500 ml round-bottomed flask. The resulting suspension was sonicated for 30 min in an ultrasonic bath and refluxed for 18.5 h at its boiling point. The precipitate was mixed well with 200 ml of ethanol to dissolve the unreacted fumaric acid. The obtained mixture was filtered and the filtrate was dried in the air oven at 80 °C. All solutions were prepared with deionized water. Solutions were freshly prepared from the standard ammonium solution for each experimental run.

### 2.4. Preparation of hydrogel nanocomposite

The gelatinized starch solution was prepared through mixing a quantitative amount of starch in deionized water at 80 °C for 10 min. The various amounts of synthesized Fum-A nanoparticles (1.2, 2.4, 3.6, 4.8 weight percentage of nanoparticle) of and MA were added to the gelatinized starch solution and heated again in a water bath at 80 °C for 4 h. Later, a quantitative amount of PVA was added to the above mixture and heated for another 4 h to aid the esterification reaction. The resulting solution was mixed well with excess ethanol (95%) for rapid water exchange and subsequent drying of a gel. The hydrogel nanocomposite precipitate was washed twice with 25 ml ethanol (95%) to remove any unreacted precursors such as PVA, MA and Fum-A. The purified hydrogel nanocomposite sample was dried in the oven at 50 °C for 12 h.

### 2.5. Swelling degree of hydrogel nanocomposite

0.3 g of the hydrogel and hydrogel nanocomposite (1.2, 2.4, 3.6, 4.8 weight percentage) samples were immersed in 100 ml distilled water for 24 h at room temperature until the gel reached the equilibrium state of swelling. The unabsorbed water on the surface of the swollen hydrogel nanocomposite was removed with a 100-mesh stainless screen, and weighted immediately. The degree of swelling is defined as follows:

$$\text{Degree of swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the weight of the swollen gel and the weight of dried gel, respectively.

**Table 1**  
Variable factors and their levels.

Factor	Description	Level 1 (-1)	Level 2 (0)	Level 3 (+1)
$X_1$	Concentration (mg/l)	10	50	90
$X_2$	Adsorbent weight (g)	0.1	0.5	0.9
$X_3$	Shaking time (min)	10	130	250
$X_4$	Temperature (°C)	25	35	45

### 2.6. Batch adsorption experiments

The standard solution (1000 mg/L) of  $NH_4^+$  was prepared through dissolving an adequate amount of ammonium standard solution in 1000 ml of deionized water. The experiments were carried out in a series of 50 ml conical flasks containing hydrogel nanocomposite adsorbent and 25 ml  $NH_4^+$  solution and shaken in a thermostatic shaker (Pars Azma, IN12) at 120 rpm for a certain time (Table 2), then the adsorbents were separated. The solutions were filtered using 0.5  $\mu$ m microporous membrane filters. The concentration of ammonia in the aqueous solutions was determined using Nessler's reagent colorimetric method (UV Apel PD-303). The removal efficiency and adsorption capacity of hydrogel nanocomposite for  $NH_4^+$  ion adsorption was calculated from the following equations, respectively:

$$R\% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (2)$$

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (3)$$

where  $R\%$  is the removal percentage and  $q_t$  is the amount of ammonium ion uptake by the adsorbent in mg/g.  $C_0$  and  $C_t$  are the initial and final  $NH_4^+$  ion concentrations in mg/L in the solution. Also,  $V$  and  $m$  indicate the volume of solution (L) and mass of the adsorbent (g), respectively. To investigate the adsorption isotherms, a series of  $NH_4^+$  solutions with different initial concentration (50, 100, 150, 200, 300, 400 mg/L) were held in contact with 0.9 g the hydrogel nanocomposite for 250 min at natural pH.

### 2.7. Design of experiments

In this research, four factors in 3 levels with 27 run order designs were used to investigate the effect of the initial concentration of ammonia (10, 50 and 90 mg/L), the adsorbent mass (0.1, 0.5 and 0.9 g), time (10, 130, and 250 min), and adsorption temperature (25, 35, 45 °C) separately and their interactions on the removal efficiency of  $R\%$  in the natural pH. A total of 27 experiments were planned and analyzed by Design Expert<sup>®</sup> 8.0.6.1 software (trial version). The independent variables were converted to dimensionless ones ( $X_1, X_2, X_3, X_4$ ) with the coded values at three levels: -1, 0 and +1. The arrangement of the factorial design is shown in Table 1.

Box-Behnken design matrix for coded values along with experimental and predicted values for removal efficiency ( $R\%$ ) and adsorption capacity ( $q_t$ ) of ammonium ion by the hydrogel nanocomposite are given in Table 2. The dependent variable or objective function was ammonium ion removal efficiency  $R\%$ . Capacities were also calculated for each experiment. A non-linear regression method was used to fit the polynomial equation (Eq. (4)) to the experimental data to recognize the relevant model terms.

### 2.8. Characterization

The hydrogel nanocomposites were characterized using FTIR and SEM analyses. Fourier-transform infrared (FTIR) spectra were recorded between 400 and 4000  $cm^{-1}$  with KBr pellets at room temperature (Bruker Alpha, Germany). SEM micrographs of all samples were taken, using.

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