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# Fast removal of ammonium ion using a hydrogel optimized with response surface methodology

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ABSTRACT

Response surface methodology (RSM) based on a three-level, three-variable, Box–Behnken design (BBD) was used to optimize the preparation parameters of a hydrogel consisted of polyvinyl alcohol (PVA), acrylic acid (AA) and tourmaline (Tm). With the adsorption capacity for ammonium ion ($NH_4^+$) as the response, the effects of three variables, i.e. neutralization degree (ND) of AA, ratio of PVA to AA, and ratio of Tm to AA, were investigated. The predicted appropriate preparation conditions for the hydrogel were ND of AA of 70%, PVA:AA of 0.0833 and Tm:AA of 0.5, under which a hydrogel was prepared and used as the adsorbent to remove $NH_4^+$. The effects of contact time, ion strength, $NH_4^+$ concentration, temperature, and pH value on the adsorption capacity were investigated using a batch experiment. The results indicated that the as-prepared hydrogel showed entangled three-dimensional network and had the advantages of fast adsorption rate and high adsorption capacity for $NH_4^+$ in a pH range from 3.0 to 8.0. The regeneration and reusable experiments were also performed, and it was observed that the as-prepared hydrogel was stable and regenerable using strong acid (HCl) or base (NaOH) as the desorbing agents.

## 1. Introduction

Hydrogels are three-dimensional crosslinked polymeric networks and receiving great interest due to their promising applications such as sensors, separation membranes, adsorbents, and materials in medicine and pharmacy as drug delivery systems, in solving some ecological and biological problems as well as in modern technologies [1]. Hydrogels possess functional groups that can be easily ionized and hence repulse each other, by which more water molecules are captured. The higher water content and porous three-dimensional structured network can diminish the mass transfer resistance, allowing thus the solute to diffuse easily through the hydrogel structure [2]. Moreover, the presence of ionized functional groups affords the hydrogels to absorb and trap many kinds of pollutants with the opposite ionic charges. Therefore, hydrogels as the potential adsorbents have attracted much attention in recent years for the removal of cationic pollutants, such as heavy metals [3,4], dyes [5,6] and ammonium ion ($NH_4^+$) [2,7].

Anionic hydrogels such as polyacrylate are the most widely used adsorbents for removing toxic pollutants or recovering precious metal ions from an aqueous solution. Xie et al. studied the adsorption behaviors of a hydrogel made from acrylic acid and acrylamide and found that the maximum adsorption capacities for $Cu^{2+}$ and $Fe^{3+}$ were 247 and 173 mg/g [8]. Li et al. obtained a macroporous, hydrophobically modified poly(acrylic acid-acrylamide) hydrogel using poly(ethylene glycol) as the pore-forming agent, and found that this hydrogel can be used as an effective adsorbent for the removal of cationic dyes, crystal violet and basic magenta [9]. By consideration of the limitations of pure polymeric hydrogels, such as poor gel strength and stability, some studies have focused on clay incorporation into the hydrogel network to prepare organic-inorganic hydrogel. Kaşgöz et al. obtained a hydrogel–clay nanocomposite using acrylamide and 2-acrylamido-2-methylpropane sulfonic acid sodium salt as the organic monomers and montmorillonite as the inorganic component, and found that the incorporation of a low amount of clay (10 wt%) into the polymeric network increased the adsorption rate and capacity for heavy metals [3]. Our previous studies revealed that owing to the unique reducing ability of biotite, a poly(acrylic acid)/biotite hydrogel could be prepared at room temperature via a self-induced redox reaction, and the resulting hydrogel showed higher adsorption capacity for $NH_4^+$ [10]. Considering the biodegradability of traditional hydrogel, it was promising to prepare hydrogels that gave the required performance profile combined with environmental friendliness. Starch, chitosan, cellulose and humic acid had been used as the backbones to graft

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acrylic acid, obtaining a series of biocompatible and biodegradable hydrogels, which showed high affinity to many kinds of cationic pollutants [11–14].

Hydrogel can be prepared by simultaneous copolymerization and crosslinking of one or more functional monomers. Most optimization studies during the development of a novel hydrogel involve variation of one factor at a time, keeping all other factors constant [15–17]. This traditional optimization method is time-consuming and expensive. Today, a statistical-based technique of response surface methodology (RSM) is used extensively to elucidate the interaction between reaction parameters for optimization. RSM is a technique whereby reaction parameters are varied simultaneously in a suitable manner to generate data for development of empirical models. It is a faster and more economical analytical approach than the traditional one, and has been applied successfully for the optimization of medium components in submerged culture of *Aspergillus flavus* for enhanced heparinase production [18], Orange II photocatalytic degradation [19], lipase-catalyzed synthesis of betulinic acid ester [20], determination of enzyme kinetic constants [21], coagulation–flocculation process for palm oil mill effluent [22], preparation of uniform silicon dioxide nanoparticles [23] and, some adsorption parameters for removing heavy metals, such as $Cu^{2+}$, $Pb^{2+}$ and $Cd^{2+}$ [24–26]. However, to the best of our knowledge, little information was reported using RSM to optimize the process parameters for obtaining hydrogels with desired properties specific to a particular application.

Acrylic acid (AA) is the mostly used functional monomer to prepare the hydrogels [15–17]. Polyvinyl alcohol (PVA) has been widely explored as water-soluble polymers for numerous biomedical and pharmaceutical applications due to its advantages of non-toxic, non-carcinogenic and bioadhesive properties [27,28]. Tourmaline (Tm) belongs to the group of silicate minerals called cyclosilicates. The general chemical formula of the tourmaline group, as a whole, can be expressed as $XY_3Z_6\text{–}(T_6O_{18})(BO_3)_3V_3W$, where $X = Na^+$, $Ca^{2+}$, $K^+$, or vacancy, $Y = Li^+$, $Fe^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$, $V^{3+}$, $(Ti^{4+})$, $Z = Al^{3+}$, $Fe^{3+}$, $Mg^{2+}$, $Cr^{3+}$, $V^{3+}$, $(Fe^{2+})$, $T = Si^{4+}$, $Al^{3+}$, $(B^{3+})$, $B = B^{3+}$ or vacancy, $V = [O(3)] = OH^-$, $O^{2-}$, $W = [O(1)] = OH^-$, $O^{2-}$, $F^-$ and metal ions in () indicate minor or possible substitution [29]. Based on these information, we prepared a series of hydrogels based on AA, PVA and Tm. The present study is an attempt to optimize the preparation process of PVA/PAA/Tm hydrogel using RSM, with the adsorption capacity of resulting hydrogel for $NH_4^+$ (an important pollutant promoting eutrophication) as the reference. The parameters that need to be optimized are neutralization degree (ND) of AA, ratio of PVA:AA, and ratio of Tm:AA. When the preparation parameters were chosen, a hydrogel with desired properties was obtained and used as the adsorbent to remove $NH_4^+$ using batch adsorption experiments. The adsorption kinetics, adsorption isotherms, pH effect, desorption and reusability were investigated and evaluated.

## 2. Materials and methods

### 2.1. Materials

Acrylic acid (AA, chemically pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), *N*,*N*′-methylene-bisacrylamide (MBA, chemically pure, Shanghai Yuanfan Additives Plant, Shanghai, China), polyvinyl alcohol (PVA with the average polymerization degree of 1700 and alcoholysis degree of 99%, Lanzhou Vinylon Factory, Lanzhou, China) were used as received. Tourmaline (Tm, Jinjianshi Nano Technology Co., Ltd., Hebei, China) was milled through a 200-mesh screen prior to use. All other agents used were of analytical grade and all solutions were prepared with distilled water.

**Table 1**
Experimental ranges and levels of the independent variables.

| Variables | Ranges and levels | | |
|---|---|---|---|
| | −1 | 0 | +1 |
| $X_1$, ND of AA (%) | 20 | 50 | 80 |
| $X_2$, PVA:AA | 0.0833 | 0.104 | 0.125 |
| $X_3$, Tm:AA | 0 | 0.25 | 0.50 |

### 2.2. Preparation of PVA/PAA/Tm hydrogel

In a four-neck flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line, an appropriate amount of PVA was dispersed in 60 mL distilled water and heated to 80 °C under stirring until PVA was dissolved completely. Then the temperature was lowered to 70 °C while 4 mL solution containing 0.2 g APS was added dropwise for 10 min. After that, a premixed solution containing 20 mL distilled water, 0.3 g MBA, 7.2 g AA with different ND and an appropriate amount of Tm was added dropwise into the flask from a constant pressure funnel. Nitrogen atmosphere was kept throughout the experiments. The solution was stirred at 70 °C for 3 h to complete the polymerization reaction, and the resulting hydrogel was immersed in distilled water to remove any impurities present and then dehydrated with ethanol. Finally, the product was dried at 70 °C and the hydrogel adsorbent used during the adsorption process was milled through a 40–80 mesh screen.

### 2.3. Experimental design

The Box–Behnken factorial design was used to optimize the preparation parameters with adsorption capacity of resulting hydrogel for $NH_4^+$ as the response. Since different variables are usually expressed in different units and/or have different limits of variation, the significance of their effects on response can only be compared after they are coded. For statistical calculations, the variable $X_i$ was coded as $x_i$ according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \tag{1}$$

where $X_i$ is the real value of the *i*th independent variable, $X_0$ is the real value of an independent variable at the centre point and $\Delta X_i$ is the step change. ND of AA ($X_1$), PVA:AA ratio ($X_2$) and Tm:AA ratio ($X_3$) were chosen as three independent variables during the preparation process. Their range and levels were listed in Table 1. The adsorption capacity for $NH_4^+$ was selected as the dependent variable. The response variable was fitted by a second-order model in the form of quadratic polynomial equation:

$$Y = \beta_0 + \sum \beta_i x_i + \Sigma \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{2}$$

where $Y$ is the response variable to be modeled; $\beta_0$, $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are constant regression coefficient of the model; $x_i$ and $x_j$ ($i = 1 \rightarrow 3$; $j = 1 \rightarrow 3$; $i \neq j$) represent the independent variables in the form of coded values. The actual design of this work was presented in Table 2. Based on this table, the experiments were conducted for obtaining the response, i.e. adsorption capacity for $NH_4^+$, at the corresponding independent variables addressed in the experimental design matrix by applying quadratic model. The parameters of the response equations and corresponding analysis on variables were evaluated using Design Expert Software Version 7.1.3 (STAT-EASE Inc., Minneapolis, USA).