



Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer



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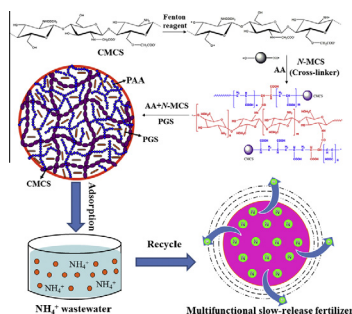
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HIGHLIGHTS

- One-step *in situ* grafted polymerization synthesis of palygorskite nanocomposites.
- The palygorskite nanocomposite exhibited excellent adsorption property for NH_4^+ .
- Various adsorption models were applied to study the adsorption mechanism.
- The nitrogenous adsorbent could be used as a multifunctional slow-release fertilizer.

GRAPHICAL ABSTRACT



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ABSTRACT

With the aim of minimizing the negative impact of nitrogen pollution and improving fertilizer use efficiency, a novel palygorskite (PGS) nanocomposite adsorbent was prepared, characterized and used for removal and recovery of NH_4^+ from ammonium wastewater with the agronomic reuse as a multifunctional slow-release ammonium fertilizer (MSAF). Batch adsorption experiments were conducted at varied operational conditions. The adsorption kinetic was well described by pseudo-second-order kinetic model, whereas adsorption isotherm results elucidated that Freundlich model provided the best fit for the equilibrium data. Results indicated that the adsorption equilibrium can be achieved within 12 min, with the adsorption capacity of 237.6 mg g^{-1} even if 30 wt% PGS was incorporated as nanofiller. The as-prepared MSAF product not only had high removal efficiency for ammonium in a wide pH range of 4.0–8.0 but also exhibited an excellent slow-release property. The nitrogen-laden carrier material with a nitrogen content of 13.2% exhibits preferable slow-release properties with nitrogen being 60% released in soil for 10 days. Moreover, due to the composite material had preferable water-absorbing and water-retention capacity, thus it can improve soil moisture content and reduce soil moisture evaporation rate. The results suggested that the product with good water-holding and slow-release capacities could conserve soil moisture and was economical and eco-friendly for wide applications in modern agriculture and horticulture.

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Abbreviations: MSAF, multifunctional slow-release ammonium fertilizer; PGS, palygorskite; CMCS, carboxymethyl chitosan; N-MCS, N-maleyl chitosan.

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1. Introduction

Over the last century, increasing population and industrialization have resulted in the degradation of various ecosystems on which human life relies on. In terms of lake and river quality, such pollutions lead to frequent occurrences of low dissolved oxygen, fish kills, algal blooms and bacterial contamination [1]. Its main cause is disposal of nutrients (N and P) directly from industrial effluents or indirectly from agriculture runoff and leaching from sewage sludge deposited in landfills [2]. Therefore, numerous techniques have been applied to removing NH_4^+ from wastewater, such as reverse osmosis [3], nitrification–denitrification processes [4], electrochemical and biological technologies [5,6], ion-exchange and supercritical water oxidation [7,8]. Strict operating conditions, high cost for physical and chemical methods, long periods, a secondary waste sludge disposal and unacceptable peaks of ammonia on bacteria for biological methods make them inconvenient to use in practical industrial applications [9]. Compared to these methods, adsorption offers a superior solution for stripping NH_4^+ from wastewater due to its considered to be a reliable, economical, low energy input and easy operation technology [10]. Various adsorbents have been developed and studied for NH_4^+ removal, but the adsorption kinetics is slow and the adsorption capacity is also limited [11–13]. In addition, the regeneration of these adsorbents is still a restricting factor governing the water treatment cost [14].

Hydrogel, loosely crosslinked hydrophilic polymers, possesses functional groups and three-dimensional polymeric networks. It is expanded throughout its whole volume by absorbing a large amount of water while maintaining their structural integrity [15]. Owing to its super-hydrophilicity and tailored functionality, the resulting hydrogel shows obvious advantages over traditional adsorbents, such as high adsorption capacity, fast adsorption rate, wide pH application range and easy separation [16]. Therefore, hydrogels are considered to have extensively potential applications in the removal of various aquatic pollutants. However, the low kinetics properties and the poor mechanical properties hinder their further practical application in wastewater treatment [17]. Comparing with traditional hydrogels, composite hydrogels can overcome these disadvantages by combining the advantages of the components. Besides, composite hydrogels, to some extent, can be prepared as a part of efforts to reduce high production cost and the environmental impact resulting from petroleum-based polymers [18]. Furthermore, the residuum of composite hydrogel treated NH_4^+ pollutions can be recovery and potentially reused as a slow-release nitrogen fertilizer [19]. To our best knowledge, few papers were involved in the removing NH_4^+ from aqueous solution onto composite hydrogel and reusing it as a multifunctional slow-release fertilizer.

Composite hydrogel used as a carrier material to control the release rate of nutrients exhibits many advantages over traditional used fertilizers, such as improving fertilizer use efficiency, lowering application frequency and minimizing negative effects associated with over dosages [20]. Moreover, a test of composite hydrogels for agriculture application showed encouraging results, as they have been observed to help reduce irrigation water consumption and amelioration of soils [21]. Among the numerous materials used for composite hydrogel formation, polysaccharide and inorganic clay have particular advantages compared with synthetic polymers, due to their economical, biocompatible, nontoxic and biodegradable properties [22]. In this study, biodegradable carboxymethyl chitosan (CMCS) and *N*-maleyl chitosan (*N*-MCS) were used as graft copolymerization material and crosslinker, respectively. Palygorskite (PGS) was incorporated into polymer matrices as nanofiller to form composite hydrogel. Its fibrous morphology, large specific surface area and moderate cation exchange capacity

are beneficial to the adsorption and fertilizer retention [23]. In addition, PGS can provide many nutrients for plant growth due to its abundant elements content, such as P, K, Ca, Fe, Mg, and Mn [20].

The major objectives of this study were to: (a) prepare a novel nanocomposite hydrogel and measure the potential of the as-prepared adsorbent for NH_4^+ adsorption capacity; (b) investigate the adsorption kinetics process, equilibrium adsorption isotherms and mechanism governing the adsorption of ammonium onto the as-prepared adsorbent; (c) evaluate the potential of using the as-prepared composite hydrogel as the carrier material for a multifunctional slow-release fertilizer system.

2. Materials and methods

2.1. Materials

Chitosan (CS, with a degree of deacetylation of 0.9, Haidebei Co. Ltd., Jinan, China) with an average molecular weight of 5.0×10^5 and 2.0×10^4 were used to synthesis of carboxymethyl chitosan and *N*-maleyl chitosan, respectively. Acrylic acid (AA, analytic reagent, Tianjin Fine Chemical Reagent Factory, Tianjin, China) was used as a monomer. Natural palygorskite (PGS, supplied by Gansu Haozhou PGS Co. Ltd., Gansu, China) was milled and sieved through a 200-mesh screen before use. Ferrous ammonium sulfate (FAS, analytical grade, Tianjin Chemical Reagent Factory, Tianjin, China) and hydrogen peroxide solution (H_2O_2 , analytical grade, Chengdu Aikeshiji Reagent Co., Ltd., Chengdu, China) were used as received. Analytic grade ammonium chloride (NH_4Cl) and distilled water were used for the preparation of a stock solution of 1 mol L^{-1} NH_4Cl . Ammonium solutions of different concentrations were prepared by diluting the NH_4Cl stock solution with distilled water. Other reagents were all of analytical grade and were used without further purification.

2.2. Synthesis of CMCS

Carboxymethyl chitosan (CMCS) was synthesized as the method reported in the literature [24]. The substitution degree of CMCS was determined to be 0.95.

2.3. Synthesis of *N*-MCS cross-linker

N-MCS was synthesized according to a method previously reported in the literature [25]. Chitosan (CS, 0.5 g, and $M_n = 20,000 \text{ g mol}^{-1}$) was dissolved in 40 mL of 2 wt% acetic acid aqueous solution with stirring and transferred to a three necked flask. Maleic anhydride (0.25 g) in a small amount of acetone was added into the solution, and then the reaction was carried out at room temperature for 8 h. The mixture was then poured into acetone to precipitate the polymer. The precipitate was washed with acetone and then freeze-dried. The substitution degree of *N*-MCS was determined to be 14.5%.

2.4. Preparation of CMCS-*g*-PAA/PGS composite hydrogel

The composite hydrogel was synthesized according to the following procedure. Typically, 0.5 g CMCS was dissolved in 50 mL of distilled water in a four-necked flask equipped with a stirrer, reflux condenser, thermometer and gas inlet tube. After being purged with nitrogen for 30 min, 0.10 g $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$ and 5 mL of 3% H_2O_2 were added dropwise into the flask from a constant pressure funnel to initiate CMCS to generate radicals. After generation of the radicals, a premixed solution containing 2.8 g

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