



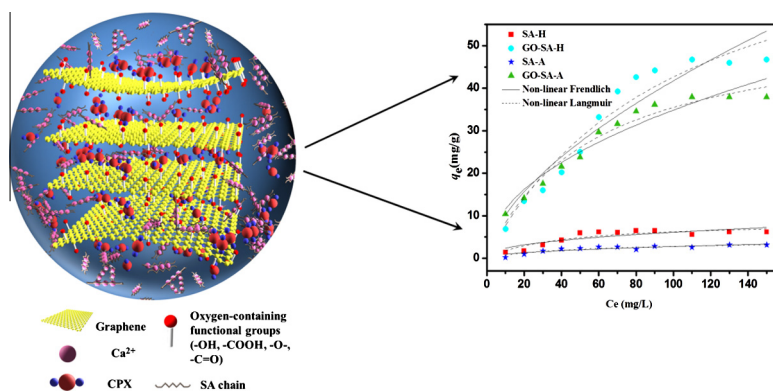
## Regular Article

## Adsorptive removal of ciprofloxacin by sodium alginate/graphene oxide composite beads from aqueous solution

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## GRAPHICAL ABSTRACT

Graphene oxide was encapsulated into environmentally benign sodium alginate to prepare composite hydrogel beads, and then used as adsorbents to remove ciprofloxacin.



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## ABSTRACT

Graphene oxide (GO) was encapsulated into environmentally benign sodium alginate (SA) to prepare a GO-SA composite hydrogel and an aerogel, which were then used as adsorbents to remove ciprofloxacin from aqueous solutions. The characteristics of these materials were investigated using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The characterizations demonstrated that the incorporation of GO improved the pore uniformity of the gels and decreased the pore sizes. Kinetic studies showed that the adsorption capacity of SA composite gels increased approximately seven to nine times after the incorporation of GO, matching with pseudo-second-order models. Non-linear fitting parameters of adsorption isotherm studies indicated that a Langmuir model could precisely represent the adsorption behavior. GO-SA aerogels exhibited high tolerance to changes in pH and ionic strength; changes in these parameters minimally influenced the adsorption capacity of the GO-SA aerogels for ciprofloxacin. This work is especially relevant for environmental applications. These

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graphene-based composites are environmentally benign adsorbents and can remove organic contaminants from aqueous solutions.

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## 1. Introduction

The discovery of antibiotics has greatly improved our capacity to treat and prevent a number of diseases. However, abuse of antibiotics can result in compromised human immunity and certain poisonous side effects [1]. Ciprofloxacin (CPX,  $C_{17}H_{18}FN_3O_3$ ), a synthetic third-generation quinolone antibacterial drug, has been widely used due to its efficient antimicrobial activity. However, CPX is not readily biodegradable [2]. CPX exists in three states in solution (see Fig. S1): a cationic  $CPX^+$  form (with a protonated amine group in solutions with pH values below  $5.90 \pm 0.15$ ), an anionic  $CPX^-$  form (with a deprotonated carboxylic group in solutions with pH values above  $8.89 \pm 0.11$ ), and a zwitterionic  $CPX^0$  form (a mixture of cationic  $CPX^+$  and anionic  $CPX^-$  forms) [3]. The presence of CPX in aqueous environments, whether from the production process or as partially metabolized molecules excreted by humans [4], will accelerate the appearance of antibiotic-resistant bacteria [1], and at high concentrations, causes damage to the immune system. In turn, higher dosages of CPX would be required to treat more tolerant bacterial infections, and a vicious cycle could ensue. This vicious cycle will lead to increases in CPX concentrations in the environment, which may pose a threat to human health. Therefore, it is necessary to regulate CPX levels to more permissible levels prior to discharge [5].

A variety of physical and chemical methods have been used to remove CPX from wastewaters, e.g., membrane separation [6], oxidation reaction [7], adsorption treatment [2], activated sludge treatment [8], microbial degradation [9] and photocatalytic degradation [10]. The adsorption treatment method has been considered a promising method due to its simple theoretical design, ease of operability, relatively low costs and relatively lower amounts of toxic byproducts [11–13]. Various adsorbents, including activated carbon [3], montmorillonite [14], carbon nanotubes [2], hydrous iron oxides [15], kaolinite [14] and graphene [16], have been explored for the removal of CPX from aqueous solutions.

Sodium alginate (SA), the sodium salt of alginic acid, consists of copolymers of  $\beta$ -1,4-glycosidic linked  $\alpha$ -L-mannuronic acid (M-unit) and  $\beta$ -D-guluronic acid (G-Unit) [17] (see Fig. S1). SA is biocompatible, nontoxic, and rich in hydroxyl and carboxyl groups and is thus readily crosslinked by various polyvalent ions, such as  $Ba^{2+}$ ,  $Ca^{2+}$ , and  $Fe^{3+}$ . SA has been used as an adsorbent to remove heavy metals [18], dyes [19], and antibiotics [5]. In these studies, pores in the SA gels play crucial roles in the adsorption process. However, SA solutions and gels also are easily contaminated with bacteria [20]. Various studies have attempted to improve the pore structure of alginate gels to impart antimicrobial properties and to increase adsorption capacities [21–23].

Graphene oxide (GO), one of the most popular carbon materials in recent years, has a two-dimensional sheet-like carbon structure of graphene and randomly distributed hydroxyl, epoxy, and carboxyl groups on its surface and edges. These properties impart excellent dispersibility in aqueous solutions, enables  $\pi$ - $\pi$  stacking, hydrogen bonding, cation bonding interactions with adsorbates, large specific surface area, and additional unique physicochemical and excellent mechanical properties [24]. GO and its composites have been used in the removal of  $Hg^{2+}$  [25], arsenic [26], tetracycline antibiotics [27], and methyl blue [28]. However, GO is nano-toxic [29], which limits its application in the environment

to some extent. Furthermore, the adsorption of antibiotics by GO has proven difficult.

In this work, GO was encapsulated into SA to form a GO-SA gel. This process lowered the nano-toxicity of GO and decreased the pore size and improved the pore uniformity of SA. After lyophilization, the resultant GO-SA aerogel was easier to handle, storable for later use, and had excellent antibacterial activity. The influences of pH, contact time and ionic strength were also investigated on the adsorption of CPX by SA and GO-SA gels.

## 2. Experimental section

### 2.1. Materials and reagents

SA was purchased from Shanghai Titan Technology Co., Ltd (Shanghai, China). Calcium chloride (analytical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ciprofloxacin,  $\geq 90\%$ , was purchased from Sigma, Yanyu Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were used as received without any further purification. All solutions were prepared using deionized water.

### 2.2. Preparation of SA hydrogel and aerogel

Sodium alginate hydrogel (SA-H) was prepared using a  $CaCl_2$ -hardening method. Briefly, 1 g SA was dissolved in 40 ml deionized water under magnetic stirring. Then, the SA solution was treated with ultrasound for approximately 20 min to disperse the SA. The SA solution was then added drop-wise using a peristaltic pump (BT100-1L, Longer Precision Pump Co., Ltd, Baoding, China) at a flow rate of  $6 \text{ ml min}^{-1}$  into a  $0.2 \text{ mol L}^{-1}$   $CaCl_2$  solution under constant and gentle magnetic stirring. The solution was continually stirred to guarantee solution density uniformity and prevent SA agglomeration. Afterward, the hydrogel was kept in a  $CaCl_2$  solution for 2–3 d without stirring. Then, the hydrogel was washed with deionized water three to four times and stored in a refrigerator ( $4^\circ\text{C}$ ). The SA aerogel (SA-A) was acquired by lyophilizing the SA hydrogel.

### 2.3. Preparation of GO-SA hydrogel and aerogel

Graphite oxide was prepared using the modified Hummer's method and subsequently dispersed in deionized water. The graphite oxide solution was treated with ultrasound for 10 h to obtain an aqueous dispersion of GO flakes ( $1.0 \text{ mg ml}^{-1}$ ). Next, SA powder was slowly mixed into the GO aqueous solution with magnetic stirring. An SA-only hydrogel was also prepared in parallel. Briefly, an SA mixture was sonicated for 20 min and was then added drop-wise to a  $0.2 \text{ mol L}^{-1}$   $CaCl_2$  solution under constant and gentle magnetic stirring using a peristaltic pump (BT100-1L, Longer Precision Pump Co., Ltd., Baoding, China) at a flow rate of  $6 \text{ ml min}^{-1}$ . This process was performed under constant magnetic stirring to guarantee solution density uniformity and to prevent agglomeration in the final GO-SA hydrogel (GO-SA-H). The formed GO-SA hydrogel was kept in a  $CaCl_2$  solution for 2–3 d without stirring to form the final GO-SA hydrogel. The GO-SA hydrogel was then washed with deionized water three to four times and stored at

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