



# Evaluation of perchlorate removal from aqueous solution by cross-linked magnetic chitosan/poly (vinyl alcohol) particles



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## ABSTRACT

Perchlorate is an emerging trace contaminant and has been detected in groundwater, surface water, soil, and food globally. Cross-linked magnetic chitosan/poly (vinyl alcohol) beads (CM-CS/PVA Bs) were synthesized and tested to remove perchlorate from water. The complex was characterized by Fourier transform-infrared spectroscopy, transmission electron microscopy, energy-dispersive spectroscopy, and vibrating sample magnetometry. The influence of pH, co-existing anions, contact time, and temperature on adsorption was investigated. Particles were super-paramagnetic and could be recovered easily using an external magnetic field. The CM-CS/PVA Bs could adsorb perchlorate efficiently in a wide pH range from 4 to 10. Co-existing anions would inhibit the adsorption of perchlorate on CM-CS/PVA Bs. Kinetic data were well-described by the pseudo-second-order model. Langmuir and Freundlich isotherms fitted the equilibrium data well. The negative Gibbs standard free energy and enthalpy show that the adsorption process was spontaneous and exothermic. The exhausted adsorbent could be regenerated efficiently by 0.1% NaCl eluent. Therefore, the magnetic property and reusability of the CM-CS/PVA Bs make it suitable for potential application in perchlorate removal from aqueous solution.

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## 1. Introduction

As a strong oxidizer, perchlorate has been used extensively in the manufacture of rocket propellants, fireworks, weapons, automobile airbags, and safety flashboards for highway construction [1]. Its use and the improper disposal of wastes have led to perchlorate release into the environment [2]. Increasing amounts of perchlorate have been detected in groundwater, surface water, soil, and food globally [3–5]. Perchlorate is an inorganic endocrine disruptor because it is a potent competitive inhibitor of sodium-iodide symporter on the basolateral membrane of thyroid cells [6]. It can interfere with natural iodine uptake by the thyroid gland, inhibit thyroid hormone production, disturb normal metabolism, and subsequently lead to a series of diseases [7]. Because of its harm to human health, the United States Environmental Protection Agency set an Interim Drinking Water Health Advisory level of 15  $\mu\text{g/L}$  in 2008, and some states in the United States have established lower action levels [8].

Perchlorate's high solubility and chemical stability make it challenging to remove from water. Technologies available for perchlorate-contaminated water remediation include ion-exchange,

adsorption, biological treatment, and chemical/catalytic reduction [9]. Compared with other treatment methods, adsorption is attractive because of its advantages of low cost, high treatment efficiency and easy operation. As the most common adsorbent, activated carbon is also used to remove perchlorate from water. However, it usually needs to be modified by cationic surfactants or other methods to improve its adsorption capacity, which may lead to increasing costs or second pollution [10]. Recently, chitosan has often been chosen as an effective bio-adsorbent for the removal or recovery of hazardous dyes, proteins, and heavy metals because of its non-toxicity, good biodegradability, excellent chemical resistance, and good mechanical properties [11]. Because of its cationic behavior in acidic media, the protonation of amine groups in chitosan exhibited high affinity with perchlorate in water in our previous study. But dissolved chitosan is difficult to separate from solution after adsorption of the contaminant, and usually needs separation or modification processing [12].

To overcome problems related to the ease of separation and regeneration of chitosan sorbents, considerable attention has been focused on magnetic adsorbents in recent years. The main advantages of magnetic composites include: (1) a fast adsorption rate; (2) a high efficiency, even in dilute solutions; (3) their micrometer size and stable structure; (4) simple recovery using an external magnetic field; and (5) their ability to be regenerated easily [13]. Chitosan is chosen as a base matrix to manufacture magnetic

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composites because of its high content of amino ( $-\text{NH}_2$ ) and hydroxyl ( $-\text{OH}$ ) functional groups, which are able to interact with iron on the magnetic particle surface [14,15]. Chitosan can also be modified easily by chemical/physical processes or react with other polymers to prepare chitosan derivatives or form new composites. Polymer blending has increasingly become an alternative technique for preparing new desirable polymeric materials and improving the cost-performance ratio of commercial products [16]. Polyvinyl alcohol (PVA) has been used in many biomaterial applications because of its nontoxicity, water solubility, good biodegradability, and excellent chemical/mechanical properties [17]. Chitosan blended with PVA exhibits good chemical and mechanical properties because of the specific intermolecular interactions between chitosan and PVA in the blend through hydrophobic side chain aggregation and intermolecular and intramolecular hydrogen bonds [17,18].

Although the preparation of magnetic chitosan composites is tedious, the composites have been used to treat various toxic pollutants in aqueous solution and exhibit good adsorption capability [13]. For instance, Monier and Abdel-Latif [19] used cross-linked magnetic chitosan-phenylthiourea (CSTU) resin to adsorb  $\text{Hg}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Zn}(\text{II})$  metal ions in water. The maximum adsorption capacities for  $\text{Hg}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Zn}(\text{II})$  were determined to be  $135 \pm 3$ ,  $120 \pm 1$  and  $52 \pm 1$  mg/g respectively. Chen and Wang [20] investigated  $\text{Cu}(\text{II})$  removal by magnetic chitosan nanoparticles of which the particle size varied from 8 to 40 nm. The maximum sorption capacity was estimated to be 35.5 mg/g. Hritcu et al. [21] prepared magnetic chitosan composite particles with an average particle size of 40  $\mu\text{m}$ , which showed a high adsorption capacity both for uranyl (666.67 mg/g) and thorium (312.50 mg/g) ions in aqueous solutions.

Apart from heavy metals, magnetic chitosan composites and their modification particles can also remove dyes from aqueous solutions efficiently. For instance, Zhu et al. [22] discovered that the introduction of multi-walled carbon nanotubes (MWCNTs) can increase the adsorption capacity of methyl orange (MO) onto a magnetic composite bio-adsorbent by 2.2 times. Zhu et al. [16] studied Congo Red removal by magnetic chitosan/poly (vinyl alcohol) hydrogel beads (m-CS/PVA HBs), which showed an adsorption capacity of 470.1 mg/g. No information has been reported on perchlorate removal by magnetic chitosan composites.

To improve the absorbent structure and recovery properties, cross-linked magnetic chitosan/polyvinyl alcohol beads (CM-CS/PVA Bs) were prepared and tested to remove perchlorate from water. The composite material structure was characterized by Fourier transform-infrared spectroscopy (FTIR), transmission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDS), and vibrating sample magnetometry (VSM). The optimum conditions for perchlorate removal were investigated. Experimental data were applied to different isotherms and kinetic models to investigate the adsorption process. This work may provide an alternative method for perchlorate removal from water.

## 2. Materials and methods

### 2.1. Materials

Chitosan powder was purchased from Golden-shell Biochemical Co. (Zhejiang, China), and had a molar mass of  $10^5$  Da and a deacetylation degree of 95.38%.  $\text{Fe}_3\text{O}_4$  particles (purity >99.5%, 20 nm spherical particles) were supplied by Aladdin Industrial Co. (Shanghai, China). Polyvinyl alcohol-1788 (purity >99.0%), with an average molar mass of  $8 \times 10^5$  Da, was obtained from Kelong Chemical Co., Ltd. (Chengdu, China). All other chemicals were of analytical grade and were available commercially. All solutions were prepared with deionized water.

### 2.2. Cross-linked magnetic chitosan bead preparation

The synthesis of CM-CS/PVA Bs used in this study was changed based on previous research [16]. Firstly, 5 g of chitosan powder was dissolved in 250 mL of 2% (v/v) aqueous acetic acid to form chitosan solution. PVA solution was prepared by dissolving 5 g of PVA powder in 250 mL of deionized water. After the chitosan and PVA powder had dissolved, the two solutions were mixed together and 5 g of  $\text{Fe}_3\text{O}_4$  was added to the mixture. The composite gel-forming solution was formed after stirring for 3 h at  $303 \pm 1$  K. Then, the gel-forming solution was dropped into 1.0 M sodium hydroxide, and spherical hydrogel beads were formed instantaneously. The beads were gelled for 2 h and then washed using deionized water several times. Finally, the wet beads were dipped into 40% (w/v) glutaraldehyde solution (determined by preliminary tests) and stirred for 12 h at  $303 \pm 1$  K to obtain the cross-linked magnetic chitosan. After thorough washing using deionized water, the cross-linked magnetic beads were filtered and dried at  $60^\circ\text{C}$  for 36 h.

### 2.3. Sample characterization

CM-CS/PVA Bs surface morphologies were visualized using a cold field transmission electron microscope (Inspect F50, Holland). EDS (INCA ENERGY 300, England), which can analyze elements ranging from 4Be to 92U, was used to determine the elemental percentage composition of the samples. Infrared spectra were obtained with a Fourier transform-infrared spectrometer (Nicolet 6700, Thermo Fisher). A vibrating-sample magnetometer (Model 155, USA) was used to characterize the magnetic properties of the CM-CS/PVA Bs at room temperature.

### 2.4. Batch adsorption studies

#### 2.4.1. Effect of pH and co-existing anions

The effect of pH on adsorption was determined by adjusting the pH from 3 to 11.5 using HCl and NaOH solutions. Approximately 0.05 g CM-CS/PVA Bs were added to 50 mL perchlorate solution with an initial concentration of 10 mg/L. The mixture was agitated for 4 h at 200 rpm.

The effects of co-existing  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$  anions with initial concentrations ranging from 0 to 50 mg/L, on perchlorate adsorption were investigated. The experiments were conducted with the same procedure as the pH effect tests described above without adjusting the pH.

#### 2.4.2. Effect of contact time

Adsorption kinetics were studied at different perchlorate concentrations (0.74, 4.75, 10.29, and 20.57 mg/L) by keeping the adsorbent dosage at 1 g/L. Mixtures were agitated on a shaker at 200 rpm and  $303 \pm 1$  K. Samples were taken at time intervals to analyze the residual perchlorate concentrations in solution.

#### 2.4.3. Effect of temperature

Uptake experiments were implemented by placing 0.05 g dry CM-CS/PVA Bs in a series of flasks containing 50 mL perchlorate solution. The initial perchlorate concentrations varied from 1 to 200 mg/L. The flasks were agitated on a shaker for 4 h at  $308 \pm 1$ ,  $318 \pm 1$ , and  $328 \pm 1$  K, respectively. After adsorption equilibrium had been achieved, the solution was filtered, and the residual perchlorate concentration was determined.

All experiments were conducted in triplicate. The amount of adsorbed perchlorate at equilibrium ( $q_e$ , mg/g) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

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