



# Structural evolution of chitosan–palygorskite composites and removal of aqueous lead by composite beads



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## ABSTRACT

This paper investigates the structural evolution of chitosan–palygorskite (CP) composites in relation to variable mass ratios of their individual components. The composite beads' performance in lead (Pb) adsorption from aqueous solution was also examined. The composite beads were prepared through direct dispersion of chitosan and palygorskite at 1:1, 1:2 and 2:1 mass ratios (CP1, CP2 and C2P, respectively). Analyses by Fourier transform Infrared (FTIR) spectroscopy, Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the dependence of the composites' structural characteristics on their composition mass ratio. The chitosan–palygorskite composite beads exhibited a better Pb adsorption performance than the pristine materials (201.5, 154.5, 147.1, 27.7 and 9.3 mg g<sup>-1</sup> for CP1, C2P, CP2, chitosan and palygorskite, respectively). Adsorption of Pb by CP1 and CP2 followed Freundlich isothermal model, while C2P fitted to Langmuir model. Kinetic studies showed that adsorption by all the composites fitted to the pseudo-second order model with pore diffusion also acting as a major rate governing step. The surface properties and specific interaction between chitosan and palygorskite in the composites were the most critical factors that influenced their capabilities in removing toxic metals from water.

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## 1. Introduction

Heavy metal contamination in the environment is a major concern due to their toxicity and persistence towards microbial detoxification. Lead (Pb) is one such heavy metal which is used as a major component in many industrial products like paint, plumbing, home appliances and electronic devices [1]. It is highly toxic and thus its improper disposal, accidental release or leaching into the groundwater pose a serious threat to the environment and humans. Lead poisoning may result in kidney damage, anaemia, miscarriage, and breakdown of central nervous system especially in children [2]. In Australia, Pb contamination poses a significant

risk to humans and animals due to the intensive mining, smelting and port activities [3] that may release Pb into the environment.

Adsorptive removal of Pb and other toxic metals from contaminated water is often practised due to the simplicity of the process, effective removal capabilities at low metal concentration, and ease of adsorbent modification to tailor specific cleaning up operation [4]. Recently, increasing public awareness about sustainable clean environment has driven the search of more cost-effective, biodegradable and non-toxic materials as contaminant adsorbents. Chitosan is a natural polysaccharide derived from deacetylation of chitin, a  $\beta$ -(1→4)-2-acetoamido-2-deoxy-D-glucose polymer, which source mainly from the shell of crustacean animals. These shells are usually discarded as wastes in food and fishery industries. Thus, utilisation of chitin to synthesise chitosan can provide significant economic advantage. In addition, chitosan is a non-toxic biodegradable material [5] which exhibits strong adsorption capabilities due to its reactive functional amine and hydroxyl groups. These reactive groups facilitate the removal of heavy metals through electrostatic attraction, chelation and ion exchange reaction [6]. However, high solubility of chitosan in acidic solution and low mechanical strength may restrict its applications. These issues can be overcome by modifying chitosan with crosslinking agent or

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by combining it with other materials such as clay minerals through forming clay–chitosan composites.

Over the last decade, composites of chitosan and natural aluminosilicate minerals have been studied as a new potential adsorbent for wastewater remediation. Research showed that chitosan–clay composite could improve mechanical strength of the material and also the adsorption capacity compared to its pristine components [7,8]. Montmorillonite and bentonite were commonly used for the preparation of chitosan–clay nanocomposites giving only a little attention to fibrous clay minerals such as palygorskite. Interestingly, palygorskite, which has moderate surface area and reactive silanol groups, can also participate in removing toxic cations from wastewater [9]. Thus, it is expected that combination of chitosan with palygorskite could have a synergic effect towards the adsorption of toxic metals. Moreover, being a non-swelling clay mineral, palygorskite would maintain better permeability during the composite's use under flow conditions [10,11]. However, the structural characteristics of such composites in relation to different mass ratio of chitosan and palygorskite were rarely reported. This research aims to investigate how synthesis routes of chitosan–palygorskite composites at varying component mass ratios affect the products' structural properties and evaluate their performances in removing Pb from aqueous solutions through adsorption.

## 2. Materials and methods

### 2.1. Chemicals

Chitosan (average molecular weight (MW) 400,000, maximum degree of deacetylation 85%) and sodium tripolyphosphate (85%, technical grade) were purchased from Sigma–Aldrich, Australia. Palygorskite originated from Western Australia was purchased from Hudson Resource Limited, Australia. Lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] was obtained from Fisher–Scientific, Australia. All other reagents were of analytical grade and purchased from Sigma–Aldrich, Australia.

### 2.2. Preparation of chitosan–palygorskite (CP) composites

The composites were prepared according to a previous published method [12] with some modification. In addition, instead of preparing powdered adsorbents, which involve additional labour, time and costs for grinding, sieving and centrifugal sedimentation following adsorption, spherical beads were developed for Pb adsorption tests.

To improve the surface area of palygorskite, it was first activated with 4M HCl under reflux condition at 70 °C for 2 h, followed by heating at 300 °C for 4 h. Chitosan was dissolved in 1% (v/v) acetic acid at 50 °C for 4 h and left for at least 2 h in order to remove any entrapped bubbles. A calculated mass of palygorskite was separately dispersed in 10 mL of Milli-Q water (18.2 Ω cm<sup>-1</sup> resistivity) for 30 min and then the dispersion was added to chitosan solution with continuous stirring at 60 °C forming specific chitosan–palygorskite mass ratios (1:1, 1:2 and 2:1). The mixture was allowed to react overnight. Then, 50 mL of chitosan–palygorskite mixture was added drop-wise with a mild agitation into 100 mL of 3% (m/v) sodium tripolyphosphate solution (pH 8.9) through a 0.45 mm syringe nozzle. Sodium tripolyphosphate acted as the neutralising and crosslinking agent which allowed the formation of chitosan–palygorskite beads. The distance between the nozzle and precipitation bath was fixed at 40 mm and the dropping rate was approximately 60 drops per min. The beads formed were cured for 24 h for hardening and complete phase inversion. The beads, known as chitosan–palygorskite composite (CP), were washed thoroughly with Milli-Q water, and kept in

Milli-Q water at 4 °C until used. The chitosan–palygorskite composites with mass ratio 1:1, 1:2 and 2:1 were denoted as CP1, CP2 and C2P, respectively (C represents chitosan, P represents palygorskite).

### 2.3. Material characterisation

#### 2.3.1. Physical characteristics

Physical characteristics of the CP beads were studied through determining their diameter, water content, average density and porosity. The diameter of the beads (wet and air-dried) was measured macroscopically by using a Vernier Calliper. Average diameter of 20 beads was reported for each sample. To determine the water content, wet beads were first blotted with filter paper to remove surface water and immediately weighed. The beads were then dried at room temperature for 24 h until a constant weight was achieved. Average weight of 10 beads (wet and dry) in triplicate was recorded. The water content ( $W_c$ ) was calculated according to Eq. (1):

$$W_c = \frac{W_h - W_d}{W_h} \quad (1)$$

where  $W_h$  and  $W_d$  are the weights of beads weighed before and after drying, respectively. Average density of chitosan–palygorskite beads was estimated by measuring the mass of dried beads over the calculated volume ( $v = 4/3\pi r^3$ , where  $v$  is volume and  $r$  is radius of sphere) of perfect spheres ( $d = m/v$ , where  $m$  and  $v$  are mass and volume, respectively). The average value of 15 calculated densities was reported for each sample. Liquid (water) displacement method was applied for porosity calculation [13] (Eq. (2)):

$$\text{Porosity} = \frac{(W_h - W_d)\rho_{H_2O}}{W_d/\rho_{mat} + (W_h - W_d)\rho_{H_2O}} \times 100\% \quad (2)$$

where  $W_h$  (g) denotes the weight of wet bead;  $W_d$  (g) the weight of dried bead;  $\rho_{H_2O}$  ( $\rho_{H_2O} = 1.0 \text{ g cm}^{-3}$ ) and  $\rho_{mat}$  are the density of water and material (chitosan–palygorskite composite), respectively.

Physical appearance of the beads (wet, air-dried and freeze dried) was observed by a digital microscope (Digitech Computers, Model QC-3199, resolution 5 Megapixel).

#### 2.3.2. Surface area and pore size distribution

BET (Brunauer–Emmett–Teller) surface area of each composite was determined through N<sub>2</sub> gas adsorption–desorption on a Micromeritics Gemini 2380 surface area analyser at 77 K. The pore diameter and size distribution were calculated through Barrett, Joyner and Halenda (BJH) technique. Approximately 0.5 g of freeze-dried sample was used for the analysis following an overnight degassing at 60 °C under vacuum.

#### 2.3.3. Scanning electron microscopy (SEM)

Surface morphology of the beads was examined by using a FEI Quanta 450 FEG environmental scanning electron microscope (SEM) equipped with an Apollo energy dispersive X-ray spectroscopy (EDS) detector. Mildly ground uncoated samples were placed on adhesive tape mounted on aluminium stubs. EDS spectra were acquired for measuring the elemental composition.

#### 2.3.4. X-ray diffraction (XRD)

Samples were powdered and pressed into stainless steel sample holders. Analysis was performed on a PANalytical Empyrean X-ray diffractometer using CuK<sub>α</sub> radiation operating at 40 mA and 40 kV with a step size of 0.0130. The XRD pattern was recorded from 4 to 90° 2θ.

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