

## Regular Article

# Synthesis and characterization of alginate beads encapsulated zinc oxide nanoparticles for bacteria disinfection in water

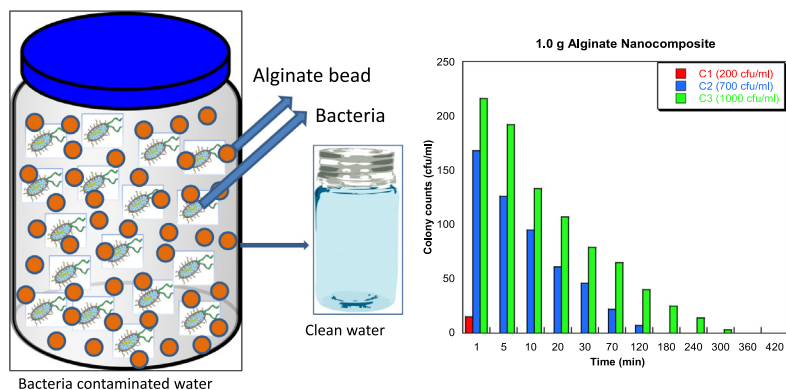


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## GRAPHICAL ABSTRACT



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## ABSTRACT

The use of polymer nanocomposites as novel materials for water remediation has emerged as a promising alternative for disinfection of bacteria contaminated water. Sodium alginate, a natural biopolymer has been investigated in this study by encapsulating antimicrobial zinc oxide nanoparticles supported bentonite. The confirmation of the alginate nanocomposites was done by use of TEM, SEM-EDS and XRD. The antimicrobial activity of the alginate nanocomposites was investigated by batch studies using surface water and synthetic bacteria contaminated water containing *Staphylococcus aureus*. The effect of nanocomposite amount and initial bacteria concentration has been studied. The inactivation results indicated that the nanocomposite effectively inactivated bacteria in both the synthetic and surface water. With an amount of 0.5 g of the nanocomposites, no bacteria was observed in the water after 70 min of contact time with initial bacteria concentration of 200 cfu/ml for synthetic water and within a min, no bacteria was observed in the water for surface water. It is worth noting that 200 cfu/ml is the bacteria concentration range in which environmental water is likely to contain. Therefore, the results of this study have indicated that the alginate nanocomposites can be deemed as a potential antimicrobial agent for water disinfection.

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## 1. Introduction

The presence of bacteria in water is of major concern to the global economy due to the threat they pose to humans and animal life.

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Although water is an essential part of life, in developing countries, some communities are still largely dependent on the use of water from open sources such as rivers, streams and dams. Often times this water is not clean and safe for human consumption as it is infested with bacteria. The World Health Organisation (WHO) has reported that almost a million people die each year in developing countries, due to lack of clean drinking water [1,2]. Various traditional disinfectants such as chlorination, ozonation and ultraviolet radiation are effective at disinfecting bacteria contaminated water to desired levels. However, some of these methods are often time-consuming, costly and produce harmful disinfection by-products or even require that a secondary treatment be used. For example, chlorination is by far the simplest disinfection method used. But, chlorine reacts with the organic compounds in water forming trihalomethanes which were found to be carcinogenic and mutagenic [3,4]. Therefore, there is an urgent need to come with alternative disinfectants to provide safe and clean drinking water that will require less processing time and produce less or no disinfection by-products. To address this problem, researchers have developed new materials with cutting edge properties for water remediation [5–11]. Hence, the development of novel, environmentally friendly and cost-effective materials for the detection and remediation of pollutants in water has attracted considerable attention. Recent advances in polymer nanocomposites have brought promising solutions for the current problems faced in water quality, which comes with high-performance and multifunctional materials. The main driving force for developing polymer nanocomposites is the improvement of the polymer properties and the use of nanomaterials administered in small quantities because of their extraordinary properties [10–13]. Nanomaterials which are used as fillers in polymers include among others carbon based materials (carbon nanotubes, carbon spheres, graphene); layered silicates (clays) and inorganic materials (metal/oxides). The use of nanofillers is particularly advantageous because of their high surface area, providing great interaction which combined with their chemical properties greatly improve the properties of the resulting polymer nanocomposites.

Among the metal oxides that have received extensive attention because of their antimicrobial properties is zinc oxide (ZnO) nanoparticles. Zinc oxide nanoparticles (ZnO-NPs) possess among many other properties chemical stability [14–16], high surface area [15–17] and exert strong antimicrobial activity [15–18] even when administered in small quantities. Zinc oxide nanoparticles are inexpensive, easy to prepare and have found applications in gas sensing [19], catalysis [14], textile [20,21], medical fields [22–24] and water treatment [11,17,25]. However, for water treatment applications, the use of nanoparticles due to environmental concerns, possible toxicity and safety hazards is very stringent. It is therefore, imperative that nanoparticles be encapsulated within a polymer matrix where the nanoparticles will be contained without adding more pollutants to the water being remediated. Both synthetic and natural polymers are available to use for this purpose [26–30]. Biopolymers such as chitosan, cellulose, starch and alginates have found their way in various applications including water remediation [11,12,28–32]. In this study, sodium alginate was selected as the host polymer to encapsulate ZnO-NPs loaded bentonite to form polymer nanocomposites. Sodium alginate is a natural biopolymer that is non-toxic and biodegradable linear polysaccharide [8–10,13]. It is extracted from brown seaweed, which makes it to be inexpensive and abundantly available. The development of alginate nanocomposites for water remediation is not entirely new as various nanocomposites have been prepared for the removal of mostly dyes and heavy metal ions in water. For instance, Li et al. (2017) [8] prepared alginate microsphere nanocomposites for removal of methylene blue from water. Their nanocomposites were prepared using sodium alginate, carbon

black and magnetic iron oxide nanoparticles. The authors reported the nanocomposites were effective to adsorb the methylene blue. Also, Barna and Alka (2017) [13] prepared alginate microspheres encapsulated gold nanoparticles for the adsorption of the dye safranin orange. They reported the nanocomposites to be highly stable and reusable for the dye adsorption. Other studies reported on the effectiveness of the alginate nanocomposites on the adsorption of metal ions, such as cadmium ions [9,10]. In addition, alginate nanofibers impregnated with silver nanoparticles were prepared and their antibacterial activity tested with both gram negative and gram positive bacteria. The authors reported that the composite demonstrated good antibacterial activity against all bacteria tested and the composite had potential to be used for wound healing [31].

The open literature has shown that, although alginate nanocomposites are effective for water remediation applications, there are relatively few studies on the disinfection of water using these nanocomposites. And of the few antimicrobial studies available, most of them use the disk diffusion method to test the antimicrobial activity of the alginate nanocomposites, with no further reports for water disinfection applications [32–34]. Hence, the importance of this study. In this study, antimicrobial alginate nanocomposites were prepared by encapsulating ZnO-NPs supported on bentonite. Bentonite, an aluminium-rich smectite is mainly composed of montmorillonite and is formed by one octahedral sheet sandwiched between two silica tetrahedral sheets [26,27]. Bentonite is readily available around the world and is inexpensive. The clay, with its high surface area and chemical stability is often used as a supporting material for nanoparticles, which tend to aggregate when used alone due to their small sizes. Hence, bentonite was used in this study to support ZnO-NPs for this purpose. As a support material for nanocomposites, the enhanced or even new properties give rise to new applications in various areas of adsorption, wound healing, cosmetics, etc. This wide range of applications has led to the extensive research of the clay and its nanocomposites to take full advantage of their properties for various applications. The prepared alginate nanocomposites were tested for their antimicrobial activity using surface water and synthetic water contaminated with *Staphylococcus aureus*.

## 2. Experimental section

### 2.1. Materials, Reagents and bacteria

Natural bentonite (Bent) obtained from Ecce Holding Pty Ltd.; South Africa was used as the support for ZnO-NPs. The clay was ground and sieved to a size  $\leq 150 \mu\text{m}$ . Calcium chloride dehydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) was purchased from Minema, South Africa; sulphuric acid ( $\text{H}_2\text{SO}_4$ , 98%), phosphate buffered saline (PBS, pH 7.4), sodium chloride (NaCl), sodium alginate and zinc oxide nanoparticles dispersed in ethanol were sourced from Sigma Aldrich, South Africa. Pure cultures of gram positive *Staphylococcus aureus* (ATCC 25923) were used to evaluate the antimicrobial activity of the polymer nanocomposites. Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), Mueller-Hinton agar and Mueller-Hinton broth were sourced from Merck, South Africa.

### 2.2. Synthesis of Bent supported ZnO nanoparticles

Bentonite, received as big lumps was first ground and sieved to a size  $\leq 150 \mu\text{m}$ . The clay was then chemically activated by acid treatment with 3 M sulphuric acid. Zinc oxide nanoparticles dispersed in ethanol were calcined at  $500^\circ\text{C}$  for 5 h to obtain the powdered nanoparticles. Bentonite supported ZnO-NPs was obtained by weighing a certain amount of the nanoparticles into 1.5 g of

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