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Disinfection and removal performance for *Escherichia coli* and heavy metals by silver-modified zeolite in a fixed bed column

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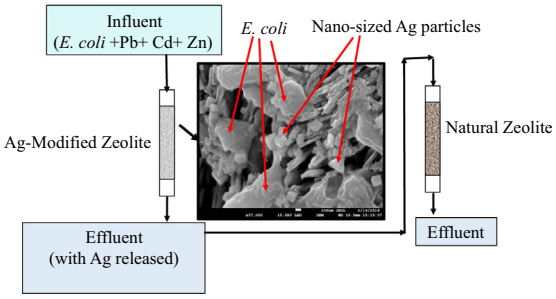
HIGHLIGHTS

- Silver-modified zeolite column simultaneously removed *Escherichia coli* and metals.
- Complete removal *of E. coli* achieved after 570 min followed by Cd and Zn (1080 min).
- No Pb breakthrough observed during the service life of the column (7920 min).
- SEM revealed damaged and lysed cells and *E. coli*-synthesised Ag particles.
- 97–98% Ag recovery achieved in the non-modified natural zeolite column.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the simultaneous removal of *Escherichia coli* and metals (Pb, Cd and Zn) in a continuous flow system and provides an insight into the mechanisms involved during bacterial cells kill when in contact with silver-modified zeolite. Results showed complete disinfection and metal removal at 570 min contact time, thereafter *E. coli* breakthrough followed by Cd and Zn at 1080 min. Due to the zeolite's high selectivity for Pb removal, no breakthrough was observed up to 7920 min run time. Column performance was influenced by changes in flow rate and bed height, as breakthrough occurred at 240 min when the flow rate was increased from 2 to 5 mL/min and the bed height decreased from 1 to 0.5 cm. Morphological characterisation of treated cells revealed extensive damage and synthesis of nano- and micro-sized silver particles as a part of their defence mechanism. The treated effluent was passed through a non-modified zeolite column with 98% silver recovery achieved. This study showed the capability of this system to simultaneously handle bacterial and heavy metals contamination while providing an insight into the mechanism of disinfection via complex *E. coli*–silver ion interactions that occur during treatment and demonstrating the potential of silver recovery for reuse.

1. Introduction

Water scarcity and water pollution are major global issues. Rapid population growth and the consequent increase in anthropogenic activities have resulted in high demand for scarce water resources, generation of large volumes of wastewater requiring treatment and diffuse pollution of surface and ground water sources [1–5]. Major pollutants of concern include pathogenic microorganisms and persistent heavy metals such as Pb, Cd, and Zn, which are harmful to humans at levels in excess of permissible limits. For instance, the World Health Organization (WHO) guideline values are 0 CFU/mL for faecal coliforms and 0.01 mg/L and

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0.003 mg/L for Pb and Cd respectively in drinking water, though there is no specific guideline value for Zn which makes water unpleasant at levels in excess of 3 mg/L [6]. Hence, more effective treatment technologies are required for their removal from water and wastewater prior to use, discharge into aquatic and terrestrial environments and/or reuse.

Silver is an effective antibacterial agent, which has been immobilized on different inorganic support materials for a wide range of antimicrobial applications including water and wastewater disinfection [7–15]. Zeolites have been used as support materials for silver ions with studies demonstrating the effective elimination of microorganisms from aqueous media by silver-modified zeolites [1,16–21]. Most of these studies have focused on the antibacterial properties of silver with the zeolites acting as inert supports with the exception of Krishnani et al. who investigated the combined disinfection and ammonia removal performance of silver ion-exchanged zeolites [21]. However natural zeolites possess excellent ion exchange and adsorption properties due to their physical and structural characteristics and have been extensively applied for the removal of metal ions from aqueous solutions with high metal removal efficiencies achieved in batch and column systems [2–4,22–26].

Preliminary results showed that silver-modified zeolite exhibited potential for disinfection and heavy metal removal and non-modified zeolites displayed no antibacterial effect [27]. Consequently, the aim of this study is to (1) investigate the performance of silver-modified zeolites for the removal of *Escherichia coli* and metal ions in a continuous fixed-bed column system including the effects of flow rate and bed height on removal performance; (2) provide an insight into the mechanism of disinfection via morphological characterisation of treated cells; and (3) from an environmental and economic point of view, evaluate the potential of silver recovery for reuse.

2. Materials and methods

2.1. Natural and silver-modified zeolites

The natural zeolites-clinoptilolite (NZ) (particle size: 0.2–0.6 mm) purchased from Planet Care Products, UK were washed with deionized water to remove surface dust and dried overnight at 60 °C.

Silver modification of NZ was achieved via ion exchange by shaking 100 g of NZ in 250 mL of 3% (w/v) $AgNO_3$. The pH of the solution was adjusted to pH 5 to prevent precipitation of silver ions and the solution was shaken for 24 h in a dark room. The silver-modified zeolites (SZ) were separated, rinsed with deionized water and dried overnight at 60 °C. The amount of silver adsorbed per gram of zeolite was 43.4 mg Ag/g. The chemical composition of representative fractions of NZ and SZ determined by EDX (Energy Dispersive X-ray Spectroscopy) as reported in our previous study [27] confirmed the presence of silver ions exchanged onto SZ.

2.2. Reagents, microorganism and aqueous solutions

Analytical grade reagents were used to prepare metal stock solutions in deionized water. $AgNO_3$ was purchased from Sigma Aldrich, UK. Pb $(NO_3)_2$, $CdN_2O_6{\cdot}4H_2O$, and Zn $(NO_3)_2{\cdot}6H_2O$ were purchased from Fisher Scientific, UK.

E. coli NCTC 9001 from the Public Health England Culture Collection used as an indicator of faecal contamination of water was grown overnight in nutrient broth (Oxoid, UK) at 37 °C. The cells were pelleted by centrifugation, rinsed to remove excess media and re-suspended in deionized water at 10^9 CFU/mL.

Aqueous solutions were prepared by diluting *E. coli* and metal stock solutions in deionized water to give initial *E. coli* concentration: 10^8–10^9 CFU/100 mL and initial metal concentrations: 0.5 mg/L Pb, 0.5 mg/L Cd and 0.5 mg/L Zn. The pH of the feed solution was adjusted to 5 to prevent metal precipitation.

2.3. Fixed-bed column experiments

Experiments were carried out using polyethylene columns of 1.5 cm internal diameter and 30 cm height packed with 1–5 g of SZ between two supporting layers of glass wool. The feed solution was pumped into the column in down flow mode using a peristaltic pump at 1–5 mL/min. Columns were wrapped with aluminium foil to prevent the formation of black silver oxide on the zeolites due to the light sensitivity of silver ions. Prior to each experiment, deionized water was passed through the column for 30 min to ensure that the zeolite particles were properly packed to minimise channelling. The influent was monitored and replaced with fresh stock at regular intervals to maintain microbial concentration levels required. All experiments were conducted at room temperature (22 °C ± 2).

The effects of flow rate (1, 2 and 5 mL/min) and bed height (0.5, 1 and 2.5 cm) were investigated until breakthrough and exhaustion of disinfection capacity. Control columns packed with 2 g of SZ and NZ were fed with *E. coli* solution at 2 mL/min and operated under the same conditions.

Samples were collected periodically for immediate microbiological analysis while samples for metal analysis were syringe-filtered, acidified to pH < 2 and refrigerated at 4 °C.

2.4. Scanning electron microscopy

E. coli cells were examined before and after exposure to SZ. Samples (5 μL) were dropped or smeared on pre-sterilized silicon substrates and air dried under sterile conditions with no further fixing done [28]. The samples were painted with high purity silver, gold coated to improve conductivity and analysed using a JEOL JSM-7100F Field Emission Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Detector (EDX).

2.5. Silver recovery

The potential of recovering silver ions was achieved by passing the treated effluent through a column packed with 1–12 g of NZ at flow rates 1–2 mL/min at pH 4 for optimum silver uptake.

2.6. Analytical methods

The membrane filtration technique was used for enumeration of *E. coli* [29]. A quarter strength Ringer's solution tablets (Oxoid UK) were used to prepare Ringer's solution for serial dilution of water samples prior to enumeration of *E. coli*. M-lauryl sulphate broth (MLSB) (Sigma Aldrich, UK) was used for enumeration of *E. coli* using the membrane filtration technique. Aliquots samples (0.1 mL) were serially diluted in Ringer's solution and filtered through sterile 0.45 μm membrane filters. The filters were placed on adsorbent pads saturated with MLSB and incubated overnight at 37 °C. *E. coli* colonies were counted and recorded as colony forming units per 100 mL (CFU/100 mL).

The concentration of metal ions in solutions was determined by ICP-OES (Perkin Elmer ICP-OES Optima 5300DV).

2.7. Theoretical calculations

Breakthrough curves of effluent pollutant concentration against time were plotted from the results of the fixed-bed columns experiments. For *E. coli* removal, the amount of *E. coli* removed at breakpoint, X_b (CFU) in the column was calculated using the equation: