Journal of Hazardous Materials 279 (2014) 190–196

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of waterborne microorganisms by filtration using clay–polymer complexes

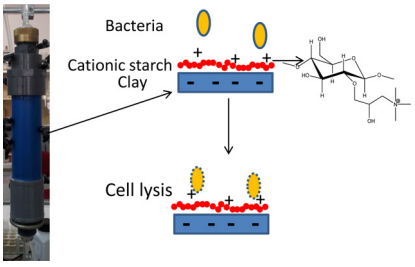
Tomas Undabeytia[a,*], Rosa Posada[a], Shlomo Nir[b], Irene Galindo[a], Leonila Laiz[a], Cesareo Saiz-Jimenez[a], Esmeralda Morillo[a]

[a] Institute of Natural Resources and Agrobiology, IRNAS-CSIC, P. O. Box 1052, 41080 Seville, Spain
[b] The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot 76100, Israel

HIGHLIGHTS

- Clay–polymer complexes were designed with bactericidal activity.
- Clay–polymer complexes were more toxic to bacteria than the polymers alone.
- Clay–polymer complexes yielded much higher filtration efficiency than GAC.
- Clay–polymer complexes saturated with bacteria were successfully regenerated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form 4 July 2014
Accepted 5 July 2014
Available online 14 July 2014

Keywords:
Water purification
Filtration
Clay–polymer complexes
Bacteria
Modeling

ABSTRACT

Clay–polymer composites were designed for use in filtration processes for disinfection during the course of water purification. The composites were formed by sorption of polymers based on starch modified with quaternary ammonium ethers onto the negatively charged clay mineral bentonite. The performance of the clay–polymer complexes in removal of bacteria was strongly dependent on the conformation adopted by the polycation on the clay surface, the charge density of the polycation itself and the ratio between the concentrations of clay and polymer used during the sorption process. The antimicrobial effect exerted by the clay–polymer system was due to the cationic monomers adsorbed on the clay surface, which resulted in a positive surface potential of the complexes and charge reversal. Clay–polymer complexes were more toxic to bacteria than the polymers alone. Filtration employing our optimal clay–polymer composite yielded 100% removal of bacteria after the passage of 3 L, whereas an equivalent filter with granular activated carbon (GAC) hardly yielded removal of bacteria after 0.5 L. Regeneration of clay–polymer complexes saturated with bacteria was demonstrated. Modeling of the filtration processes permitted to optimize the design of filters and estimation of experimental conditions for purifying large water volumes in short periods.

1. Introduction

Disinfection processes are crucial in water treatment utilities. Disinfection is traditionally performed in drinking water treatment plants (WTPs) by chlorination, which reduces significantly pathogens in water but may pose a serious risk to human health due to formation of disinfection by-products (DBPs) [1]. The presence of a minute amount of natural organic matter in chlorinated waters can induce the formation of trihalomethanes (THMS) and haloacetic acids (HAAS), which are carcinogenic. The use of chloramination instead reduces the formation of these chemicals but leads to the formation of nitrosamines [2].

Ozone is also a very powerful disinfectant able to remove a wide range of microorganisms including those resistant to other oxidative means, such as chlorination. However, it is a very unstable molecule, which decomposes very

* Corresponding author. Tel.: +34 954624711; fax: +34 954624002.
E-mail address: undabeyt@irnase.csic.es (T. Undabeytia).

http://dx.doi.org/10.1016/j.jhazmat.2014.07.006
0304-3894/

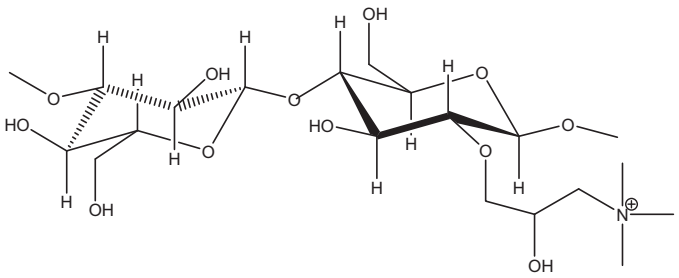


Fig. 1. Chemical basic structure of the cationic starches.

quickly. Studies have shown undesired effects after ozonation, such as formation of nitrosamines [3] and cyanogen halides [4]. Advanced oxidation processes based on the attack of the target molecules by hydroxyl radicals generated by UV irradiation in the presence of oxidants, such as ozone, H_2O_2 or TiO_2, are capable of degrading very efficiently numerous prions [5].

Disinfection processes are greatly improved in combination with other water treatment processes such as filtration technologies [6–8]. Depth filtration is incorporated in the vast majority of WTPs, and helps to reduce the loading of waterborne pathogens by physical sorption or entrapment in addition to removal of particles to which they are associated. Moreover, it may be effective for removal of DBP precursors. Membrane filtration processes are mostly advantageous for very stringent water quality standards because of their high operational costs [9].

One of the most widely-used materials in column filtration is GAC; however, this material has very poor performance for removal of pathogens. Therefore, present research is focusing on GAC modification and the synthesis of new composite materials to be used as media for microorganism [10–14]. An alternative is the use of polymer-based composites due to the antimicrobial properties exerted by cationic polymers [15]. These composites are of particular interest when dealing with water soluble polymers, where surface anchorage is needed for their preparation. Tashiro [16] prepared polymers based on polystyrene supported in alumina granules, which presented high adsorption rate constants in *Escherichia coli*'s removal. Madkour et al. [17] eliminated *E. coli* and *Staphylococcus aureus* from water by using glass surfaces grafted with poly(butylmethacrylate)-*co*-poly(boc-aminoethyl methacrylate). However, studies showing the potential use of polymer based composites in water filtration processes for removal of microorganisms are scarce [18]. Clay–polymer composites can be designed by adsorption of cationic polymers onto negatively charged clay mineral platelets. The driving forces for polymer sorption are the translational entropic gain due to removal of water molecules and counter ions from the clay surface, and the electrostatic attraction between the polymer and the clay surface [19]. Adsorption of certain polycations on clay minerals was considered irreversible [20]. The use of clay–polymer composites in the removal of microorganisms from water by filtration has not been thoroughly studied yet. In the current study, we aimed at (i) designing clay–polymer composites with antibacterial properties based on the sorption of cationic starches onto a commercial bentonite; (ii) elucidating the mechanisms and factors involved in the development of toxicity of the new composites; (iii) testing their efficiency in the removal of the pathogenic enteroindicator *E. coli* by filtration; and (iv) analysis of the kinetics of filtration for generating estimates for a variety of situations, e.g., upscaling. The polymers used were cationic starches which are widely used as additives in paper-making, textile and cosmetic industry.

2. Materials and methods

2.1. Materials

The cationic starches employed were a gift from Penford Co. (Centennial, CO) and are based on the reaction of hydroxyl groups of pristine starch with 3-chloro-2-hydroxypropyltrimethylammonium (chemical structure in Fig. 1). Three types of polymers were studied differing in their degree of substitution (DS). All of them are commercial: Topcat L-98 (DS = 0.22) (denoted hereafter as P1); Topcat L-95 (DS = 0.15) (denoted as P2) and Penbond 1000 (DS = 0.05) (P3). Their charge densities (CD) were determined to be respectively, 1.19 meq/g for P1, 0.846 meq/g for P2, and 0.29 meq/g for P3. A commercial Na-bentonite (Bentonil A, CEC 0.8 $mmol_c/g$) was kindly supplied from Süd-Chemie Spain. Granular activated carbon (GAC) (NUSORB GC60, 12 × 30 mesh) was purchased from NUCON International, Inc. (Columbus, OH).

The bacterial strain *E. coli* was purchased from the Spanish Type Culture Collection (CECT): the Luria–Bertani growth medium and the Agar for the microbial assays were supplied by Merck (Darmstadt, Germany). The LIVE/DEAD BacLight Bacterial Viability kits were obtained from Life Technologies (Carlsbad, CA, USA).

2.2. Sorption of polymers onto the clay

Sorption isotherms of the polymers onto the commercial bentonite were carried out by mixing 15 mL of polymer solutions (0–40 g/L) with 24 mg of clay. The clay concentration was 1.6 g/L. After shaking for 24 h at 20 °C, the suspensions were centrifuged at 12,000 × *g* for 10 min, the supernatants were discarded and the pellets were dry-frozen. The sorbed amount of polymer was determined by elemental C analysis.

The zeta potential (ξ) of the polymer–clay complexes obtained after sorption was measured by redispersing with distilled water at a concentration of 1.6 g/L. The samples were allowed to equilibrate for 1 h and few milliliters of dispersion were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA).

X-ray diffraction of oriented samples on glass slides was also measured using a Philips X'Pert diffractometer (model Anton Paar HTK) at low and higher angles on a Siemens diffractometer (model D5000). The samples were prepared from the paste obtained after centrifugation of the polymer–clay suspensions of the adsorption experiments.

Several clay polymer complexes were prepared for their study in the next sections. In general, clay powder was added to a polymer solution; the suspension was shaken for 24 h and centrifuged; the pellet was dry-frozen yielding the clay–polymer composite. A nomenclature for the different clay–polymer composites was introduced where the first two characters indicate the type of polymer, the following number denotes the polymer concentration added in g/L and the last number the clay concentration used in g/L.

2.3. Determination of bactericidal effects of clay–polymer composites

E. coli were incubated for 24 h at 37 °C in Luria–Bertani nutrient broth, and a bacteria suspension with a 10^5 CFU/mL concentration was prepared. Clay–polymer complexes were added to this suspension in centrifuge tubes at a 1.5:100 solid: water ratio. This ratio was chosen after preliminary trials to see differences in the bactericidal activity of the prepared clay–polymer complexes. After 1 h incubation at 25 °C, the suspensions were centrifuged at 1000 rpm for 10 min at 4 °C, and 0.1 mL of the suspensions were removed and mixed with 0.9 mL of sterile distilled water, and then successive decimal serial dilutions were prepared. From the suspensions and successive dilutions, the surviving bacteria were counted on nutrient media by the spread-plate method and expressed as colony forming units (CFU) per milliliter of sample. The plates were incubated at 37 °C and the colonies were counted after 24 h. The counting was done in four replicates every time. The limit of quantification (LOQ) for bacteria analysis with the spread-plate method is 10 CFU/mL. If no colonies are recovered, the limit of detection (LOD) is reported to be <10 CFU/mL for a 1:10 dilution according to the ASTM International.

In a parallel experiment, the deactivation of the cells after interaction with the clay complexes was examined by using a LIVE/DEAD stain methodology. Briefly, 1 mL of the suspension was incubated in darkness for 15 min with 4 μL of a mixture of propidium iodide and the SYTO 9 dye. After centrifugation, the pellets were mounted on slides and examined with a Zeiss Axioskop epifluorescence microscope at 40× magnification counting the dead and live cells on the clay–polymer surfaces by emission of red and green light,