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Comparison study of Ag(I) and Au(III) loaded on magnetic thiourea-formaldehyde as disinfectants for water pathogenic microorganism's deactivation

Mohamed Azab El-Liethy[a], Khalid Z. Elwakeel[b,c,*], Mohammed S. Ahmed[d]

[a] Environmental Microbiology Lab., Water Pollution Research Department, National Research Centre, P.O. Box 12262, Dokki, Giza, Egypt
[b] Chemistry Department, Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia
[c] Environmental Science Department, Faculty of Science, Port-Said University, Port-Said, Egypt
[d] Water Quality Audit Department, Egyptian Water and Wastewater Regulatory Agency (EWRA), New Cairo City, Egypt

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ABSTRACT

Magnetic disinfectants were achieved through the polymerization of thiourea and formaldahyde in the presence of magnetite nano particles (MTUF), the as-prepared MTUF was loaded with Ag(I) or Au(III). The obtained disinfectants (MTUF-Ag and MTUF-Au) were test for some selected pathogenic strains deactivation. The toxicity of MTUF before and after Ag(I) or Au(II) loading was estimated. The antimicrobial activity tests of MTUF-Ag and MTUF-Au were carried out against *Escherichia coli*, *Salmonella* typhimurium and *Pseudomonas aeruginosa* as examples of Gram negative bacteria; *Listeria monocytogenes, Staphylococcus aureus, Enterococcus faecalis,* and *Bacillus subtilis* as examples of Gram positive bacteria; *Candida albicans* as representative for fungi. The results showed that the minimum inhibitory concentration (MIC) of MTF-Ag against *Escherichia coli, Salmonella typhimurium, Listeria monocytogenes, Staphylococcus aureus and Candida albicans* were 1.5, 2.0, 1.5, 1.0 and 2.5 mg mL^{-1}, respectively after 40 min of contact time. While MTUF-Au showed higher MIC concentrations: 6.0, 4.0, 4.0, 4.0 and 6 mg mL^{-1} for the mentioned strains, respectively. The studied MTUF-Ag and MTUF-Au were successfully tested for deactivation of the studied pathogenic microorganism's water and wastewater samples. It can be concluded that, MTUF-Ag and MTUF-Au are good candidates for water disinfection.

1. Introduction

Water borne diseases have been extended because of inadequate water supply, hygiene and sanitation. Every year, about four million people suffer from waterborne diseases and 2.2 million people die [1]. The risks of pathogenic microorganisms to human are associated with ingestion of contaminated water with human or animal feces [2]. Meanwhile, wastewater discharges into fresh waters, lakes, ground waters and coastal seawaters are the main sources of fecal that are contaminated with microorganisms, including pathogens [3,4]. Conventional disinfectants including chlorine and their derivatives are a strong disinfecting oxidant, which can effectively inactivate bacteria and viruses. Chlorine interacts readily with natural organic matter present in all source surface waters to generate numerous disinfection by-products [5]. Moreover, the increased resistance of some pathogens, such as Cryptosporidium, Giardia, and viruses, to conventional chemical disinfection requires the application of extremely high disinfectant dosages that make worse disinfection by-products formation and elevate operational costs. As a result, the effort to provide safe, appropriate, effective, and affordable drinking water disinfection alternatives continues, as new and old technologies are estimated [6]. Recently, solar radiation, UV disinfectants and photocatalytic oxidations using metal oxide have been used for a wide range of organic compounds and bacteria as pollutant disinfectants [7,8]. Solar radiation is still has some disadvantages concluded in required large space to set up the apparatus and also this process works best for water of low turbidity [9]. Moreover, UV disinfectants and photocatalytic oxidation processes have some drawbacks including high energy is required and there is no residual effect for visible light and/or UV disinfectants, which is important to keep the treated water free from the pathogens in an extensive distribution network or long term storages [6].

Metallic ions have been used for water disinfection. Some metal ions, such as that of potassium, silver, gold and copper are known to possess some disinfection property [10,11]. The metal ions mode of action as a disinfectant is result from effect of these ions on the microbial cell, capsid protein surface and/or on the nucleic acid of cells or

* Corresponding author at: Environmental Science Department, Faculty of Science, Port-Said University, Port-Said, Egypt.
E-mail address: khalid_elwakeel@sci.psu.edu.eg (K.Z. Elwakeel).

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viruses. As well, metals ions are able to modify enzyme structure and function or facilitate hydrolysis or nucleophilic displacement [6].

Polymer metal complexes are a novel and excellent type of materials that combine some of the mechanical properties of the organic polymer and some of those of the metal ions. A large number of such polymers have been synthesized and studied and have been found to be of interest because of their biological applications such as antibacterial effects [12]. Chelating resins with metal ions have many practical applications in the fields of chemical analysis and environmental applications [13,14]. Chelating resins with silver and gold ions were used in several environmental and medical applications but not previously used as water disinfectants against pathogenic microorganisms [15–17]. Thus, the scope of this work is to synthesis a new magnetic disinfectants based on thiourea-formaldehyde polymer loaded with silver (MTUF-Ag) and/or gold ions (MTUF-Au) for water pathogenic microorganism's deactivation. The effect of the as-prepared disinfectants on *Escherichia coli, Salmonella typhimurium, Listeria monocytogenes, Staphylococcus aureus and Candida albicans* strains were evaluated using well diffusion and disc diffusion method. The operating parameters such as disinfectant concentration, contact time and minimum inhibitory concentration (MIC) were also estimated. Moreover the influences of the studied MTUF-Ag and MTUF-Au disinfectants on the studied strains on water and wastewater samples were evaluated.

2. Material and methods

2.1. Materials

Thiourea, formaldehyde solution (solution 37% w/w), Dimethyl sulfoxide (DMSO), Ferric chloride, ferrous sulphate and silver nitrate were supplied by Sigma-Aldrich (Germany) as analytical grade reagents, while gold solution was prepared by dissolving a known weight of metallic gold in an aqua regia mixture (HNO_3: HCl, 1:3 v/v).

Preparation of the inoculum was carried out one day before each test to determine the initial counts. Stock microbial strains with 10% glycerol in −20 °C were inoculated in 10 mL tryptic soya broth (TSB) (Merck, Germany). The tubes were incubated at 37 °C for 24 h. The counts between 10^5 and 10^6 CFU mL^{-1} were chosen by 10 serial dilution using pour plate method according to American Public Health Association (APHA) [18]. Briefly 1 mL from the suitable dilution was inoculated into plate count agar (Merck, Germany) and the plates were incubated at 37 °C for 24 h. The resulting colonies were counted and expressed as colony forming unit (CFU mL^{-1}). *Bacillus subtilis* and *Candida albicans* were isolated from wastewater sample and confirmed using Biolog GEN III.

2.2. Magnetic disinfectant synthesis

2.2.1. Magnetite nanoparticles synthesis

The synthesis of Fe_3O_4 nanoparticles was already described [19,20]. Fe_3O_4 nanoparticles were synthesized by co-precipitation of ferric and ferrous salts. Firstly, iron solutions of $FeSO_4{\cdot}7H_2O$ (3.334 g) and $FeCl_3{\cdot}6H_2O$ (6.480 g) are dissolved in 150 mL of deionized water. The iron mixture is heated up to 60 ± 1 °C in a 250 mL flask being equipped with a reflux. The reaction solution is magnetically stirred under condition of N_2 gas for 60 min. Then NaOH (3 mol) solution is added to the mixture in a slowly and drop wise fashion, while the temperature is kept at 318 K until pH is reached to 12; then the reaction is continued for 300 min. The resulted particles are magnetically separated and washed repeatedly with deionized water and ethanol until the pH reaches 7. The products are then dried at 60 ± 1 °C in vacuum for 300 min.

2.2.2. Preparation of thiourea- formaldehyde polymer (MTUF)

In a 250 mL two necked round flask equipped with a stirrer and condenser, 15.2 g (0.2 mol) of thiourea and 40 mL of distilled water were mixed. The reaction flask was heated until thiourea was dissolved. After that 7.6 g of magnetite nanoparticles Fe_3O_4 was added with continuous stirring, then 15 mL of formaldehyde (37% aqueous solution, containing 0.2 mol formaldehyde) was added to the reaction flask. The pH of the reaction the medium was adjusted to approximately 3 by adding 2 mL of glacial acetic acid. The reaction was carried out for 6 h with heating at 95 ± 1 °C with stirring. The product was washed with dilute NaOH solution, distilled water, ethanol, and acetone in turn. The obtained black powder material was dried for 10 h and kept for use.

2.2.3. Loading of MTUF polymer with Ag(I) or Au(III) ions

Three grams of MTUF polymer were put in 1000 mL conical flask containing 500 mL of $AgNO_3$ aqueous solution (0.11 mol L^{-1}), the pH was 4.6. The conical flask was wrapped with black paper to exclude light. The mixture was vibrated for 2 h after remaining motionless for 20 h and was then filtrated. The separated sorbents from Ag and Au solutions were labeled MTUF-Ag and MTUF-Au, respectively. The same method was used for loading MTUF with Au(III) ions using 0.16 mol L^{-1} Au(III) solution at pH 2.2. The mount of sorbed Ag(I) or Au(III) ions was calculated the mass balance equation:

$$q_e = \frac{(C_i - C_{eq})\,V}{m} \tag{1}$$

where q (mmol g^{-1}) is the amount sorbed, C_i (mmol L^{-1}) is the initial metal ion concentration, C_{eq} (mmol L^{-1}) is the equilibrium metal ion concentration, V (mL) is the volume of metal ion solution and m (g) is the mass of the sorbent. The residual concentration of the metal ions was determined by using Agilent atomic absorption spectrophotometer model FS240 (USA).

2.3. Disinfectant characterization

2.3.1. Morphology study and structural properties

The surface morphology of MTUF-Ag and MTUF-Au disinfectants were determined using field emission scanning electron microscope FE-SEM, QUANTA FEG 250 (FEI, Japan) equipped with energy-dispersive X-ray micro analysis system (EDX) operated with an accelerating voltage of 20 kV and a working distances of 9.7 and 9.8 mm. Powder of the magnetic disinfectant was spread on the holder, The specimens were examined at different magnification power.

2.3.2. Textural properties

The textural properties of the sorbent (BET surface, pore volume and pore size) were characterized using a Quantachrome NOVA 3200e surface area and pore analyzer; data analysis was performed using NovaWin software (v11.0) (Quantachrome Instruments, Boynton Beach, FL, USA). The magnetic properties of MTUF, MTUF-Ag and MTUF-Au were measured on a vibrating-sample magnetometer (VSM) (Lake Shore 730 T, Westerville OH, USA) at room temperature.

The particle size distribution of MTUF was determined by dynamic light scattering (DLS) technique. DLS was done on the fixed scattering angle Zetasizer Nano-S system (Malvern Instruments Ltd., Malvern, UK).

2.3.3. Magnetic properties

The magnetic properties of the materials were determined using VSM (vibrating sample magnetometry) (Lake Shore, 7400-S). The VSM utilizes the Faraday's Law to measure absolute magnetic moment of a magnetic sample.

2.3.4. Toxicity assay

Toxicity tests of MTUF, MTUF-Ag MTUF-Au were measured using microtox analyzer 500 Luminometer. Microtox analyzer 500 is an in vitro test instrument using toxins sensitive bioluminescent bacteria called *Vibrio fescheri.* The toxicity results are given as effective