Journal of Hazardous Materials 168 (2009) 38–43

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Application of DNA condensation for removal of mercury ions from aqueous solutions

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ARTICLE INFO

Article history:
Received 29 October 2008
Received in revised form
26 December 2008
Accepted 28 January 2009
Available online 7 February 2009

Keywords:
DNA condensation
Mercury adsorption
Mercury ion
Water purification

ABSTRACT

DNA has a unique character that allows it to combine with various chemical substrates at the molecular level, and the DNA binding with chemical pollutants can cause serious damage to the organism. The purpose of this research was to apply the strong bonding character of DNA for the removal of mercury ions. In this research, we used DNA condensation promoted by the action of DNA condensing agents, such as cetyltrimethylammonium bromide and a commercially available combination flocculant made of zeolite, to precipitate out the DNA bound with mercury ion in an aqueous solution. When solutions of mercury at 0.02–100 ppm (parts per million) concentrations at a pH range of 2–11 were treated with double-stranded DNA followed by the condensing agent, more than 95% of the mercury ions could be removed after simple filtration or sedimentation.

1. Introduction

Mercury and its derivatives have been used for thousands of years and have afforded many benefits in human culture, but expanded use of mercury compounds and cumulated mercury wastes have caused serious damages to the environment as well as to human health. Therefore, environmental remediation for mercury pollution, that is, the removal of metallic, ionic, and organic mercury substances from environmental media, has been considered to be one of the most important aims for environmental scientists and engineers. Accordingly, various kinds of adsorbents for mercury in aqueous solutions, like synthetic polymers, surface modified materials and so on, have been investigated in the last several decades [1–24]. Some of these sorbents are suitable to use in a large-scale apparatus for the treatment of a large amount of waste solutions, but the disadvantage of such practical-scale mercury decontamination process would be to operate for a small amount of waste solution. For small laboratories of high schools and colleges, where a few amounts of mercury salts are used, small-scale treatment of waste solutions by industrial processes might be a problem due to bad cost and scale performances. It is worth searching for a high performance adsorbent which works for the treatment of a small amount of waste solutions with hazardous materials.

We focused our attention on DNA as we considered the issue of mercury adsorption. DNA is a commonly existing macromolecule in life, and it has never been considered that DNA and nucleic acids, except pathogenic viruses, are hazardous to humans or cause significant environmental damages. At the molecular level, DNA can interact with many kinds of chemical substances by means of widely known intermolecular bonding mechanisms, such as +/− charge (or dipole) attraction, hydrophobic (or hydrophilic) interaction, hydrogen bonding, and intercalation. Among such DNA-combining chemicals, there are many chemical pollutants such as heavy metal compounds and persistent organic pollutants (POPs). For example, mercury and mercury ions strongly interact with DNA, and the bond formation of DNA with mercury causes various harmful effects in humans [25–28].

Viewed from another perspective, however, such characteristic binding interactions of DNA with mercury could be useful to reduce (uptake) mercury and its compounds from various media. Although this idea has not been considered practical, there have been reported a few laboratory-scale studies in which researchers used designed materials consisting of DNA for removing mercury ions or POPs from aqueous solutions [29–32]. These reported successes have supported our work using untreated DNA, but until recently there were two major problems to be solved before DNA could be applied for environmental treatment. One was the high cost of DNA, and the other was the difficulty of separating DNA complexes with pollutants from aqueous solutions. Recently, the development of a method for accomplishing large-scale preparation of DNA from major wastes disposed of by the sea food industry resolved the first problem. Because DNA is a hydrophilic polymer with many negative charges on the surface, it is not easy to separate the DNA complex with pollutants from an aqueous colloidal

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doi:10.1016/j.jhazmat.2009.01.121

solution. The desired DNA separation was accomplished using DNA condensation which gave tightly compacted and easily precipitated DNA particles [33–37], and in this way the second problem was solved. In this paper, a report of our preliminary studies on the application of the complex formation of DNA for environmental remediation, we describe the removal of mercury ions from an aqueous solution by the combination of the complex formation of DNA with mercury ions and DNA condensation protocols.

2. Experimental

2.1. General procedures, materials, and instruments

Double-stranded high-molecular-weight DNA (L-DNA; >10,000 base pairs) and double-stranded low-molecular-weight DNA (S-DNA; 500–2000 base pairs) were obtained from Nippon Chemical Feed Co., Ltd., and Wako Pure Chemical Industry Co., Ltd., respectively, and were used as received. The concentration of DNA (C_{DNA}) as used in this paper represents the molar concentration (M) of the nucleotide pair per volume. Since an average molecular weight of nucleotides is generally considered to be 333, a DNA solution of C_{DNA} = 100 μM corresponds to 67 mg/L, that is equal to 67 ppm. Artificial zeolite powder, Circulash®, prepared from fly ash of coal incineration [38,39] and the combination flocculant, named Zeflock®, made of zeolite, both of which are available in industrial scales, were obtained from Chubu Electric Power Co., Inc., Japan. Cetyltrimethylammonium bromide (CTAB), a 1.00 g/L standard solution of mercury, dithizone (diphenylthiocarbazone), analytical grade carbon tetrachloride, and humic acid were purchased from Wako Pure Chemical Industry Co., Ltd. Water using in this research was purified using a Millipore Corp. Milli-Q Labo®. UV spectra were taken on a JASCO® V-550 spectrometer.

2.2. Determination of mercury ions (C_{Hg}) by dithizone method

To a mixed solution of 1.0 M sulfuric acid (4.0 mL) and 6.0 M acetic acid (0.40 mL) were added a mixture of a sample solution (1.0 mL) and a 0.002% solution of dithizone in carbon tetrachloride (5.0 mL) at 20 °C. The mixture was vigorously shaken for 1 min, and the bottom layer (1.0 mL) was subjected to UV analysis. Absorbance at 485 nm was measured, and concentrations of mercury (C_{Hg}) were calculated based on a calibration curve. If necessary, the sample solutions were diluted or concentrated to appropriate concentrations before subjecting them to the UV analysis.

2.3. General procedure for the removal of mercury ions, DNA condensation using CTAB

To water (0.50 mL) were added 500 μM solution of mercury (0.022 mL) and 5.0 mM solution of L-DNA (0.11 mL), and the volume of the solution was adjusted to 0.90 mL by the addition of water, and the mixed solution was stirred gently at 20 °C for 15 min. Next, a 5.0 mM solution of CTAB (0.11 mL) was added, and the total volume was adjusted to 1.1 mL by the addition of water. These operations gave the sample solution, the final concentrations of which are as follows: C_{Hg} = 2.0 ppm (parts per million) = 10 μM, C_{DNA} = 500 μM, and C_{CTAB} = 500 mM. After 30 min, this solution was subjected to centrifugal separation (15,000 rpm, 30 min), and the top layer (1.0 mL) was subjected to an analysis of mercury ions.

2.4. General procedure for the removal of mercury ions, DNA condensation using the combination flocculant

A sample solution (1.1 mL) of C_{Hg} = 2.0 ppm and L-DNA (C_{DNA} = 500 μM) was stirred gently at 20 °C for 15 min. To this was added the combination flocculant (Zeflock®, 10 mg), and, after 15 min, the mixture was separated by filtration through a filter paper. The resulting clear solution filtrate (1.0 mL) was subjected to an analysis of mercury ions.

3. Results and discussion

3.1. Mercury removal by the action of the DNA condensing agent: control experiments without DNA

A solution of mercury (C_{Hg} = 20 ppm) was stirred with 500 μM concentration of CTAB at room temperature (20 °C) for 30 min. After high-speed centrifugal separation (15,000 rpm, 30 min), a further decrease of mercury ion concentration was not detected based on the UV analysis. On the contrary, it is known that zeolite has ion exchange ability and can absorb mercury ions in an aqueous solution [6,9,10,38,39]. When the same solution was treated with 10 mg of the combination flocculant (Zeflock®) followed by centrifugal separation (3000 rpm, 3 min), the concentration (C_{Hg}) decreased from 20 to 14 ppm. The efficiency increased with increasing the amount of the combination flocculant, and 92% mercury removal efficiency was accomplished in the presence of 50 mg of Zeflock®.

3.2. Mercury removal using DNA condensation generated by CTAB

An aqueous solution of high-molecular-weight DNA (L-DNA; >10,000 base pairs) was treated with CTAB at room temperature, and the DNA concentration was monitored using UV absorption at 285 nm after the high-speed centrifugal separation. An equimolar amount of CTAB to the amount of nucleosides was necessary to complete DNA separation from the colloidal solution, and the following mercury removal experiments were carried out under the condition $C_{CTAB} = C_{DNA}$. The results of mercury removal using L-DNA or S-DNA (500–2,000 base pairs) and CTAB ($C_{CTAB} = C_{Hg}$) under similar conditions are summarized in Table 1. When solutions of mercury (C_{Hg} = 2.0 ppm) were treated with 100 μM and 500 μM of L-DNA at room temperature for 15 min followed by 100 μM and 500 μM concentrations, respectively, of CTAB, 68% and 97% amounts of mercury were removed from the resulting clear solutions (entries 3 and 6 in Table 1), respectively. The 15-min reaction period was long enough to complete the complex formation of DNA with mercury, and the removal efficiency using L-DNA was 73% in the case of 24-h reaction under the conditions C_{Hg} = 2.0 ppm and C_{DNA} = 100 μM (entry 4). In the mercury solution (C_{Hg} = 2.0 ppm), the removal efficiencies promoted by various concentrations of L-DNA (10–500 μM) are given in entries 1–3, 5 and 6, and comparative results employing S-DNA at the same mercury concentration (C_{Hg} = 2.0 ppm) are given in entries 7–11. It is obvious by these

Table 1
Removal efficiency of Hg^{2+} using S- or L-DNA and CTAB.[a].

Entry	DNA		Hg^{2+} removal efficiency/%
	Type	C_{DNA}/μM	
1	L-DNA	10	11
2	L-DNA	40	18
3	L-DNA	100	68
4	L-DNA	100	73[b]
5	L-DNA	200	90
6	L-DNA	500	97
7	S-DNA	10	15
8	S-DNA	40	18
9	S-DNA	100	71
10	S-DNA	200	89
11	S-DNA	500	94

[a] Unless otherwise stated, these entries were carried out under the following conditions: C_{Hg} = 2.0 ppm for 15-min and C_{CTAB} = 500 μM.
[b] The reaction period of Hg^{2+} and DNA was 24 h.