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Organic arsenic removal from an aqueous solution by iron oxide-coated fungal biomass: An analysis of factors influencing adsorption

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Abstract

A two-level seven-factor (2^{7-2}) fractional factorial design analysis was conducted to examine the parameters influencing dimethylarsinic acid (DMA) removal from an aqueous solution using iron oxide-coated *A. niger* biomass. The factors examined were the concentration of DMA in solution, the mass of the adsorbent, the solution temperature, the Ca^{2+} ions in solution, the Fe^{2+} ions in solution, the SO_4^{2-} ions in solution, and the Cl^- ions in solution. The magnitude of the influence of the factors considered on DMA removal was observed in the order: presence of Ca^{2+} ions in solution > the DMA concentration > solution temperature > presence of SO_4^{2-} in solution > presence of Fe^{2+} in solution > the mass of adsorbent > the presence of Cl^- in solution.

Keywords: Dimethylarsinic acid; Organic arsenic; Factorial design; *A. niger*; Adsorption; Iron oxide-coated fungal biomass

1. Introduction

Arsenic a toxic element is found in natural waters in both inorganic and organic forms. Inorganic arsenic species are the dominant form found in most of the groundwater and surface water sources. Information on the removal of inorganic arsenic from drinking water is widely available [1,2]. The organic arsenic species are the methylated form of inorganic arsenic. Dimethylarsinic acid (DMA) is one of the major metabolites formed in humans and rodents exposed to arsenite {As(III)} and arsenate {As(V)} [3]. The anthropogenic input of organic arsenic in the environment may be due to the use of methylarsonic and dimethylarsinic acids in agricultural industry as herbicides and pesticides [4–6]. The other source may be the methylation of inorganic arsenic present in the environment by microorganisms. The biomethylation of inorganic arsenic was thought to be a detoxification pathway [6]. The degree of toxicity of arsenic compounds was earlier reported as follows: arsine > As(III) > As(V) > methylated arsenicals [7]. However, methylation of arsenic might be a toxification rather than a detoxification pathway [8,9]. Dimethylarsinic acid (DMA) was found to cause several genotoxic or clastogenic effects, DNA damage, chromosomal aberrations [8,10]. Longtime exposure to DMA was found to cause cancer in humans and rodents [3].

Inorganic arsenic is the predominant arsenic species found in most of the groundwaters. A recent report suggested that quite a number of surface water sources in Canada and in the United States of America were found to be contaminated with organic arsenic. DMA was the dominant organic arsenic species in the oxidizing environment [11]. A number of sub-arctic lakes in the Yellowknife area, Northwest Territories, Canada were found to be contaminated with elevated levels of arsenic; 10% of which was found to be methylated form of arsenic [12]. Similarly, a number of lakes and estuaries in California were reported to be contaminated with methylated form of arsenic (1–59% of total As) and DMA was found to be the dominant species among the methylated form [13]. Methylated form of arsenic consisted of 53–60% of the total dissolved arsenic in river and estuarine waters analyzed in the southwest Spain [14].

Recent information on the high degree of toxicity of methylated arsenicals and the abundance of organic arsenic species in the fresh water environment make it necessary to direct research on processes for its removal. Kuhlmeir and Sherwood [15] examined activated carbon, activated alumina, ferrous sulphide and a strongly basic ion exchange resin to remove mixed inorganic and organic arsenic. Ferrous sulphide was found to be the most effective. DMA removal by iron filing was found to be quite low compared to the removal of monomethylarsinic

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acid (MMA) [16]. DMA adsorption by goethite and ferrihydrite was reported to be low compared to other arsenic species [17]. DMA removal was reported to be in the following order: ion exchange resin > iron oxide-coated sand (IOCS)-2 > manganese greensand > IOCS-1 [18]. The adsorption of MMA was found to be 100% at pH 7.5 while DMA removal was only 65% at pH 5.5 by nanocrystalline titanium oxide [19]. Only limited information is available in the literature on the removal of organic arsenic species [5]. The objective of the present study was to examine the removal of DMA by iron oxide-coated *A. niger* biomass (IOCB) from water and various factors that influence the removal process.

2. Materials and methods

2.1. Preparation of standards and reagents

Distilled deionized water (VWR International, USA) was used in the preparation of standards, modifier, and wash solutions {for a sample dispenser of graphite furnace atomic absorption spectroscopy (GFAAS)}. Deionized water obtained from a local supplier was used in the preparation of all sample solutions. DMA stock solution (1000 mg l^{-1}) was prepared by dissolving 0.4266 g of cacodylic acid ($C_2H_6AsO_2Na$; Sigma Chemical, Ontario) in deionized water to make a solution volume of 200 ml. The stock solution was preserved with 1% trace metal grade nitric acid. The required working solution was prepared daily from the stock solution.

2.2. Preparation of adsorbent

2.2.1. A. niger

A. niger strain (ATCC #11414) was routinely maintained on potato dextrose agar plates. *A niger* was grown by shake flask method in aerobic conditions. The growth medium (pH 5) comprised a homogeneous mixture of the following (g l^{-1}): dextrose (20); peptone (10); NaCl (0.2), $CaCl_2{\cdot}2H_2O$ (0.1); KCl (0.1); K_2HPO_4 (0.5); $NaHCO_3$ (0.05); $MgSO_4$ (0.25); $FeSO_4{\cdot}7H_2O$ (0.0005). One hundred millilitres of the medium thus prepared was transferred into a series of 250 ml conical flasks; the flasks were covered with aluminum foil and subsequently autoclaved at a temperature of 121 °C and a pressure of 124 kPa for 15 min. The solution was allowed to cool down to room temperature (21 ± 1 °C); subsequently inoculated by *A. niger* strain, covered with the glass wool to facilitate aeration and was shaken at a speed of 135 rpm in an orbital shaker (Lab-Line Instruments, Inc., USA). The biomass was harvested after 5 days of cultivation. The biomass was separated from the growth medium by filtering through 160 μm sieve. The biomass was washed thoroughly with a generous amount of deionized water until the filtrate showed crystal clear color. The washed biomass was autoclaved at 121 °C and a pressure of 124 kPa for 30 min, allowed to cool down, washed again with deionized water, and dried in an oven at 60–70 °C for approximately 36 h. The dried biomass was powdered into a fine size using a commercial coffee grinder. The biomass passing through 400 μm sieve was coated with iron oxide (see Section 2.2.2).

2.2.2. Iron oxide-coated biomass

A solution of 80 ml of 2 M $Fe(NO_3)_3{\cdot}9H_2O$ was prepared and 1 ml of 10 M NaOH was added to this solution and mixed thoroughly. The autoclaved biomass powder (20 g) was taken in a porcelain pot. The mixture of iron oxide and NaOH solution was poured into the porcelain pot and homogenized; kept in an oven at 80 °C for about 3 h. After 3 h the oven temperature was raised to 110 °C for another 24 h. The coated biomass powder was found to be sticky and was crushed with mortar and pestle. The crushed biomass powder passing through a 400 μm sieve was used in biosorption experiments. The iron oxide-coated biomass powder used in the experiments was found to have a surface area of 2 m^2 g^{-1}, a density of 0.7188 g cm^{-3}, and an iron content of 254 mg g^{-1}. As(III) and As(V) removal capacities of IOCB were found to be generally similar to those of other iron oxide-coated materials but much less than those shown by activated carbon and activated alumina [20]. The difference may be due to the fact that initial arsenic concentration of 100 μg l^{-1} was used for IOCB studies [20] where as in the case of activated carbon and activated alumina studies, the initial arsenic concentration was 100 mg l^{-1} [21,22].

2.3. pH and equilibrium study

pH of the solution is one of the influential parameters in adsorption but the optimum pH is guided by the DMA chemistry and needed a detailed study instead of a factorial effect. So, a detailed study was conducted to find the optimum pH and the equilibrium time. A volume of 100 ml of the DMA solution of a concentration of 100 μg As l^{-1} was contacted with 0.1 g of the biomass in a series of conical flasks at pH 5–8 and samples were collected at an interval of 1 h. The DMA solutions and the adsorbent (IOCB) were mixed thoroughly at a speed of 175 rpm in a platform shaker (model: Classic C2), manufactured by New Brunswick Scientific, New Jersey, USA. pH was kept constant during each run using 0.1 M *tris* buffer (Invitrogen Life Technologies, USA) for pH 6 and above. The initial pH of the 0.1 M *tris* buffer was 10 and it was adjusted to desired pH by adding 0.5 M HNO_3. For pH 5, a mixture of acetic acid and acetate was used [23]. All experiments were conducted in duplicate and average values were used in data analysis.

2.4. Factorial design of experiments

A two-level seven-factor (2^{7-2}) fractional factorial experiment was designed to observe the effect of various parameters influencing DMA removal by iron oxide-coated *A. niger* biomass. The factorial experiments were conducted at the optimum pH and equilibrium time. The seven factors considered were—(1) *A*: concentration of solution [low 50 μg l^{-1} and high 500 μg l^{-1}], (2) *B*: mass of the adsorbent [low 0.02 g and high 0.12 g], (3) *C*: temperature [low 5 °C and high 30 °C], (4) *D*: Ca^{2+} ions in solution [low 100 mg l^{-1} and high 1000 mg l^{-1}], (5) *E*: Fe^{2+} ions in solution [low 100 mg l^{-1} and high 1000 mg l^{-1}], (6) *F*: $SO_4{}^{2-}$ ions in solution [low 100 mg l^{-1} and high 1000 mg l^{-1}] and (7) *G*: Cl^- ions in solution [low 100 mg l^{-1} and high 1000 mg l^{-1}]. Ca^{2+}, Fe^{2+}, $SO_4{}^{2-}$ and Cl^- are com-