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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-

Table 1
Design matrix, response (%DMA removal) and statistical parameters

Run order	*A*	*B*	*C*	*D*	*E*	*F*	*G*	Obs. (%)	Pred. (%)	Std. dev. (residual)	Residual (%)	Stand. res. (%)
1	−1	1	−1	−1	−1	−1	−1	65.8	65.7	0.7	0.1	0.1
2	1	1	1	−1	1	−1	−1	66.7	67.8	0.7	−1.1	−1.6
3	−1	1	−1	−1	−1	−1	−1	65.6	65.7	0.7	−0.1	−0.1
4	−1	−1	−1	−1	−1	1	1	76.6	76.9	0.7	−0.3	−0.4
5	1	1	1	1	1	1	1	61.0	60.9	0.7	0.1	0.1
6	−1	1	1	1	−1	−1	1	75.8	75.5	0.7	0.3	0.4
7	−1	−1	1	1	1	1	1	62.2	61.7	0.7	0.5	0.7
8	1	−1	1	1	1	−1	−1	47.0	47.3	0.7	−0.3	−0.4
9	1	−1	−1	1	1	1	−1	49.7	49.5	0.7	0.3	0.4
10	1	−1	−1	1	−1	1	1	57.4	56.3	0.7	1.1	1.6
11	1	−1	1	−1	1	1	1	74.1	73.7	0.7	0.4	0.6
12	−1	1	1	−1	1	1	1	78.8	79.8	0.7	−1.0	−1.4
13	1	1	−1	1	1	−1	1	44.3	43.2	0.7	1.1	1.6
14	1	1	1	−1	1	−1	−1	68.8	67.8	0.7	1.0	1.4
15	1	−1	1	1	−1	−1	1	55.3	52.9	0.7	2.4	3.4
16	−1	1	1	1	1	−1	−1	62.6	61.0	0.7	1.6	2.3
17	1	−1	−1	1	−1	1	1	55.2	56.3	0.7	−1.1	−1.6
18	−1	−1	1	−1	1	−1	−1	67.8	67.6	0.7	0.2	0.3
19	−1	−1	1	−1	−1	−1	1	74.8	75.3	0.7	−0.5	−0.7
20	1	1	1	−1	−1	−1	1	72.1	72.5	0.7	−0.4	−0.6
21	1	1	−1	−1	−1	1	1	73.3	73.5	0.7	−0.2	−0.3
22	−1	1	1	−1	−1	1	−1	77.6	77.0	0.7	0.6	0.9
23	−1	−1	−1	1	1	−1	1	52.4	54.7	0.7	−2.3	−3.3
24	1	1	−1	−1	1	1	−1	68.3	68.2	0.7	0.1	0.1
25	1	−1	1	−1	−1	1	−1	73.6	73.9	0.7	−0.3	−0.4
26	1	−1	−1	1	1	1	−1	49.2	49.5	0.7	−0.3	−0.4
27	1	−1	1	1	−1	−1	1	50.4	52.9	0.7	−2.5	−3.6
28	1	1	1	1	−1	1	−1	62.8	63.3	0.7	−0.5	−0.7
29	1	1	1	1	−1	1	−1	63.7	63.2	0.7	0.5	0.7
30	1	−1	−1	−1	1	−1	1	58.6	60.6	0.7	−2.0	−2.9
31	−1	−1	1	−1	1	−1	−1	67.4	67.6	0.7	−0.2	−0.3
32	−1	1	1	−1	1	1	1	80.8	79.8	0.7	1.0	1.4
33	−1	1	−1	1	1	1	−1	59.8	58.4	0.7	1.4	2.0
34	−1	1	−1	1	−1	1	1	60.8	60.7	0.7	0.1	0.1
35	−1	1	−1	1	−1	1	1	60.6	60.7	0.7	−0.1	−0.1
36	−1	−1	−1	−1	−1	1	1	77.2	76.9	0.7	0.3	0.4
37	−1	1	1	−1	−1	1	−1	76.4	77.0	0.7	−0.6	−0.9
38	1	1	1	1	1	1	1	60.7	60.9	0.7	−0.2	−0.3
39	−1	1	−1	1	1	1	−1	57.0	58.4	0.7	−1.4	−2.0
40	−1	−1	1	1	−1	1	−1	66.4	66.4	0.7	0.0	0.0
41	−1	−1	−1	1	1	−1	1	57.0	54.7	0.7	2.3	3.3
42	1	−1	−1	−1	−1	−1	−1	60.3	60.5	0.7	−0.2	−0.3
43	−1	1	−1	−1	1	−1	1	68.2	68.1	0.7	0.1	0.1
44	1	1	−1	1	−1	−1	−1	55.8	56.1	0.7	−0.3	−0.4
45	1	−1	−1	−1	−1	−1	−1	60.6	60.4	0.7	0.2	0.3
46	−1	−1	1	1	−1	1	−1	66.4	66.4	0.7	0.0	0.0
47	1	−1	1	−1	−1	1	−1	74.2	73.9	0.7	0.3	0.4
48	−1	−1	1	−1	−1	−1	1	75.8	75.3	0.7	0.5	0.7
49	−1	1	1	1	1	−1	−1	59.4	61.0	0.7	−1.6	−2.3
50	−1	1	1	1	−1	−1	1	75.2	75.5	0.7	−0.3	−0.4
51	−1	−1	1	1	1	1	1	61.2	61.7	0.7	−0.5	−0.7
52	1	1	−1	1	1	−1	1	42.1	43.2	0.7	−1.1	−1.6
53	1	1	1	−1	−1	−1	1	72.8	72.5	0.7	0.3	0.4
54	−1	−1	−1	−1	1	1	−1	71.6	70.8	0.7	0.8	1.1
55	−1	−1	−1	−1	1	1	−1	70.0	70.8	0.7	−0.8	−1.1
56	1	1	−1	−1	−1	1	1	73.6	73.5	0.7	0.1	0.1
57	−1	−1	−1	1	−1	−1	−1	58.6	59.7	0.7	−1.1	−1.6
58	1	1	−1	−1	1	1	−1	68.1	68.2	0.7	−0.1	−0.1
59	1	−1	1	1	1	−1	−1	47.5	47.3	0.7	0.2	0.3
60	1	−1	−1	−1	1	−1	1	62.5	60.6	0.7	1.9	2.7
61	1	−1	1	−1	1	1	1	73.3	73.7	0.7	−0.4	−0.6
62	1	1	−1	1	−1	−1	−1	56.3	56.1	0.7	0.2	0.3
63	−1	−1	−1	1	−1	−1	−1	60.8	59.7	0.7	1.1	1.6
64	−1	1	−1	−1	1	−1	1	68.0	68.1	0.7	−0.1	−0.1

Notes:

(1) *A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}).
(2) The number 1 represents high value of factor and −1 represents low value of factor.
(3) Obs.: observed value of percentage DMA removal (%); Pred.: predicted value of the DMA removal (%); Std. dev. (residual): standard deviation of residual; Std. res.: standardized residual.

mon ions present in most of the water sources. These ions were found to influence As(III) and As(V) removals using IOCB in earlier studies (data not shown). Thus, Ca^{2+}, Fe^{2+}, SO_4^{2-} and Cl^- were selected to observe the influence of these ions on DMA adsorption. The low value of factor is represented by −1 and high value of factor is represented by 1 in the design matrix (Table 1).

A solution volume of 100 ml was taken in a conical flask of 250 ml capacity for each run and the temperature was controlled using an air bath. The adsorbent and the DMA solution were contacted for 7 h at a rotational speed of 175 rpm in a platform shaker with different combinations of factors (Table 1). Each experiment in this design was duplicated. The samples were filtered through 0.4 μm filter (Osmonic Inc.) and were analyzed for arsenic using a graphite furnace atomic absorption spectrometer (GFAAS). The factorial design data were analyzed using *MINITAB* [24].

2.5. Arsenic analysis

Samples were preserved using 0.1% trace metal grade nitric acid. Arsenic was analyzed using Varian type SpectraAA-600 Zeeman GFAAS equipped with GTA 100-graphite tube atomizer and programmable sample dispenser. Pyrolytically coated graphite tubes (notched partition, Varian Canada Inc., Toronto) were used in the experiment, and argon gas (ultra-high purity 99.995%, Praxair Products Inc., Ontario) was used to sheath the atomizer and to purge internally. Arsenic hallow cathode lamp (Varian Canada Inc., Ontario) was used at a wavelength of 193.7 nm with a slit width of 0.5 nm. A mixture of palladium (II) nitrate solution (1500 mg l^{-1}) and magnesium nitrate (1000 mg l^{-1}) was used as a matrix modifier. An external reference standard from National Water Research Institute, Environment Canada, Ontario, was used to verify the calibration.

3. Results and discussion

Fig. 1 shows the effect of pH on DMA removal by iron oxide-coated *A. niger* biomass. The optimum pH and equilibrium time were found to be 6.0 and 7 h, respectively. This optimum pH value coincides with the pK_a value of 6.14 where more than 50% of the DMA is in the anionic form. DMA was found to be better removed by natural zeolite compared to iron hydroxides [25]. The surface charges at various pH values are as follows: +17 mV (pH 2.0), −16 mV (pH 3.0), −25 mV (pH 4.0), −31 mV (pH 5.0), −33.5 mV (pH 6.0), −31.5 mV (pH 7.0), −35 mV (pH 8.0) and −32 mV (pH 9.0). The surface charge of the iron oxide-coated biomass was almost the same in the pH range of 6–9 [26]. In an earlier investigation of As(III) and As(V) by the iron oxide-coated biomass [26], almost 95% of the As(V) and 75% of the As(III) were removed whereas the DMA removal by the same adsorbent was found to be only approximately 50% or below (this study). It is likely that the mechanisms of removal of inorganic forms of arsenic and methylated arsenic are different.

The design matrix of the factors, and observed and predicted values of the response in terms of the percent DMA are presented

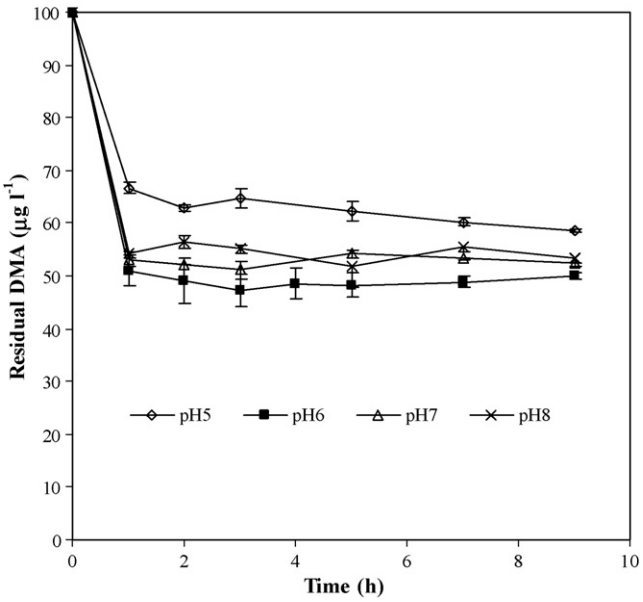

Fig. 1. Residual DMA using iron oxide-coated *A. niger* biomass [initial DMA concentration, 100 μg l^{-1}; adsorbent dosage, 1 g l^{-1}].

in Table 1. The experimental data (response in percentage DMA removal) were evaluated using software *MINITAB*. A statistical analysis (normal probability plot) of the data in terms of the standardized residual was also conducted. A linear regression model was fitted for the experimental data using the least square technique using *MINITAB*. The magnitude and the direction of the effect of the factors as well as their coefficients of regression and statistical significance of the experimental data for DMA removal are provided in Table 2.

The net effect is a difference between the responses of two levels (high and low level) of factors and the regression coefficients are obtained by dividing the net effects by two. The standardized effects are obtained by dividing the regression coefficients by standard error coefficient [27]. The combined effect of DMA concentration and temperature (p-value = 0.356), DMA concentration and Fe^{2+} concentration (p-value = 0.620), mass of adsorbent and Fe^{2+} concentration (p-value = 0.888), mass of adsorbent and Cl^- concentration (p-value = 0.963), solution temperature and Ca^{2+} concentration (p-value = 0.198), solution temperature and Fe^{2+} concentration (p-value = 0.829) and solution temperature and SO_4^{2-} concentration (p-value = 0.104) were found to be not significant at 95% confidence level. Details of the estimated effect and the significance of the data fit are provided in Table 2. The significance of the data is judged by its p-value being closer to zero (0.00). For a 95% confidence level the p-value should be 0.05.

3.1. Main effect plot

A main effect is a plot of the mean response values at each level of a design parameter [27]. It indicates the relative strength of effects of various factors. The sign of the main effect indicates the direction of the effect. Fig. 2 shows the main effect

Table 2
Estimated effects and coefficients for DMA removal (% coded units)

Term	Net effect	Regression coefficient	Standard error coeff.	Standardized effect (T)	p-Value
Constant		64.3	0.165	389.5	0.000
A	−6.2	−3.1	0.165	−18.9	0.000
B	2.7	1.4	0.165	8.3	0.000
C	5.9	2.9	0.165	17.7	0.000
D	−12.8	−6.4	0.165	−38.7	0.000
E	−4.6	−2.3	0.165	−13.8	0.000
F	5.2	2.6	0.165	15.6	0.000
G	2.1	1.0	0.165	6.3	0.000
AB	1.1	0.6	0.165	3.3	0.002
AC	−0.3	−0.2	0.165	−0.9	0.356*
AD	−2.4	−1.2	0.165	−7.2	0.000
AE	−0.2	−0.1	0.165	−0.5	0.620*
AF	2.2	1.1	0.165	6.5	0.000
AG	−1.2	−0.6	0.165	−3.6	0.001
BC	2.1	1.1	0.165	6.4	0.000
BD	1.1	0.5	0.165	3.3	0.002
BE	−0.05	−0.02	0.165	−0.1	0.888*
BF	−1.2	−0.6	0.165	−3.6	0.001
BG	0.02	0.01	0.165	0.05	0.963*
CD	0.4	0.2	0.165	1.3	0.198*
CE	−0.07	−0.04	0.165	−0.2	0.829*
CF	−0.6	−0.3	0.165	−1.7	0.104*
CG	1.4	0.7	0.165	4.3	0.000
DE	−2.2	−1.1	0.165	−6.7	0.000
DF	−1.8	−0.9	0.165	−5.5	0.000
DG	−1.5	−0.8	0.165	−4.6	0.000
ACE	1.6	0.8	0.165	4.7	0.000
ACG	−0.4	−0.2	0.165	−1.2	0.253*
BCE	−0.03	−0.02	0.165	−0.1	0.933*
BCG	1.4	0.7	0.165	4.2	0.000
CDE	0.05	0.02	0.165	0.1	0.888*
CDG	1.3	0.6	0.165	3.9	0.000

Notes:

(1) *A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}).
(2) Standard error coeff.: standard error coefficient.

* Data not significant at 95% confidence level (p-value > 0.05).

plots (average of the duplicate data) for DMA removal (%). This figure shows that the mass of the adsorbent, solution temperature, presence of $SO_4{}^{2-}$ and Cl^- had a positive effect on DMA removal. The concentration of DMA, presence of Ca^{2+} and Fe^{2+} had a negative effect. The magnitude of the factorial effect on DMA removal is provided in Table 2. The presence of Ca^{2+} and Fe^{2+} ions in solution on inorganic arsenic {As(III) and As(V)} removal was found to be positive (removal of arsenic increased, data not shown). The present study showed that the presence of these ions in solution decreased DMA removal using iron oxide-coated biomass. Similarly, the presence of $SO_4{}^{2-}$ and Cl^- ions had no significant effect on inorganic arsenic {As(III) and As(V)} removal while presence of these ions was found to have a negative effect on DMA removal (present study). This indicated a clear difference in the effect of these ions on the adsorption of As(III)/As(V) and DMA by iron oxide-coated biomass. The mechanism behind the effect of these ions on DMA removal is not evident.

3.2. Interaction effect plot

An interaction plot is a graphical tool which plots the mean response of two factors at all possible combinations of their settings. If the lines are non-parallel, it is an indication of interaction between the two factors [27]. Parallel lines indicate that there is no interaction between two factors. The interaction effects of the factors for DMA removal are presented in Fig. 3 based on an average of the duplicate data. Fig. 3 shows that the combined effect of DMA concentration and presence of Ca^{2+} ion, DMA concentration and presence of $SO_4{}^{2-}$ ion, DMA concentration and presence of Cl^- ion, mass of adsorbent and solution temperature, mass of adsorbent and presence of Ca^{2+} ion in solution, mass of adsorbent and presence of $SO_4{}^{2-}$ ion in solution, solution temperature and the presence of Cl^- ion in solution, presence of Ca^{2+} and Fe^{2+} ions, presence of Ca^{2+} and $SO_4{}^{2-}$ ions, presence of Ca^{2+} and Cl^- ions and presence of Fe^{2+} and $SO_4{}^{2-}$ ions had strong interaction for DMA removal

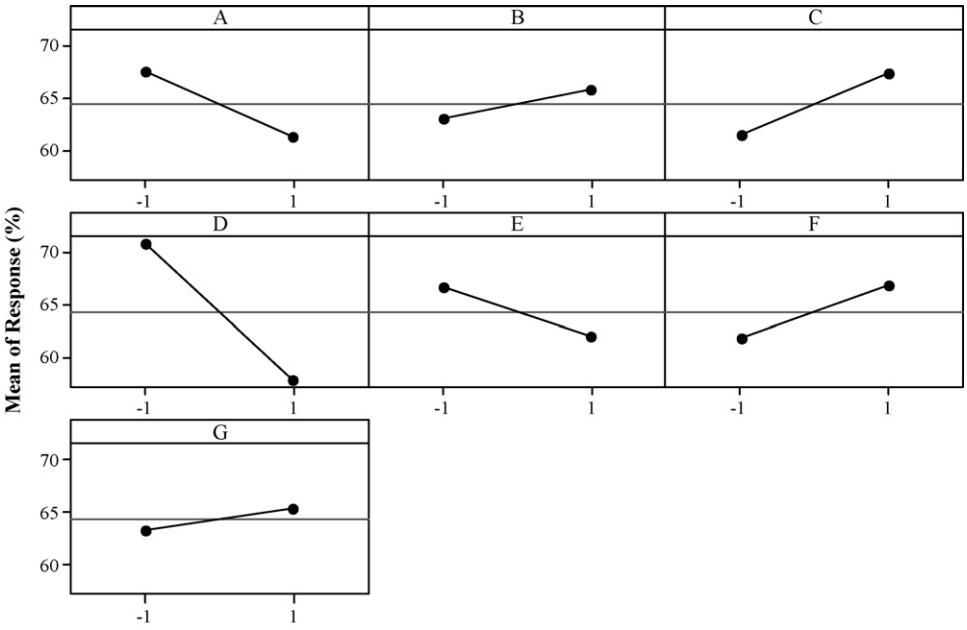

Fig. 2. Main effect plot for DMA removal (%) [*A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1})].

(the lines are converging—see Fig. 3). There was no interaction effect of other combination of factors (the lines are more or less parallel—see Fig. 3).

3.3. Pareto plot of effect

The pareto plot displays the absolute values of the effect of factors which are important in the design of the experiment for optimization. It draws a reference line to indicate that the factors which extend past this line are potentially important [27]. Fig. 4 shows the significant factors for DMA removal. The factorial influence (magnitude) in the adsorption of DMA by iron oxide-coated biomass was found to be in the following 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

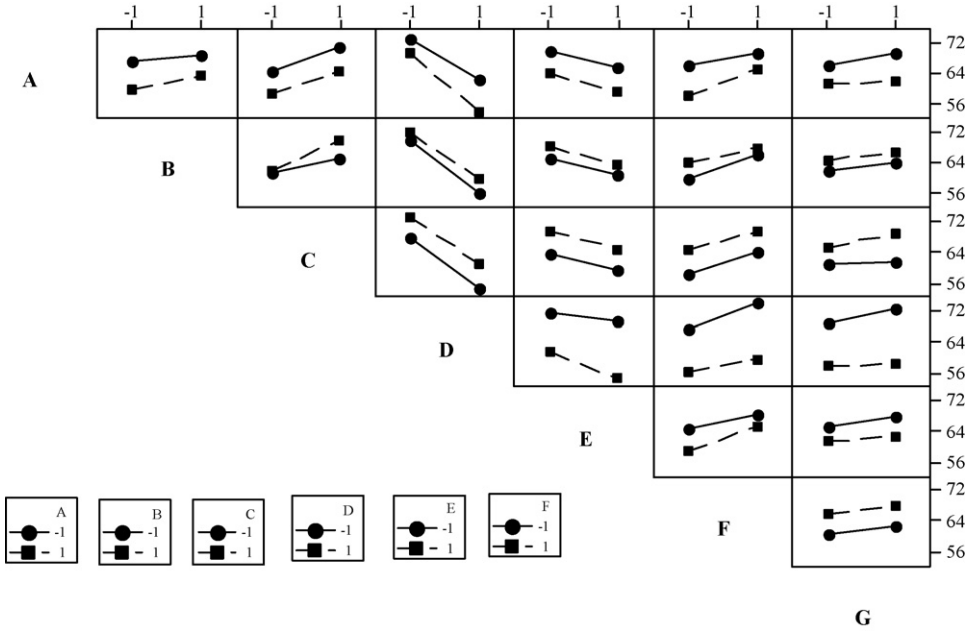

Fig. 3. Interaction effects plot for DMA removal (*X*-axis: factors and *Y*-axis: %DMA removal) [*A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1})].

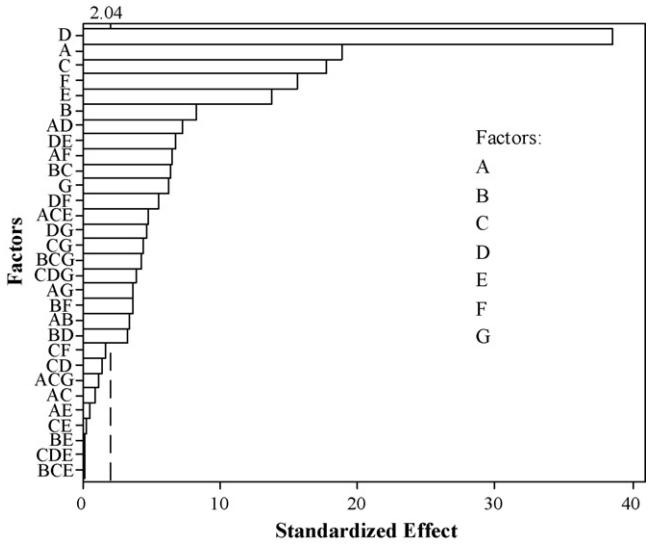

Fig. 4. Pareto chart of the standardized effects for DMA removal, $\alpha = 0.05$ [*A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1})].

solution. The combined effect of factors was also found to be significant. The relative importance of each of the factors and the combination of factors are shown in pareto plot (Fig. 4) for DMA removal.

3.4. Normal probability plot of residuals

One of the assumptions of the statistical analysis of the data from the experiment is that the data are from a normal distribution. The normality of the data can be checked by plotting a normal probability plot (NPP) of the residuals; if the points on the plot fall fairly close to a straight line, then the data are normally distributed [27]. The residual is the difference between the observed value and the predicted value (or fitted value) from the regression analysis. Fig. 5 provides the normal probability plot of the residuals for DMA removal. It shows that the data are normally distributed.

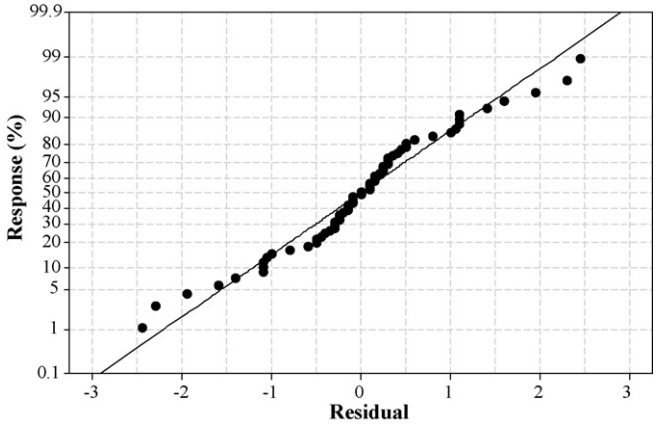

Fig. 5. Normal probability plot of the residuals [response is %DMA removal].

3.5. Prediction of regression model

A model is proposed based on the regression coefficients (for coded units) for DMA removal. Table 2 provides the regression constants and the coefficients for various factors taken into consideration. The regression model proposed for DMA removal is as follows:

$$\begin{aligned}\text{DMA removal (\%)} &= 64.3 - 3.1A + 1.4B + 2.9C - 6.4D - 2.3E \\ &+2.6F + G + 0.6AB - 1.2AD + 1.1AF - 0.6AG \\ &+1.1BC + 0.5BD - 0.6BF + 0.7CG - 1.1DE - 0.9DF \\ &-0.8DG + 0.8ACE + 0.7BCG + 0.6CDG \end{aligned} \quad (1)$$

where *A*: DMA concentration (low = 50 μg l^{-1} and high = 500 μg l^{-1}), *B*: mass of adsorbent (low = 0.02 g and high = 0.12 g), *C*: temperature (low = 5 °C and high = 30 °C), *D*: Ca^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *E*: Fe^{2+} concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}), *F*: $SO_4{}^{2-}$ concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}) and *G*: Cl^- concentration (low = 100 mg l^{-1} and high = 1000 mg l^{-1}).

The applicable range of all the parameters of the regression model is as follows: DMA concentration = 50–500 μg l^{-1}, mass of adsorbent = 0.02–0.12 g, temperature = 5–30 °C, Ca^{2+} concentration = 100–1000 mg l^{-1}, Fe^{2+} concentration = 100–1000 mg l^{-1}, $SO_4{}^{2-}$ concentration = 100–1000 mg l^{-1} and Cl^- concentration = 100–1000 mg l^{-1}.

4. Conclusions

The following conclusions were drawn based on the experimental results:

1. DMA can be removed from water using iron oxide-coated *A. niger* biomass.
2. The factors influencing the adsorption of DMA by iron oxide-coated biomass were found to be in the following order (based on the magnitude): 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.

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