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Arsenic removal from groundwater by pretreated waste tea fungal biomass

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Abstract

Arsenic contamination in ground water poses a serious threat on human health. The tea fungus, a waste produced during black tea fermentation has been examined for its capacity to sequester the metal ions from ground water samples. Autoclaved tea fungal mat and autoclaving followed by FeCl₃ pretreated tea fungal mat were exploited for removal of As(III), As(V) and Fe(II) from ground water sample collected from Kolkata, West Bengal, India. The biosorption rate tends to increase with the increase in contact time and adsorbent dosage. FeCl₃ pretreated and autoclaved fungal mats removed 100% of As(III) and Fe(II) after 30 min contact time and 77% of As(V) after 90 min contact time. The optimum adsorbent dosage was 1.0 g/50 mL of water sample. The results revealed that the FeCl₃ pretreated fungal mat could be used as an effective biosorbent for As(III) and As(V); autoclaved fungal mat for Fe(II) removal from ground water sample.

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Keywords: Tea fungus; Biosorption; Arsenic; Iron; Isotherm

1. Introduction

Environmental pollution by toxic metals arises as a result of numerous activities including industrial and agriculture wastes and sewage disposal. Metals that are discharged as solutes or particles tend to be non-biodegradable and can lead to biohazardous effects. Groundwater contamination by iron and arsenic in West Bengal and Bangladesh has been well documented (Navarro et al., 1993; Biswas et al., 1998; Thompson et al., 1999). The problem of arsenic contamination in groundwater poses a serious threat in these areas because ground water is the main source of drinking water (Pal et al., 2002). Long term exposures to arsenic levels

can result in permanent and severe damage to human health. Arsenic toxicity causes skin lesions, rhagades, and damage mucous membranes, digestive, respiratory, circulatory and nervous system and more over it is associated with skin, liver and lung cancers (Wang et al., 2001). Biswas et al. (1998) reported that arsenic exposure leads to black foot disease, diffused and spotted melanosis, diffused and spotted keratosis, nonpitting oedema, Bowen's disease and gangrene.

The chemical processes that exist are not economical for treating a large volume of dilute metal concentrations. At this juncture adsorption using microbial biomass has emerged as an option for developing economic and eco-friendly wastewater treatment processes. The potential of using nonviable fungal biomass as biosorbents for heavy metals has received considerable attention since this represents a substantial by-product from several fermentation processes and produces less sludge (Volesky et al., 1993). This technology has an

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advantage of low operating cost, is effective in treating dilute solutions and generates minimum amounts of effluent. The microbial biomass functions as an ion-exchanger by virtue of various reactive groups available on the cell surface such as carboxyl, amine, phosphate, sulfhydryl, sulfate and hydroxyl (Vasudevan et al., 2001). The present study was carried out to investigate the metal biosorptive nature of the tea fungus (a symbiont of two yeasts viz., *Pichia* sp. NRRL (Northern Regional Research Laboratory) Y-4810 and *Zygosaccharomyces* sp. NRRL Y-4882 and a bacterium *Acetobacter* sp. NRRL B-2357), which is used in black tea fermentation. The influence of agitation time and adsorbent dosage for metal recovery by the fungal cells was optimized with a view of adopting it for ground water treatment.

2. Methods

2.1. Tea fungus

The tea fungus (a symbiont of two yeasts viz., *Pichia* sp. NRRL Y-4810 and *Zygosaccharomyces* sp. NRRL Y-4882 and a bacterium *Acetobacter* sp. NRRL B-2357) was obtained from the Kolli hills of Tamil Nadu. The fungus was grown in tea medium (Hesseltine, 1965). To 1 L of water, two tea spoons (10.50 g) of tea powder was mixed and boiled, after which 100 g of sucrose was added and boiled for 5 min. The tea extract was filtered and used as a medium. The fungal mat (FM) was inoculated in tea medium and incubated at 30 ± 2 °C statically for ten days. New fungal mat was produced over the mother culture. The rapid extensive production of fungal mat was used as adsorbents for metal recovery.

2.2. Biosorbent

The tea FM was washed with an adequate amount of deionized water until free from the media components. The washed fungal mat was autoclaved at 15 psi for 15 min. A portion of the autoclaved fungal mat was immersed in FeCl_3 solution (15 mg/L) for 120 min. These two modified FMs were then tested for its efficacy to remove As and Fe from ground water. To determine the adsorption capacity of the FMs, 1.0 g of the biosorbent was added to 50 mL of sample and agitated in a rotary shaker at 160 rpm for predetermined time intervals at 30 °C. The adsorbate and biosorbent were separated by centrifugation at 10,000 rpm for 20 min. The remaining metals in the adsorbate were analysed. No adsorption on to the container walls was observed. The rate constant and the Freundlich isotherm were studied using the previously generated equilibrium data.

2.3. Ground water

The ground water sample was collected from Ram Nagar, Old Hotkola, Kolkata, West Bengal, India in a pre-cleaned 5 L plastic container. The metal contents were estimated spectrophotometrically (UV-1601, Shimadzu, Japan) using Phenanthroline for Fe(II) (APHA, 1995), ammonium molybdate for As(III) (Bassett et al., 1994) and ammonium molybdate and rhodamine B for As(V) (Palanivelu and Ramakrishna, 1990).

2.4. Adsorption studies

The efficiency of autoclaved and FeCl_3 pretreated fungal mats for the adsorption of Fe(II), As(III) and As(V) were performed by batch mode studies. To 50 mL of ground water sample 1.0 g of biosorbent was added and incubated in an orbital shaker (160 rpm) at 30 °C for predetermined time intervals. The equilibrium time for the adsorption of three metals was determined. After determining the equilibrium time, the optimum dosage was determined by agitating different concentrations of adsorbent (0, 0.5, 1.0, 1.50, 2.0 and 2.50 g/50 mL) with water sample for the corresponding equilibrium time. Since the pH of the sample was near neutral (pH 7.20) and used for drinking purposes, the effect of pH on metal adsorption was not studied. After adsorption studies, the adsorbents (autoclaved and FeCl_3 treated fungal mats) were gently washed with distilled water to remove the unadsorbed metal ions. The adsorbents were then resuspended in flask containing 50 mL of 0.1 N NaOH and agitated for different time intervals to fix the equilibrium time for maximum desorption of metal ions. After optimizing the equilibrium time, the freshly prepared metal laden adsorbent was resuspended in 50 mL of different concentrations (0.1–0.5 N) NaOH. The metal ion desorbed in to the solution was separated by centrifugation and quantified.

2.5. Statistical analysis

The values presented in the study were means of five replicates. The SPSS (Statistical Package for Social Sciences) 9.05 version was employed to determine the standard deviation and standard error.

3. Results and discussion

As(III) and As(V) content of the sample were estimated to be 1.3 and 0.9 mg/L, respectively. But the permissible level of total arsenic in drinking water prescribed by WHO is 0.01 mg/L, which is far below the sample level. Biswas et al. (1998) has reported the occurrence of various health problems to people consuming bore well water containing 0.05–1.0 mg/L of

arsenic. Consequently the arsenic level in the sample taken for study is very high. For Fe(II) the permissible limit is 0.3 mg/L, whereby the same concentration was noted in the sample. Hence there should be minimal possibility for any potential health hazard by Fe(II) in the sample. Since the sample contains all the three metals, the removal efficacy of the biosorbent towards Fe(II) was also tested.

Metal uptake increased with an increase in contact time but remained constant after equilibrium time period. Equilibrium time varied with metals due to the difference in initial metal concentration and affinity of biosorbent for a particular metal ion. In the groundwater sample, Fe(II) was completely removed in 30 min by autoclaved FM and in 45 min by FeCl₃ treated FM. For As(III) the equilibrium times were 45 min and 60 min for autoclaved and FeCl₃ treated FM respectively. For As(V) the equilibrium time was 75 min for autoclaved and FeCl₃ pretreated fungal mats. The experiment was carried out using different adsorbent dosages until equilibrium time (Fig. 1a and b). It was noted that the dosage level of 1 g/50 mL sample removed 100% of Fe(II) and As(III); 76% of As(V).

The Freundlich isotherm was applied for the adsorption of metal ions by modified fungal mats.

$$X/m = k_f C_e^{1/n} \quad (1)$$

Rearranging the Eq. (1) gives,

$$\log X/m = \log k_f + 1/n \log C_e \quad (2)$$

where C_e is the equilibrium concentration (mg/L), X/m is the amount of metal adsorbed at equilibrium time (mg/g) and k_f and n are Freundlich constants (n gives an indication of the favourability and k_f [mg/g (l/mg)^{*n*}], the capacity of the adsorbent) (Pollards et al., 1991).

Linear plots of $\log C_e$ vs $\log X/m$ show that the adsorption of metal ions onto fungal mats follows the Freundlich isotherm model (Fig. 3). It also indicates that the average energy of adsorption decreases with increasing adsorption density. Similar results were reported by Senthilkumar (1998). Values of n and k_f were calculated from the slope and intercept (Table 1).

The rate constant of adsorption is determined from the following first order rate expression

$$\log(q_e - q) = \log q_e - k_{ad}/2.303t \quad (3)$$

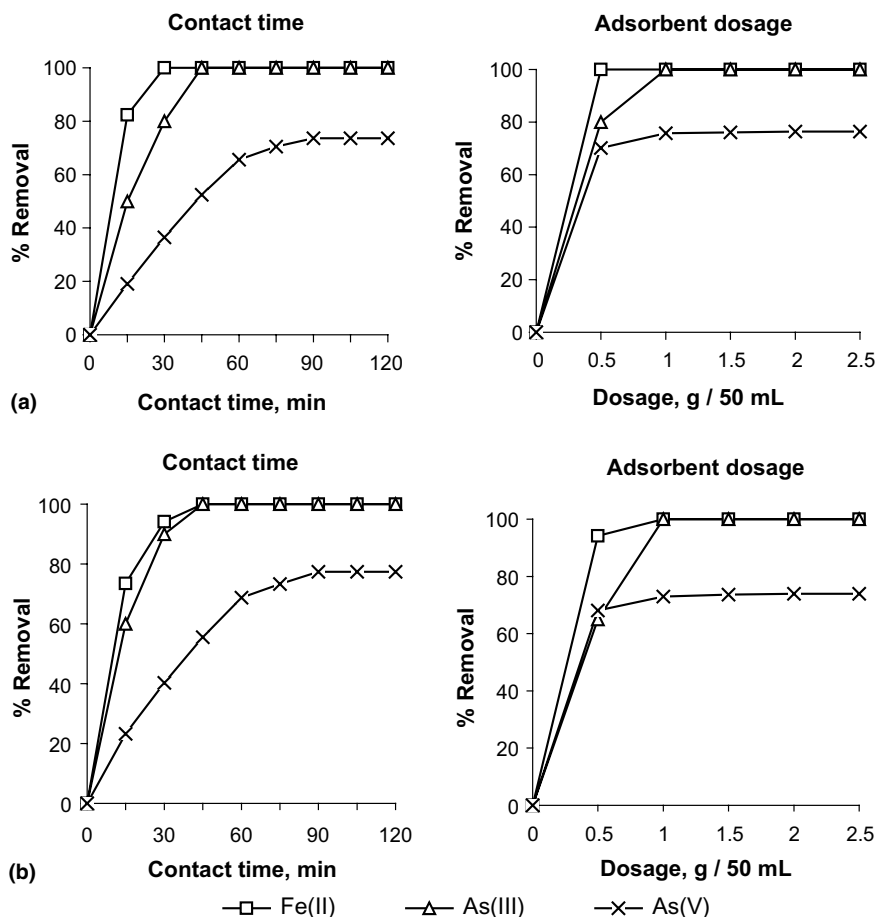


Fig. 1. Optimum conditions for the removal of Fe(II), As(III) and As(V) from groundwater by (a) autoclaved biomass, (b) FeCl₃ pretreated biomass.

where q and q_e are the amounts of metal adsorbed (mg/g) at time, t (min) and at equilibrium, respectively. In addition k_{ad} is the rate constant for adsorption (l/min).

The straight line plots of $\log (q_e - q)$ vs t for different metal ion concentration indicate the applicability of the above equation (Fig. 2). Values of k_{ad} were calculated from the slope of the linear plots and are given in Table 1. The rate constant was higher at lower concentrations. These are comparable with the k_{ad} values reported by Oscarson et al. (1983) and Senthilkumar (1998). Desorption studies revealed that 70% of As(III) and 55% of As(V) can be desorbed from the tea FM using 0.5 N NaOH. After treatment, the treated and untreated groundwater samples were plated on malt agar plates to check for presence of tea fungal colonies in the treated sample. However, no fungal growth was detected. This is due to the use of autoclaved-FeCl₃ treated FM as a biosorbent in which the mat was killed. Therefore

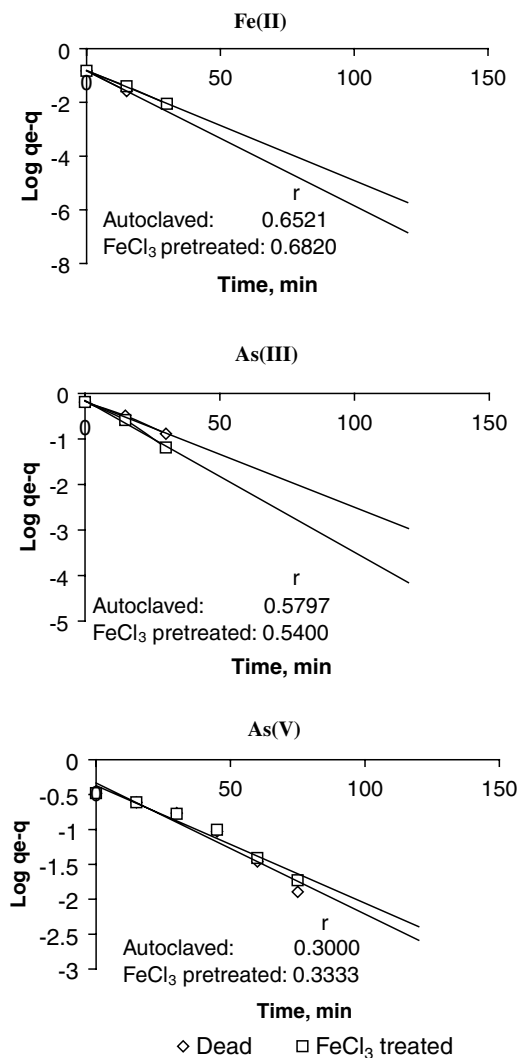


Fig. 2. Lagergren plot for the removal of Fe(II), As(III) and As(V) from ground water.

Table 1
Isotherm constants

Metal ions	Freundlich		Lagergren
	n	$k_f, \text{mg/g(L/mg)}^n$	$k_{ad}, 1/\text{min} \times 10^{-3}$
<i>Fe(II)</i>			
Nonviable	1.281	2.777	-0.116
FeCl ₃ treated	0.888	2.651	-0.094
<i>As(III)</i>			
Nonviable	1.166	1.109	-0.580
FeCl ₃ treated	1.720	5.404	-0.078
<i>As(V)</i>			
Nonviable	0.263	4.951	-0.043
FeCl ₃ treated	1.104	10.261	-0.039

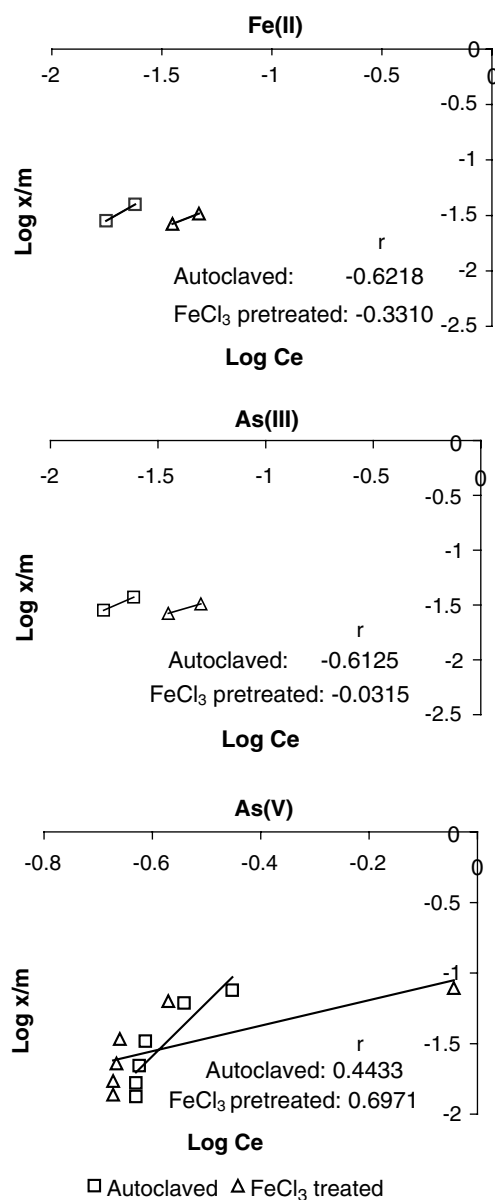


Fig. 3. Freundlich plot for removal of Fe(II), As(III) and As(V) from water.

using the autoclaved and FeCl₃ treated FM ground-water treatment would be considered a safer and more effective process.

In general, all biological materials have a high affinity for toxic metals and radionuclides. Specific metal-binding proteins and peptides were found in all microbial groups and extensive studies have been carried out with yeasts (Vasudevan et al., 2001; Volesky and May-Phillips, 1995). The metal adsorption capacity of the microorganisms may be due to metallothioneins, a small cysteine-rich polypeptide that can bind essential and non-essential metals, and metal α -glutamyl peptides (phytochelatins), short peptides involved in heavy metal detoxification in algae, plants, some fungi and yeasts (Gadd and White, 1993).

The results revealed that the FeCl₃ treated FM and autoclaved fungal mat are efficient in removing As(III), As(V) and Fe(II) from ground water sample respectively. FeCl₃ treated FM works better because iron has an affinity towards arsenic in forming arsenic-iron oxides. Also Welch et al. (2000), Pierce and Moore (1980), Singh et al. (1998), Hodi et al. (1995), Zouboulis et al. (1993), Thirunavukkarasu et al. (2003), Senthilkumar (1998) had reported that iron has more affinity towards arsenic. Hence FeCl₃ pretreated fungal mat work better than nontreated mat. In batch mode studies, the adsorption was dependent on contact time, initial metal ion concentration and biosorbent dosage. The adsorption of metal ions followed the Freundlich isotherm model. The rate constant data would be useful for the designing of water treatment plants. The tea fungal mat produced during black tea fermentation was exploited for metal removal. Moreover, the fungal mat is easily biodegradable. After adsorption studies, the metals can be desorbed by resuspending the tea FM in flask containing 50 mL of NaOH (0.1–0.5 N) and agitated for different time intervals to fix the equilibrium time for maximum desorption of metal ions. Later the tea FM can be separated from the NaOH solution. So, after adsorption process, the metals can be desorbed from the mat and the mat can be easily degraded which is not possible in chemical adsorbents.

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