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R. Selvakumar[a][b]; S. Kavitha[c]; M. Sathishkumar[d]; V. Jayavignesh[e]; K. Swaminathan[a][e]
[a] Department of Microbial Biotechnology, School of Biotechnology and Genetic Engineering, Bharathiar University, Coimbatore, India [b] PSG Institute of Advanced Studies, Coimbatore, India [c] Department of Biotechnology, Karunya School of Biotechnology, Karunya University, Coimbatore, India [d] Department of Food Science and Technology, College of Agriculture, Chonbuk National University, Chonju, South Korea [e] Environmental Management and Biotechnology Division, DRDO-BU Centre for Life Sciences, Bharathiar University, Coimbatore, India

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Liquid Phase Separation of As(V) from Aqueous Solution Using Pretreated *Paecilomyces variotii* Biomass

R. Selvakumar,[1,2] **S. Kavitha,**[3] **M. Sathishkumar,**[4]
V. Jayavignesh,[5] **and K. Swaminathan**[1,5]
[1]*Department of Microbial Biotechnology, School of Biotechnology and Genetic Engineering, Bharathiar University, Coimbatore, India*
[2]*PSG Institute of Advanced Studies, Coimbatore, India*
[3]*Department of Biotechnology, Karunya School of Biotechnology, Karunya University, Coimbatore, India*
[4]*Department of Food Science and Technology, College of Agriculture, Chonbuk National University, Chonju, South Korea*
[5]*Environmental Management and Biotechnology Division, DRDO-BU Centre for Life Sciences, Bharathiar University, Coimbatore, India*

Biosorption of As(V) was carried out using *Paecilomyces variotii* biomass in batch and column mode experiments. Various pretreatments like autoclaving (APV), iron doping (FePV), and PVP K25 doping (PVPPV) of biomass were carried out to increase and compare the adsorption efficiency of As(V) onto the biomass. At maximum concentration of 2.5 mg/L of As(V), the removal was observed to be 58.4, 51.29, and 47.7% with FePV, PVPPV, and APV biomass respectively. PVPPV required comparatively less time (135 min) to attain equilibrium when compared to other adsorbents (165 min). FePV showed higher As(V) adsorption capacity (Q_o) of 1.563 mg/L in batch mode. The batch mode data were analysed using Langmuir and Freundlich isotherms and first order and pseudo second-order kinetic models. The maximum removal was observed at pH 2 with FePV. In column mode experiments, the change in the flow rate and the bed volume affected the adsorption capacity of the adsorbent. FePV showed maximum adsorption of As(V) in column mode experiments also. The desorption experiments revealed that the adsorbents could be reused so that it can be a cost-effective adsorbent for As(V) removal from drinking water.

Keywords arsenic; batch and column mode; desorption; kinetics; *Paecilomyces variotii*

INTRODUCTION

Ground water contamination by arsenic has been a major problem in the northeastern parts of India like West Bengal, Assam, and in a few pockets of Orissa and in many parts of the world. Continuous consumption of arsenic contaminated water has lead to hyperkeratosis, skin cancers, and pigmentation of the palm. Due to these clinical manifestations caused by the arsenic contaminated drinking water, the World Health Organization (WHO) has recommended 0.01 mg/L as maximum contaminant level (MCL) in drinking water (1). Considering its clinical significance, extensive studies have been carried out for As(III) and As(V) removal using various methods like precipitation (2), ion exchange (3), and adsorption (4). Scientific evidence suggested that adsorption is an efficient method to control the mobility and bioavailability of arsenic when compared to other methods. Adsorption of arsenic has been tried with various adsorbents like activated carbon (4), sulphate modified iron oxide coated sand (5), orange juice residues (6), iron oxide loaded alginate beads (1), $FeSO_4$ doped coir pith carbon (7), nanoscale zerovalent iron (8), and polyvinyl pyrrolidone K25 coated cassava peel carbon (9). Amidst these adsorbents, plant and fungal biomass has been viewed as a potential biosorbents for arsenic removal (10,11). Micro fungi offer low-cost adsorbents for heavy metal removal from aqueous solution (12). Fungal biomass produced as a by-product from the fermentation and pharmaceutical industries has been used as a promising alternative to biosorbents to adsorb metallic ions having possible application in water and wastewater treatment (13). During the last decades, the use of biosorbents has become interesting due to high adsorption capacities and regenerability of the sorbent (14,15). This technology has an advantage of low operating cost, is effective in treating dilute solutions and generates minimum amounts of the effluent. The microbial biomass functions as an ion exchanger by virtue of various reactive groups available on the cell surface such as carboxyl,

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Address correspondence to Dr. R. Selvakumar, Lecturer in Nanobiotechnology, PSG Institute of Advanced Studies, Coimbatore-641004, India. Tel.: +91 9944920032. E-mail: selvabiotech@gmail.com

amine, phosphate, sulfhydryl, sulfate, and hydroxyl groups (16,17).

Since the adsorption of metal ions takes place mainly on the fungal biomass surface, increasing the sorption active sites on the surface by pretreatment would be an effective approach to enhance the adsorption capacity. The effect of physical pretreatment processes like heat, autoclaving, freeze drying, or boiling and chemical pretreatment processes like acid, alkali, and polymers enhances the metal sorption capacity of the biosorbents (18,19). Loukidou et al. (18) demonstrated the increased removal of arsenate using hexadecyl-trimethylammonium bromide and dodecylamine surfactant pretreated *Penicillium chrysogenum* biomass. The bioremediation of As(III) and As(V) containing aqueous solutions and groundwater by live and pretreated biomass of *Aspergillus fumigatus* was studied by Sathishkumar et al. (11,20). It was reported that pretreatment with iron compounds increased the adsorption capacity of the adsorbent. Similar results have been obtained by using non-viable fungal biomass of *A.niger* and tea fungus coated with iron compounds (17,21). Seki et al. (22) employed methylated yeast strains for the removal of arsenic and chromium. Deng and Ting (13) removed As(V) and As(III) from water with polyethylene imine modified *Penicillium chrysogenum* biomass. These reports indicate that pretreatment of fungal biomass has the potential to increase the adsorption capacity of the adsorbent.

Polymer composites play an important role in today's adsorption technology. Arsenic removal has been tried with metal loaded polymers, strong cation exchange resins, macroporous polymers, chelating resins, or biopolymer gels (23). Polyvinylpyrrolidone (PVP) (Fig. 1), an organic polymer has been used as an intermediate sizing material to increase the adhesion property of carbon fiber to vinyl ester matrix. The interdiffusion of PVP had been a key factor in improving the adhesion property of the carbon fiber. PVP is currently used in the adsorption of different polyphenols from apple juices and the mechanism of adsorption mainly relies on carbonyl adsorption sites of PVP (24). PVP is used in the pharma industry for preparing blends of different drug especially in controlled drug release delivery systems (25). Poly 4-vinyl pridine has been used as a coating agent on silica gel for chromium removal (26). Similar reports are available for uranyl sulphate recovery using poly 4-vinyl pridine cross-linked silica gel (27).

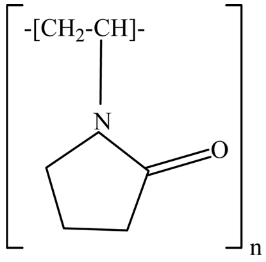

FIG. 1. Structure of PVP.

In the present study, *Paecilomyces variotii* biomass has been analyzed for its efficiency to remove As(V) from aqueous solution. Adsorption studies have been carried out with native (NPV), autoclaved (APV), iron pretreated (FePV), and PVP K25 pretreated *Paecilomyces variotii* (PVPPV) biomass for As(V) removal in batch and column mode experiments. The properties of the PVP K25 used in this study have been reported in our earlier paper (9). The experimental data were fitted to the Langmuir and Freundlich isotherm followed by first-order and pseudo second-order kinetic models. BDST plot was used to analyse the data obtained during the column mode studies. The effect of pH towards arsenic adsorption was analyzed. The reusability of biosorbents were studied after desorption. This is the first study for comparing the effect of various pretreatments like moist heat (autoclaving), metal doping, and polymer doping onto fungal biomass for As(V) removal from aqueous solution.

MATERIALS AND METHODS

Biosorbent

One milliliter (10^6 spores) of *Paecilomyces variotii* (isolated from soil and deposited at MAC's culture collection centre, Agarkar Research Institute, Pune, India) spore suspension was inoculated into Czapex dox broth in 250 mL Erlenmeyer flasks and incubated at room temperature (27°C ± 3°C) for 5 days in an orbiatary shaker at 125 rpm. At the end of the 5th day, the mycelial pellets were separated by filtration using Whatmann No.1 filter paper. Biomass was then washed with generous amount of deionised water till it was free from media components. The washed native biomass (NPV) was used as an adsorbent after squeezing out excess water with the use of filter paper. The biomass was subjected to various pretreatments to test its efficiency to adsorb As(V). The pretreatment of NPV was carried out as mentioned below.

Autoclaved biomass (APV): The NPV was autoclaved for 30 min at 121°C at 124 kpa.

Iron modified biomass (FePV): The modification of APV with $FeCl_3$ was carried out according to Selvakumar et al. (7). In brief, a known quantity of biomass was added to 0.1 M $FeCl_3$ and agitated on a rotary shaker at 125 rpm for 24 h at room temperature. The resultant biomass was washed several times until the filtrate was free from metal ions. Residual iron in the washed filtrate was estimated using 1,10-phenanthrolein method.

PVP modified biomass (PVPPV): The modification of APV with PVP was carried out according to Loukidou et al. (18). In brief, a known quantity of autoclaved biomass was treated with 100 mL of 0.1 M PVP K25 solution in a rotary shaker at 125 rpm for 48 h at room temperature. The polymer doped biosorbent was washed generously with distilled water, air dried and used for further studies.

Spectrophotometric Determination of As(V)

As(V) estimation was carried out according to Lenoble et al. (28). The methodology of As(V) estimation has been already reported in our previous paper (9). In brief, a known quantity of ammonium molybdate was mixed with 9 M sulphuric acid making upto 100 mL and named as "Reagent A." Ten percent ascorbic acid was prepared daily before use. As(V) estimation was carried out using a known quantity of ascorbic acid solution and 2 mL reagent A and successively added to a 40 mL sample aliquot in a 50 mL volumetric flask. The volume was completed with deionized water. A blank was prepared according to the same procedure using the appropriate volume of deionised water. The minimum detection limit of As (V) determination by this method is 20 µg/L. The analysis was carried out in 1 cm quartz cells with a Shimadzu 1800 UV visible spectrophotometer.

Batch Mode Studies

Batch biosorption experiments were carried out by agitating 1.0 g of the biosorbent with 50 mL of As(V) solution of desired concentration and pH at 125 rpm at room temperature. The concentration of As(V) in the solution was analyzed according to Lenoble et al. (28). The samples were withdrawn at predetermined time intervals, the supernatant solution was separated from the adsorbent by centrifugation and the residual As(V) concentration was analyzed. The pH of the aqueous solution was adjusted by adding a small amount of 0.1 M HCl and NaOH solutions and 2-[4-(2-hydroxyethyl)-1-piperazinyl} ethanesulfonic acid (HEPES) was used as a buffer reagent (6). The concentration ranging from 0.5–2.5 mg/L of As(V) was used to determine the effect of concentration. The initial concentration of 2.0 mg/L and 1 g/50 mL of biosorbents was used to determine the pH effect. Langmuir and Freundlich isotherm was employed along with pseudo first-order and second order kinetic models to study the adsorption equilibrium.

Column Mode Studies

The efficiency of pretreated biomass showing maximum As(V) adsorption was studied in column mode. 5 cm bed height of pretreated fungal biomass was packed in a glass column (30 × 4.2 cm) and the solution containing 2 mg/L of As(V) was passed through the column after adjusting its pH to the optimum value. A varying flow rate of 2.5, 5.0, 7.5 and 10 mL/min was used in the experiment. Fractions were collected at regular time intervals and analyzed for As(V) concentration. The study was repeated with best flow rate and different As(V) concentrations (0.5, 1.0, 1.5, 2.0, and 2.5 mg/L). Data obtained were used to plot Bed-depth-service-time model (BDST) curves. BDST model proposed by Hutchins (29) is a simple method to correlate the service time, t, with process variables in fixed bed adsorber.

$$C_o t = N_o H/\mu - 1/k_a \times \ln(C_o/C_t - 1) \qquad (1)$$

where t is service time to breakthrough; min, N_o is the adsorption capacity; mg/L, of the adsorbent bed, C_o is the influent concentration; mg/L, μ is linear flow rate; cm/min, H is the depth of bed; cm, k_a is the rate constant of adsorption; L/mg/min, C_t is the effluent concentration at time t; mg/L.

Desorption Studies

Desorption studies were carried out with adsorbate laden FePV obtained from batch and column process. The mycelium was washed gently with distilled water to remove unadsorbed As(V). After washing, the spent adsorbent was mixed with 50 mL of distilled water at different pH values (2–11) adjusting the pH of the solution using 0.1 to 0.6 N HCl and NaOH and agitated at equilibrium time. The desorbed As(V) was estimated spectrophotometrically. The experiments were carried out in duplicate and mean values were taken for calculation.

RESULTS AND DISCUSSION

Effect of Contact Time and Initial Adsorbate Concentration

Equilibrium time and adsorbate uptake are important considerations for economical treatment of water and wastewater and vary with adsorbates and adsorbents (30). In the present study, adsorption of As(V) increased with time and at a certain point, it reached a constant value where no more adsorbate was removed from the solution and the system attained a state of dynamic equilibrium. The equilibrium time increased with the increase in the initial concentration of the adsorbates studied. At maximum concentration of 2.5 mg/L, PVPPV required less time (135 min) to attain saturation when compared to other adsorbents (165 min) used in this study. The increase in the initial adsorbate concentration from 0.5 to 2.5 mg/L, decreased the adsorption of As(V) onto the adsorbents. The iron doping increased the percent removal when compared to other pretreatments. At As(V) concentration of 2.5 mg/L, pretreatment of autoclaved biomass with $FeCl_3$ showed increased As(V) removal (58.4%) when compared to live (42.3%), autoclaved (47.1%) and PVP (51.29%) pretreatment. Although PVP pretreatment was not as effective as the $FeCl_3$ pretreatment, it was more effective than NPV and slightly higher than APV. The increased rapid phase of adsorption in the initial stages may be due to the availability of more number of adsorption/vacant sites at the initial stage of adsorption. Because of the availability of such vacant sites, there exists an increased concentration gradient between the adsorbate in the solution and the adsorbate in the adsorbent (11). This increase in As(V) adsorption by $FeCl_3$ doped adsorbents can be explained through ligand exchange mechanism. Cells when subjected to death or autoclaving can suffer rupture and denaturation of the cell wall, allowing free access of chemicals used for pretreatment into cell wall binding sites thereby increasing the possibility of arsenic adsorption (19,32). When this autoclaved fungal biomass is treated with $FeCl_3$, the process of crosslinking of iron with various negatively charged surface sites in the cell wall occurs. Ghimire et al. (33) reported that the iron group mainly crosslinks with the phosphate group of the biomass through cation exchange mechanism. During the cation exchange mediated adsorption, substitution of water molecule or hydroxyl ion within the octahedral coordination sphere of the loaded Fe occurs with As(V). The electrostatic binding of soluble arsenic to the external surface of the insoluble metal hydroxide may also be a possible reason for efficient arsenic removal by $FeCl_3$ pretreated adsorbent (34). The possible mechanism for $FeCl_3$ pretreatment onto adsorbents may be as follows

$$\text{X-Fe(OH)}_2^+ + \text{H}_3\text{AsO}_4^- \longrightarrow [(\text{X-FeO})_2\text{-AsO(OH)}]^- + \text{H}_3\text{O} + \text{H}_2\text{O} \tag{2}$$

$$\text{X-Fe(OH)}_2^+ + \text{H}_3\text{AsO}_4^- \longrightarrow [(\text{X-Fe-O})_2\text{-AsO(OH)}]^- + \text{H}_3\text{O} \tag{3}$$

The product of this reaction is ferric arsenate complex which has a very low solubility profile (35). The possible reason for increased adsorption by PVPPV might be due to the presence of a lone pair of electrons on protonated N-center (Fig. 1) containing +NH at which As(V) anion could bind with the electrostatic force of attraction. The decrease in the arsenic uptake, especially at increased concentrations, could be attributed to the interionic repulsion between different types of arsenic oxyanion and hydroxyl ions present on the surface of the adsorbent (31). The results were in accordance with previous findings (11,17,20).

Effect of pH

The extent of the adsorption of ions onto the adsorbent is governed strongly by the pH of the solution. The pH of the aqueous solution is an important variable which controls the adsorption process by affecting the nature of the surface charge of the adsorbent at water interface and the speciation of the adsorbate in the water (36,37). Experiments were performed to investigate the effect of initial pH on adsorption of As(V) at fixed concentrations of 2 mg/L with 120 min of contact time and 1 g/50 mL of adsorbent dosage. The experimental results revealed that the pH in the range of 2–5 favored As(V) adsorption onto the adsorbents. The As(V) adsorption onto adsorbents was high at pH 2 where after it gradually decreased till pH 5. After pH 5, the adsorption of As(V) reduced drastically until pH 9.0. The maximum adsorption at pH 2 was found to be 83.54% with FePV followed by PVPPV (76.3%) and APV (67.2%) (Fig. 2). The native biomass removed only 57.3% of As(V). Above pH 2.0, As(V) is present in anionic

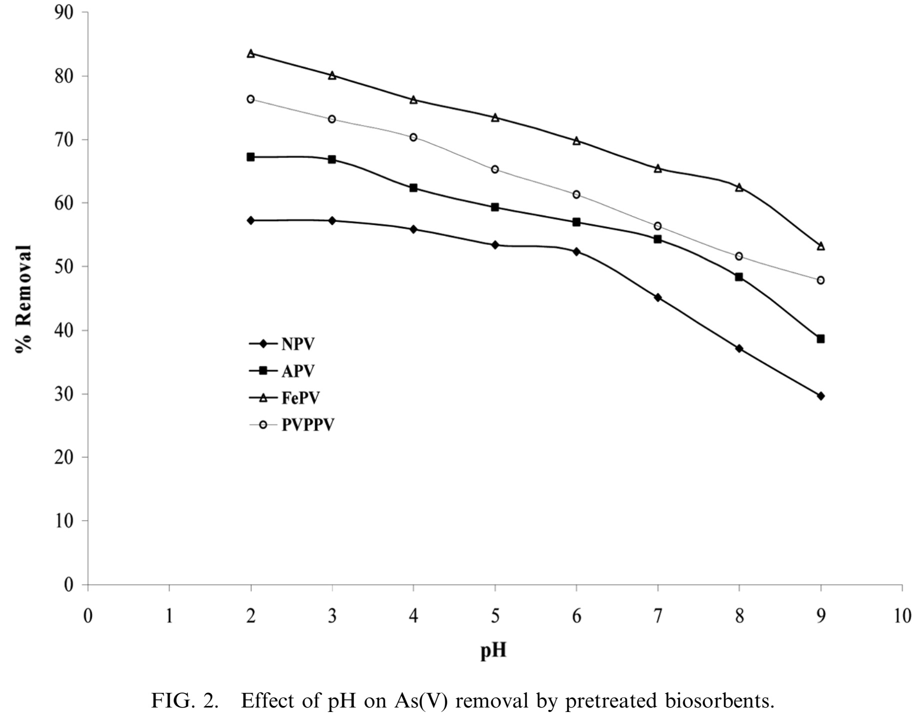

FIG. 2. Effect of pH on As(V) removal by pretreated biosorbents.

forms and therefore, it can be effectively removed by the iron hydroxides, which at this pH range are present as cationic monomers ($Fe(OH)_2^+$). Hence higher adsorption of As(V) could be related to the strong electrostatic attraction between positively charged surface sites and the predominant As(V) species $H_2AsO_4^-$. Decrease of As(V) adsorption above pH 7 could be due to electrostatic repulsion between the negatively charged As(V) species, $HAsO_4^{2-}$, and the adsorbent surface, which had crossed the point of zero charge and become negatively charged (38). Thus, decrease in As(V) adsorption with increase in pH can be attributed to the repulsion of anion on a negatively charged surface.

Adsorption Isotherms

Adsorption isotherms, Langmuir and Freundlich, were used to describe the adsorption data for a range of adsorbate concentrations. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites (39). The model assumes uniform energies onto the surface and no transmigration of adsorbate in the plane of surface (40).

The isotherm is represented by the following equation.

$$q_e = Q_o b C_e / 1 + b C_e \quad (4)$$

where C_e is the equilibrium concentration (mg adsorbate per liter of solution) and q_e is the amount adsorbed (mg adsorbate per g of adsorbent) at equilibrium. The constant Q_o signifies the monolayer adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). A linear expression for the Langmuir equation is

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (5)$$

Plots of q_e vs C_e showed agreement of experimental data with Langmuir plots for As(V) removal using fungal biomass. Langmuir constants, Q_o and b were determined from the slope and intercept of the respective plots. The values of the correlation coefficient (r^2), which is a measure of the goodness of fit, confirms the Langmuir equation results in closure prediction of the isotherm as compared to the experimental data. The Langmuir Q_o and b values for adsorption of As(V) by various previously reported adsorbents and adsorbents studied in the present investigation are given in Table 1.

The data presented in the Table 1 revealed that, the FePV biomass had a higher adsorption capacity for As(V) than NPV, APV, and PVPPV fungal biomass. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L (41)

$$R_L = 1/(1 + bC_o) \quad (6)$$

where, b is the Langmuir constant and C_o is the initial adsorbate concentration (mg/L). In the present study, it was observed that R_L values decreased with increasing concentration of adsorbate used. R_L values ranged between 0.257 to 0.065, 0.219 to 0.053, 0.173 to 0.04 and 0.141 to 0.032 for NPV, APV, FePV, and PVPPV biomass respectively. The R_L values of the adsorbents used were always less than one and more than zero thereby indicating favorable adsorption of As(V) onto the adsorbents. Kavitha (42), reported R_L value of 0.399 and 0.062, for As(III) and As(V) removal respectively using $FeCl_3$ doped *Aspergillus wentii* biomass. Sathishkumar et al. (11), reported a R_L value in the range of 0.559–0.202, 0.417–0.125, 0.394–0.115, 0.282–0.073, 0.344–0.095, 0.343–0.095, and 0.315–0.084 for live autoclaved, acid, alkali, formaldehyde, $FeCl_3$, and $FeSO_4$ pretreated biomass respectively showing favourable adsorption. Similar results were observed for the adsorption process of arsenic onto various adsorbents (19,43).

TABLE 1
Langmuir and Freundlich constants for adsorption of As(V) by pretreated biomass

	Langmuir constants		Freundlich constants		
Adsorbent	Q_o (mg/g)	b (L/mg)	K_F (mg/g (L/mg)^n)	n	Reference
$FeCl_3$ pretreated tea fungal biomass	0.456	–	10.261	1.104	(17)
Native *Aspergillus wentii* biomass	1.467	3.966	–	–	(19)
Autoclaved *Aspergillus wentii* biomass	1.925	4.95	–	–	”
$FeCl_3$ modified *A. fumigatus*	0.053	–	0.493	1.27	(20)
Methylated yeast	7.5	–	–	–	(22)
Iron-coated light expanded clay aggregates	3.12	0.398			(49)
NPV	1.170	5.796	1.013	3.213	Present study
APV	1.290	13.05	2.558	3.765	”
FePV	1.563	9.588	1.506	3.178	”
PVPPV	1.338	12.206	1.287	3.660	”

TABLE 2
First and second order adsorption rate constants for As(V) adsorption by APV, FePV and PVPPV

Adsorbent/initial As (V) conc (mg/L)	C_e (Exp) (mg/g)	First order kinetic model			Second order kinetic model		
		k_1 (L/min)	Q_e (cal) (mg/g)	R^2	k_2 (g/mg/min)	Q_e (cal) (mg/g)	R^2
APV							
0.5	0.45	2.0	0.38	0.9359	5.0	0.50	0.9764
1.0	0.76	3.2	0.91	0.9367	3.5	0.82	0.9901
1.5	0.96	2.8	0.89	0.9629	7.4	1.04	0.9911
2.0	1.13	2.6	1.30	0.8578	9.1	1.23	0.9802
2.5	1.18	2.2	1.06	0.9491	10.2	1.30	0.978
FePV							
0.5	0.47	2.8	0.27	0.9455	25.4	0.49	0.997
1.0	0.86	2.1	0.38	0.9827	14.2	0.89	0.9971
1.5	1.15	2.4	0.67	0.9326	8.9	1.19	0.9954
2.0	1.31	3.1	0.95	0.9558	8.3	1.37	0.9861
2.5	1.46	2.3	0.69	0.9781	8.1	1.51	0.9966
PVPPV							
0.5	0.45	2.3	0.25	0.9631	21.1	0.47	0.9951
1.0	0.79	2.0	0.46	0.9525	9.2	0.94	0.9912
1.5	1.07	2.1	0.75	0.9467	5.6	1.14	0.9881
2.0	1.18	1.8	1.27	0.9406	4.3	1.27	0.9800
2.5	1.28	2.0	1.26	0.9393	4.9	1.37	0.9886

The Freundlich isotherm is a limiting form of Langmuir isotherm and is an empirical equation employed to describe heterogeneous surface systems (44). It is a common model used in wastewater studies, which relates the residual impurity in solution at equilibrium to the amount adsorbed and it is given as

$$q_e = K_F \log C_e^{1/n} \tag{7}$$

in logarithmic form,

$$\log q_e = \log K_F + 1/n \log C_e \tag{8}$$

where, K_F[mg/g (L/mg)^n] denotes approximate adsorption capacity and n is related to the intensity of adsorption. Agreement of experimental data with Freundlich isotherm (plots log q_e vs log C_e) for As(V) adsorption suggested that the average energy of adsorption decreases with increasing adsorption density. The Freundlich constants, K_F and n were determined from the linear plots of log q_e vs log C_e. The K_F and n values of various adsorbents and that of presently studied adsorbents for As(V) is presented in Table 1.

In As(V) adsorption, $FeCl_3$ pretreatment of biomass enhanced the K_F values indicating that the doping of $FeCl_3$ onto the adsorbents could increase the adsorption capacity of the adsorbent by creating a higher affinity for As(V) on the surface of adsorbents when compared to other pretreatment process (11). The values of n in the range of 1 to 10 denote good adsorption of the adsorbate onto the adsorbent for As(V) as suggested by McKay et al. (45).

Adsorption Kinetics

Adsorption kinetics provides information about the rate of adsorption, which is important to determine the efficiency of the process. Adsorption kinetics can be determined using the Lagergren first order (46) and pseudo second-order equations (37). In order to investigate the mechanism of adsorption and potential rate controlling steps, kinetic models have been used to test the experimental data. A straight line of log (q_e-q) versus t will suggest the applicability of Lagergren first order kinetic model.

The Lagergren first order model can be represented as:

$$\log(q_e - q) = \log q_e - k_1 t/2.303 \tag{9}$$

where q_e and q are the amounts of As(V) adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant of first order adsorption (1/min). Values of q_e and k_1 were calculated from the slope and intercept of the plot of log (q_e-q) vs t for different concentrations of As(V).

The pseudo second-order equation is also based on the adsorption capacity of the solid phase (37). Contrary to the other model it predicts the behavior over the whole time adsorption and is in agreement with the adsorption mechanism being the rate controlling step.

The second-order kinetic model is represented as:

$$t/q = 1/k_2 q_e^2 + t/q_e \tag{10}$$

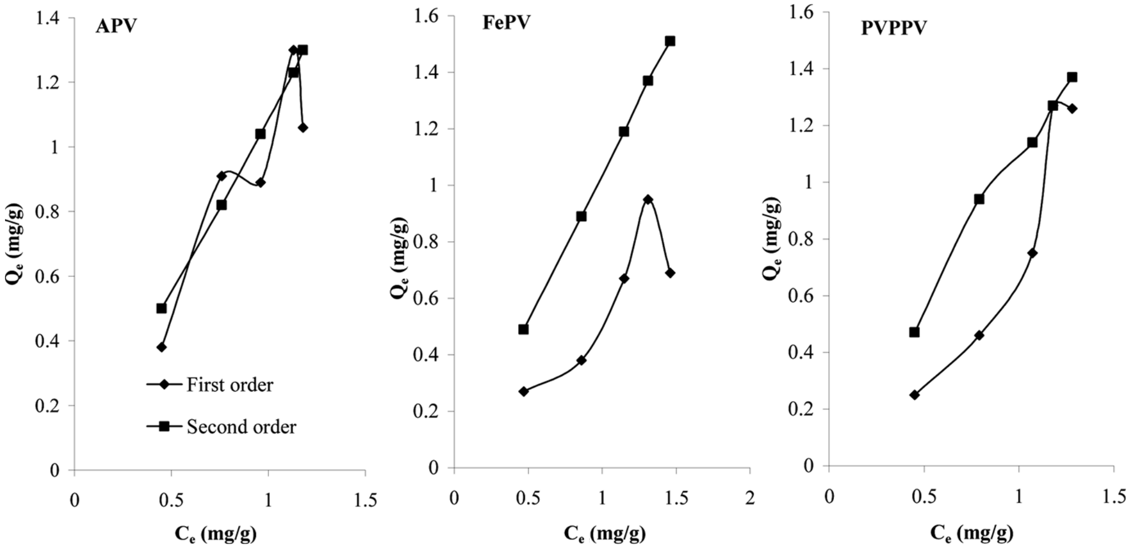

FIG. 3. Comparison of experimental C_e and the calculated Q_e values.

Values of k_2 and q_e were calculated from the slope and intercept of the plots t/q vs t. The results of fitting kinetic data to the first and second order model are presented in Table 2.

Second-order kinetic models showed a good agreement between the experimental C_e values and the calculated q_e values when compared to Lagergren first order reaction (Fig. 3). This indicated that the adsorption process of As(V) followed second order reaction mechanism. The correlation coefficients for the linear plots obtained from the second order equations were also of best fit ($r^2 > 0.99$) (Table 2). Deng and Ting (13) observed similar type of adsorption kinetics for adsorption of As(III) and As(V) using polyethylenimine (PEI)-modified *Penicillium chrysogenum*. Sathishkumar et al. (11) reported that adsorption of As(III) onto *Aspergillus fumigatus* biomass followed pseudo second-order kinetics and failed to obey Lagergren first-order kinetics.

Column Studies

Column studies were carried out using FePV which showed maximum removal of As(V) in batch mode studies.

Effect of Flow Rate and Bed Volume on As(V) Adsorption

Increasing the flow rate decreased the removal of As(V) and after a certain period of time no more adsorption was taking place and the removal was nil. The removal ceased at 470 min with the flow rate of 2.5 mL/min; 210 min with the flow rate of 5.0 mL/min; 150 min with the flow rate of 7.5 mL/min, and 120 min with the flow rate of 10.0 mL/min. Initially at 15 min 99%, 99%, 85.67%, and 73.26% of As(V) was removed with the flow rate of 2.5, 5.0, 7.5, to 10.0 mL/min respectively but the removal decreased with increase in time. The increase in the flow rate decreases the contact time between the adsorbate and adsorbent, but increases the volume contacting the adsorbent. When the available adsorption sites have all been used, the metal removal process terminates. Hence the rate of adsorption decreases as the flow rate was increased.

The effect of bed volume on As(V) adsorption was studied with 2 mg/L of As(V) concentration at a constant flow rate of 2.5 mL/min and increasing the bed volume of 6.36 cm^3, 12.73 cm^3, 19.09 cm^3, and 25.46 cm^3. The As(V) removal was found to increase from 83.59%, 89.71%, 94.56%, and 99% and the removal ceased at an effluent volume of 600, 750, 900, and 1087.5 mL for increasing the bed volume of 6.36, 12.73, 19.09, and 25.46 cm^3 respectively, beyond which no adsorption took place. The result shows that the number of available sites for As(V) adsorption increased with increase in bed volume owing to the increased amount of effluent volume with higher percent removal. The empty bed contact time (EBCT) was considered as the time that the water needs to fill the empty column and was calculated according to the following equation (1).

$$\text{EBCT (min)} = \text{Bed volume (cm}^3\text{)/Flow rate (mL/min)} \qquad (11)$$

The EBCT for As(V) adsorption was found to be 5.09, 2.55, 1.69, and 1.27 min for a flow rate of 2.5, 5.0, 7.5, and 10.0 mL/min respectively with a constant bed volume of 12.73 cm^3. When the bed volume was increased from 6.36 cm^3 to 25.46 cm^3 keeping the flow rate (2.5 mL/min) as constant, the EBCT increased. The EBCT was observed to be 2.54, 5.09, 7.64, and 10.18 min with increasing bed volume of 6.36 cm^3, 12.73 cm^3, 19.09 cm^3 and 25.46 cm^3 respectively. At optimum flow rate of 2.5 mL/min and bed volume of 25.46 cm^3, the EBCT was 10.18 min and the As(V) removal in empty bed was found to be below the detection limit.

BDST Plot

The BDST plot showed linearity, suggesting the fixed bed removal of As(V) obeys to the model. Adsorption rate constant ka and No were calculated from the slope and interceptof the BDST curves. No and ka values for As(V) adsorption by FePV is presented in Table 3.

Desorption Studies

The recovery of the adsorbed material and regeneration of the adsorbent is an important aspect of wastewater technology. The success of adsorption technology, for environmental and economic reasons, depends on the possibility of desorbing the target contaminant and reusing the adsorbent. Desorption studies also help to elucidate the mechanism of adsorption. In the present study, desorption of As(V) from $FeCl_3$ doped biomass was carried out using 0.1 to 0.6 N hydrochloric acid and sodium hydroxide. Maximum desorption of the adsorbates was observed with 0.4 N sodium hydroxide for As(V) (40.18%). HCl could desorb only 6.81–10.64% of As(V) and NaOH desorbed 26.48–40.18% of As(V) at an increasing concentration of 0.5 to 2.5 mg/L (Fig. 4). Low desorption of arsenic by HCl might be attributed to the formation of neutral H_3AsO_3 at acidic pH, which does not exchange with the positive surface of adsorbent (47). When the adsorbents are desorbed using NaOH, a high alkaline condition is created around the adsorbate laden adsorbents in the solution. At this high alkaline pH, all adsorption sites are deprotonated. This deprotonation process causes the Donnan co-ion exclusion effect under this condition leading to efficient desorption of the arsenate (48).

TABLE 3
BDST constants for As(V) removal by FePV

	FePV		
Conc. (mg/L)	N_o (mg/g) × 10^{-2}	Ka (L/min/mg) × 10^{-2}	R^2
0.5	0.011	0.176	0.9269
1.0	0.019	0.099	0.8443
1.5	0.020	0.087	0.8965
2.0	0.018	0.053	0.9335
2.5	0.016	0.049	0.9219

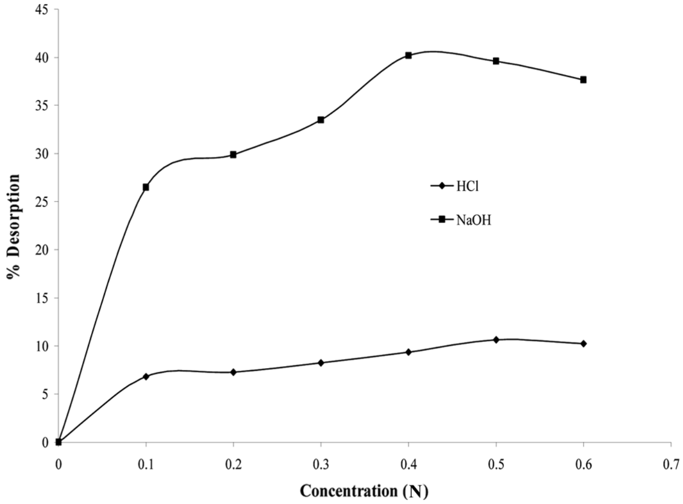

FIG. 4. Desorption pattern.

CONCLUSION

The present study showed that when the *Paecilomyces variotii* biomass was doped with iron and PVP K25, the adsorption efficiency varied considerably when compared to autoclaved and native biomass. Iron doping showed higher arsenic removal when compared to PVP doping and autoclaving. The experimental data obtained from the batch mode when fitted to the Langmuir and Freundlich isotherm showed that the data is fitting onto both the isotherms. The reaction kinetics followed pseudo-second-order kinetics with very high correlation coefficient of above 0.99. The adsorption capacity of FePV was higher ($Q_o = 1.563$ mg/g) when compared to PVPPV ($Q_o = 1.338$ mg/L) and the adsorption was effective at pH 2. In the column mode, the flow rate and the bed volume along with the initial concentration of As(V) influenced the rate of adsorption. Maximum desorption of 40.18% was achieved using 0.4 N NaOH as desorbing agent. Hence this comparative study showed that iron doping is more effective than polymer doping and autoclaving and the adsorbed As(V) could be desorbed effectively and reused.

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