Focused Ion Beam Analysis of Banana Peel and Its Application for Arsenate Ion Removal

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Abstract

Banana peel, a common fruit waste, has been investigated for its ability to remove arsenate ions from ground water as a function of pH, contact time, and initial metal ion concentration. Focused ion beam (FIB) analysis revealed the internal morphology of the banana peels. Arsenate ions were entered into micropores of banana peel. pH was seen to have no effect on the sorption process. Retained species were eluted using 5 mL of 2 M H_2SO_4. The kinetics of sorption were observed to follow the pseudo first order rate equation. The sorption data followed Freundlich and D-R isotherms. The energy value obtained from the D-R isotherms indicated that the sorption was physical in nature for arsenate species. Our study has shown that banana peel has the ability to remove arsenate species from ground water samples.

Keywords: Banana peel; Arsenate ions; Sorption; Kinetics; Adsorption isotherms

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Introduction

Arsenic is particularly difficult to characterize as a single element because its chemistry is so complex and there are many different arsenic compounds [1]. It may be trivalent (e.g. arsenite) or pentavalent (e.g. arsenate) and is widely distributed in nature. In surface water, it is mostly present as As(V) (arsenate) [2]. Arsenic is released into the environment from a number of anthropogenic sources, which include copper, zinc and lead smelters, glass manufacturers that add arsenic to raw materials, manufacturers of pesticides, herbicides and other agricultural products. It has been reported that over 137 million people in more than 70 countries are probably affected by arsenic-contaminated drinking water [3]. The drinking water guideline recommended by the World Health Organization (WHO) for total arsenic is 10 μg L^{-1} [4].

Due to its toxic effects, it is important to develop an effective, fast, precise, accurate and repeatable method. Removal of arsenic by sorption has been studied on hydrated cement, marble powder and brick powder [5], akaganeite decorated graphene oxide composite [6], bagasse fly ash-iron coated and sponge iron char [7], leonardite char [8], raw and acidified laterite [9], blue pine (Pinus wallichiana) and walnut (Juglans regia) [10], immobilized rice husk [11], iron coated rice husk [12], sorghum biomass [13], iron oxide-coated cement [14], iron hydroxide coated alumina [15] and red mud [16].

In the present study, an attempt has been made to describe the use of an effective and inexpensive banana waste material for the removal of arsenate species from ground water samples. The porosity of the material has been explored and measured using focused ion beam (FIB). The effects of relevant parameters (pH, contact time

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and initial metal ion concentration) have been investigated and we have demonstrated its higher sorption capacity for arsenate ion than the above materials reported.

Materials and Methods
Materials

All the chemicals were supplied by Merck (Darmstadt, Germany) and of analytical grade. Sodium arsenate was used to prepare a stock standard solution. Different pH range buffer solutions were prepared and employed for conducting experiments.

Methods
Preparation of sorbent

Preparation of material and analysis of different parameters was already reported by the authors [17].

Equipment and instruments for chemical analysis

A HORIBA Jobin Yvon (Stanmore, UK) inductively coupled plasma atomic emission spectrophotometer (ICP-OES) model Ultima was used to determine the concentration of arsenate ions in solution. ICP-OES analysis was performed after setting of the experimental parameters (arsenic, λ = 193.695 nm). As per the operation manual, the instrument was allowed to warm up for about 30 min, with de-ionized water being aspirated all the time. Before analysis, a calibration curve was constructed for the arsenate ions.

All pH measurements were made with a WTW (Weilheim, Germany) digital pH meter model inolab pH level 1 equipped with a calibrated combined pH glass electrode.

A Barloworld Scientific (Staffordshire, UK) Stuart rotator model SB3 was used for the batch experiments.

An FEI Strata (Hillsboro, Oregon, USA) FIB 201 gallium FIB instrument was used to mill or cut and cross section samples by sputtering in precisely defined areas. Platinum was deposited over selected areas prior to sectioning in order to save the top surface of the sample during ion milling, though this was commonly not found to be essential for sectioning the small particles.

Equilibrium metal sorption experiments

The batch equilibrium experiments were conducted to explore the metal sorption performance of banana peel. 20 mL of As(V) ion solution (100 mg L^{-1}) maintained at optimum pH and 20 ± 1 ^{o}C was equilibrated with 0.1 g of banana peel and shaken at 40 rpm for the designated time (0–24 h). The mixtures were filtered and metal ions adsorbed were desorbed by shaking with 5 mL of 2 M H_2SO_4 solution before being analyzed after dilution by ICP-OES. Experiments were conducted in triplicate and the results presented here are the average of those triplicate measurements. Precision in all cases is close to ±1%.

Results and Discussion

The banana peel used in this study has been characterized previously using FT-IR and scanning electron microscopy (SEM) coupled with the energy dispersive X-ray analysis (EDX) [17]. Here, it was analyzed using FIB to evaluate the sorption behavior of the arsenate ions.

FIB analysis

FIB analysis of banana peel was performed by selecting particles from the aggregate and imaging both as-received (e.g. Fig. 1, which reveals clearly the microporous structure) and after cross sectioning. The radius of a typical pore was found to be 2.67 µm.

Influence of aqueous solution pH on the arsenate sorption

As the pH of the system controls the sorption capacity through its influence on the surface properties of the adsorbent and species of adsorbate in solution, sorption experiments were carried out over a pH range of 1–11, whilst maintaining all other parameters constant. The uptake of metal ions onto banana peel as a function of pH is shown in (Fig. 2). The sorption of arsenate species was found to be independent of pH. 95% sorption was observed at all pH values, suggesting

no interaction of the arsenite species with surface groups. The major species of As(V) in the pH range < 2.26, 2.26-6.76, 6.76-11.29 and > 11.29 are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} [18]. However, in this present work, it was arsenate species entering into the banana peel micropores (Fig. 1). Pauling has calculated and reported the ionic radius of arsenite ($HAsO_4^{2-}$) ion to be 10.68×10^{-16} µm [19] which is v.v. much smaller than the pore size of banana peel (2.67 µm) as calculated from (Fig. 1).
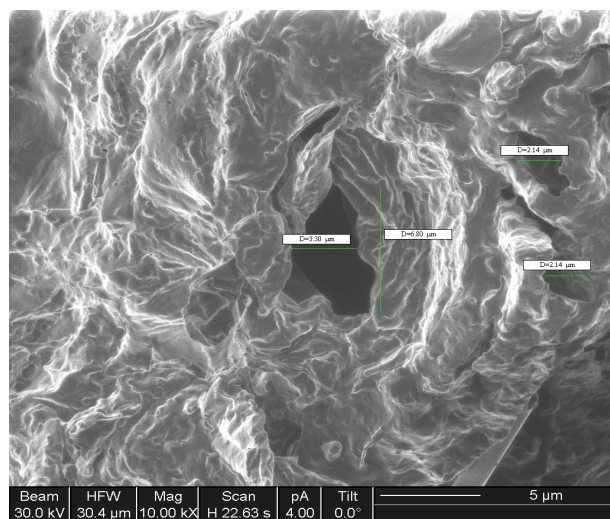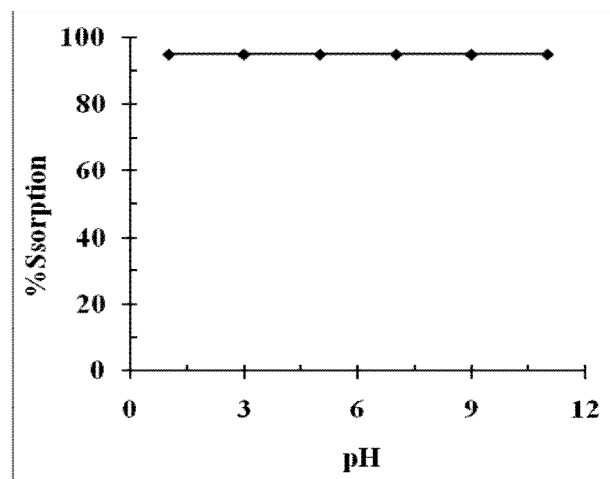

Figure 1. **Focused ion beam image of banana peel**

Figure 2. **Sorption of As(V) ions onto banana peel as a function of pH.**

Recovery of arsenic species

Desorption of As(V) ions from the banana peel surface was studied using 5 mL of different concentrations of HNO_3, H_2SO_4, HCl and NaOH. Percent recoveries are given in (Table 1). Elution was found to be complete (100%) with 5 mL of 2 M H_2SO_4. NaOH forms precipitating hydroxides with As(V) ions by increasing the pH. However, because of the low concentration of NaOH used, it cannot completely remove the As(V) ions. HNO_3 and HCl do not formed soluble As(V) compounds whereas H_2SO_4 forms soluble sulphates. Therefore, 5 mL of 2 M H_2SO_4 can recover the As(V) ions from the banana peel surface.

Table 1. **Reagent used for the elution of As(V) ions.**

Reagent [a]	Concentration (M)	Recovery (%)
HCl	0.5	10
HCl	1	16
HCl	2	27
HNO_3	0.5	8
HNO_3	1	15
HNO_3	2	23
H_2SO_4	0.5	25
H_2SO_4	1	52
H_2SO_4	2	100
NaOH	0.5	5
NaOH	1	12
NaOH	2	18

[a]Volume of each reagent used = 5 mL.

Kinetics of sorption

A kinetic study was carried out at optimized conditions over times of 0 to 30 min. The sorption process was initially found to be rapid, 90% at 0 min, but became slower as time increased. Equilibrium was established within 30 min and 95% sorption was recorded for As(V) ions. There was no significant increase in the percent sorption after 30 min. Therefore, for further investigations 30 min agitation time was applied. The recorded kinetic data were fitted to different equations namely, Morris–Weber, Lagergren and Reichenberg. The adsorbed

concentration q_t (µmol g^{-1}) at time t, was plotted against $\sqrt{t}$ to test the Morris-Weber equation [20] in the following form:

$$q_t = R_d \sqrt{t} \tag{1}$$

where, R_d is the rate constant of intra-particle transport. Up to 10 min, Eq (1) held well, with a regression coefficient of 0.993, but it deviated as the agitation time increased. From the slope of the plot in the initial stage (Fig. 3), the value of R_d, was found to be 2.04 ± 0.10 µmol g^{-1} min$^{-1/2}$. The Lagergren equation [21].

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \tag{2}$$

was tested by plotting $\log(q_e-q_t)$ versus time t (Fig. 4), where q_e is the adsorbed concentration of As(V) ions on banana peel (mol g^{-1}) at equilibrium. In the initial stage up to 15 min, the plot shown in Fig. 4 appeared to be linear. The overall value of rate constant (k) was estimated to be 0.214 ± 0.008 min^{-1} from the slope of the plot with a regression coefficient of 0.994. The effectiveness of the diffusion of exchanging ions within the adsorbent particles of radius r and control of film diffusion in sorption may be deduced from the linear fit of the data to the Reichenberg equation [22]:

$$Q = 1 - \frac{6e^{-Bt}}{\pi^2} \tag{3}$$

where $Q = q_t/q_m$, $Bt = \Pi_2 \, D_i/r^2$, q_t and q_m are adsorbed concentrations at time t and the maximum sorption capacity of the adsorbent, respectively, and D_i is the effective diffusion coefficient of ions exchanging inside the adsorbent particle. The value of Bt (a mathematical function of Q) can be evaluated for each value of Q, using the following equation:

$$Bt = -0.4977 - \ln(1 - Q) \tag{4}$$

The plot of Bt versus time (Fig. 5) was linear from 0 to 15 min with a regression coefficient of 0.994. However, the regression line plot did not pass through origin, indicating the formation of a thin As(V) film on the surface.
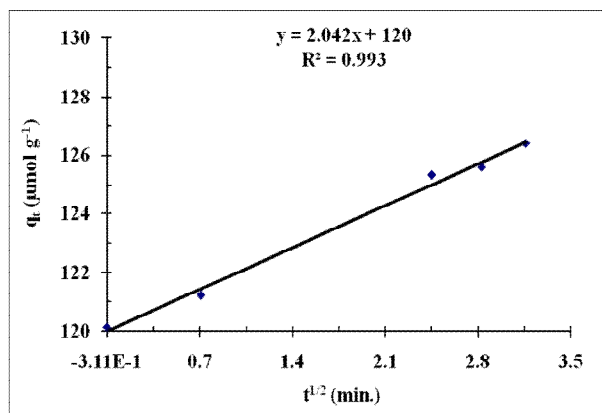

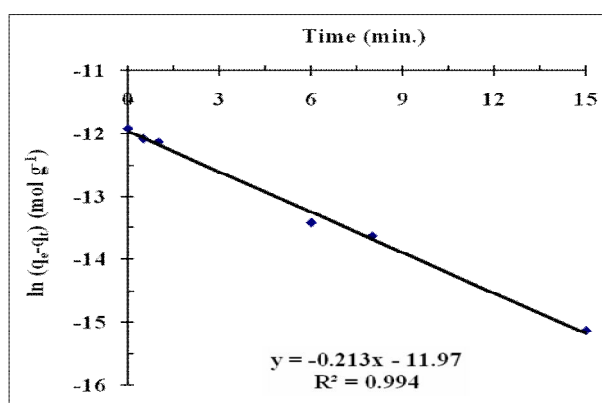*Figure 3.* **Morris–Weber plot for the sorption of As(V) ions onto banana peel**

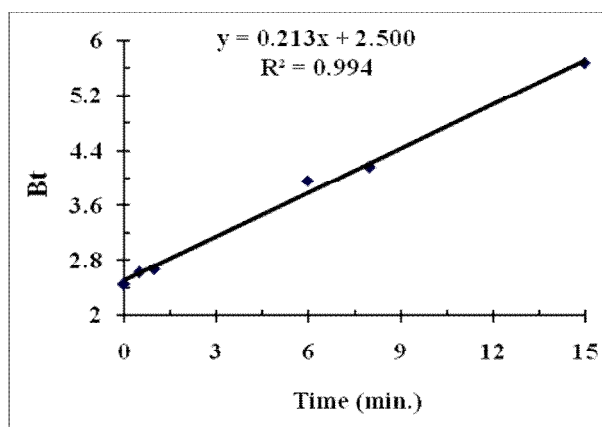*Figure 4.* **Lagergren plot for the sorption of As(V) ions onto banana peel**

Figure 5. **Reichenberg plot for the sorption of As(V) ions onto banana peel**

Sorption isotherms

The sorption of As(V) ions was also investigated as a function of its concentration at

room temperature in the range 0.5–1000 mg L^{-1} using 0.1 g of adsorbent, 20 mL of adsorbate solution and 30 min. shaking time. The metal ion uptake increased with increasing concentration up to 100 mg L^{-1} but then a decreasing trend was observed. These results reflect the efficiency of the adsorbent for the removal of As(V) ions from the aqueous solution. The effect of the tested metal ion concentration on banana peel was analyzed in terms of the Freundlich (log C_{ads} = log A + (1/n) log C_e), Langmuir ((C_e/C_{ads}) = (1/Qb) + (C_e/Q)), and Dubinin–Radushkevich (D–R) (ln C_{ads} = ln X_m $-\beta\varepsilon^2$) and ε = RT ln (1 + (1/C_e)) equations, where C_{ads} is the concentration of metal ions sorbed per unit mass of sorbent, C_e is the concentration of metal ions in the liquid phase at equilibrium and A and n, Q and b, and X_m and β are the Freundlich, Langmuir and D–R constants, respectively. The sorption data were seen to follow the Freundlich and D–R isotherms. Therefore, the Freundlich and D–R isotherms were used to evaluate the sorption capacity of banana peel for As(V) ions. The Freundlich and D–R constants were evaluated using the slopes and intercepts of the linear plots studied at room temperature; results are listed in (Table 2). The numerical values of the Freundlich constant 1/n > 1 for arsenate species indicated high adsorptive capacity at high equilibrium concentrations that rapidly diminishes at lower equilibrium concentrations. The value of E evaluated from the slope (β) of the D–R plot using equation ($E = \dfrac{1}{\sqrt{-2\beta}}$) was (7.94 ± 0.06 kJ mol^{-1}), which is in the range expected for physical adsorption (8–16 kJmol^{-1}) [23]. Hence, it was very likely that the metal ions were sorbed onto banana peel predominantly by physical adsorption. The calculated values of sorption capacity were different and in the range of 1.7-4.7 mmol g^{-1}. This difference in sorption capacity can be interpreted in terms of the assumptions taken into consideration while deriving these sorption models. Comparison of sorption capacity of arsenic on banana peel with data from previously reported sorbents (Table 3) highlights the efficiency of this cheaper material.

Table 2. **Freundlich and D-R constants of As(V) ions onto banana peel at room temperature.**

Freundlich			Dubinin–Radushkevich			
A (mmol g^{-1})	1/n	R^2	X_m (mmol g^{-1})	$\beta \times 10^{-3}$ (kJ^2 mol^{-2})	E (kJ mol^{-1})	R^2
4.7 ± 1.4	1.05 ± 0.03	0.99	1.7 ± 0.2	-(8.7 ± 0.3)	7.94 ± 0.06	0.99

Table 3. **Comparison of sorption capacities for arsenic species with previously reported adsorbents.**

Adsorbent	Adsorption capacity (mg g^{-1})	Reference
Hydrated cement	1.92	[5]
Marble powder (waste)	0.02	[5]
Brick powder(waste)	0.04	[5]
Akaganeite decorated graphene oxide composite	77.5	[6]
Bagasse fly ash-iron coated	0.04	[7]
Sponge iron char	0.03	[7]
Leonardite char	4.46	[8]
Raw laterite	0.13	[9]
Raw laterite	0.2	[9]
Quaternized rice husk	0.775	[11]
Activated alumina	0.18	[11]
Sorghum biomass	1.02	[13]
Iron hydroxide coated activated alumina	0.04	[15]
Red mud	0.7	[16]
Banana peel	**352.13**	**This study**

Analytical application

The analytical applicability of banana peel was tested for the removal of total arsenic from ground water samples collected from different regions of Sindh, Pakistan. After acid digestion, the samples were analyzed using ICP-OES (Table 4, found values). A 20 mL aliquot of each sample was agitated with 1 g of banana peel for 30 min. (Table 4, removal values). The metal ions were then eluted with 5 mL of 2 M H$_2$SO$_4$ and determined by ICP-OES, 100% recovery was achieved. The R.S.D. was always within 2%,

clearly showing the efficiency of banana peel for the removal and recovery of As(V) ions from these ground water samples.

Table 4. **Determination, removal and recovery of arsenic species from ground water samples.**

Sample location	Found (µg L⁻¹)	Removal (%)
Sonara Muhallah Hala (new)	29.1	100
Pir Pinealdho Coloni Hala (new)	36.6	99
Talib-ul-Mola Coloni Hala (new)	34.2	100
Quaid-e-Awam University of Engineering Science and Technology (QUEST), Nawabshah	18.7	100
Latifabad No. 4 Hyderabad	41.8	98
Matiari (city)	44.1	97
Khairpur (city)	32.8	99

Conclusions

Removal and recovery of As(V) ions was successfully accomplished using a cheap and economic adsorbent – banana peel. Low materials cost, rapid attainment of phase equilibrium and high sorption capacity, along with the pH independency, were some of the significant features. Focused ion beam (FIB) analysis of banana peel revealed clearly the microporous structure. The radius of arsenate ions calculated by Pauling is very small as compared to the calculated radius of pores present at the surface of banana peel using FIB. No role of surface groups was seen but the As(V) ions were entering into pores of banana peel. The kinetics of sorption for As(V) followed a pseudo first order rate equation. Sorption of As(V) on banana peel followed the Freundlich and D–R isotherms. The energy value obtained from the D–R isotherm showed that the sorption was physical in nature. Banana peel can be effectively used to remove and recover As(V) ions from ground water samples.

Acknowledgements

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