ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 15, No. 1 (2014) 35 – 41

Citrus paradisi: An Effective Bbio-adsorbent for Arsenic(V) Remediation

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Received 04 February 2014, Revised 13 April 2014, Accepted 13 June 2014

Abstract

In the present study As(V) was removed by *citrus paradisi* (grape fruit) peel. Kinetics of the adsorption reaction was analyzed by the Pseudo second order and Morris-weber equations. Freundlich and Langmuir isotherm models were utilized for understanding of the relationship between the arsenic ions and *citrus paradisi* peel adsorbent. The maximum measured uptake capacity of *citrus paradisi* was 37.76 mg.g^{-1} at pH 4. FT-IR characterization of unloaded and As(V) loaded *citrus paradisi* peel adsorbent showed the participation of carbonyl (CO) and hydroxyl (OH) groups in adsorption process. The proposed *citrus paradisi* peel adsorbent with optimized parameters was used for the removal of arsenic from arsenic contaminated real water samples.

Keywords: Citrus paradisi; Kinetics; Langmuir; FT-IR characterization

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Introduction

Increasing water contamination poses a threat to bio-environment. The word arsenic is derived from Greek *arsenikon*, means potent [1]. Arsenic, a tasteless poison, has adverse impact on the life of flora and fauna. Metals especially arsenic contamination is found throughout the world. In 1999 World Health Organization (WHO) ranked arsenic as “major public health issue”. USEPA and IARC classified arsenic as group A and category 1 human carcinogen [2]. Arsenic exists mostly as oxy-anions in an oxidizing environment [3]. Generally two oxidation states – arsenic (III) and arsenic (V) are common in nature.

In 1993 WHO and 2002 USEPA reduced the tolerable limit of arsenic in drinking water to 10 µgL^{-1}. Use of drinking water containing arsenic above tolerable limit causes muscular weakness, skin thickening (hyperkeratosis), loss of appetite, pigmentation, neurological disorders, nausea and cancer in kidney, bladder, lungs and skin [4-6]. Severity of arsenic poisoning causes vomiting, bloody “rice water” diarrhea, abdominal pain and esophageal pain [7-8].

Various methods like physio-chemical methods (coagulation, adsorption, precipitation, ion exchange, membrane filtration), and biological methods (living microbes/bio-filtration) have been developed [9]. In past two decades bio-sorption has received much attention due to the availability of variety of bio-sorbent materials [10]. In comparison to other metal removal methods, bio-sorption has various advantages such as high metal binding efficiency, short operational time, improved selectivity for specific metals, no production of secondary toxic compounds and reusability of biosorbent [11]. Further applicability of this method is very suitable for small scale industries [12].

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Literature survey reveals that various economical materials have been utilized for the adsorption of arsenic such as shrimp shells, modified coconut coir pith, methylated yeast biomass, acid-washed crab shells, bone char, iron oxide coated fungal biomass, modified fungal biomass, residue rice polish, modified cotton cellulose, spruce saw dust, HDTMA-modified zeolite, modified orange waste gel, surfactant-modified zeolite, iron-coated zeolite and coconut fiber [13-27]. Most of the mentioned adsorptive materials were utilized after simple or special treatment and their performance was not encouraging at very lower concentrations. Keeping in view the effectiveness and performance those new adsorbents were selected which were economical and simple. Their activity was pronounced even at lower concentrations. In this respect *citrus paradisi* peel adsorbent showed very effective arsenic (V) removal response even at parts per million concentration levels.

Materials and Methods

Reagents and equipment

A suitable amount of arsenic (V) salt was dissolved in de-ionized water to prepare stock solution. For experiments fresh solutions of desired concentrations were made from stock solution. For maintaining the pH of sample solutions, different buffers like CH_3COOH, $CH_3COO^- Na^+$, KCl, HCl and NaOH were used. 0.2% w/v of sodiumborohydride was added to 0.05 % w/v of sodium hydroxide for preparing the reducing agent for arsenic. All solutions used were of analytical grade.

pH meter Thermo Scientific Orion 5 Star (pH. ISE. Cond. DO Benchtop, 8102BNUWP; USA), Shaking Incubator Model 1- 40000 Irmeco GmbH (Geesthacht/Germany) and Atomic Absorption Spectrometer (AAS) (Analyst 800, Perkin Elmer, Singapore) connected with Flow Injection System for hydride generation (FIAS 100 Perkin Elmer, Singapore) were used during the adsorption experiments.

Sorbent: Collection and preparation

The *citrus paradisi* peel adsorbent material was obtained from the fresh juice sellers, Hyderabad, Pakistan. The collected peels possessed dust and other extraneous dirt particles. So peels were simply washed with tap water and de-ionized water to make them clean from unwanted material. Then washed adsorbent material was dried in incubator at 60 °C for six hours.

Dried material was ground and meshes size of 120 (~125 micron) was obtained by electrical sieve shaker. pH and chemical oxygen demand (COD) of the effluent of adsorbent material was measured. Initially COD of the material was greater than the European Union (EU) permissible limit. For maintaining the COD material was washed several times with de-ionized water till the accepted value of COD was achieved. Finally washed adsorbent material was dried at 60 °C for 24 hours.

Characterization of adsorbent

Fourier transform-infrared spectroscopy (FT-IR). The samples were dried for 12 hours in incubator, in order to remove reined water; the dried samples then were scanned into transmission mode by employing FT-IR spectrometer. IR spectra of free and metal loaded sorbents were recorded in the wavelength range of 400 – 4000 cm^{-1}.

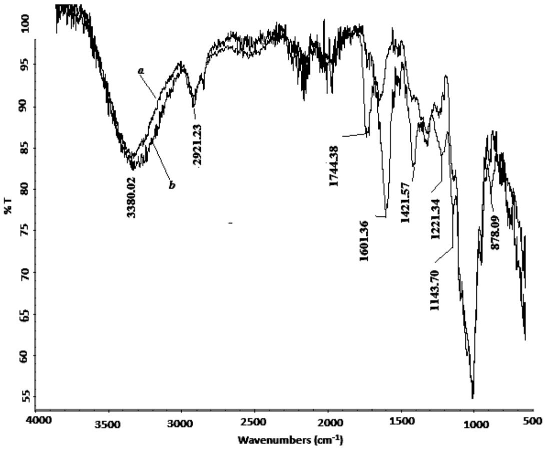

Figure 1. **FT-IR spectra of a) *Citrus paradise* peel b) Citrus paradise peel loaded with As(V)**

Fig. 1a and b shows FT-IR spectrum of plain *citrus paradisi* peel and As (V) loaded peel respectively. Bands at 3380.02, 2921.23, 1601.36

and 1421.57 cm^{-1} in free grapefruit peel can be assigned to –OH and C-H stretching, C=O stretching and O-H bending respectively [28]. Characteristic peak for polysaccharide appears at 1030.64 cm^{-1}. Noticeable decrease in intensities and shift of peaks at 1601.36 and 1421.57cm^{-1} can be seen from Fig. 1b indicates the involvement of C=O and –OH for the uptake of As(V) by grapefruit peel.

Batch equilibrium adsorption of As(V)

As (V) adsorption on *citrus paradisi* peel was investigated using batch equilibrium experiments. An aliquot (15 mL) containing 0.01 – 50 mgL^{-1} of As (V) maintained at pH 4 was agitated (200 rpm) with 200 mg of adsorbent at 25 ^{o}C for 15 minutes. Concentration of metal ions in filtrate was examined by AAS connected with Flow Injection System.

For the calculation of adsorption (%) following equation was employed.

$$\text{Adsorption (\%)} = \left(\frac{C_{b-a}}{C_b}\right)\times 100 \qquad (1)$$

Where

C_b = Metal ions concentration (mol.L^{-1}) of solution before adsorption.

C_a = Metal ions concentration (mol.L^{-1}) of solution after adsorption.

Treatment of arsenic contaminated water samples

Actual efficiency of developed method can only be evaluated by analyzing real water samples. Plastic bottles were used for the collection of arsenic contaminated drinking water samples. The samples S1, S2 and S3 were collected from Sachal colony District Larkana, Chak No.159 Taluka Sadiqabad District Rahimyar Khan and village Bakhtiarpur Taluka Sehwan District Jamshoro respectively. These real samples were filtered and their initial arsenic concentrations were analyzed by Atomic Absorption Spectrometer connected with FIAS system. A suitable amount of real sample was spiked with standard arsenic solution. The adsorption experiments were performed under optimum conditions. Uptake efficiency of the adsorbent with un-spiked and spiked real water samples were carried out.

Result and Discussion

pH Effect on arsenic removal

Citrus paradisi peel adsorbent performance for arsenic (V) removal is shown in (Fig. 2.) Initially (up to pH4) the increase in sorption was registered but the sorption showed a decreased trend with further increase in pH value. Same trend was noticed in case of arsenic adsorption on rice polish [15].

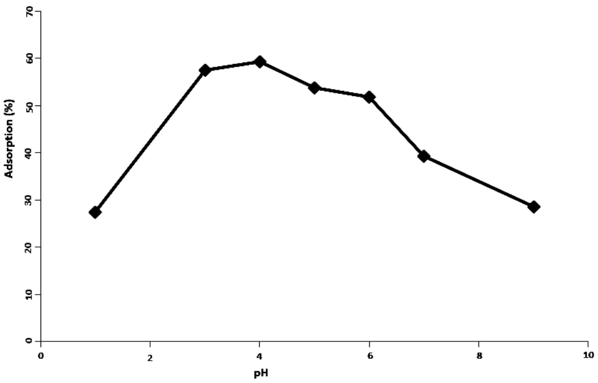

Figure 2. **Effect of pH on removal of As(V) on *Citrus paradise* peel**

Adsorption kinetics

Equilibrium study has important role in determining the efficiency of the adsorbent and adsorption reaction. By maintaining the optimum shaking speed, amount of *citrus paradisi* peel adsorbent, volume of arsenic (V) solution, agitation speed and pH reaction time was varied from 0 minute (the time when just adsorbent is added to arsenic solution and immediately filtered without shaking of mixture is termed as 0 time) to 24 hours. Flasks were shaken at different times and then taken out for analysis of the residual concentrations. In first 15 min the sorption was found to be very fast and then slowed down till the equilibrium was achieved in 2 hours. This phenomenon can be attributed to the condition that in the initial stage the surface of the adsorbent is free so sorption becomes fast and diffusion process takes place (arsenic ions sorbed from bulk solution to the surface of the sorbent) [29]. In the later stage process can be attachment-controlled. For determining the rate constant of intra particle diffusion, Morris-Weber equation $qt = k_{id} t^{\frac{1}{2}} + C$

was employed. High value of correlation coefficient (0.997) up to 30 min. indicates that equation follows the sorption up to 30 minutes (R_d = 0.4356 mgg^{-1}) and then deviates as shaking time is increased According to Morris-Weber plot q_t versus $t^{1/2}$ (Fig. 3), the sorption process is consisted in two phases (first phase up to 30 minutes and second phase up to 24 hours). It suggests that intra-particle diffusion is not the only the rate limiting step for the whole sorption process [30]. The linear part of the curve which is not passing through the origin reveals that sorption mechanism was complex and both the surface adsorption as well as intra-particle diffusion occurred. Similar mechanism was observed for the sorption of arsenic on bone char [20].

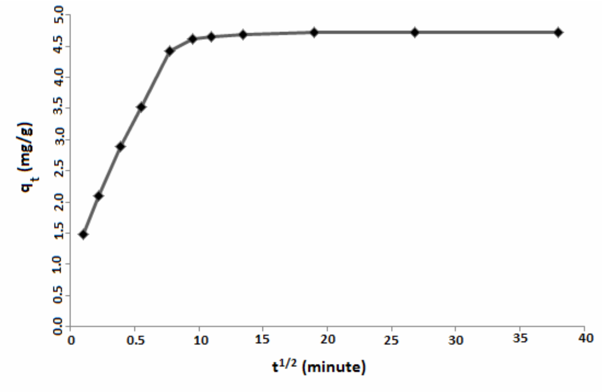

Figure 3. **Morris-Weber plot for the adsorption of As(V) on *Citrus paradise* peel**

For further understanding the kinetics of sorption pseudo-first order, pseudo-second order equation and Richenberg equations were used. Except first order rate equation, pseudo second order rate and Richenberg equations were fitted to the data. The linear form of pseudo second order rate equation is given below.

$$\frac{t}{qt} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (2)$$

Where *k* is rate constant (gmg^{-1} min^{-1}), q_e the amount of metal ion at equilibrium (mgg^{-1}), and q_t amount of metal ion at specified time (mgg^{-1}). The constants of pseudo second order rate equation were determined from the plot of t/q_t against *t*. High value of correlation coefficient (r = 1.00) indicates that experimental data is well fitted to the pseudo second-order kinetic model. From this it is assumed that reaction between *citrus paradisi* peel adsorbent and As (V) is chemisorption [31]. In the adsorption of As (V) onto metal oxides forms inner and outer surface complexes [32]. Thus, the formation of chemical bond between As (V) and *citrus paradisi* peel adsorbent is involved. Similar observation was seen in the case of As (V) adsorption on sawdust and bone char [20-21].

Richenberg equation describes diffusion of metal ions within the sorbent particles. Following linear form of Richenberg equation was employed.

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

Where Q = qt/qm, $Bt = \pi^2 Di/\gamma^2$, r is radius of adsorbent particle, qt adsorbed concentration at time t, Di an effective diffusion coefficient of ions exchanging, qm maximum sorption capacity. Bt is determined by the following equation.

$$Bt = -0.4977 - \ln(1-Q) \qquad (4)$$

The Richenberg constants were calculated by plotting the Bt against t. It was observed that regression line (r = 0.945) is linear from 0 to 180 min and does not passing through origin (Fig. 4) means that mechanism of the sorption reaction is not the sole rate controlling step [15].

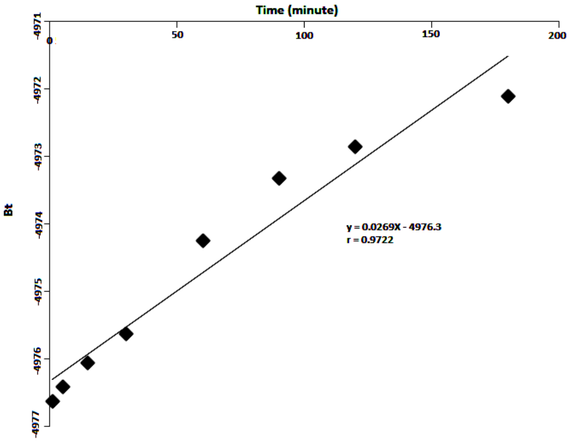

Figure 4. **Reichenberg plot for adsorption of As(V) on *Citrus paradise* peel**

Adsorption isotherms

Various isotherm equations have successfully been employed for examining the observed data [33-34]. Here experimental data is tested by two parameter models a monolayer Langmuir model (eq. 6) and multilayer Freundlich model (eq. 8) over the concentration range of 6.6×10^{-7}-6.6×10^{-4} $molL^{-1}$.

Langmuir isotherm

This adsorption isotherm studies the formation of monolayer of metal ions on the surface of adsorbent. K_L and q_m are the two main parameters of Langmuir model [33].

The Langmuir equation is given below:

$$q_e = \frac{q_{max}(K_1C_e}{1+(K_LC_e} \qquad (5)$$

Different linear equations of Langmuir model are used but here experimental data is tested by following linear equation.

$$\frac{q_e}{C_e} = K_L q_{max} - K_L q_e \qquad (6)$$

Where C_e is equilibrium concentration of metal ions ($molL^{-1}$), q_e amount of adsorbate on surface of adsorbent at equilibrium ($molg^{-1}$), q_m maximum amount of metal ions adsorbed and K_L binding energy of solute. Langmuir constants which were determined by the eq. 6 are given in (Table 1). It is evident from the co-relation coefficient that the experimental data follow the eq. 6. Increase in the value of K_L with the rise of temperature indicates that sorption is endothermic in nature [34]. Dimensionless constant separation factor R_L is an essential characteristic of Langmuir isotherm which is calculated by following equation [35].

Table 1. **Estimated Langmuir equation constants for the adsorption of As(V) ions onto *Citrus paradise* peel.**

Temp: (K)	Concentration range (μgL^{-1})	R_L	K_L (10^4)	q_m (10^{-4})	Capacity (μgg^{-1})	r
293	200-50000	0.42-1	0.33	2.20	16502	0.97
298	200-50000	0.37-1	0.37	2.30	17524	0.98
303	200-50000	0.34-1	0.46	2.50	18881	0.98
308	200-50000	0.20-1	0.52	3.44	25787	0.95
313	200-50000	0.17-1	0.83	4.30	32226	0.92
318	200-50000	0.15-0.99	1.08	5.04	37765	0.91

$$R_L = \frac{1}{1+(K_LC_1)} \qquad (7)$$

R_L determines the shape of isotherm. According to the values of R_L if R_L is greater than one, equal to one, equal to zero and between zero and one indicates the unfavorable, linear, irreversible and favorable respectively sorption reaction [35]. Table 1 shows the R_L values in the range of 0.15 - 0.99 for all temperatures indicates that the adsorption of As (V) on *citrus paradisi* peel was favorable.

Freundlich isotherm

Like langmuir equation, Freundlich equation is commonly used in the isotherm study of adsorption. Linear form of the equation is given below:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (8)$$

Where K_F is adsorption capacity, 1/n sorption intensity; q_e and C_e are described in Langmuir isotherm study. (Table 2) shows the values of 1/n are greater than 1(n less than 1) indicates that there is concave isotherm [36]. For the sorption of Cd (II) on maize husk, Igwe reported the 0.38 value of n and similar trend was observed in literature [37-39]. It can be assumed that concave curve may be due to the complex nature of the sorbent (sorbent contains various active sites for the sorption) [34].

Table 2. **Freundlich constants for the adsorption of As(V) ions onto *Citrus paradise* peel.**

Temperature (K)	Capacity (mgg^{-1})	1/n	r
293	0.78	1.33	0.99
298	1.05	1.29	0.99
303	2.10	1.31	0.99
308	2.31	1.38	0.99
313	5.27	1.27	0.99
318	6.14	1.30	0.99

Effect of matrix electrolytes

In the adsorption study the effect of electrolytes has immense importance. Real water samples contain various electrolytes with varying concentrations. These electrolytes may affect the efficiency of *citrus paradisi* peel adsorbent on the removal of As (V). 1:10 and 1:100 metal-electrolyte ratios were examined in 20 mL volumetric flasks. In 1:10 ratio 7.5 mL of As (V) (10 mgL^{-1}) and 0.075 mL of an electrolyte (10000 mg.L^{-1}) and in case of 1:100 ratio 7.5 mL of arsenic (10 mg.L^{-1}) and 0.75 mL of an electrolyte (10000 mg.L^{-1}) were taken in separate volumetric flasks.

During electrolytic study optimized values of different parameters (temperature 45^{o}C, pH-4, time 15 min, agitation speed 200 rpm, volume 15 mL and amount of sorbent 0.1 g) were maintained. According to the histogram (Fig. 5) common ions present in the solution puts no any pronounced adverse effect on adsorption of As (V) on *citrus paradisi* peel. But the presence of iron(II) and carbonate ions increased the removal efficiency of the sorbent up to 5%. This shows the practical applicability of *citrus paradisi* peel adsorbent for the removal of As (V).

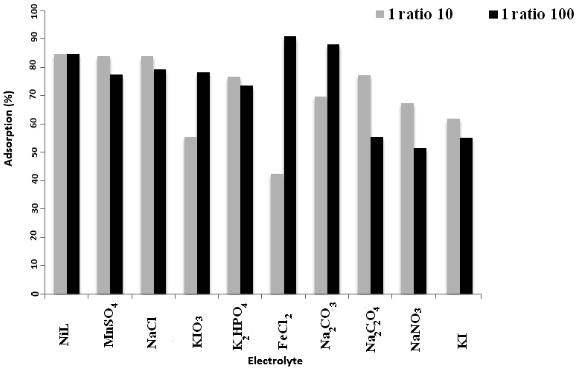

Figure 5. **Effect of electrolyte on removal of As(V) by *Citrus paradise* peel**

Applications

The proposed *citrus paradisi* peel adsorbent was successfully applied to the arsenic contaminated real water smples (Table 3) shows the removal efficiency of *citrus paradisi* peel for the arsenic contaminated real water samples. It has been observed that in most of the cases *citrus paradisi* peel proved to be an effective sorbent for the treatment of arsenic contaminated water samples up to the safe limit recommended by WHO.

Table 3. **Removal of As(V) from environmental water samples.**

Samples	Actual concentration (µgL^{-1})	Amount spiked (µgL^{-1})	Removal (%)	Residual concentration (µgL^{-1})
S1	1.03	0.0	89.29	0.11
S1		50	93.52	3.31
S2	0.00	-	-	-
S2		50	80.44	9.78
S3	18.0	0.0	76.50	4.23
S3		50	89.52	7.12

S1: Water sample collected from Hand-pump in Sachal colony. District Larkana, Sindh-Pakistan.
S2: Water sample collected from Hand-pump in, Chak No.159 TalukaSadiqabad, District Rahimyar Khan, Pujab-Pakistan.
S3: Water sample collected from Well in Village Bakhtiarpur, TalukaSehwan, District Jamshoro, Sindh-Pakistan.

Conclusion

Citrus paradisi peel adsorbent demonstrated the removal efficiency for As (V). Kinetically adsorption process followed the Morris-Weber, Pseudo second order and Richenberg equations. To examine the relationship between adsorbent and adsorbate at equilibrium, linear form of Langmuir, and Freundlich isotherms were employed. According to Langmuir isotherm maximum arsenic uptake was 37.765 mg per gram of adsorbent at pH 4.0 and 45 ^{o}C. Further sorption was found to be endothermic in nature.

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