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Utilization of *Punica granatum* carpellary membrane for removal of arsenic trivalent ions from aqueous medium

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ABSTRACT

The present study focuses on adsorption of arsenic trivalent ions from water on pristine *Punica granatum* carpellary membrane (PPC) under different conditions including initial arsenic ions concentration in water, dose of PPC, pH, and time of contact. Scanning electron microscope, atomic emission spectroscopy, Brunauer–Emmett–Teller and energy-dispersive X-ray (EDX) techniques were used for confirmation of adsorption process. EDX spectrum of PPC did not exhibit any arsenic peak. However, additional arsenic peak was visible in EDX of PPC after adsorption which confirmed the adsorption of arsenic on adsorbent. Batch adsorption studies were performed to analyze the adsorption of arsenic trivalent ions on the adsorbent surface in various conditions. Optimum removal of arsenic was achieved at 60 mg/L of arsenite solution on 0.06 g/L of adsorbent dose at pH 5.0 for 120 min of contact time. Maximum adsorption (Langmuir) capacity was found to be 83.33 mg/g on the surface of PPC with 0.998 R^2 value. Pseudo-second-order kinetic model was found to be the best fitted model with 0.998 R^2 value. Pseudo-second-order calculated adsorption capacity at equilibrium (48.70 mg/g) was closed to experimental value (52.63 mg/g) also confirmed the best fitted model.

Keywords: Adsorption; Arsenic; Kinetics; Langmuir isotherm; Pristine *Punica granatum* carpellary membrane

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1. Introduction

Worldwide, more than 1.8 billion inhabitants use contaminated drinking water and the linked health affects impedes the survival of poor families across the world [1–6]. Arsenic contamination is of great concern and enters the water through numerous geographical reasons and anthropogenic activities. Notably in recent eras, the wide usage of arsenic-based pesticides/fertilizers and mineral exploitation has greatly lifted the arsenic levels in the ecosystem. Millions of people in Bangladesh got affected and suffering from liver, kidney, bladder and skin disorders as well as cardiac issues due to ingestion of arsenic contaminated water [7,8]. Number of studies confirms the existence of arsenic in various varieties of rice [8–10]. Chronic exposure to arsenic has been well known to raise the threat of cancer, cardiovascular, and nervous system malfunctions [11]. As per guidelines laid down by WHO and EPA, concentration up to 0.01 mg/L of arsenic in water is permissible, whereas the standard specification for certain locations raises up to 0.05 mg/L due to some practical reasons [8,12,13]. Exposure to arsenic via numerous routes should be curtailed as much as possible. Once it gets registered in the food chains via agriculture produce, water, flora or fauna, it is very difficult to avoid the ingestion of arsenic.

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Arsenic elimination from potable water is most important for the well-being of humans. Membrane filtration, oxidation, bioremediation, coagulation, ion exchange, and adsorption methods have been widely used for remediation of the arsenic from water. Membrane filtration, oxidation, bioremediation, and ion exchange methods are quite expensive, low efficient and difficult to manage [14–16]. However, adsorption is one of the highly recommended technologies by the researchers for removal of arsenic and other impurities from water because of low cost, highly efficient and manageable options [17–19].

Nanomaterials, synthetic and modified other materials have been widely applied as adsorbent for removal of arsenic and other contaminants from water [5,6,16–19]. However, there are certain practical/ economical/ availability constraints to utilize these materials for water purification [20,21]. Groundnut shells, rice polish, coconut fibres, biochar of rice straw, banana peel, *Momordica charantia*, guava leaf biomass, *Psidium guajava*, orange peel, sugarcane bagasse, mango bark, bagasse, moringa lamarck seed, mosambi citrus peel, water melon rind, corn cob, java plum seed, pomegranate peel, tea waste, water chestnut shell, *Hydrilla verticillata*, egg shell, rice husk biochar, saw dust, *Acacia auriculiformis*, corncob husk, *Acacia nilotica* [36–38]. In order to surmount the problem easily available natural adsorbents in its pristine or modified form need to be further explored and tested for the elimination of arsenic ions from water as these natural adsorbents offer more viable, frugal and cost-effective solution [22].

Punica granatum (pomegranate), belonging to the family *Punicaceae*, also known as the Jewish Torah or the paradise fruit. Pomegranate is a unique fruit indigenous to Iran and is cultivated nowadays in Mediterranean region, Arabian Peninsula, South East Asia, Afghanistan, and India. The fruit consists of many parts such as seeds (fertilized ovule), and carpellary membrane which separates seeds in the fruit. 30% of the total fruit weight corresponds to the peel [23]. Carpellary membrane used in the present research study is usually disposed as waste residue. The constituents of carpellary membrane are poly phenols (epigallocatechin-3-gallate (EGCG), phenols, flavonoids (catechin, luteolin, epicatechin, quercetin), hydrolysable tannins condensed tannins, proanthocyanidin, gallotannins, ellagitannin compounds, minerals, phenolic acid (Gallic acid, ellagic acid and caffeic acid) complex polysaccharides [24,25]. Present study is focused for adsorption of arsenic trivalent ions from prepared water samples using *Punica granatum* carpellary membrane (PPC) adsorbent at different conditions including initial arsenic ions concentration, dose of PPC, pH, and time of contact.

2. Material and methods

100 ppm stock solution of arsenic trivalent ions was prepared from analytical grade sodium arsenite ($NaAsO_2$) purchased from Central Drug House Pvt. Ltd., in distilled water. Different concentration solution for batch study was prepared from 100 ppm stock solution after dilution. pH of prepared solutions was maintained between 1–9 using sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) obtained from Loba Chemia. All the chemicals used in the research work are used as received. All apparatus used in research work was subjected to wash with aqua regia followed by double distilled water. Fresh *Punica granatum* was taken from market of Faridabad India, washed with double distilled water and eatable part was removed from it. The carpellary membrane collected from the fruit was dried for one week in sunlight and then grinded to get fine powder then sieved (Mesh no 4).

2.1. Characterization techniques

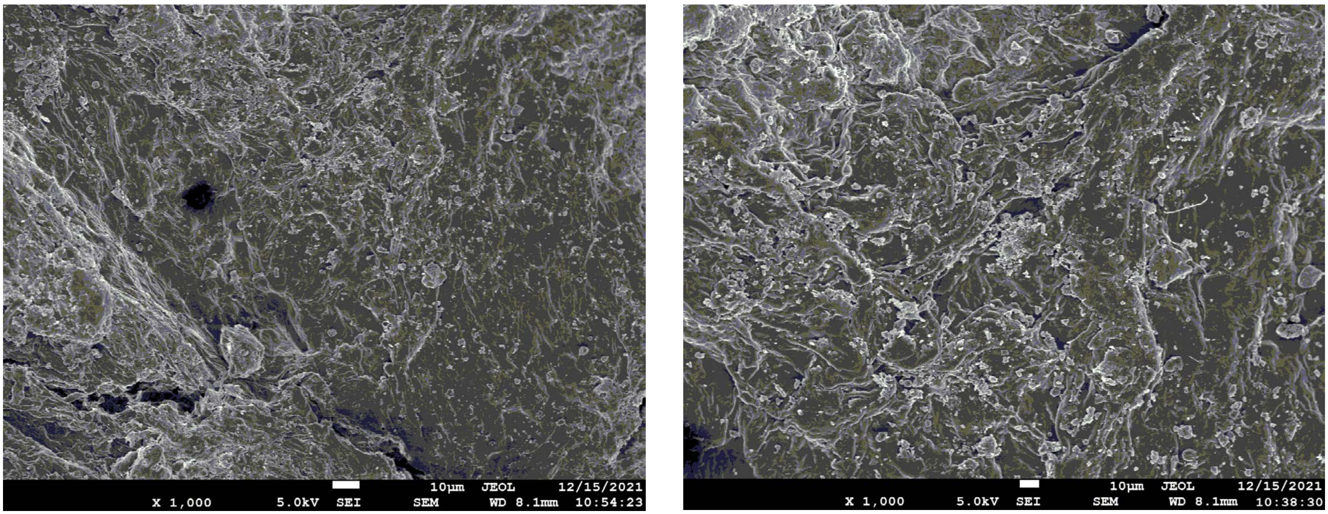
Fourier transform infrared (FTIR) Affinity 1S Shimadzu instrument was used to measure the spectrums of pristine adsorbent before and after adsorption of arsenic ions using KBr pallets. Groups on the surface were identified and characterized using FTIR technique. Brunauer–Emmett–Teller (BET) equipment, Micromeritics ASAP 2020 (Germany), porosity and surface analyser, was employed to know the surface area and size of samples through N_2 adsorption. Surface morphology of PPC before and after adsorption was characterized using scanning electron microscope (SEM) technique. The SEM imaging of samples (before and after adsorption) was carried out through JSM 6510Lv SEM instrument manufactured by Jeol Japan, operating at 15 kV accelerating voltage. 1 cm to 5 μ area may be imaged with magnification 20x–30000x and spatial resolution of 50–100 nm by using conventional SEM. Composition of PPC before and after adsorption was analyzed using energy dispersive X-ray (EXD) technique. Energy-dispersive X-ray (EDX) of adsorbents was carried out by the Oxford INAX-ACT model instrument manufactured by Oxford (London), to know the chemical composition of PPC. Microwave plasma-atomic emission spectrophotometer (MP-AES 4200) Agilent Technologies Inc. (USA) was used for detection arsenic concentration in the solution.

2.1.1. Fourier transform infrared (FTIR) analysis

Functionalization on the surface of PPC was identified using FTIR. PPC spectrum exhibits carbonyl stretching (1,729 cm^{-1}) band and –OH stretching (3,169 cm^{-1}) band due to presence of poly phenol of adsorbent. The peak observed at 2,882 cm^{-1} indicates $-CH_2$ group symmetric stretching. The peak at 1,372 cm^{-1} confirmed the presence of –CH (stretching vibration) group in the compound. The peak at 1,020 cm^{-1} is due to C–O stretching vibration of [22]. However, FTIR spectrum of PPC was slightly changed after adsorption of arsenic trivalent ions because of interaction of arsenic with the different groups.

2.1.2. SEM analysis

Surface morphology of PPC before and after adsorption was characterized using SEM technique provides high resolution image. Fig. 1a shows SEM images of PPC and 1b shows after adsorption of arsenic trivalent ions, respectively at 1,000X magnification. It was noticeable that empty sites available on PPC surface of 10 μm size were occupied by arsenic trivalent ions after adsorption. Many bright points are visible in image obtained after treatment of arsenic ions contaminated water with PPC indicated the presence of arsenic ions due to adsorption [26,27].



(a) (b)

Fig. 1. SEM images of (a) PPC and (b) As(III)-PPC.

2.1.3. Energy dispersive X-ray analysis

Elemental and quantitative composition of adsorbent samples were analyzed using EDX which is a non-destructive technique. Extremely energetic electron beam is descended on the sample causing emission of X-rays emitted from the sample that is used to identify elemental and quantitative composition of PPC. EDX spectrum of PPC did not display any arsenic peak. However, PPC examined after adsorption studies displayed additional arsenic peak (at 10.8 eV) which confirmed the adsorption of arsenic on PPC (Fig. 2).

2.1.4. BET analysis

BET, is used to measure the specific surface area as well as pore size of the adsorbent in presence of nitrogen. BET surface area of 0.2001 ± 0.0570 m^2/g and Langmuir surface area equal to 0.2224 ± 0.0594 m^2/g with BJH adsorption average pore diameter (4 V/A) 540.52 Å was found under nitrogen atmosphere. High surface area as well as pore volume of the adsorbent helps to hold arsenic trivalent ions on the surface of adsorbent material under study [22].

2.1.5. Thermal analysis

Stability of the PPC adsorbent can be analyzed using thermogravimetric analysis (TGA). The TGA and derivative thermogravimetry (DTG) analysis of the PPC adsorbent is shown Fig. 3. TGA analysis was performed from 25°C (room temperature) to 1,000°C temperature with 10°C/min heating rate. Gradual weight loss was observed during whole TGA analysis. 8.77% weight loss was observed from 25.10°C–132.16°C could be attributed to evaporation of water present in adsorbent matrix. Sharp weight loss was observed after 132.16°C. 58.23% weight loss was observed from 132.16°C to 547.88°C could be attributed to primary degradation of the PPC adsorbent. Also gradually weight loss was observed after 547.88°C could be attributed to the further degradation of PPC adsorbent. Thus PPC adsorbent showed excellent thermal stability before 132.16°C.

3. Results and discussion

3.1. Adsorption batch studies

Adsorption studies for removal of arsenic trivalent ions were carried out by the batch technique. Batch studies help to identify the optimal values for the arsenic ions remediation from water.

3.1.1. Effect of adsorbent (PPC) dose

In order to evaluate the effect of PPC (adsorbent) dose; different dosage of PPC were taken and keeping other factors constant (60 mg/L of arsenite solution, pH 5, contact time 120 min) (Fig. 4). 60 mg/L of arsenite solution along with 0.03, 0.06, 0.12, 0.18, 0.24 and 0.3 g/L of PPC adsorbent was taken in 6 different 250 mg/L conical flask and were agitated via rotatory shaker, after subjecting the mixture for agitation for fixed period of time, the mixture was removed and filtered. The filtrate obtained was subjected to atomic emission spectrophotometer in order to determine the concentration arsenic trivalent ions in the solution. From the results obtained it was determined that adsorption increased rapidly up 0.12 g/L and negligible change was examined after that. The initial ascend in amount of arsenic trivalent ions adsorbed is due to enhanced accessibility of active sites for adsorption (Fig. 4b).

3.1.2. Effect of initial arsenic ions concentration

The adsorption capacity of PPC was affected by concentration of arsenic ions (Fig. 4a). The effect of initial arsenic trivalent ions on adsorption was studied using 20–100 mg/L concentrations of the solutions at other constant factors (0.06 g/L PPC dose, pH 5, contact time 120 min) and same procedure. It was observed that adsorption increases with increase in the concentration of arsenic trivalent ions. Results showed that adsorption rate was slightly fast in the beginning due to more availability of more sites. Further it was slightly slow due to non-availability or less availability of sites.

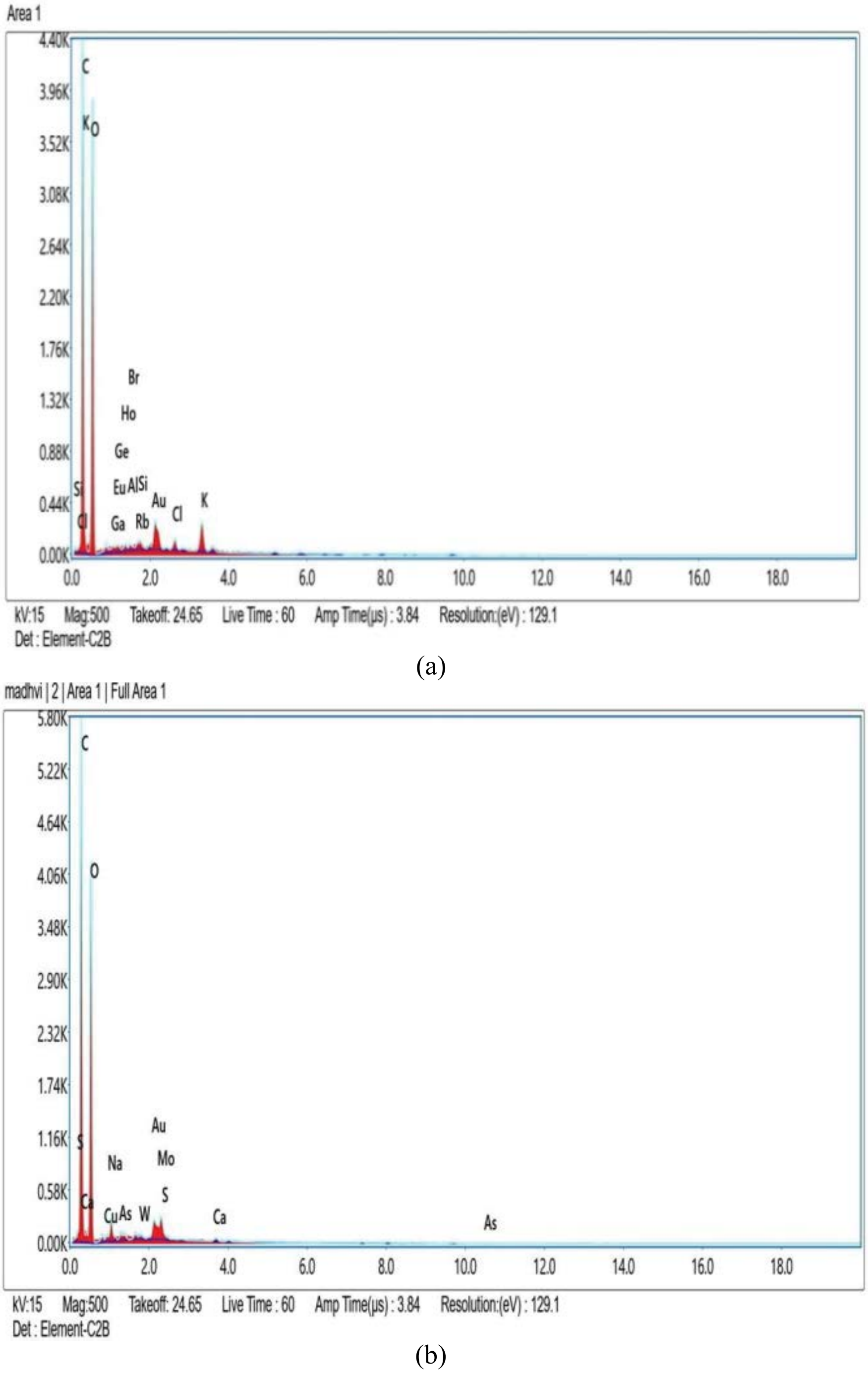


Fig. 2. EDX images of (a) PPC and (b) As(III)-PPC.

3.1.3. *Effect of pH*

pH of medium has prominent effect on adsorption process. Zero point charge pH (pH-ZPC) represents zero surface charge of the adsorbent. Surface of adsorbent is positive below the pH-ZPC and negative above the pH-ZPC. Negatively charged species are attracted from the solution towards the adsorbent below the pH-ZPC and positively charged species are attracted from the solution towards the adsorbent above the pH-ZPC. Zero point charge pH of PPC adsorbent was measured as per standard method [28]. Zero point charge can be obtained by plotting a graph between initial and final pH with or without adsorbent (Fig. 4d) and it is the value where the change in the pH is zero. In present study 3.5 is the pH-ZPC of PPC adsorbent. It indicated that PPC adsorbent surface was having positive charge below 3.5 pH and negatively charged above 3.5 pH. In order to evaluate the effect of pH, the adsorption study was carried out in conical flask at

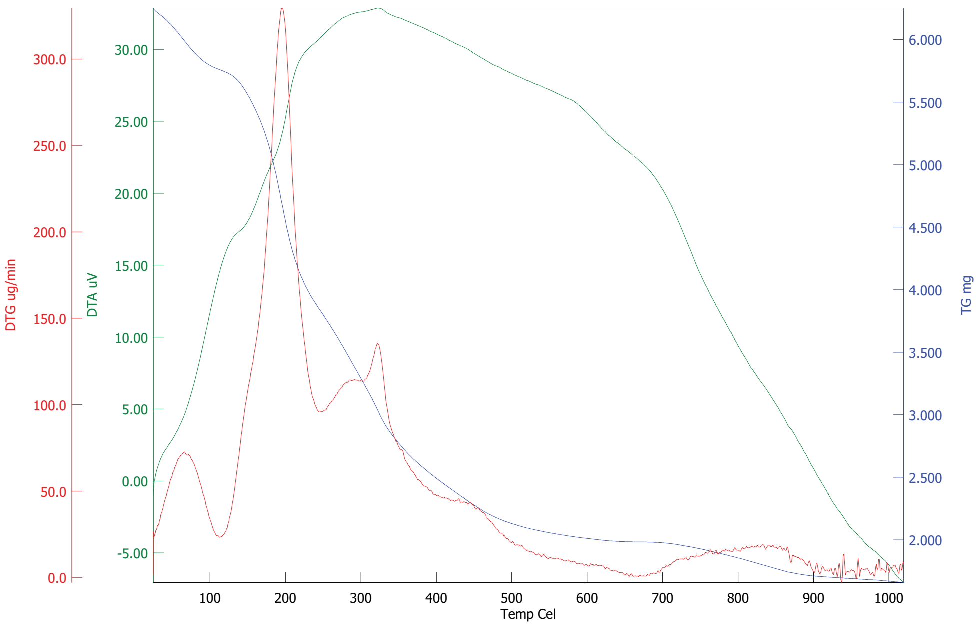
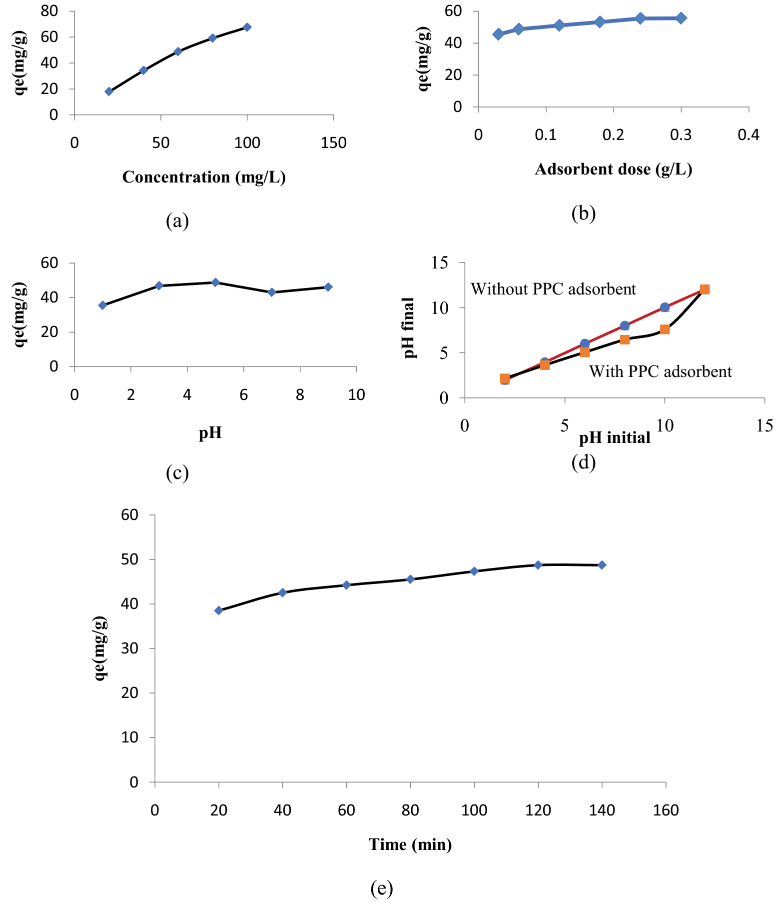


Fig. 3. TGA-DTG-DTA analysis of PPC adsorbent.



(a)

(b)

(c)

(d)

(e)

Fig. 4. Effect of (a) different initial arsenic trivalent ions concentration, (b) adsorbent dose, (c) pH, (d) pH-ZPC value graph of adsorbent and (e) contact time for removal of trivalent arsenic. Constant conditions (60 mg/L solution of arsenite, 0.06 g/L of PPC dose, pH 5, and contact time 120 min).

solution pH 1–9 keeping at other constant factors (0.06 g/L PPC dose, 60 mg/L of arsenite solution, contact time 120 min) and same procedure. pH of solution was maintained by using 1–2 drops of acid (H_2SO_4) or base (NaOH). The filtrate so obtained was subjected to atomic emission spectrophotometer in order to determine the concentration arsenic trivalent ions in the solution. Uptake of arsenic trivalent ions by PPC was found accelerate with rise in pH. Maximum remediation of arsenic was achieved at pH 5.0 (Fig. 4c).

3.1.4. Effect of contact time

Contact time is one of the significant parameters that play important role in the adsorption of arsenic trivalent ions from the solution. In order to evaluate the impact of contact time on the uptake of arsenic from the adsorbate solution, the batch experiment was conducted at different time intervals (20–120 min) while keeping other factors constant. Results demonstrated that adsorption of arsenic trivalent ions by the adsorbent increased with time. In the initial phase, numerous vacant sites are available for adsorption of arsenic trivalent ions but with time (after 120 min) adsorption becomes steady because of decrease in the number vacant sites for uptake of arsenic trivalent ions (Fig. 4e).

Results of adsorption batch study showed that pH 5 and 120 min of contact time are favorable conditions for maximum removal with different concentration of arsenic ions keeping PPC dose from 0.03–0.3 g/L.

3.1.5. Effect of temperature

Temperature has a key role of the adsorption of contaminants on the surface of adsorbents. Effect of temperature was studied at 293, 303, 313, 323 K at other constant factors (arsenic initial concentration = 60 mg/L; adsorbent dose = 0.06 g/L; contact time = 120 min; and pH = 5). Result indicates that arsenic ions adsorption increases with increase in temperature from 293–323 K. At high temperature mobility of the ions as well as activity of the surface binding sites increases which increase the adsorption of arsenic ions on the surface.

3.2. Adsorption isotherm

Batch study experiments are utilized to optimize the maximum adsorption capacity using adsorption isotherms. Maximum removal of arsenic was achieved at 120 min of time. 0.06 g/L of PPC was selected for further studies to check the effects of pH, contact time, and concentration of the arsenic. Langmuir, Freundlich, and Temkin models were applied to check the homogenous or heterogeneous surface with uni-layered or multi-layered binding and adsorption capacity of PPC for arsenic trivalent ions.

3.2.1. Langmuir isotherm

Experiments were conducted under the optimized conditions (adsorbent dose 0.06 g/L, pH 5, contact time 120 min). This model assumes that monolayer adsorption occurs on the sorbent surface and it is a reversible process, that is, adsorbate molecule can adsorb as well as can get desorbed according to the Langmuir model. Adsorption can occur by chemisorptions or by physiosorption. Langmuir model in the linear form can be represented as [29]:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_{\max}}\right) + \left(\frac{C_e}{q_{\max}}\right) \tag{1}$$

where C_e is concentration of arsenic trivalent ions at equilibrium after adsorption, q_e is the concentration of arsenic trivalent ions adsorbed on PPC in mg/g, K_L represents Langmuir constant and $q_{\max}$ indicates maximum adsorption capacity of PPC in mg/g. Langmuir isotherm helps to calculate separation factor R_L. The value of separation factor obtained from Langmuir isotherm provides indication that whether the set-up is favorable or unfavorable for adsorption process.

$$R_L = \left(\frac{1}{1+\left(K_L C_o\right)}\right) \tag{2}$$

Separation factor (R_L) may vary from zero to positive or negative value. If the value of separation factor is zero, it means irreversible isotherm will be obtained indicating very strong adsorption, linear isotherm will be attained in case R_L is one; similarly, if R_L is less than one but greater than zero the conditions are favourable for adsorption and if separation factor (R_L) has value greater than one the conditions are unfavorable for adsorption. R_L value is less than one indicated that conditions are favourable for adsorption of arsenic ions (Table 1). Maximum adsorption capacity, $q_{\max} = 83.33$ mg/g as well as Langmuir constant, $K_L = 0.123$ were obtained from the slope and intercept of the plot (Fig. 5a).

3.2.2. Freundlich isotherm

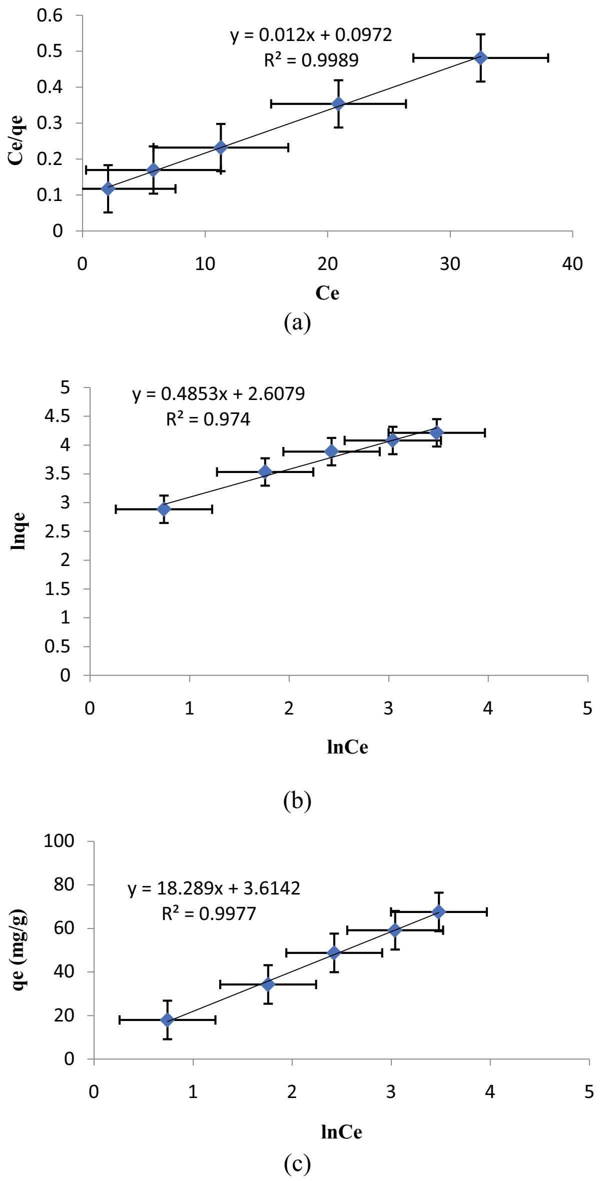
Freundlich isotherm describes the multilayer reversible adsorption process, heterogeneity of the surface as well as reflects the exponential allocation of the active sites [29]. Freundlich isotherm can be expressed as

$$q_e = K_f C_e^{1/n} \tag{3}$$

Linear form of the Eq. (3) can be expressed as [28]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where Freundlich constant K_f is related to the adsorption capacity, q_e represents arsenic trivalent ions adsorbed on the PPC at equilibrium (mg/g), C_e represents concentration of arsenic trivalent ions at equilibrium after adsorption, $1/n$ is potency of adsorption, n denote the adsorption intensity in addition to deviation from linearity of adsorption [22]. The value of n ranges from 1–10 for favorable adsorption. The parameters of the model can be calculated from a straight line obtained by plotting $\ln C_e$ vs. $\ln q_e$ with $1/n$ as the slope and $\ln K_f$ as an intercept (Fig. 5b). The value of n is 2.06 also indicates the favorable adsorption. The other results obtained are summarized in Table 1.



(a)

(b)

(c)

Fig. 5. Isotherms (a) Langmuir, (b) Freundlich, (c) Temkin for removal of arsenic trivalent ions by using 0.06 g/L of PPC at pH 5 for 120 min of contact time.

3.2.3. Temkin isotherm

Temkin isotherm model take into consideration the consequence of adsorbate/adsorbate interactions on the adsorption potential. The Temkin isotherm is not valid for extremely large and low ion concentrations. Temkin isotherm model is best suited for an intermediate range of concentrations values [30]. Temkin isotherm is expressed in Eq. (5):

$$q_e = b\ln AC_e \tag{5}$$

where q_e is the amount adsorbed by adsorbent at equilibrium, C_e corresponds to equilibrium concentration, A represents Temkin equilibrium binding constant (L/mg), b corresponds to heat sorption constant (J/mol) and is calculated from $b = RT/B$, where R is the gas constant, B Temkin constant (J/mol), T is temperature in Kelvin. The value of equilibrium binding constant (A) and heat sorption constant (b) was calculated from slope and intercept of the graph plotted against $\ln C_e$ vs. q_e (Fig. 5c). The results obtained are summarized in Table 1. The value of b was found to be 137.74 J/mol.

From the comparative analysis of the values, specifically regression correlation coefficients, it can be inferred that the Langmuir isotherm model ($R^2 = 0.998$) explains best for adsorption of arsenic trivalent ions on the surface of PPC compared to Freundlich ($R^2 = 0.974$) and Temkin ($R^2 = 0.997$) isotherm models. The regression correlation coefficient of the Langmuir isotherm model is more closed to unity as compared with the other two isotherms indicated monolayered coverage of arsenic trivalent ions on the surface of PPC.

3.3. Kinetics of adsorption

In order to conclude the adsorption rate as well as the mechanism of adsorption it becomes foremost important to study the adsorption kinetics. The adsorption rate can be calculated by fitting the recorded data into different kinetic models (pseudo-first-order, pseudo-second-order) [29]. The unique nature of equilibrium kinetics was studied to establish the rate-limiting steps indulged in the course of adsorption of arsenic trivalent ions.

3.3.1. Pseudo-first-order and pseudo-second-order kinetic models

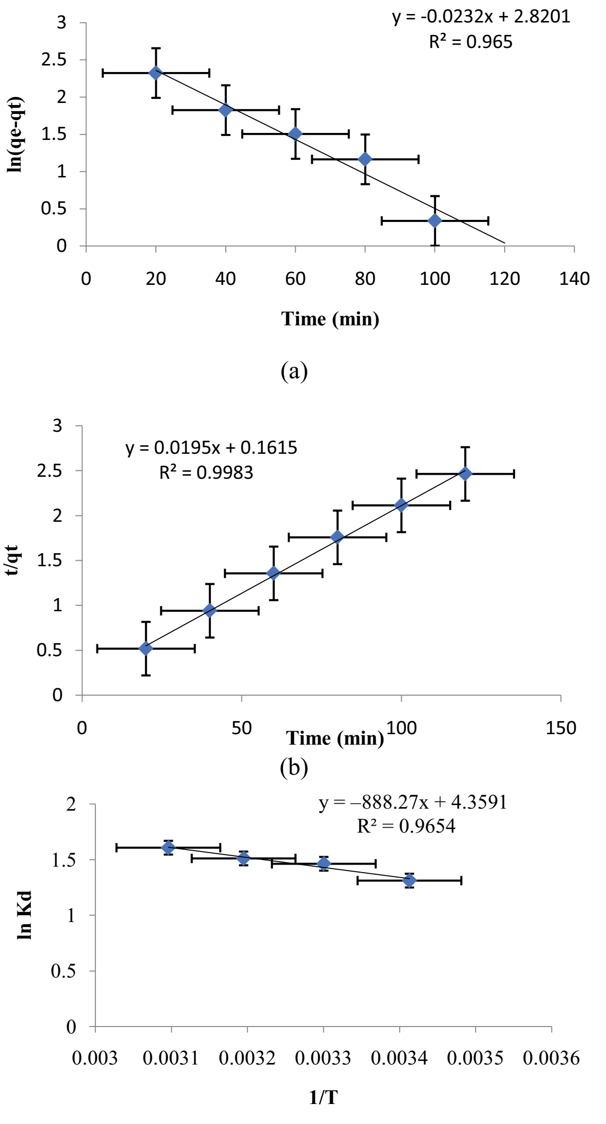
The pseudo-first-order (PFO) parameters were obtained from Lagergren's model rate equation whose linear form is expressed as [28]:

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 t \tag{6}$$

The pseudo-second-order (PSO) kinetic model assumes that chemisorption as rate limiting step and as per this adsorption rate does not depend on the concentration of adsorbate but depend on adsorption capacity [29,30]. In order to determine the rate constant for adsorption, the PSO kinetic model can be expressed in form of Eq. (7) [31–33]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{7}$$

where Eqs. (6) and (7) k_1 and k_2 (L/mg/min) are I and II order rate constants respectively. Value of these constants can be evaluated from the linear plot of $\ln(q_e - q_t)$ vs. time (t) (Fig. 6a) and linear plot of t/q_t vs. time (t) (Fig. 6b). The results obtained are summarized in Table 2. PSO was the better fitted model compared to PFO due to high value of regression correlation coefficient (R^2). Calculated adsorption capacity at equilibrium was 16.77 and 48.70 mg/g for pseudo-first-order and pseudo-second-order model respectively. Pseudo-second-order model calculated value was closed to experimental value (52.63) also confirmed best fitted model for adsorption of arsenic ions.



(a)

(b)

(c)

Fig. 6. Kinetics (a) pseudo-first-order, (b) pseudo-second-order, models for removal of arsenic trivalent ions by PPC (c) Van't Hoff equation, for adsorption of arsenic trivalent ions on PPC adsorbents.

3.3.2. Thermodynamics study

Thermodynamic study was investigated using different temperature to evaluate spontaneity and feasibility of adsorption in terms of Gibbs energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) parameters, which can be calculated by using the below equation [34,35]

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{8}$$

where K_d is thermodynamic constant $\{K_d = (q_e/C_e)\}$, q_e (mg/g) is arsenic trivalent ions adsorbed on the PPC at equilibrium, C_e is concentration of arsenic trivalent ions at equilibrium after adsorption, R is universal gas constant, and T (K) is absolute temperature.

Energy change ($\Delta G°$) can be calculated by using standard Gibbs free energy change equation ($\Delta G° = \Delta H° - T\Delta S°$) in which change in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were evaluated from the slope and intercept of a linear plot shown in Fig. 6c.

Analysis of thermodynamic data summarized in Table 3 showed that adsorption of arsenic trivalent ions on adsorbent was spontaneous and endothermic in nature due to negative value Gibbs free energy change ($\Delta G°$), positive value of enthalpy ($\Delta H°$) and entropy changes ($\Delta S°$).

3.4. Regeneration of PPC

For the sake of making the adsorption process cost effective and secure for environment, recycling and resumption of the adsorbent from the desorbing agent is one of the most crucial aspects in the adsorption study. PPC adsorbents were regenerated by designing column batch study by utilizing 20% H_2SO_4 to it with desorption efficiency of 80%–85% obtained in the first cycle followed by subsequent five cycles and 90%–95% efficiency was obtained in the next five cycles. After regeneration, washing of PPC was done with deionized water and heated overnight at 120°C. Recovered adsorbent was stored for further use. It was observed that there was no significant change in desorption of arsenic trivalent ions within the temperature range (25°C–40°C).

3.5. Mechanism of removal of arsenic trivalent ions from water

Removal of arsenic trivalent ions from water by PPC depends on availability of various binding site and ion exchange capacity of the PPC groups present on the surface. Arsenic trivalent ions are adsorbed on the surface of PPC by physiochemical mechanism. However, ion exchange mechanism also facilitate because of presence of carboxylic group on the surface of PPC.

3.6. Column study

Column study was performed to check the practical applicability of this adsorbent in real scenario. Fixed bed packing was prepared using PPC adsorbent in the column of 25 mL capacity of the length 79.75 cm (outer and inner diameter 1.4 and 0.8 cm) at a uniform 5 mL/min flow rate for 20 mL arsenic solution. 0.1 mg/L synthetic arsenic solution at pH 5 was passed through this column. Glass wool was placed at top and at the end of the column to prevent adsorbent loss. More than 97% efficiency was observed for PPC. Thus PPC can be applied as a packing material in the column for removal of arsenic from water.

3.7. Comparative studies of *Punica granatum* carpellary membrane adsorbent with other adsorbents

Availability of adsorbent, its ability to regenerate, and capacity of adsorption are some of the important parameters to be considered while assessing the adsorbent materials. Removal of heavy metals by adsorption especially arsenic

Table 1
Results of different isotherms

Ads.	Isotherm model									
	Langmuir			Freundlich			Temkin			
	$q_{\max}$ (mg/g)	K_L (L/g)	R^2	n	K_f	R^2	A	B	b	R^2
PPC	83.33	0.123	0.998	2.06	13.55	0.974	1.2	18.28	137.74	0.997

Table 2
Results of different kinetic studies

Ads.	Pseudo-first-order kinetics			Pseudo-second-order kinetics			$q_{e,\exp}$ (mg/g)
	q_e	k_1	R^2	q_e	k_2	R^2	
PPC	16.77	0.023	0.965	48.70	0.002	0.998	52.63

Table 3
Results of thermodynamic studies for adsorption of arsenic trivalent ions on PPC

Adsorbent	Thermodynamic parameters					
	$\Delta G°$ (kJ/mol)				$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol·K)
Temp. (K)	293 K	303 K	313 K	323 K	–	–
PPC	–3.16	–3.52	–3.88	–4.24	7.38	0.036

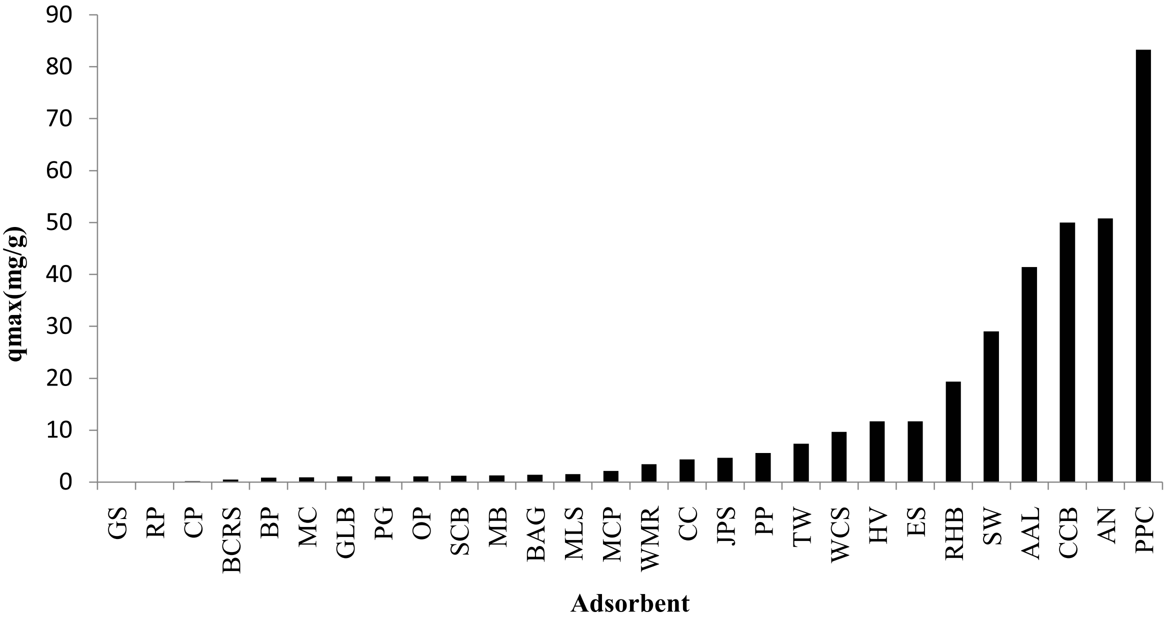


Fig. 7. Performance diagram of different natural adsorbent for removal of arsenic trivalent ions from water.

trivalent ions from aqueous media was carried out using many synthetic and natural materials in their pristine as well as derivatized form. Reported studies have been reviewed for a wide range of natural adsorbents in their pristine form used elimination arsenic trivalent ions from water samples. On evaluating the reported data, maximum adsorption capacities ($q_{\max}$) for arsenic trivalent ions from aqueous media by PPC under a specific set of experimental settings followed the below given sequence. Subject to the fact that it is very difficult to do analysis or comparison of the performance of the adsorbent ensuring all conditions similar as varying optimized conditions has been used to examine the adsorption capacity of different reported adsorbents. In general all the studies have been performed in the pH range of 4–9, 0.01–250 mg/L initial arsenic ions concentration, 20°C–40°C temperature, 0.014–50.8 mg/g maximum adsorption capacity with 60%–99% removal of arsenic from water samples [36–38].

For natural adsorbents comparative arsenic trivalent ions uptake capacity is listed as: groundnut shells (GS) 0.014 < rice polish (RP) 0.04 < coconut fibres (CP) 0.12 < biochar of rice straw (BCRS) 0.4476 < banana peel (BP) 0.84 < *Momordica charantia* (MC) 0.88 < guava leaf biomass (GLB) 1.05 < *Psidium guajava* (PG) 1.06 < orange peel (OP) 1.08 < sugarcane bagasse (SCB) 1.20 < mango bark (MB) 1.25 < bagasse (Bag) 1.35 < moringa lamarck seed (MLS) 1.5 < mosambi citrus peel (MCP)2.12 < water melon rind (WMR) 3.4 < corn cob(CC) 4.33 < java plum seed (JPS) 4.63 < pomegranate peel (PP) 5.57 < tea waste (TW) 7.36 < water chestnut shell (WCS) 9.61 < *Hydrilla verticillata* (HV) 11.65 < egg shell (ES) 11.69 < rice husk biochar (RHB) 19.3 < saw dust (SW) 29 < *Acacia auriculiformis* leaf (AAL) 41.41 < corncob husk (CCB) 50 < *Acacia nilotica* (AN) 50.8 < pristine *Punica granatum* capillary membrane (PPC) 83.33 (Fig. 7) [36–38].

4. Conclusion

Punica granatum carpellary membrane (PPC) is a promising economic material that can be utilized for arsenic remediation at different conditions. Batch studies were performed at different arsenic concentration in solution, different pH, different contact time and different adsorbent dose to get the optimum removal of arsenic from water sample. Langmuir, Freundlich and Temkin models were applied for adsorption of arsenic trivalent ions. Optimum removal of arsenic was achieved at 60 mg/L of arsenite solution on 0.06 g/L of adsorbent dose at pH 5.0 for 120 min of contact time. Results showed that Langmuir isotherm model was the best fitted model ($R^2 = 0.998$) with high regression coefficient value compared to other models. Langmuir maximum adsorption capacity was 83.33 mg/g. Pseudo-second-order model kinetic model was the best fitted model with high regression coefficient value. Further studies may be conducted using PPC as economical and viable adsorbent for simultaneous removal of multiple contaminants from aqueous medium.

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