

Research Article

## Sorption of Arsenic(III) from wastewater using *Prosopis spicigera* L. wood (PsLw) carbon-polyaniline composite

**Ramasubbu Dhana Ramalakshmi\***

Department of Chemistry, Rani Anna Government College for Women, Tirunelveli - 627008 (Tamil Nadu), India; Research centre (St. Xavier's College (Autonomous), Tirunelveli - 627002), Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli-627012 (Tamil Nadu), India

**Mahalingam Murugan**

Department of Chemistry, Sri K.G.S. Arts College, Srivaikuntam, Thoothukudi - 628619 (Tamil Nadu), India

**Vincent Jeyabal**

Department of Chemistry, St. Xavier's College (Autonomous), Palayamkottai, Tirunelveli - 627 002 (Tamil Nadu), India

\*Corresponding author. Email: dhana.ram11@gmail.com

### Article Info

<https://doi.org/10.31018/jans.v13i4.2969>

Received: September 5, 2021

Revised: November 3, 2021

Accepted: November 7, 2021

### How to Cite

Ramalakshmi, R. D. *et al.* (2021). Sorption of Arsenic(III) from wastewater using *Prosopis spicigera* L. wood (PsLw) carbon-polyaniline composite. *Journal of Applied and Natural Science*, 13(4), 1283 - 1293. <https://doi.org/10.31018/jans.v13i4.2969>

### Abstract

Water contamination by toxic heavy metal ions causes a serious public health problem for humans. The present work reports the development of a new adsorbent of PsLw carbon-polyaniline composite by direct oxidation polymerisation of aniline with PsLw carbon for the removal of arsenic (As). The structure and morphologies of the adsorbent were characterised by Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). The ability of the adsorbent for the removal of As(III) was estimated by batch and kinetic studies. The optimum adsorption behaviour of the adsorbent was measured at pH=6.0. The equilibrium process was found to be in good agreement with Langmuir adsorption isotherm and the maximum adsorption capacity was 98.8 mg/g for an initial concentration of 60 mg/L at 30 °C. The kinetic study followed pseudo-second-order kinetics. Thermodynamic parameters predict the spontaneous, feasible and exothermic nature of adsorption. Column operation was carried out to remove As(III) bulk and column data obeys the Thomas model. The results indicated that PsLw carbon-polyaniline composite can be employed as an efficient adsorbent than polyaniline for removal of As(III) from wastewater.

**Keywords:** Adsorption, Isotherm, Mass transfer, Polyaniline, PsLw carbon, Thomas model

### INTRODUCTION

Arsenic (As) is released into groundwater and surface water through human activities and natural phenomena. Even though arsenic is essential to human health, its accumulation into the tissues of humans and other organisms through the food chain poses health hazards. A large amount of arsenic ingestion causes adverse effects such as chronic symptoms (dermatitis, pigmentation, myelopathy, peripheral neuropathy, jaundice, renal failure) and acute symptoms (nausea, vomiting, diarrhoea) (Ogata *et al.*, 2006). Arsenic concentrations are found at an elevated level (several thousand times than the potable limit), notably in West Bengal (India), Bangladesh, Taiwan, northern China, Mexico, Chile, Argentina, and parts of the United States of America Japan. World Health Organisation (WHO) lowered the

potable limit of arsenic in drinking water from 50 to 10 µg/L (Mohan and Pittmann, 2007; Fayazi *et al.*, 2016). Various methods are available to remove arsenic from wastewater, and the adsorption method is more advantageous than others in terms of cost, ease of operation, flexibility, simplicity of design, and insensitivity to toxic pollutants. For adsorptive removal of arsenic adsorbents such as activated carbon, activated alumina, gibbsite, aluminium loaded materials, lanthanum compounds, fly ash, natural solids etc., have been used (Munoz *et al.*, 2002). However, activated carbon plays a major role in any other adsorbents. The adsorption capacity of activated carbon can be enhanced by heteroatoms such as oxygen, hydrogen, nitrogen and phosphorous. They form acidic and basic functional groups and contribute to additional adsorption. This surface modification of the carbon matrix can be affect-

ed by the impregnation of metals/metal oxides or composite formation with the polymeric material.

Polymer based adsorbents have a wide range of pore structures, strong binding affinities, high adsorption capacity and good mechanical, chemical and thermal stability. Polyaniline is one such polymer that can be used for composite formation with carbon due to easy synthesis, the feasibility of doping, good physicochemical characteristics, mechanical flexibility, environmental stability and easy availability of its monomer. In wastewater treatment, polyaniline is used as an adsorbent due to amine and imine groups that interact with molecules of various contaminants present in polluted water (Li *et al.*, 2015). Pure and modified forms of polyaniline behave as an effective adsorbent for the removal of arsenic and heavy metals (Boeva and Sergeev, 2014; Jiang *et al.*, 2018; Nodeh *et al.*, 2018; Mahmoud *et al.*, 2018). Polyaniline contains many amine and imine functional groups. It is expected to have interactions with some metal ions, which have the strong affinity to nitrogen atoms in the structure. In the present study, *Prosopis spicigera* L. wood (PsLw) carbon prepared from cheaply available plant material is impregnated with polyaniline and used for removal of As(III) from wastewater.

## MATERIALS AND METHODS

### Preparation of PsLw carbon-polyaniline composite

PsLw plant material used in the present work was collected from the dry land area of Palayamkottai in Tirunelveli district, Tamilnadu State, India. The branch and roots of the plant were cut into pieces and piled up on a firing hearth. Before firing, the heaped wood pieces were enclosed by fresh plantain pith and the whole mass was covered and plastered with layers of wet clay. This arrangement prevented the direct entry of air into wood pieces and, hence, prohibited burning wood and becoming ash. After 48 hours of continuous firing and subsequent natural cooling, the activated carbon was obtained. After removing the non-carbonaceous materials, the carbon was isolated, crushed and sieved to 75 micron particles. The composite adsorbent was prepared using the slightly modified literature procedure (Schwarz *et al.*, 1984; Chang *et al.*, 2010). The adsorbent was dried in an air oven at 100 °C for 8 hours and finally kept in clean air-tight containers. 20 g of PsLw carbon was mixed with 10 ml of distilled aniline in 1.0 M H<sub>2</sub>SO<sub>4</sub> and the mixture was cooled in an ice-bath with constant stirring for 2 hours. A pre cooled solution of 0.5 M Ammonium peroxydisulphate in 100 ml of distilled water was added drop by drop under constant stirring for 1 hour. After the addition of APS, the constant stirring was continued for further 3 hours. The reaction mixture was then kept in the refrigerator overnight. The next day it was filtered to recover the product and

washed several times with distilled water till the filtrate became colourless. It was washed with acetone and the sample was dried in an air oven at 110 °C for 5 hours. The dried product was weighed and stored in an airtight container.

### Characterisation of adsorbent

The functional group and surface morphology were analysed by Fourier Transformer Infrared Spectroscopy (JASCO FT/IR – 4700 type A) and Scanning Electron Microscope (Joel, JSM 6390, Oxford Instruments, UK), respectively. The point of zero charge (pH<sub>zpc</sub>) of PsLw carbon-polyaniline composite was determined by potentiometric titration with acid/alkali (Schwarz *et al.*, 1984). The textural property of the surface area of the adsorbents was studied by the methylene blue method (Palit and Moulik, 2000; Adamson, 1990; Potgiefer, 1991) and Brunauer-Emmett-Teller (BET) nitrogen adsorption method.

### Batch adsorption studies

Batch equilibrium studies were carried out for adsorption of arsenic on PsLw carbon-polyaniline composite. Standard As(III) stock solution of 1000 mg/L was prepared for batch studies by dissolving 1.32 g of As(III) oxide with 1000 mL of deionized water. The effect of pH, initial concentration, contact time, in the presence of other ions and solution temperature of the adsorbate solution on PsLw carbon-polyaniline composite were studied. The sample solutions were analysed at particular time intervals using the literature procedure (Jeffery *et al.*, 1989) for higher concentrations. Samples from the column study were analysed using Atomic Absorption Spectrophotometer (concentration less than 1.0 mg/L) (Shimadzu, AA-6300). The lower detectable limit of the spectrophotometric method is 0.25 µg/ml. Each sample was analysed twice and the results are reproducible within ±1 percent error limit. Further, the results obtained from the spectrophotometric method are comparable with the AAS method (lower detectable limit is 0.01 µg/ml) and the deviation is ±3 percent only, which is within the error limit in order to make use of this process for large scale treatment and small scale for potable water.

The amount of adsorption of As(III) per unit mass of adsorbent ( $q_e$ ) was calculated using Eq. (1)

$$q_e = (C_o - C_e)V/W \quad \text{Eq. 1}$$

Where, C<sub>o</sub> and C<sub>e</sub> (mg/L) are the initial and equilibrium concentration of As(III) respectively, V is the volume of the solution (L) and W is the mass of adsorbent (g).

### Adsorption Isotherm Models

Equilibrium adsorption isotherm expresses the relationship between the surface of the adsorbent and the adsorbate molecule and adsorption efficiency. The linear

form of Langmuir and Freundlich models were used for isotherm modelling for arsenic sorption on PsLw carbon-polyaniline composite and can be expressed as

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \tag{Eq. 2}$$

$$\log q_e = \log K_f + 1/n \log C_e \tag{Eq. 3}$$

Where,  $C_e$  (mg/L) and  $q_e$  (mg/g) are the free and sorbed concentration of As(III) species respectively at equilibrium,  $Q_0$  (L/mg) is the monolayer sorption capacity and  $b$  is the Langmuir adsorption equilibrium constant.  $K_f$  ( $\text{mg}^{1-n} \text{g}^{-1} \text{L}^n$ ) and  $1/n$  are the Freundlich constants related to the adsorption capacity and heterogeneity, respectively.

### Adsorption Kinetics

The kinetics of the adsorption arsenic on PsLw carbon-polyaniline composite are described using pseudo first and second-order models at different concentrations and temperatures. The pseudo first-order rate equation of Lagergren is expressed as

$$\log(q_e - q) = \log q_e - k_1 t / 2.303 \tag{Eq. 4}$$

where  $q_e$  and  $q$  are the amounts of As(III) adsorbed at equilibrium and at a time 't' and  $k_1$  is the rate constant for first-order adsorption. The pseudo second-order Ritchie kinetic rate equation can be written as

$$t/q = (1/k_2 q_e^2 (cal)) + t/q_e(cal) \tag{Eq. 5}$$

where  $k_2$  is the reaction rate constant of second order adsorption and  $q_e (cal)$  is the numerically determined parameter.

### Column Study

The experimental unit consists of a glass column of 48 cm height by 3.5 cm diameter packed with 5 g of PsLw carbon-polyaniline composite. The column was fitted with cotton screens to separate the adsorbent from the top and bottom stoppers. The arsenic solution was drawn into the column from a height of 1 meter. Elutents were collected at regular interval of time and

**Table 1.** Physico-chemical characteristics of PsLw carbon-polyaniline composite

Parameters	Values
pH	6.5
Moisture Content % (W/W)	0.0009
Surface area ( $\text{m}^2/\text{g}$ ) (Nitrogen BET adsorption method)	245.39
Surface area ( $\text{m}^2/\text{g}$ ) (Methylene Blue dye adsorption method)	90.21
$\text{pH}_{zpc}$	7.3
Bulk density (g/cc)	0.3834
Particle density (g/cc)	0.4182

analysed. The data were analysed using Thomas model (Thomas, 1948; Reynolds and Richards, 1996), which is given by the equation.

$$\log(C_0/C_e - 1) = k q_e M/Q - k C_0 V/Q \tag{Eq. 6}$$

where,  $C_0$  and  $C_e$  are the influent and effluent As(III) concentrations (mg/L) respectively,  $k$  is the Thomas rate constant (mL/min/mg),  $q_0$  is the maximum solid-phase concentration of solute (mg/g),  $M$  is the mass of the adsorbent (g),  $Q$  is the influent flow rate (mL/min) and  $V$  is the through put volume (mL/min).

## RESULTS AND DISCUSSION

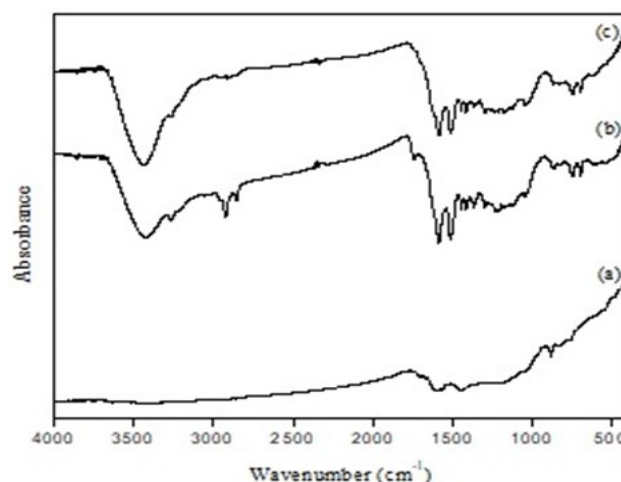
### Characterisation of adsorbent

The physico-chemical characteristics of PsLw carbon-polyaniline composite are listed in Table 1.

### Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) characterisation

FTIR is used to confirm aniline's polymerization and composite formation with PsLw carbon and As(III) adsorption onto the PsLw carbon. The FTIR spectra of pure PsLw carbon, PsLw carbon-polyaniline composite and As(III) loaded PsLw carbon-polyaniline composite are illustrated in Fig. 1a, 1b and 1c, respectively.

The free PsLw carbon shows three weakly intense peaks at  $1613 \text{ cm}^{-1}$  (due to ketone moiety),  $1423 \text{ cm}^{-1}$  (O-H in-plane bending) and  $961 \text{ cm}^{-1}$  (C-O stretching) (Fig. 1a). Fig. 1b of PsLw carbon-polyaniline composite shows the peak at  $3432$  and  $3266 \text{ cm}^{-1}$  due to the presence of -N-H stretching vibration. The peak at  $2915$  and  $2864 \text{ cm}^{-1}$  are due to the presence of -C-H stretching in alkanes, while the peak at  $1738 \text{ cm}^{-1}$  corresponds to C-N stretching of amino group. The adsorp-



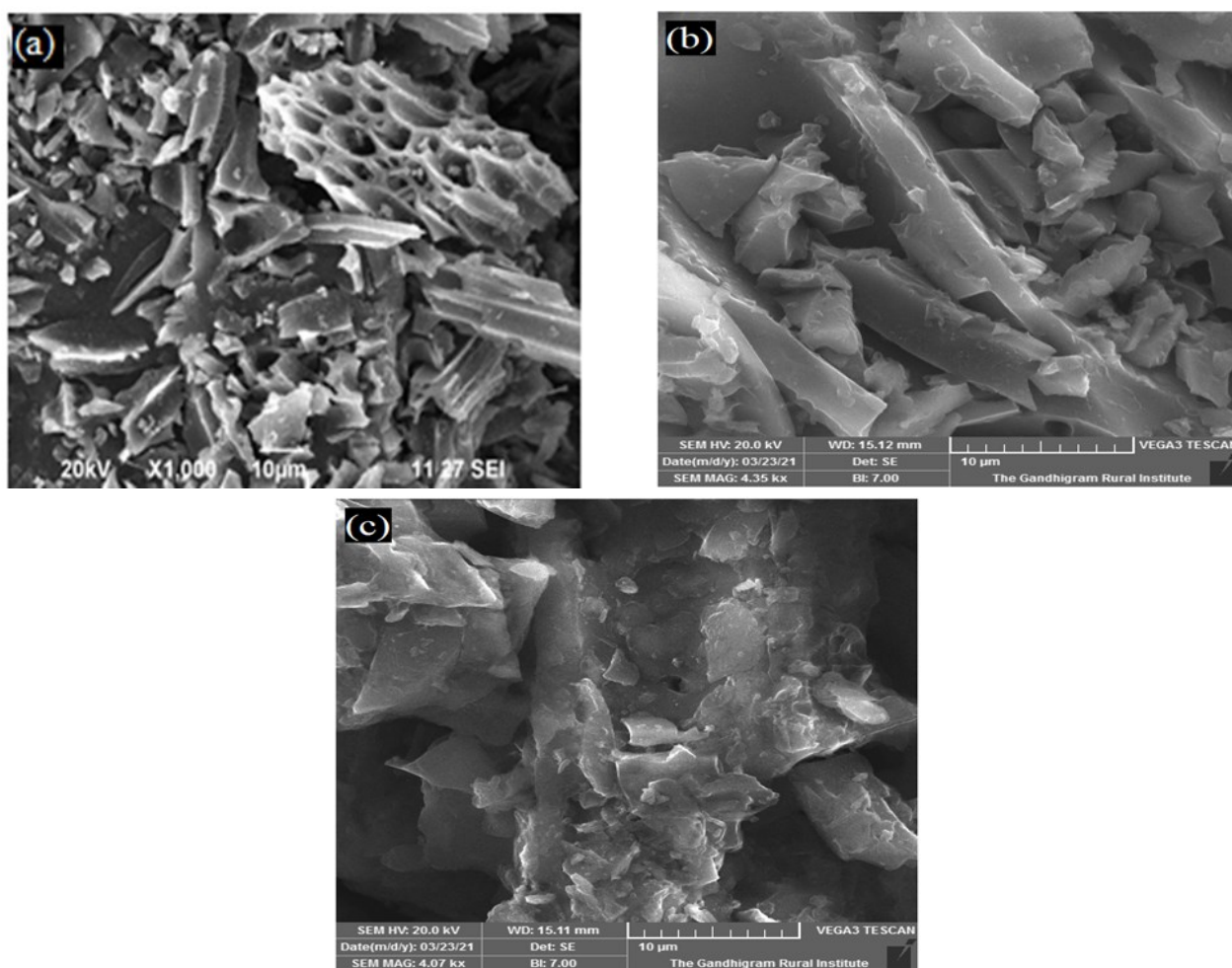
**Fig. 1.** FTIR spectra of (a) pure PsLw carbon (b) PsLw carbon-polyaniline composite (c) As(III) loaded PsLw carbon-polyaniline composite.

tion peaks at 1582, 1490 and 1211  $\text{cm}^{-1}$  are assigned to the C=C stretching mode of the quinoid ring, C=C stretching vibration of the benzenoid ring and C-N stretching mode, respectively (Yang *et al.*, 2009; Zhou *et al.*, 2015). The weak adsorption band at 1035, 860, 736 and 684  $\text{cm}^{-1}$  exhibits the presence of C-O stretching in polymeric structure, =C-H bending in alkenes, aromatic C-H bending and out plane O-H bending, respectively. These stretching frequencies indicate that the modification of PsLw carbon surface with polyaniline is successfully performed.

### Effect of pH

The pH of the solution is identified as one of the important variables for metal adsorption. The surface of the adsorbent is altered by the solution pH and changes occur in adsorption process due to the reaction of  $\text{H}^+$  with the functional groups on the active sites at the surface of the adsorbent. The effect of pH on the removal of As(III) has been studied by varying the initial pH of the solution in the range of pH = 1.0-11.0 for an initial concentration of 50 mg/L and 0.5 g/L adsorbent dose (Fig. 3). It is evident from Fig. 3 that the amount of As

(III) adsorption increases with rise in pH and reaches a maximum at pH = 7.0 and then decreases. This observation can be correlated with zero point charge of PsLw carbon-polyaniline composite. The zero point charge of PsLw carbon-polyaniline composite is 7.3 and the adsorption of As(III) is controlled by the surface charge of the adsorbent, which mainly depends on the solution pH (Zhu *et al.*, 2009; Purwajanti *et al.*, 2016; Shabnam 2017). Below pH = 7.0 As(III) exists as  $\text{H}_3\text{AsO}_3$  and above pH = 7.0 As(III) is present as  $\text{H}_2\text{AsO}_3^-$  and  $\text{HASO}_3^{2-}$ . But in the polyaniline composite at  $\text{pH} \leq 4$ , the amine group is protonated and therefore, hydrostatic repulsion could be operative between As(III) species and a protonated amine group. But the adsorption increases with an increase in pH, and therefore complexation between the composite and the As(III) species could not be ruled out (Nodeh *et al.*, 2018). This is evident from the FTIR spectral study and SEM analysis. The FTIR spectra of As(III) loaded PsLw carbon-polyaniline composite is represented in Fig. 1 c. The major changes that occur at the vibration modes of 3266, 2915 and 2864  $\text{cm}^{-1}$  are diminished and the adsorption bands in the region of 1500-800  $\text{cm}^{-1}$  are weak-



**Fig. 2.** SEM images of (a) Pure PsLw carbon (b) PsLw carbon-polyaniline composite (c) As(III) loaded PsLw carbon-polyaniline composite.

ened. These changes confirm the structural modification via complex formation due to As(III) adsorption on PsLw carbon-polyaniline composite. SEM images give information about the surface morphology of the adsorbents. The SEM image of PsLw carbon (Fig. 2 a) exhibits a rough surface with porous and pristine carbon particles. The bright rod-like agglomerated particles are present in the image of PsLw carbon-polyaniline composite and small white patches show the presence of polyaniline on the surface of PsLw carbon (Fig. 2 b). PsLw carbon-polyaniline composite surface is further agglomerated due to the adsorption of As(III) than the free adsorbent shown in Fig. 2 c. These structural changes clearly reveal the adsorption of As(III) on PsLw carbon-polyaniline composite through complex formation.

At pH>8.0, the efficiency decreases due to the repulsion between the anionic species of As(III) ( $H_2AsO_3^-/HAsO_3^{2-}$ ) and the negatively charged surface of the adsorbent. Thus the solution pH controls the sorption process and the batch studies are carried at the neutral pH=6.0 for applying the process to household applications.

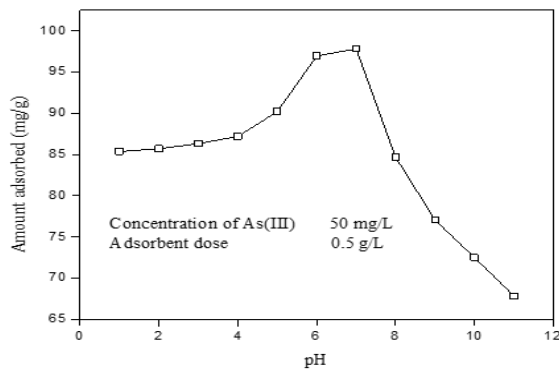
**Effect of contact time and initial concentration**

The effect of contact time and initial concentration on

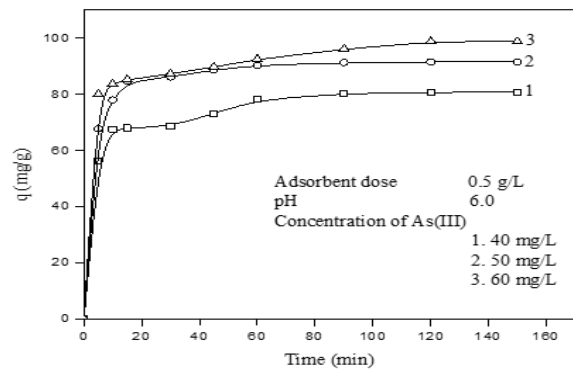
As(III) sorption on PsLw carbon-polyaniline composite is depicted in Fig. 4. The As(III) removal capacity increases with contact time and initial concentration and equilibrium are attained within 60 min. The maximum As(III) uptake capacities of PsLw carbon-polyaniline composite are 80.8, 91.5 and 98.8 mg/g for initial concentrations 40, 50 and 60 mg/L at 150 min, respectively. After equilibrium, the adsorption efficiency is almost constant because the active sites of the adsorbent are saturated with As(III) species.

**Effect of temperature**

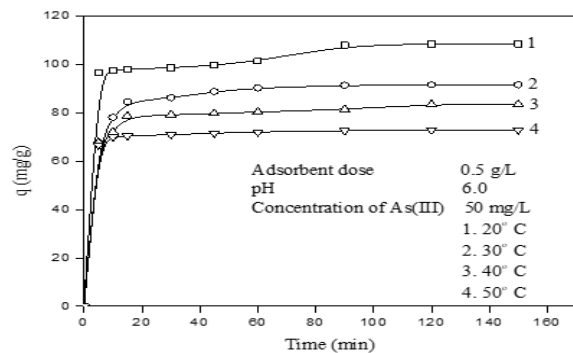
The As(III) removal efficiency of PsLw carbon-polyaniline composite is studied under different temperatures ranging from 20-50 °C and is shown in Fig. 5. The maximum adsorption capacity obtained at 20, 30, 40 and 50 °C are 108.4, 91.5, 83.5 and 72.8 mg/L respectively for an initial concentration of 50 mg/L and adsorbent dosage 0.5 g/L. The maximum removal was noted at 20 °C and a further increase in temperature resulted in a decrease in removal efficiency. This indicated that the sorption process is exothermic in nature and the increase in temperature is unfavourable for As(III) adsorption. This decrease in adsorption with increased temperature may be due to the weakening of adsorptive forces between the active sites of the PsLw



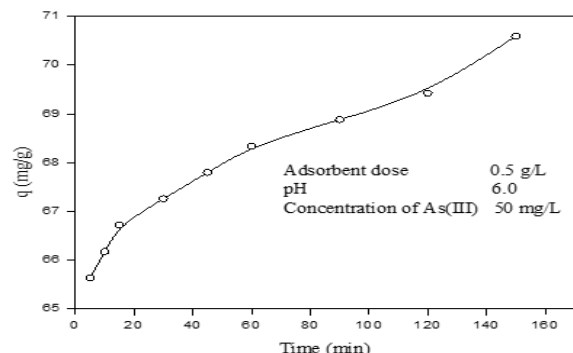
**Fig. 3.** Effect of pH on the adsorption of As(III) by PsLw carbon-polyaniline composite



**Fig. 4.** Effect of contact time and initial concentration on the removal of As(III) by PsLw carbon-polyaniline composite



**Fig. 5.** Effect of temperature on the removal of As(III) by PsLw carbon-polyaniline composite



**Fig. 6.** Effect of As(III) removal by PsLw of carbon-polyaniline composite in the presence of  $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $CO_3^{2-}$  ions

carbon-polyaniline composite and As(III) species and between the adjacent molecules of the adsorbed phase (Lashkenari *et al.*, 2011).

### Effect of coexisting anions

The effect of coexisting anions such as carbonate, chloride, nitrate and sulphate of concentration 0.001 M each on the adsorption of As(III) was examined and are presented in Fig. 6. The sorption of As(III) increases with contact time and equilibrium was attained at 90 min. The amount of As(III) sorbed is found to be 70.5 mg/g for an initial concentration of 50 mg/L As(III) and adsorbent dosage 0.5 g/L. This is lower than the adsorption of As(III) in the absence of these ions. This may be due to the competitive interaction of As(III) on the same site of the adsorbent surface with the above ions. (Bhaumik *et al.*, 2015)

### Adsorption isotherms

Adsorption isotherms are used to describe the distribution of molecules between the liquid and solid phase at adsorption equilibrium. Langmuir and Freundlich adsorption isotherms are classical models used to evaluate the equilibrium between metal ion adsorbed onto adsorbent and the metal ion in solution. The experimental data obtained under various concentrations and temperatures were fitted with a linearised form of Langmuir and Freundlich isotherms represented by equations (2) and (3), respectively. The Langmuir isotherm plots at different initial concentrations and temperatures are shown in Fig. 7. The maximum adsorption capacity  $Q_o$  (mg/g) and the Langmuir adsorption constant  $b$  (L/mg) were calculated from the slope and intercept of the linear plot  $C_e/q$  vs  $C_e$ , respectively. Freundlich constants related to adsorption capacity ( $K_f$ ) and heterogeneity ( $1/n$ ) are calculated from the slope and intercept of the linear plot between  $\log q_e$  and  $\log C_e$ , respectively (Figures not shown). Table 2 exhibits the isotherm constants for both isotherms and correlation coefficients of Langmuir and Freundlich isotherms. The correlation coefficients ( $R^2$ ) showed the sorption process best fit to Langmuir isotherm than Freundlich and it confirms that the chemical forces govern the adsorption process. The maximum adsorption efficiency of PsLw carbon-polyaniline composite is found to be 88.18 mg/g for an initial concentration of 50 mg/L and at 20 °C. Further, it is observed that the Freundlich adsorption isotherm parameter  $n$  is negative;  $K_f$  value deviates from the experimental values, which makes the Freundlich isotherm model unsuitable for the given system. But the adsorption isotherm fits well the Langmuir isotherm model, which shows a monolayer coverage of As(III) onto PsLw carbon-polyaniline composite.

Weber and Chakraborti (1974) expressed the feasibility of the sorption process in terms of a dimensionless constant known as separation factor ( $R_L$ ) given by

equation 7.

$$R_L = 1/(1 + bC_o) \tag{Eq. 7}$$

The  $R_L$  values of the sorption process at different concentrations and temperatures are exhibited in Table 2 and the values fall in the range of  $0 \leq R_L < 1$ , which implies that the sorption process is favourable under the studied conditions (Mckay *et al.*, 1982).

### Adsorption kinetics

The kinetics of the removal study is important to evaluate adsorption dynamics. The rate of adsorption of As(III) onto PsLw carbon-polyaniline composite was investigated using Lagergren's (1898) pseudo first order and Ho and McKay (1999) pseudo second-order models, which are represented by equations 4 and 5, respectively. The linear plot of  $t/q_t$  vs  $t$  for the pseudo second-order model at different concentrations and temperatures is given in Fig. 8 (For the first order the plots are not given). The parameters obtained for the pseudo first and pseudo second-order kinetics are exhibited in Table 3. The experimental data showed a good agreement with the pseudo-second order. The regression coefficient value ( $R^2$ ) for pseudo second order was higher than the pseudo first order model at different concentrations and temperatures. The  $q_e$  (cal) values of pseudo second-order are close to the  $q_e$  (exp) than the  $q_e$  (cal) of pseudo first-order model. These results confirm that the removal of As(III) using PsLw carbon-polyaniline composite is better described and controlled by pseudo second-order kinetics (Lashkenari *et al.*, 2011).

### Thermodynamic parameters

The mechanism and nature of the adsorption process are determined with the thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ). The relationship between the equilibrium constant  $K_o$  and free energy change ( $\Delta G^\circ$ ) of the adsorption process is given by equation (8). The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be obtained from the equations (9) and (10).

$$\Delta G^\circ = -RT \ln K_o \tag{Eq. 8}$$

$$\ln K = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \tag{Eq. 9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{Eq. 10}$$

where  $R$  is the universal gas constant (8.314 J/mol K) and  $T$  is the absolute temperature (K). Using Khan and Singh method, the equilibrium constant  $K_o$  is calculated

**Table 2.** Langmuir and Freundlich constants at different concentrations and temperatures

C <sub>o</sub> (mg/L)	Temp (°C)	Langmuir Isotherm				Freundlich Isotherm		
		Q <sub>o</sub> (mg/g)	b (L/mg)	R <sub>L</sub>	R <sup>2</sup>	n	K <sub>f</sub>	R <sup>2</sup>
40	30	55.16	1.32	0.0185	0.9880	-7.0116	94.1217	0.7456
50	30	68.49	0.42	0.0453	0.9958	-5.2348	143.6250	0.9509
60	30	77.88	0.29	0.0541	0.9964	-2.1793	255.1937	0.8881
50	20	88.18	0.90	0.0217	0.9984	-6.2861	162.1586	0.9947
50	30	68.49	0.42	0.0453	0.9958	-5.2348	143.6250	0.9509
50	40	59.40	0.33	0.0571	0.9952	-3.2347	117.0760	0.9772
50	50	52.61	0.25	0.0737	0.9994	-2.1193	113.5952	0.9627

**Table 3.** Comparison of pseudo-first order and pseudo-second order kinetic parameters

C <sub>o</sub> (mg/L)	Temp (°C)	q <sub>e</sub> (exp) (mg/g)	Pseudo first Order			Pseudo second Order		
			k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> (cal) (mg/g)	R <sup>2</sup>	k <sub>2</sub> (g/mg/min)	q <sub>e</sub> (cal) (mg/g)	R <sup>2</sup>
40	30	80.83	0.0342	30.61	0.7999	0.0038	83.80	0.9958
50	30	91.52	0.0202	17.88	0.6865	0.0073	92.03	0.9997
60	30	98.8	0.0190	15.21	0.8192	0.0085	99.94	0.9991
50	20	108.41	0.0259	05.40	0.6631	0.0144	109.77	0.9999
50	30	91.52	0.0202	17.88	0.6865	0.0073	92.03	0.9997
50	40	83.52	0.0198	19.56	0.9588	0.0035	84.01	0.9999
50	50	72.88	0.0182	21.11	0.9801	0.0032	73.21	0.9991

by plotting  $\ln(q_e/C_e)$  versus  $q_e$  and extrapolating  $q_e$  to zero under different temperatures (Figures not shown). The slope and intercept values of the plot of  $\ln K_o$  against  $1/T$  give enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ), respectively.

The thermodynamic parameters are listed in Table 4. The negative  $\Delta G^\circ$  values at different temperatures confirmed the spontaneous nature of the adsorption process. The negative  $\Delta H^\circ$  values indicate that As(III) adsorption on PsLw carbon-polyaniline composite is exothermic. The positive  $\Delta S^\circ$  value indicates the degrees of freedom increased at the solid-liquid interface during the adsorption of As(III) on the adsorbent. Thus the adsorption of As(III) on PsLw carbon-polyaniline composite is spontaneous, feasible and exothermic in nature (Zhou *et al.*, 2015).

**Pore diffusion and Mass transfer**

In the batch sorption process, the intraparticle diffusion is the rate-controlling step and the uptake of adsorbate varies with time which are analysed by Finkiam diffusion law. The intra-particle diffusion is given as

$$q = k_i t^{1/2} + c \tag{Eq.11}$$

Where,  $k_i$  is the intra-particle diffusion rate constant and  $c$  gives the thickness of the boundary layer. In the ad-

sorption process, adsorbate molecules moved from the bulk of the solution into solid adsorbent surface through an intra-particle diffusion process and it is the rate-limiting step (Semerjian, 2010). The multi-linear nature of intra-particle diffusion model is obtained by the plot of amount of adsorbed (mg/g) against  $t^{1/2}$  (min<sup>1/2</sup>), which is shown in Fig. 9 (a). The plot is linear for some initial contact time and do not pass through the origin. The slope of the initial linear portion characterises the rate of intra-particle diffusion (Table 4). This indicates that the adsorbate molecules get adsorbed in the first step and slowly entered into the pores of PsLw carbon-polyaniline composite in the second step (Podder and Majumder, 2016).

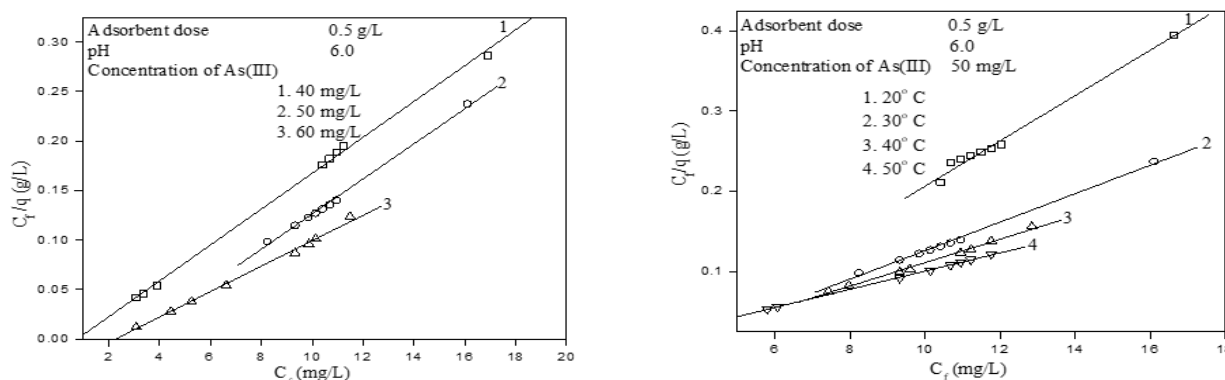
The extent of transfer of adsorbate molecules from the bulk solution to the solid adsorbent surface is governed by intra-particle diffusion and the intra-particle diffusion is verified by mass transfer equation. McKay proposed the mathematical model of mass transfer, which is used for the study of the present system and is given by

$$\ln(C_i/C_o - 1/1 + mk) = [(1 + mk/mk)\beta_L S_s]t + (mk/1 + mk) \tag{Eq. 12}$$

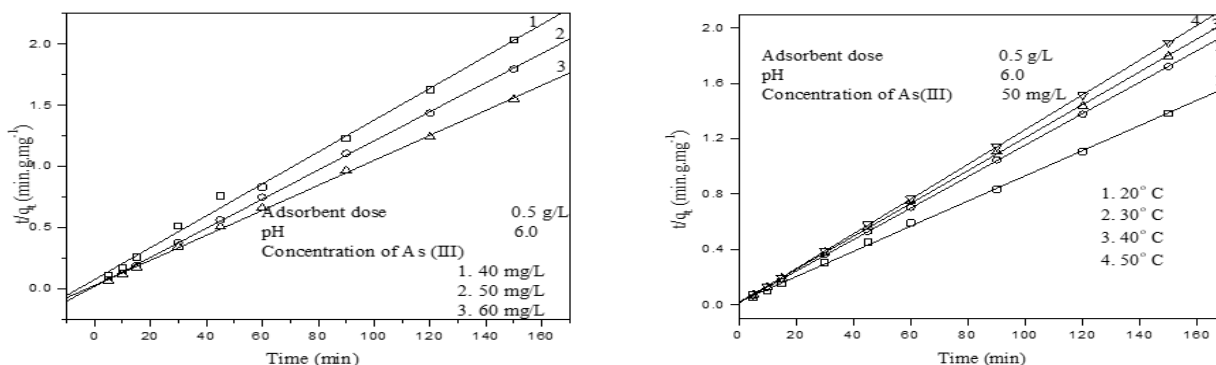
Where  $C_o$  (mg/L) is the initial adsorbate concentration and  $C_t$  (mg/L) is the adsorbate concentration after time  $t$ , 'm' is the mass of adsorbent per unit volume of parti-

**Table 4.** Thermodynamic parameters, pore diffusion and mass transfer coefficients

T (K)	C <sub>o</sub> (mg/L)	-ΔG° (KJ/mol)	-ΔH° (KJ/mol)	ΔS° (J/mol K)	(k <sub>i</sub> ) (mg/g/min <sup>1/2</sup> )	β <sub>L</sub> × 10 <sup>-4</sup>
303	40	-	-	-	3.2494	-
303	50	-	-	-	6.3335	-
303	60	-	-	-	7.5368	-
293	50	63.12	47.81	0.54	5.3568	0.3626
303	50	64.11	-	-	6.3335	0.5094
313	50	64.61	-	-	6.9214	0.5473
323	50	64.98	-	-	7.1028	0.6558



**Fig. 7.** Langmuir isotherm for As(III) adsorption onto PsLw carbon-polyaniline composite at different concentrations and temperatures.



**Fig. 8.** Pseudo-second order plot of As(III) onto PsLw carbon-polyaniline composite at different concentrations and temperatures.

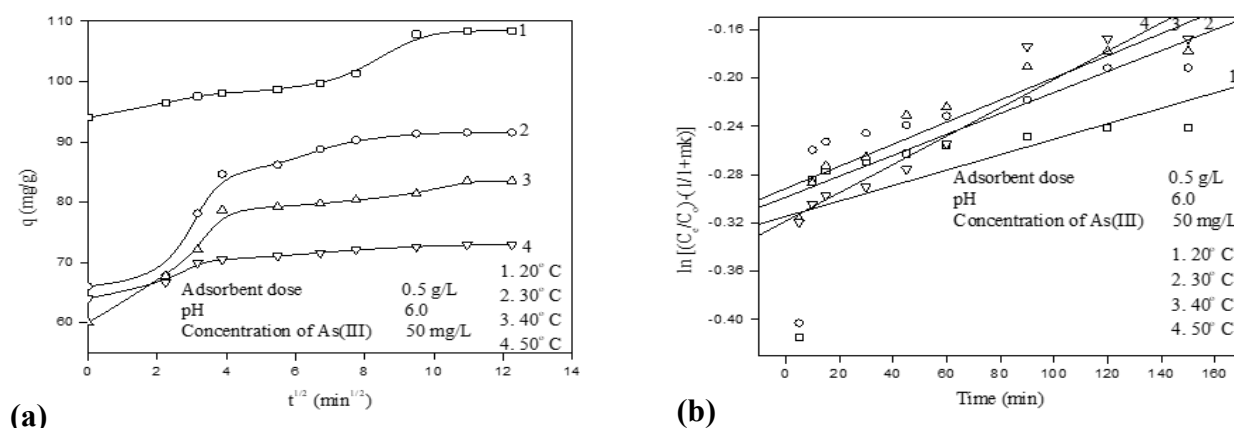
cle free solution (g/L), k (L/g) is the product of Langmuir constants Q<sub>o</sub> and b, β<sub>L</sub> (cm/s) is the mass transfer coefficient while S<sub>s</sub> is the outer surface area of adsorbent per unit volume of particle free slurry (cm<sup>-1</sup>). The values of 'm' and 'S<sub>s</sub>' were calculated using the relations (13) and (14),

$$m = W / v \tag{Eq. 13}$$

$$S_s = 6m / (1 - \epsilon_p) d_p \rho_p \tag{Eq. 14}$$

Where W is the weight of adsorbent (g), 'v' is the volume of particle free adsorbate solution (L), d<sub>p</sub> is the particle diameter (cm), ρ<sub>p</sub> is the density of adsorbent (g/cm<sup>3</sup>) and ε<sub>p</sub> is the porosity of adsorbent particle. The plot of ln [(C<sub>i</sub>/C<sub>o</sub>)-(1/1+mk)] against t is a straight line and is shown in Fig. 9 (b). From the slope and intercept of the plot, the mass transfer coefficient β<sub>L</sub> was calculated and is given in Table 4. The linear behaviour of the plot exhibits the fast movement of As(III) from the bulk solution to the solid adsorbent surface.





**Fig. 9.** Plots of As(III) adsorption of (a) intraparticle diffusion (b) mass transfer onto PsLw carbon-polyaniline composite at different temperatures.

The mass transfer coefficient increases with an increase in temperature. This shows that mass transfer is also a part of the sorption process.

### Column study

Column study can be used to apply the adsorption of As(III) on PsLw carbon-polyaniline composite for large scale treatment. The Thomas kinetic model (Thomas, 1948) is one of the most widely used methods to study fixed bed columns. The maximum solid phase concentration of the solute on an adsorbent and the adsorption rate constant for continuous adsorption process in column studies is determined from equation 6 (Roy *et al.*, 2013). In column operation, the breakthrough curve for As(III) adsorption at optimum pH = 6.0 onto PsLw carbon-polyaniline composite with flow rate (3 mL/min) is displayed in Fig. 10. The effluent concentration of As(III) was found to be zero for the first 169 bed volumes.

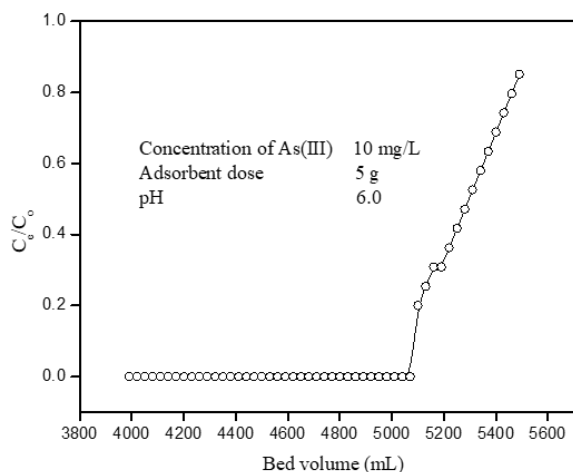
After 169 bed volumes, the retention concentration of As(III) slowly decreased with the increase of bed volumes. Thomas rate constant ( $K=1.026$  mL/min/mg) and maximum solid phase concentration ( $q_0=0.9069$  mg/g) was determined from the slope and intercept of the plot  $\log(C_0/C_e-1)$  versus  $V$ . When the column was saturated with As(III), it was eluted with 0.1 M NaOH. The column study is thus useful for the practical applicability of PsLw carbon-polyaniline composite in removing As(III).

### Desorption studies

Desorption is one of the important factors in adsorbent marketing that can influence the cost of the removal process. The pH of the adsorbate plays an important role in the adsorption of As(III) on PsLw carbon-polyaniline composite. The uptake of As(III) decreases with increasing pH and therefore, desorption is carried out using 0.1 M NaOH. As(III), desorption is 93%, 89%,

**Table 5.** Adsorption efficiency of other adsorbents

Adsorbents	Adsorption capacity (mg/g)	References
Hollow Polyaniline Microsphere/Fe <sub>3</sub> O <sub>4</sub> nano composite	28.27	Dutta <i>et al.</i> , 2020
Magnetic polyaniline-doped strontium-titanium nanocomposite	67.11	Nodeh <i>et al.</i> , 2018
Polyaniline/Nickel Ferrite-polyaniline composite	25.2/25	Agrawal & Singh 2016
Polyaniline/Fe <sup>0</sup>	232.5	Bhaumik <i>et al.</i> , 2015
Fe <sub>3</sub> O <sub>4</sub> @Polyaniline	1.066	Zhou <i>et al.</i> , 2015
PsLw carbon	65.41	JansiRani <i>et al.</i> , 2014
Polyaniline/polystyrene	52	Davodi & Jahangiri 2014
Polyaniline/rice husk nano composite	34.48	Lashkenari <i>et al.</i> , 2011
Polyaniline/Sawdust	2.08	Ansari <i>et al.</i> , 2008
PsLw carbon-polyaniline composite	98.8	Present study



**Fig. 10.** Breakthrough curve for adsorption of As(III) on PsLw carbon-polyaniline composite

and 86% for first, second and third cycles, respectively.

#### Comparison with other adsorbents

The adsorption efficiency varies with the nature and characteristics of adsorbent, adsorbate pH, dosage of adsorbent, temperature and initial concentration of adsorbate solution. The As(III) adsorption capacity of PsLw carbon-polyaniline composite compared with other adsorbents is given in Table 5. PsLw carbon-polyaniline composite has comparable adsorption capacity with other adsorbents.

#### Conclusion

PsLw carbon-polyaniline composite was prepared by direct oxidative polymerisation of aniline mixed with PsLw carbon. The removal of As(III) from aqueous solution at different initial concentration and temperature in a batch sorption mode was carried out at pH=6.0. The adsorption capacity decreased with increase in pH and temperature. Adsorption of As(III) followed pseudo-second order kinetics and Langmuir isotherm was suitable for describing the adsorption of As(III) onto PsLw carbon-polyaniline composite. Thermodynamic parameters indicated that As(III) adsorption on PsLw carbon-polyaniline composite was spontaneous, feasible, and exothermic in nature. The sorption of As(III) took place through complex formation, inter-particle diffusion and mass transfer. Column study provided the applicability of this process to a large/industrial scale. Modified polyaniline with PsLw carbon showed an improved ability to adsorb As(III) from wastewater than the pristine polyaniline. PsLw carbon-polyaniline composite is a simple, easily available low-cost adsorbent and it could be used for the treatment of drinking water/groundwater contaminated with arsenic.

#### ACKNOWLEDGEMENTS

We acknowledge the administration of Sri K.G.S Arts College, Srivaikuntam, St. Xavier's College (Autonomous), Palayamkottai and Rani Anna Government College for Women, Tirunelveli for all the laboratory studies.

#### Conflict of interest

The authors declare that they have no conflict of interest.

#### REFERENCES

1. Adamson, A.W. (1990). Physical Chemistry of Surfaces, (5th edition) John Wiley & Sons Inc, Newyork, USA.
2. Agrawal, S. & Singh, N.B. (2016). Removal of arsenic from aqueous solution by an adsorbent nickel ferrite-polyaniline nanocomposite. *Indian J. Chem. Technol.*, 23, 374-383.
3. Ansari, R., Feizy, J. & Delavar, A.F. (2008). Removal of Arsenic ions from aqueous solutions using conducting polymers. *E. J. Chem.*, 5(4), 853-863.
4. Bhaumik, M., Noubactep, C., Gupta, V.K., McCrindle, R.I. & Maity, A. (2015). Polyaniline/Fe<sup>0</sup> composite nanofibers: An excellent adsorbent for the removal of arsenic from aqueous solution. *Chem. Eng. J.*, 271, 135-146.
5. Boeva, Z.A., & Sergeev, V.G. (2014). Polyaniline: synthesis, properties, and application, *Polym. Sci. Ser. C.*, 56, 144-153.
6. Chang, Q., Lin, W. & Ying, W.C. (2010). Preparation of iron-impregnated granular activated carbon for arsenic removal from drinking water. *J. Hazard. Mater.*, 184(1-3), 515-522.
7. Davodi, B. & Jahangiri, M. (2014). Determination of optimum conditions for removal of As (III) and As (V) by polyaniline/polystyrene nanocomposite. *Synth. Met.*, 194, 97-101.
8. Dutta, S., Manna, K., Srivastava, S.K., Gupta, A.K. & Yadav, M.K. (2020). Hollow polyaniline microsphere/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as an effective adsorbent for removal of arsenic from water. *Sci Rep.*, <https://doi.org/10.1038/s41598-020-61763-z>
9. Fayazi, M., Ali, M. & Afzali Detal. (2016). Synthesis and application of novel ion-imprinted polymer coated magnetic multi-walled carbon nanotubes for selective solid phase extraction of lead (II) ions. *Mater. Sci. Eng. C.*, 60, 365-373.
10. Ho, Y.S. & McKay, G. (1999). Pseudo-Second Order Model for Sorption Processes. *Proc. Biochem.*, 34, 451-465.
11. JansiRani, M., Murugan, M., Subramaniam, P. & Subramanian, E. (2014). Adsorptive removal of arsenic from aqueous solution on PSLW carbon (*Prosopis spicigera* L. wood): Equilibrium, kinetics, thermodynamics and home-water treatment studies. *Res. J. Chem. Environ.*, 18(2), 16.
12. Jeffery, G.H., Bassett, J., Mendham, J. & Denny, R.C. (1989). Vogel's Textbook of Quantitative Chemical Analysis (5<sup>th</sup> edition). *Longmann Scientific & Technical*, England.
13. Jiang, Y., Liu, Z., Zeng, G., Liu, Y., Shao, B., Li, Z., Liu,

- Y., Zhang, W. & He, Q. (2018). Polyaniline-based adsorbents for removal of hexavalent chromium from aqueous solution: a mini review. *Environ Sci Pollut Res.*, 25, 6158–6174. <https://doi.org/10.1007/s11356-0171188-3>
14. Lagergren, S. (1898). Zurtheorie der sogenannten adsorption gelösterstoffe, Kungligasvenska Ventenskapsakademien. *Handlingar*, 24, 1–39.
  15. Lashkenari, M.S., Davodi, B. & Eisazadeh, H. (2011). Removal of arsenic from aqueous solution using polyaniline/rice husk nanocomposite. *Korean. J. Chem. Eng.*, 28, 1532–1538.
  16. Li, J., Huang, Y. & Shao, D. (2015). Conjugated polymer-based composites for water purification. In: Saini P (ed) Fundamentals of conjugated polymer blends, copolymers and composites: synthesis, properties, and applications. *Scrivener*, 581-620.
  17. Mahmoud, M.E., Saad, E.A. & El-Khatib, A.M. (2018). Green solid synthesis of polyaniline-silver oxide nanocomposite for the adsorptive removal of ionic divalent species of Zn/Co and their radioactive isotopes  $^{65}\text{Zn}/^{60}\text{Co}$ . *Environ Sci Pollut Res.*, 25, 22120- 22135. <https://doi.org/10.1007/s11356-018-2284-8>
  18. McKay, G., Balir, H.S. & Garden, J.R. (1982). Adsorption of dyes on Chitin I equilibrium studies. *J. Appl. Polym Sci.*, 27, 3043-3057.
  19. Nodeh, M.K.M., Gabris, M.A., Nodeh, H.R. & Bidhendi, M.E (2018). Efficient removal of arsenic(III) from aqueous media using magnetic polyaniline-doped strontium– titanium nanocomposite. *Environ Sci Pollut Res.*, 25, 16864-16874. <https://doi.org/10.1007/s11356-018-1870-0>
  20. Mohan, D., Pittman, C.U. (2007). Arsenic removal from water/wastewater using adsorbents-a critical review. *J Hazard Mater.*, 142, 1–53.
  21. Munoz, J.A., Gonzalo, A. & Valiente, M. (2002). Arsenic adsorption by Fe(III)-loaded open-celled cellulose sponge. Thermodynamic and selectivity aspects. *Environ. Sci. Technol.*, 36, 3405-3411.
  22. Ogata, F., Kawasaki, N., Nakamura, T. & Tanada, S. (2006). Removal of arsenious ion by calcined aluminium oxyhydroxide (boehmite). *J. Colloid Interface Sci.*, 300, 88-93.
  23. Palit, D. & Moulik, S.P. (2000). Adsorption of methylene blue on cellulose from its own solution and its mixture with methyl orange. *Indian J. Chem.*, 39 A, 611-617.
  24. Podder, M.S. & Majumder, C.B. (2016). Kinetic, mechanistic and thermodynamic studies of removal of arsenic using *Bacillus arsenicus* MTCC 4380 immobilized on surface of granular activated carbon/MnFe<sub>2</sub>O<sub>4</sub> composite. *Groundw. Sustain. Dev.*, 2, 53-72.
  25. Potgieter, J.H. (1991). Adsorption of methylene blue on activated carbon: An experiment illustrating both the Langmuir and Freundlich isotherms. *J. Chem. Edu.*, 68, 349.
  26. Purwajanti, S. (2016). Mesoporous magnesium oxide hollow spheres as superior arsenite adsorbent: Synthesis and Adsorption Behavior. *ACS Appl. Mater. Interfaces*. 8, 25306–25312.
  27. Reynolds, T.D. & Richards, P.A. (1996). Unit operations and process in Environmental Engineering. *PWS Boston, USA*.
  28. Roy, P., Mondal, N.K., Bhattacharya, S., Das, B. & Das, K. (2013). Removal of arsenic(III) and arsenic(V) on chemically modified low-cost adsorbent: batch and column operations. *Appl. Water Sci.*, 3, 293- 309.
  29. Schwarz, J.A., Driscoll, C.T. & Bharot, A.K. (1984). The zero point of charge of silica-alumina oxide suspensions. *J. Colloid Interface Sci.*, 97, 55-61.
  30. Semerjian, L. (2010). Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinushalepensis* sawdust. *J. Hazard. Mater.*, 173, 236-242.
  31. Shabnam, R. (2017). Novel magnetically doped Epoxide functional cross-linked hydrophobic Poly(lauryl methacrylate) composite polymer particles for removal of As(III) from aqueous solution. *Ind. Eng. Chem. Res.*, 56, 7747–7756.
  32. Thomas, H.C. (1948). Chromatography: a problem in kinetics. *Ann. N.Y. Acad Sci.*, 49, 161-182.
  33. Weber, T.W. & Chakraborti, R.K. (1974). Pore and solid diffusion models for fixed-bed adsorbents. *J. Am. Inst. Chem. Eng.*, 20, 228-238.
  34. Yang, P.C., Du, J., Peng, Q., Qiao, R., Chen, W., Xu, C., Shuai, Z. & Gao, M. (2009). Polyaniline/Fe<sub>3</sub>O<sub>4</sub> nanoparticle composite: Synthesis and reaction mechanism. *J. Phys. Chem. B*, 113, 5052–5058.
  35. Zhou, Q., Wang, J., Liao, X., Xiao, J. & Fan, H. (2015). Removal of As(III) and As(V) from water using magnetic core-shell nanomaterial Fe<sub>3</sub>O<sub>4</sub>@ polyaniline. *Int. J. Green Technol.*, 1, 54–64.
  36. Zhu, H., Jia, Y., Wu, X. & Wang, H. (2009). Removal of arsenic from water by supported nano zero-valent iron on activated carbon. *J. Hazard. Mater.*, 172, 1591–1596.