

Bio-sorption of As(V) from Aqueous Solutions by Thuja Occidentalis Leaves Activated Carbon@Al Embedded Material

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In this work, Thuja Occidentalis leaves carbon blended with Aluminum (TOLC@Al) was chosen as a precursor material for the As(V) adsorption from an aqueous solution. The parameters that affect the adsorption strength such as pH, TOLC@Al dosage, contact period, and initial arsenic concentration were studied. Characterization studies such as Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) analysis were performed to study the surface morphology. The results showed that TOLC@Al had potential for adsorption of arsenic ions (94.1% removal efficiency) at pH = 6.00 at room temperature. Langmuir adsorption isotherm ($R^2 = 0.9953$) displayed the best fit. The maximum adsorption capacity (Q_m) was 24.44 mg g⁻¹ and adsorption favored uni-layered uptake. The Kinetic study demonstrated that the pseudo-second-order model ($R^2 = 0.9959$) was the better fit and adsorption took place through chemisorption. Regeneration studies revealed that the adsorbent is regenerated using sodium hydroxide solution and can be reused for the adsorption of As(V). Higher absorption of As(V) ions was recorded using TOLC@Al compared to some other standard commercial adsorbents. Hence, TOLC@Al adsorbent can be a promising material for As(V) ion removal.

Keywords: Adsorption, As(V), Activated carbon, FTIR, SEM, TOLC@Al

INTRODUCTION

The water resources comprise 2.5% of fresh water, of which around thirty percent is groundwater, which is utilized for drinking, agricultural and industrial needs. However, the increase in industrialization together with urbanization poses a dangerous threat to groundwater quality [1]. Among different pollutants in water [2], arsenic (As) is one of the important ones. Typically, arsenic enters the groundwater via the dissolution of arsenic-containing rocks. According to the Agency for Toxic Substances and Disease Registry, arsenic is represented as the first among twenty extremely risky substances. Many people of countries such as India, Pakistan, Bangladesh, Mexico and Srilanka are exposed to various diseases related to arsenic pollution of drinking water, which is carcinogenic [3]. The primary pathway of arsenic ion

entrance into the life of human beings is through arsenic-contaminated potable water from ground wells connected to alluvium sediments [4]. The allowable limit of arsenic in potable water according to the World Health Organization (WHO) is 10 µg l⁻¹. The toxic effects of arsenic on humans and animals have been studied by several researchers [5]. Use of a higher amount of As for longer periods can cause lung disease, skin thickening, kidney disease, loss of appetite and sickness. The toxicity of arsenic is firmly identified by its oxidation state and speciation. In an aquatic environment, inorganic arsenic is principally arsenic(V) and arsenic(III), whereas organic components are monomethyl and dimethyl arsenic acid. As(III) is more toxic than As(V). Arsenite-As(III) exist in water if the water is basic whereas arsenate-As(V) exists if the water has acidic nature [6]. Given the extensive contamination and higher toxic nature of arsenic, a remarkable attention has been considered among researchers to foster appropriate and successful innovations for the

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indemnification of arsenic-polluted water [7].

Some of the methods for the removal of pollutants are electro dialysis, reverse osmosis, membrane filtration and nano-filtration. [8,9,10]. These techniques have some limitations such as high maintenance cost, large waste formation, membrane replacement, sensitivity towards specific ions and a high maintenance cost. Hence, adsorption process [11,12,13] is an affordable and successful strategy for treating poisonous components, including arsenic, from polluted water. Factors such as high porosity, increased availability of active sites for adsorption, and large surface area make activated carbon an interesting material for research. Since commercially available carbon materials are expensive, activated carbon material, synthesized naturally, can drastically reduce the overall cost of adsorption process. Generally, adsorption process is associated with chemisorption's, electrostatic interactions, surface complexation, and ion exchange. Biosynthesis of ingredients plays a vital role to reduce the cost of the experimental process [14]. Currently, materials available from industrial and agricultural wastes such as rice paddy, orange peel, peanuts, fly ash, activated *Moringa oleifera*, and walnut have been used to synthesize the activated carbon material as an adsorbent for arsenic removal [15].

To improve the adsorption strength, the surface modification of present carbon-based materials with appropriate substances has been investigated [16,17]. The anionic species such as arsenate, fluoride and chromates have high affinity toward metal ions such as Fe^{3+} , Al^{3+} and La^{3+} , hence, aluminum metal ion blended with activated carbon shows brilliant potential for the removal arsenate ions. Furthermore, utilizing low cost aluminum metal ion as an active binding site can increase the number of binding sites for arsenic interaction; this may enhance the adsorption efficiency for the As(V) chemisorption. Selecting *Thuja Occidentalis* leaves is the best choice due to the existence of surface groups and no discharge of soluble contaminants into the water. For the arsenic removal, synthesis of low-cost material utilizing *Thuja-Occidentalis* leaves (TOL) was used as economic feasibility is an important concern when implementing the purification process of water in rural areas. The TOL are usually accessible in the underdeveloped areas [18], and in the present study area. *Thuja Occidentalis* leaves carbon is blended with aluminum (TOLC@Al) can be used

as a precursor material for the removal of arsenic ion.

MATERIALS AND METHODS

Plant Description

Capacities of various assortments of accessible adsorbing materials from plants were studied to find new adsorbent material for present examinations. *Thuja Occidentalis* leaves (TOL) [19] were considered for the synthesis of activated carbon.

Preparation of TOLC@Al

TOL were collected from our functioning place, and it was dried under sunlight for about five days. The dried TOL were grounded into a powder and sulphuric acid was mixed in 1:1.8 (leave powder: H_2SO_4) [20,21] followed by heating at 300 °C in a muffle furnace for three hours. The obtained material was washed with distilled water with numerous times to remove acidic molecules and then material was dried in an electric oven to get activated *Thuja Occidentalis* leaves carbon (TOLC). Then, aluminum metal powder was mixed to the prepared TOLC in the weight ratio of 10:1(TOLC: Al powder) in a conical flask followed by adding hydrochloric acid solution drop by drop with constant stirring until a precipitate material was formed. The resultant material was washed until became free from hydrochloric acidic molecules and the material was dried in an oven. Finally, the material was grounded into a particle size of < 80 μm using mesh.

Required Chemicals and Instruments

Inorganic arsenic salt-As(V) ($Na_2HAsO_4 \cdot 7H_2O$, 98%) was taken for the preparation of stock arsenic solution (1000 ppm) and analytical grade aluminum powder was used for the composite preparation. The pH meter (Model 335-systronics) was utilized to measure the pH. The 0.05 M NaOH and 0.05 M HCl solutions were used to adjust the solution pH. Atomic absorption spectrophotometer (AAS) (Perkin Elmer-model 400AAS) was used for the measurement of arsenic ion concentration. Perkin Elmer BX FTIR was used for Fourier transformation infrared ray (FTIR) analysis and scanning electron microscopy (SEM) pictures were taken by Philips XL30. The surface area and porous volume of the TOLC@Al were determined by a quantachrome instrument

(Model Nova 3200-Surface area analyzer-), using N₂ as adsorbate at -196 °C.

Adsorption of As(V)

In batch analyses, a 50 ml of 10 ppm As(V) solution was transferred in a 250 ml flask by a predetermined adsorbent (TOLC@Al) dosage and solution pH. The contents were shaken in an orbital shaker at 200 rpm under room temperature for a particular period. Then the solution was filtered by a Whatman filter paper-50, and the filtrates containing As(V) were measured by AAS. The pH, TOLC@Al dosage, time period and initial arsenic concentration are the factors determining the adsorption efficiency. Therefore, the effect of the above variables was studied in the range of pH (3.00-10.00), TOLC@Al adsorbent (0.3-0.6 g l⁻¹ of As(V) ion solution), time period (10-70 min), and initial concentration of an arsenic solution (4-18 ppm) to acquire an optimal condition for the maximum adsorption of As(V) ion; during the experiment one parameter was changed while the remaining parameters were predetermined to a particular value.

The percentage removal of As(V) is measured by

$$\% \text{Removal of As(V)} = [(C_o - C_e)/C_o] \times 100 \quad (1)$$

Here, 'C_o' & 'C_e' are initial As(V) concentration and equilibrium concentration of As(V).

The As(V) uptake 'Q_e' (mg g⁻¹) of the TOLC@Al adsorbent at equilibrium is measured by the equation:

$$Q_e = [(C_o - C_e)/w] \times V \quad (2)$$

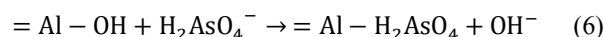
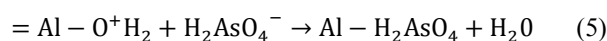
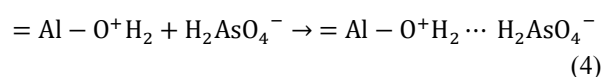
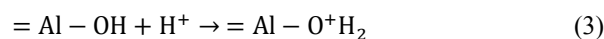
Here, 'w' is the mass of TOLC@Al (g) and V (l) is the volume of As(V).

RESULTS AND DISCUSSION

Adsorption Studies

Effect of pH. To find out the effect of the pH of the solutions on the arsenic ion removal, the batch mode studies at different pH levels were performed in the range of 3.00 to 11.00 by a preset amount of TOLC@Al dosage (0.55 g l⁻¹ of 10 ppm arsenic(V) solution) and 60 minutes time period. It is observed that arsenic adsorption is maximized (94.1%) at the

pH of 6.00 (Fig. 1a). At this pH value, the adsorbent surface is positively charged. Subsequently, there is a strong columbic interaction between the TOLC@Al surfaces with arsenic ions. The zero point charge of the TOLC@Al adsorbent (pH_{ZPC}) was obtained by a standard method [22] to identify the charge on the TOLC@Al surface. A plot of initial pH versus final pH provided an arc from; the pH_{ZPC} for TOLC@Al was recognized as a point at which the variation of pH is zero. The pH_{ZPC} of TOLC@Al was 7.31. This represents that TOLC@Al is negatively charged above pH_{ZPC} and positively charged below the pH_{ZPC}. It was identified that the removal of arsenic ion reached the maximum value at the pH of 6.00. At this pH, the surface of the adsorbent is positively charged, subsequently, there is a strong columbic interaction between the arsenic ion with the TOLC@Al surface and the As(V) exchanged with the surface hydroxyl groups of TOLC@Al. The maximum adsorption strength (17.1 mg g⁻¹) was found at pH 6.00, which decreases by an increase in pH value. Further increase in pH led to a reduction in As(V) adsorption since the TOLC@Al surface was negatively charged; indicating an increment in the electrostatic repulsions among the adsorbent surface and the negatively charged arsenic ion. The possible way of arsenic ion removal is shown in the following Eqs. (3) to (6).



Effect of TOLC@Al dosage. The adsorption studies were performed by changing the TOLC@Al adsorbent dosage from 0.3 g l⁻¹ to 0.6 g l⁻¹ of 10 ppm arsenic solution by predetermined parameters of pH (6.00) and time of contact (60 min). An increase in dosage of TOLC@Al led to an increase in adsorption of As(V) (Fig. 1b), which was due to an increase in the number of active binding sites. Additional increase in the adsorbent material does not influence the percentage removal may be due to the fact that the number of arsenic ions remains constant after reaching equilibrium. The measured value

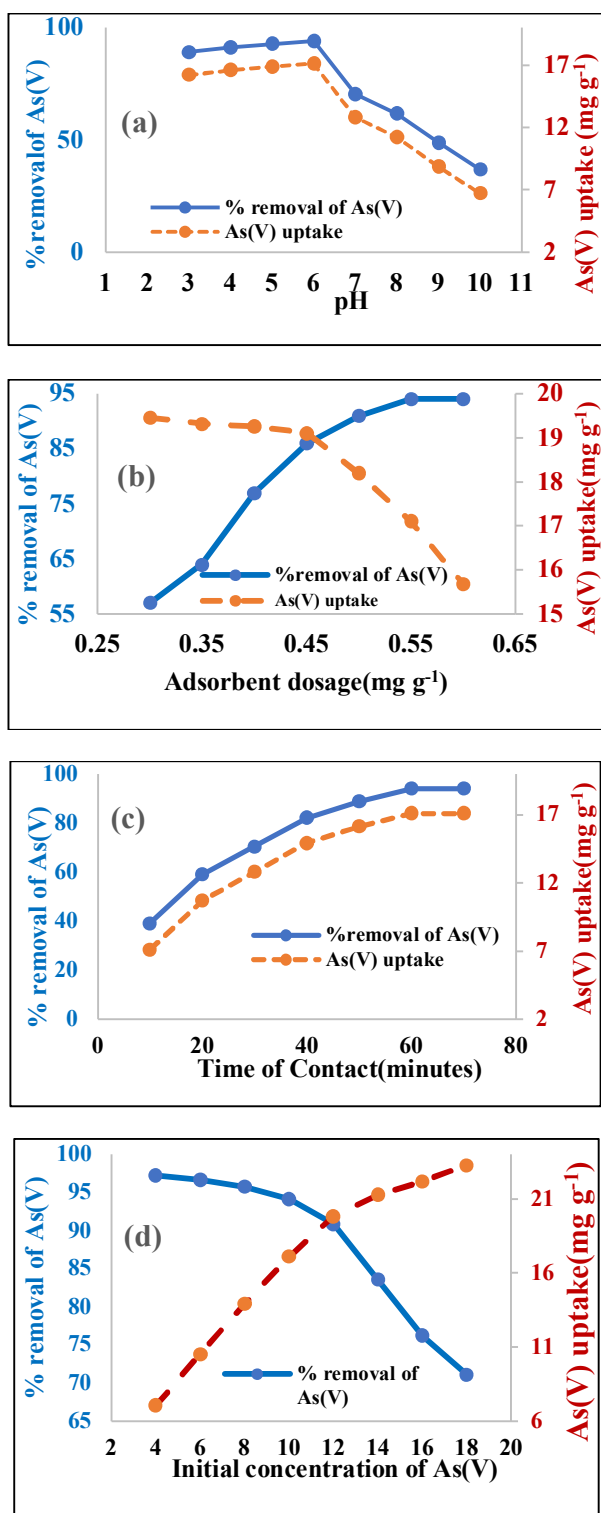


Fig. 1. Effect of parameters on the % removal of As(V) and As(V) uptake on the adsorbent (TOLC@Al) surface: (1a) pH of the solution; 1b TOLC@Al adsorbent; 1c time of contact; 1d initial concentration of As(V).

of arsenic uptake on the adsorbent surface reduced from 19 mg g⁻¹ to 15.68 mg g⁻¹ with an increase in TOLC@Al adsorbent dosage from 0.3 g l⁻¹ to 0.6 g l⁻¹ of 10 ppm As(V) solution, since the amount of arsenic ions was fixed to be adsorbed on the adsorbent material.

Effect of time of contact. Equilibrium time is an important characteristic in adsorption process. The experimentation was executed at preset conditions of pH 6.00, TOLC@Al dosage 0.55 g l⁻¹ and initial arsenic ion concentration of 10 ppm by changing the time period from 10 to 70 min. The data demonstrated that adsorption of arsenic ion increased (Fig. 1c) with an increase in the contact time. Initially, within 10 min, 39.1% removal of arsenic ion occurred due to the presence of more active sites. The time gradually increases up to 60 min (94.1% removal) and then reached an equilibrium condition in which further increment did not affect the removal efficiency due to quick exhaustion of the adsorbing sites.

Effect of initial concentration of arsenic ions. Adsorption studies were performed at preset conditions of pH 6.00 and adsorbent dosage of 0.55 g l⁻¹ arsenic solution by changing the concentration of As(V) solution from 4 ppm to 18 ppm. The experimental data (Fig. 1d) revealed that the As(V) uptake on the TOLC@Al surface enhanced from 7.07 to 17.1 mg g⁻¹ by increasing the arsenic concentration from 4ppm to 18 ppm. The percentage removal of arsenic decreased by an increase in concentration since the availability of binding sites was fixed.

Adsorption Isotherms Studies

It is useful to study the relationship between the equilibrium amounts of As(V) on the TOLC@Al adsorbent surface. Two adsorption isotherm studies, Freundlich model and Langmuir model, were done to find out the best fit. The Freundlich model assumes that the sorption continues at heterogeneous sites of the TOLC@Al adsorbent and represents the multi-layered uptake whereas the Langmuir model [23] assumes the sorption at homogeneous sites and represents the uni-layered uptake. The regression constant ($R^2 = 1$) indicates a better fit to the given adsorption isotherms. The expressions of these two models and calculated sorption parameters are presented in Table 1. The sorption constants were measured from the graphs plotted the $\ln C_e$ vs. $\ln Q_e$ and $1/C_e$ vs. $1/Q_e$, utilizing TOLC@Al

Table 1. Adsorption Isotherm, and Kinetic Data by TOLC@Al Adsorbent

Model	Adsorption isotherm data			Adsorption parameters	Measured value
	Expression	plot	R ²		
Freundlich	$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e$	$\ln C_e$ vs. $\ln Q_e$	0.8723	K_f	16.65
Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$	$1/C_e$ vs. $1/Q_e$	0.9953	n_f	3.56
				b	3.75
				R_L	0.067
				Q_m	24.44
Model	Adsorption kinetic data				Q _e
	Expression	Plot	R ²	Kinetic rate constants	
Pseudo-first order kinetic	$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$	$\ln(Q_e - Q_t)$ vs. t	0.9773	$K_1 = 0.058$	20.69
Pseudo-second order kinetic	$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t$	$\frac{t}{Q_t}$ vs. t	0.9959	$K_2 = 0.001$	23.25
Intra particle diffusion	$Q_t = K_i t^{0.5}$	Q_t vs. $t^{0.5}$	0.9658	$K_i = 2.231$	-
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	Q_t vs. $\ln t$	0.992	$\alpha = 2.001$ $\beta = 0.1839$	-

Here, 'C_e' denotes equilibrium concentration of As(V), 'Q_e' and 'Q_t' means As(V) uptake at equilibrium and at time 't', 'Q_m' is constant denotes adsorption capacity, 'b' is constant denotes the rate of adsorption, 'R_L' is dimensionless equilibrium parameter, 'R²' denotets regression constant, 'K_f' denotes adsorption capability, 'n_f' denotes amount of adsorption intensity, 'k₁' (min⁻¹) and 'k₂' (g (mg min⁻¹)⁻¹) denotes the pseudo-first-order and pseudo-second-order rate constants. 'K_i' (mg (g min^{0.5})⁻¹) denotes the intraparticle diffusion rate constant, 'α' (mg (g min) and 'β' (g mg⁻¹) denotes the adsorption rate and activation energy for chemisorption's respectively.

adsorbent and various arsenic ion concentrations (Fig. 2). The high value of R² (0.9953) of the Langmuir model indicates the uni-layered adsorption. The maximum arsenic adsorption capacity of TOLC@Al from the consistent model was 24.44 mg g⁻¹. The important characteristic of the Langmuir model is the separation factor, R_L, which determines whether the adsorption process is irreversible, favorable or unfavorable. It is measured by the expression- (1).

$$R_L = \frac{1}{1 + bC_0} \quad (1)$$

Here, 'C₀' is the initial arsenic ion concentration (mg l⁻¹) and 'b' is the constant obtained from graph. The 'obtained R_L'

value was 0.0677, which demonstrates favorable adsorption with an adsorbent TOLC@Al for the removal of arsenic ion.

Kinetic Studies

The kinetic study is usually useful to know the sorption mechanism. To demonstrate the adsorption kinetics for the adsorption of arsenic ion on the TOLC@Al surface, the results at different time intervals, related to the changes in the adsorption strength by different models (Table 1), were studied to recognize the best fit model. The individual plots are shown in Fig. 3. The expressions and determined kinetic parameters are present in Table 1. It was obtained that R² (0.9959) of the pseudo-second-order model was nearer to unity. Similarly calculated and experimental kinetic constants demonstrate that this model is a good fit and the

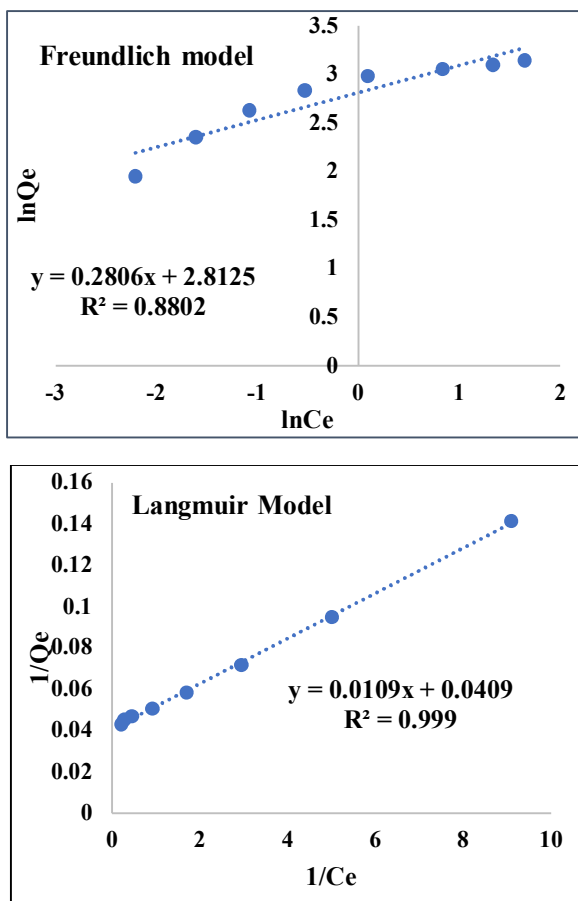


Fig. 2. Freundlich and Langmuir model curves for the As(V) removal by TOLC@Al. chemisorption.

chemisorption is the rate determining step.

Characterization Studies

The N₂ adsorption isotherm of the prepared material is shown in Fig. 4. From this figure, the material showed type I isotherms indicating that the prepared material was microporous. Typically, Type I isotherm show a convex curve and volumes adsorbed that strongly increments at low relative pressures ($P/P_0 < 0.2$); this implies that nitrogen particles are adsorbed fundamentally in the microporous structure [24]. The surface area of the TOLC@Al material was 768.3 m² g⁻¹ and the pore volume was 0.612 cm³ g⁻¹. FTIR spectra are useful for obtaining the structural data of the adsorbent. The occurrence of different functional groups

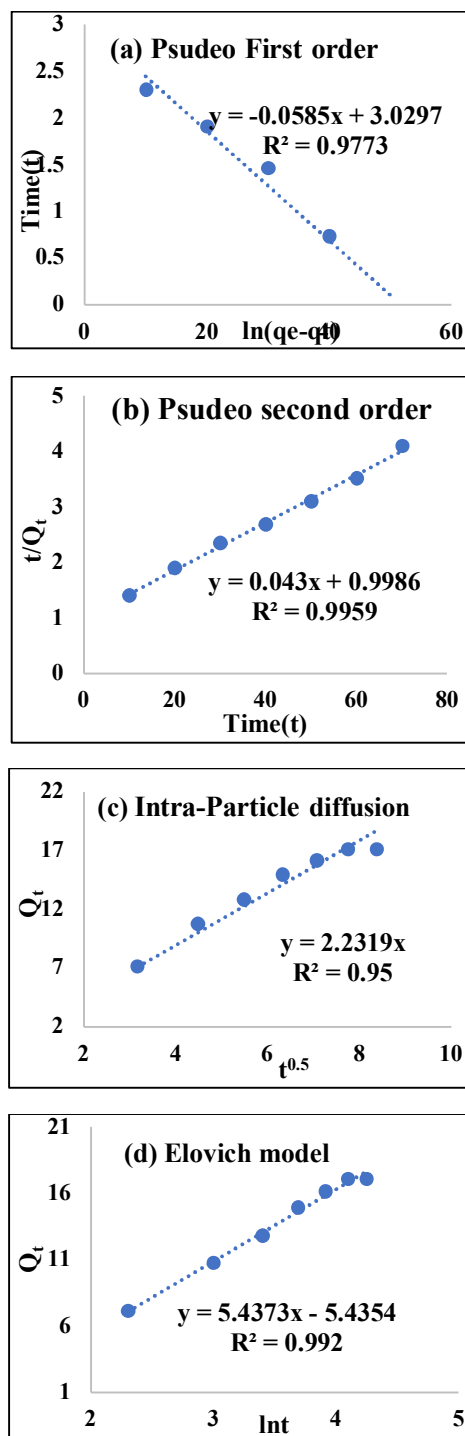


Fig. 3. The kinetic models (a) Pseudo first order, (b) pseudo-second order, (c) Intra particle diffusion and (d) Elovich model curves using TOLC@Al adsorbent to the As(V) adsorption.

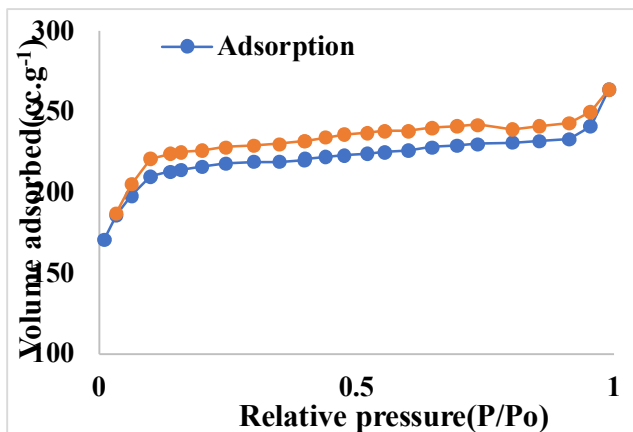


Fig. 4. Adsorption-Desorption isotherm curve of TOLC@Al Material.

in the TOLC@Al adsorbent was studied before and after the arsenic adsorption. The spectra was measured from 4000 cm^{-1} to 400 cm^{-1} (Fig. 5). The raw adsorbent showed a FTIR band at 3418 cm^{-1} [25] before adsorption of arsenic, indicating the presence of -OH stretching vibrational band; it

also showed a band at 3422 cm^{-1} after adsorption with the marginal shift. The raw adsorbent band at 2918 cm^{-1} and 2846 cm^{-1} [26] before adsorption represent the presence of -CH_2 stretching vibrational bands. There was a marginal shift of these bands at 2927 cm^{-1} and 2855 cm^{-1} after adsorption of arsenic. The presence of a band at 1612 cm^{-1} [23] before arsenic adsorption indicates the presence of carbon-carbon double bonds ($\text{C}=\text{C}$) that was shifted to 1622 cm^{-1} after adsorption. The presence of a band at 1168 cm^{-1} before adsorption indicates the C-O stretching vibration in alcohol that was moved to 1197 cm^{-1} after adsorption. A band of As-O stretching vibration was appeared within a range of $700\text{-}950\text{ cm}^{-1}$ that is a characteristic band of As(V) [27]. Less intense peaks also appeared before and after adsorption. These vibrational band values had peripheral shifts indicating the interaction of functional groups in the TOLC@Al with the negatively charged arsenate ions. SEM pictures of TOLC@Al before and after the arsenic sorption are shown in Fig. 6. The SEM image of the adsorbent exhibited small-sized particles clustered in a bigger structure with a micro-porous character. The arsenic adsorbed material exhibited a

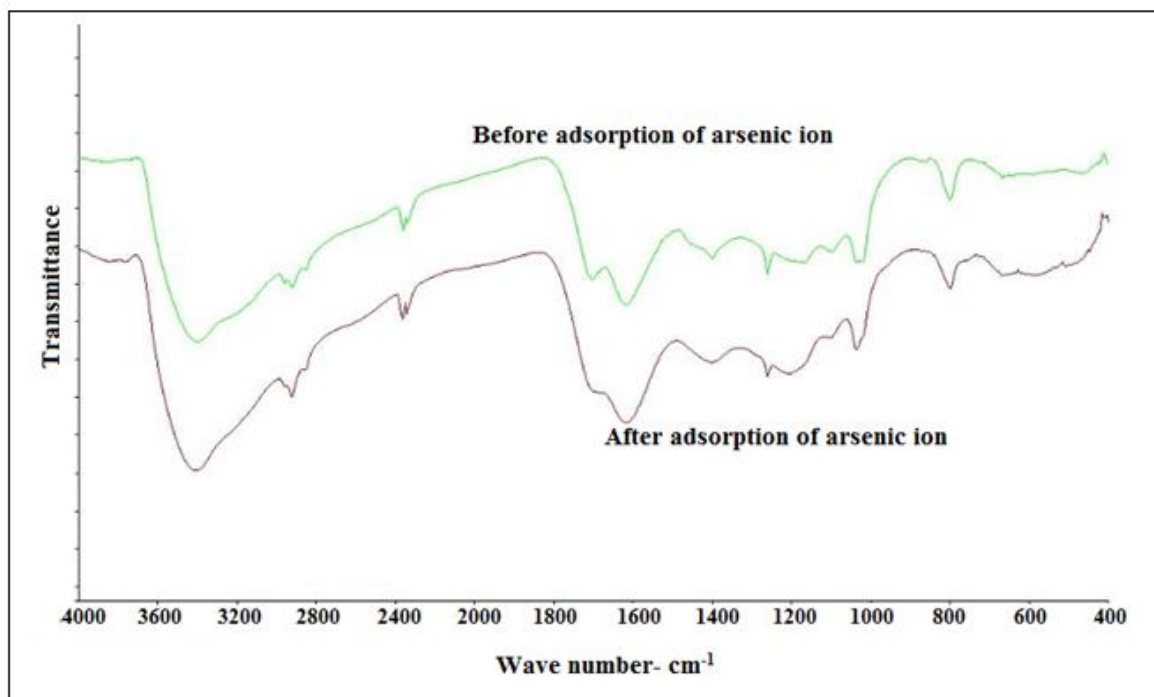


Fig. 5. FTIR Spectra of TOLC@Al before arsenic adsorption and after arsenic adsorption.

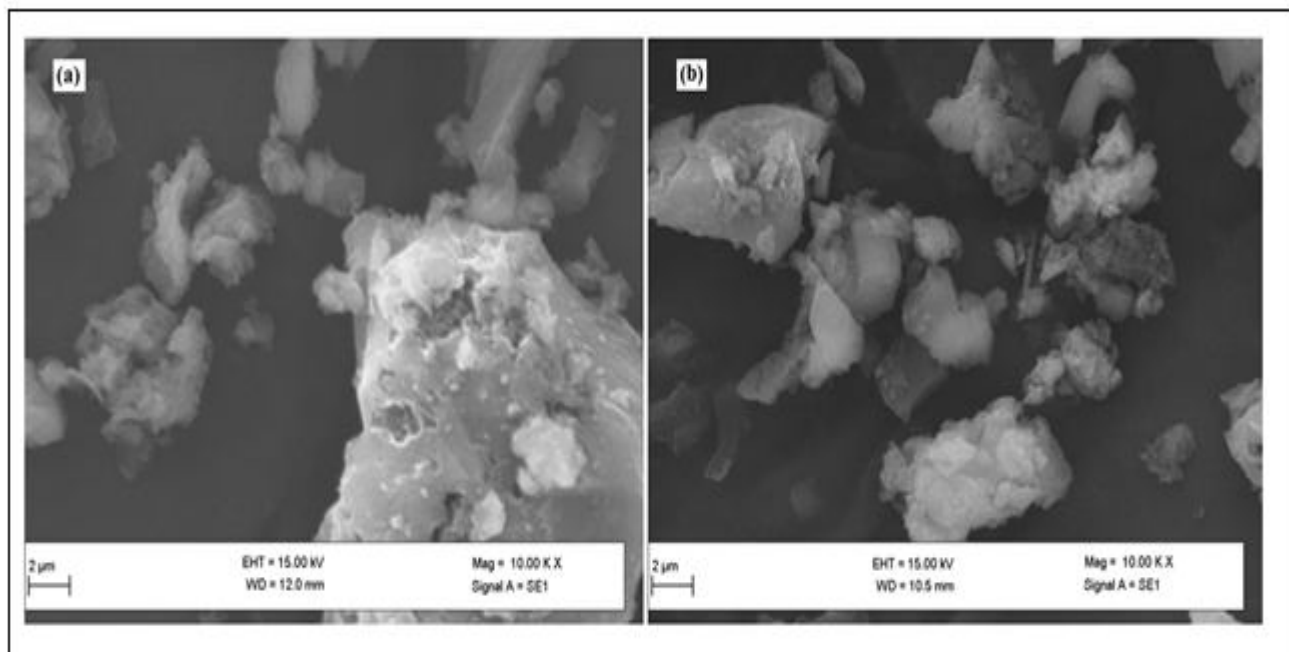


Fig. 6. Comparison of SEM picture of TOLC@Al before (a) and after (b)As(V) adsorption.

comparable structure with less comparable porosity. Small modifications in morphology may be attributed to the sorption and exchange of arsenic ions on the TOLC@Al adsorbent surface.

Desorption Studies

Recycling of the adsorbent minimizes the operational price. The Desorption of the As(V) from TOLC@Al adsorbent was done (Fig. 7) for a few cycles by sodium hydroxide solution. Desorption studies were performed using 10.0 g of arsenic loaded on adsorbent material by utilizing 100 ml sodium hydroxide. The recovered material was reused for the adsorption of an arsenic ion with the same 10ppm arsenic solution. The %removal of arsenic ion from the regenerated adsorbent was 87.3%, 78.4%, and 76.5% for the consecutive cycles. Further investigation is required for the wide use of TOLC@Al for further cycles.

Comparison of Adsorption Strength of TOLC@Al with some Reported Adsorbent Materials for Arsenic Removal

The adsorption strength of TOLC@Al is different from

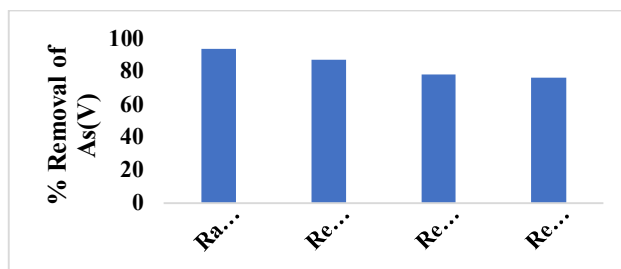


Fig. 7. %Removal of As(V) for raw adsorbent and regenerated adsorbent with few cycles.

other materials due to its different working conditions for As(V) removal Table 2 shows the comparison between adsorption capability of TOLC@Al and some other adsorbent materials. The adsorption strength of TOLC@Al is notably higher than that of the many available adsorbents.

CONCLUSIONS

The results demonstrate that TOLC@Al has the potential

Table 2. Adsorption Strength of TOLC@Al is Compared with some Described Adsorbents for As(V) Removal

Adsorbent material	pH of the solution	Maximum adsorption capability (mg g ⁻¹)	Ref.
Modified saxaul ash	7	4.203	[28]
Activated Moringa oleifera	7.0	6.23	[29]
Fe/Mn modified biochar (FMBC)	6	8.25	[30]
Paddy Husk Ash	4	0.063	[31]
Iron-impregnated biochar	6	2.16	[32]
iron oxide amended rice husk char	7	1.46	[33]
Fe(II)-loaded activated carbon	3	3.01	[34]
TOLC@Al	6.0	17.1	Present work

for the adsorption of arsenic ions (94.1% removal efficiency) at pH 6.00 at room temperature. The working pH < p_{HZPC} of TOLC@Al indicates the positively charged surface which supports a high attraction between the adsorbent surfaces and As(V) ions. FTIR studies showed the existence of polar functional groups such as hydroxyl and phenolic groups, demonstrating that the sorption may occur through ion exchange with As(V) ions. SEM spectra showed small-sized particles clustered for the TOLC@Al that resulted in a bigger structure having a micro-porous character. The adsorption isotherm study and the kinetic study revealed that the Langmuir model ('Q_m' is 24.44 mg g⁻¹) followed by pseudo-second-order were best fitted to system; this indicate the unilayered structure and that the chemisorption is the rate-determining step. Furthermore, the prepared adsorbent is regenerated by sodium hydroxide solution that reduces the cost of the adsorption method. The TOLC@Al material is one of the best adsorbents compared to the locally accessible adsorbents; it is financially feasible and naturally executed in wastewater treatment.

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