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Research Article

REMOVAL OF ARSENIC FROM AQUEOUS SOLUTIONS BY

LAWSONIA INERMIS CARBON

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ABSTRACT

Arsenic in water systems is mostly introduced from natural and anthropogenic sources. Natural sources include the erosion of arsenic-rich rocks and soils, which probably occur because of long-term geochemical changes. Arsenic removal from contaminated water is an important subject worldwide, which has recently attracted great attentions. Arsenic is a naturally occurring metalloid, which is widely distributed in nature and is regarded as the largest mass poisoning in history. In the present study, the adsorption potential of plant carbon in a batch system for the removal of As(V) from aqueous solutions was investigated. Isotherm studies were carried out to evaluate the effect of contact time (30-180 min), pH (1–6), initial arsenic concentration (10-60 μ g/L), and adsorbent dose on sorption efficiency. Maximum removal efficiency of 90% was obtained at pH 6, adsorbent dosage 150g/L, initial As(V) concentration 10 μ g/L, and contact time 180 at 30 °C to 60 °C, respectively. Also, the adsorption equilibriums were analyzed by the Langmuir and Freundlich isotherm models. Such equilibriums showed that the adsorption data was well fitted with the Freundlich isotherm model for *Lawsonia inermis carbon* at 30 °C to 60 °C. According to achieved results, it was defined that *Lawsonia inermis carbon* as effectively for As(V) removal from the aqueous environment.

Keywords: Arsenic, plant carbon, batch system, contact time, Lawsonia inermis carbon.

1. INTRODUCTION

Arsenic is a geogenic water menace affecting millions of people all over the world and is regarded as the largest mass poisoning in history. Permanent arsenic intake can lead to chronic intoxication, and prolonged arsenic exposure can damage the central nervous system, liver, and skin and results in the appearance of diverse types of cancers, such as hyperkeratosis, lung, skin, and prostate cancers 1-3. Arsenic in natural waters is a worldwide problem. Arsenic pollution has been reported recently in USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan, and India⁴. The largest population at risk among the 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India⁵. Due to high toxicity and carcinogenic effect of arsenic, the World Health Organization (WHO), the European Commission (EU), and the United States Environmental Protection Agency (USEPA) have recommended a maximum contaminant level (MCL) of $10 \mu g/L$ for arsenic in drinking water⁶. In Iran, a maximum arsenic level of $10 \mu g/L$ is permitted in drinking water by the Institute of Standard and Industrial Research of Iran (ISIRI). Arsenic (a semi metallic element) is one of the most toxic, carcinogenic, and natural contaminants found in water resources^{7,8}. Anthropogenic sources include forestry, agricultural application of various pesticides, herbicides and fertilizers, and industrial effluents from metallurgy, electronics, mining, pharmaceuticals, glass processing, ceramic, dye and pesticides manufacturing, wood preservatives, petroleum refining, and landfill leaching%.

The two states prevalent in water environment are arsenite (As(III)) and arsenate (As(V))¹⁰.

As(III) mostly exists in reducing ground waters and hydrothermal waters, whilst As(V) is more often present in surface waters and oxidizing ground waters¹¹. Several treatment technologies have been applied for the removal of arsenic from water, including chemical coagulation^{12, 13}, chemical oxidation¹⁴, dissolved air flotation (DAF) process¹⁵, adsorption³, ion exchange¹⁶, membrane processes¹⁷, electrocoagulation¹⁸, constructed wetlands¹⁹, and biological process ²⁰. Each method has its advantages and disadvantages, and individual water treatment plants may choose the method that best suits their financial and managerial situations.

Coagulation and adsorption processes are most promising for arsenic removal from high-arsenic water because of the low cost and high efficiency and are widely used in the developing world²¹. Although the coagulation process is a simple and economical way, it produces a wet bulky sludge, and furthermore could not satisfy the stringent standard of the WHO. Because of the ease of handling, sludge-free operation, and using acid or base leaching to regenerate the sorbent bed, the adsorption process appears to be the most promising one²². Also, currently, low-cost adsorption materials are popular for arsenic removal from natural water^{23, 24}. On the other hand, adsorption has a comparatively low cost, availability, and easy operation and it easily separates a small amount of toxic elements from large volumes of solutions²⁵. These advantages of adsorption have motivated several researchers to use this process for removal of arsenic from water. Some of the common adsorbents used for arsenic removal include activated alumina, activated carbon hydroxide, composites, granular ferric manganese green sand, natural laterite, rare earth oxides, bone char, surface-modified zeolite with cationic surfactant and mud, and Feexchanged natural zeolite 22,26-30.

The main objective of this research was to evaluate the feasibility of using the *Lawsonia inermis carbon* as an adsorbent for the removal of arsenic from aqueous solutions. The effects of different parameters including solution pH, adsorbent dosage, arsenic concentration, temperature of carbon produced, and contact time were studied. Additionally, the sorption isotherm was explored to describe the experimental data.

2. EXPERIMENTAL

2.1. Adsorbent Preparation

The stems of *Lawsonia inermis carbon* leaves were obtained from Nagapattinam Cauvery delta Area. These materials were firstly w carboned with distilled water to remove impurity such as sand and leaves and soluble and colored components, dried at 110°C for 12 h, burned at 500°C for 2 h, crushed in a mortar, and sieved to obtain a particle size in the range of 0-63 mesh. The powdered adsorbent was stored in an airtight container until use. No other chemical or physical treatments were used prior to adsorption experiments.

2.2. Arsenic Solution (Absorbate)

All the chemicals used were of analytical reagent (AR) grade. Stock solutions of As(V) were prepared by dissolving sodium salt heptahydrate (Na₂HAsO₄7H₂O) in double-distilled water (at a concentration of 10 mg/L) and the experimental solutions were obtained by diluting the stock solution to the required concentrations (10-60 μ g/L). The solution pH (1–6) was adjusted with 0.1 M HCl or 0.1 M NaOH.

2.3. Analysis

The residual arsenic concentration in the solutions was analyzed by silver diethyl dithiocarbamate method (SDDC) using UV-Vis spectrophotometer (Spectro UV-Vis Double Beam UVD- 3500, Labomed.Inco) at 530 nm. The pH of solution was measured using a pH meter (Digsun2012).

2.4. Batch Adsorption Experiments

The adsorption studies were carried out at 30

 \pm 1 °C. pH of the solution was adjusted with 0.1 N HCI and 0.1N NaOH. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. The batch experiments were carried out in Erlenmeyer glass flasks of 100 mL capacity. To help mixing of the solutions with the adsorbents, the mixture was shaken in a mechanical shaker (Remi make) at suitable (180) rpm for three hours. Then the mixture were filtered and the remaining metal ions/dyes concentration were determined in the filtrate using (Spectro UV-Vis Double Beam UVD- 3500, Laborned.Inco) at suitable λ_{max} .The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent, contact time t, initial concentration of metal ion C_0 , adsorbent amount , initial pH of solution and temperature. The solution volume (V) was kept constant 50 ml. The metal ion/dye adsorption (%) at any instant of time was determined by the following equation:

Metal ion/dye adsorption (%) = $(C_0 - C_e) \times 100/C_0$

Where C_0 is the initial concentration and C_e is the concentration of the metal ion/dye at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

2.4.1. Effect of Solution pH on As (V) Adsorption

The effect of solution pH on the adsorption capacity of Lawsonia inermis carbon (150 g) obtained at 30°C was investigated using a 100 mL solution of $25 \mu g/L$ of As(V) for a pH range of 1 to 6 at °C. Flasks were agitated on a rotary shaker at 180 rpm for 80 min to ensure that the equilibrium was reached. The mixtures were then filtered through Whatman 42 filter paper and the concentration of As (V) in the filtrates was analyzed using а spectrophotometer. The above procedure was repeated three times and the average value was taken.

2.4.2. Effect of Lawsonia inermis carbon Dosage

Batch adsorption experiments were done at a different *Lawsonia inermis carbon* (obtained at 30° C) concentration from 50mg to 200mg in a 100 mL solution of $25 \,\mu$ g/L of As(V) at pH 6.0, for a contact time of 80 min at °C. The samples were then agitated and filtered and the filtrates were analyzed as mentioned before.

2.4.3. Effect of Contact Time

Batch adsorption experiments were carried out at different contact times (30, 60, 120, 180 min) for an initial concentration of $25 \mu g/L$ of As (V) solution at pH 6.0. The *Lawsonia inermis carbon* (obtained at 30°C) dose was 150mg in 100 mL solution in 250 mL stoppered bottle at 30°C. The samples were then agitated and filtered. The filtrates were analyzed as mentioned before.

2.4.4. Effect of Initial As(V) Concentration

Batch experiments were carried out by contacting 150mg of *Lawsonia inermis carbon* (obtained at 30°C) with 100 mL of As(V) solution of different concentrations (10, 20,30,40,50 and $60 \mu g/L$) at pH value of 6.0 at 30°C. A series of such Stoppered bottles were shaken for 180 min with *Lawsonia inermis carbon* at a speed of 180 rpm. Samples were then agitated and filtered. The filtrates were analyzed as mentioned before.

3. RESULT AND DISCUSSION 3.1 Effect of particle Size

The effect of adsorbent's particle size was studied in the range of 0-200 microns particle size (0-63, 63-125, 125-200) for checking the maximum adsorption of As(V), and the smallest particle size (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area.

3.2.Effect of pH

The pH of the solution is one of the most critical parameters in the adsorption of pollutants from aqueous solutions. In order to determine the preferred pH for adsorption of As(V) over Lawsonia inermis carbon leaves carbon, the uptake of As(V) as a function of hydrogen ion concentration was studied. Figure 1 depicts the effect of pH on adsorption of As(V) onto the Lawsonia *inermis carbon*(30°C). Both adsorption efficiency and capacity have the same trend. The maximum adsorption capacities of Lawsonia inermis carbon for As(V) occurred at pH 5.5–6.5. Nevertheless, highest adsorption has taken place at pH 6.0 (81.2%) which was chosen as an optimum pH condition for further experiments. pH parameter is very important since it strictly depends upon the nature of adsorbate and adsorbent. Also, it is an established fact that As(V) is more strongly adsorbed than As(III) where pH is acidic or near neutral³¹. In addition, after adsorption, the pH of solution was slightly relevated. One reason for the change of pH may be the ion exchange process.

3.3. Effect of Contact Time

The contact time is one of the most important parameters for practical application. The effect of contact time onto the adsorption of arsenic by Lawsonia inermis carbon at 30°C is shown in Figure 2. The adsorption capacity and removal efficiency of As(V) onto the Lawsonia inermis carbon significantly increase during the initial adsorption stage (0–30 min) and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained after 180 min for carbon at 30°C. Because the adsorbate is adsorbed easily on the surface (or macropore surface) of the adsorbent, rapid adsorption results. In contrast, in the interior (or micropore surface) of the adsorbent, the adsorbate would be adsorbed by a pore and/or surface diffusion mechanism, resulting in a slower adsorption. On the other hand, according to Figure 2, As(V) was rapidly adsorbed in the first 30 min (55%), then the adsorption rate decreased gradually from 60 to 180 min, and finally reached equilibrium in

about 180 min. Also, the maximum efficiency of 84.1% for removal of As(V) was obtained at approximately 180 min for carbon at 30°C.

A further increase in contact time had an insignificant effect on the amount of adsorption (adsorption capacity). Therefore, contact time of 180 min was used in subsequent experiments (for carbon 30°C). Generally the removal rate of sorbate is rapid initially, but it gradually decreases with time until it reaches equilibrium. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar findings were reported by other researchers³²⁻³⁴.

3.4Effect of temperature

Temperature has an important effect on the rate percentage adsorption. of The ∩f As(V)adsorption was studied as a function of temperature in the range of 30-60 °C. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption was 84.09 % at 30 °C and maximum adsorption was 90.63 % at 60 °C for 25 ppm initial concentration of metal ion solution. The effect of temperature on the percentage adsorption of As(V)on Lawsonia inermis is shown in figure 3 and table 4.1.9. This is only natural because increase in temperature provides the necessary energy for the endothermic process of adsorption, As(V)to an increase in the rate of the process. The point to be appreciated is that even at room temperature sufficient (more than 84.09 %) adsorption has taken place. This in turn confirms the efficiency of the adsorbent in the removal of toxic As(V)ions.

3.5. Effect of Adsorbent Dose

The Lawsonia inermis carbon dose is an important parameter because this determines the capacity of the adsorbent for a given initial As(V) ion concentration. Therefore, the effect of adsorbent dose on As(V) uptake was depicted in Figure 4, which showed that the adsorption efficiency of As(V) increased very quickly with an increase in dosage of Lawsonia inermis carbon from 50 to 200mg/L a marginal increased was observed on further increase in the adsorbent dose. On the other hand, at lower adsorbent doses, the increase in the percentage of As(V) removal was very high because of the increase in adsorbent dose. However, at higher adsorbent doses, the increase in the removal efficiency of As(V) was insignificant. This may

occur because arsenic adsorption happens in two stages, which are fast formation of a monolayer followed by a slow plateau stage³⁵. Furthermore, both adsorption efficiency and capacity have the same trend. As shown in Figure 4, adsorption efficiency has gone up from 61.36% and 97.22% at a dose of 50mg/L to 200mg/L for carbon at 30°C. Increase in removal efficiency was because of the greater availability of the exchangeable sites or surface area at the higher concentrations of the adsorbent^{36, 37}. On the other hand, the increase in the efficiency of removal may be attributed to the fact that with an increase in the adsorbent dose, more adsorbent surface or more adsorption spots were available for the solute to be adsorbed. The results of this study are in accordance with obtained findings by other researchers^{3, 34}. The rate of adsorption depends upon the uncovered surface available for adsorption. Initially, as the whole surface was uncovered, the rate of adsorption was very high. As the surface was covered increasingly, the rate of adsorption decreased. Ultimately, a stage was reached when there was no more adsorption with the further addition of adsorbent, and at that time, equilibrium was achieved. The trend in adsorption capacity was because of the interference between binding sites, and higher biomass dose or insufficiency of metal ions in solution with respect to available binding sites ^{38, 39}. After studying the effect of concentration of adsorbent on carbon at both 30°C, a dose of 150mg/L was selected for subsequent experiments.

3.6. Effect of Initial Concentration of Arsenic

The initial concentration provides an important driving force to overcome all mass transfer resistance of the adsorbate between the aqueous and solid phases⁴⁰. In this study, the effect of initial As(V) concentrations on adsorption process was studied at pH 6, adsorbent concentration 25mg/L, and contact carbon at 30°C. The time 180 min for adsorption capacity decreases from 91.06% to 78.77% as the metal concentration increases from 10 to 60 mg/L. The trend is that of the result of the progressive decrease in the electrostatic interaction between the As(V)ions and the absorbent active sites. Moreover, this can be explained by the fact that less adsorption sites were being covered as the metal ions concentration decreases. Besides, lower initial concentrations As(V)to an increase in the affinity of the As(V)ions towards the active sites. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger

number of adsorbing species at lower concentrations. The experimental results of adsorption of As(V)ions on Lawsonia inermis at various initial concentrations are shown in figure5. It reveals that, the actual amount of metal ions adsorbed per unit mass of Lawsonia inermis decreased with increase in metal ion concentration. Adsorption is maximum when the initial concentration of As(V)ions were 10 mg/L.As the concentration increases, all the adsorption sites are being filled up and there remains unabsorbed metal ions, hence the decrease in percentage adsorption. This result is in favour of only monolayer coverage and suggests the application of the Langmuir isotherm model. Since 91.06% adsorption occurs when the initial concentration was 10 mg/L, Lawsonia inermis appears to be very effective adsorbent in removing even traces of As(V) ions.

3.7Adsorption Isotherm

Isotherms study can describe how an adsorbate interacts with adsorbent. The isotherm provides a relationship between the concentration of As(V) in solution and the amount of As(V) adsorbed on the solid phase when both phases are in equilibrium. Isotherm parameters, evaluated from the linear plots of equations (3.1-3.4) are illustrated in Table 1, (Fig. 6-9). The K_L (sorption equilibrium constant) value for the Langmuir isotherm, ie. 2.958 mg/g indicated the high adsorption capacity of biosorbent toward As (V) adsorption. This is in turn supported by the values of the dimensionless separation factor (R_L), which are less than 1.The R^2 (correlation coefficient) value 0.921 indicated that the Langmuir isotherm is good for explaining the As (V) adsorption. The R² value calculated for the Freundlich isotherm was found to be 0.997, indicating that the experimental data can be explained by the Freundlich isotherm. The K_F (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 3.155. The values of Freundlich constant, n, are much greater than 1, implying that the adsorption process is governed by physisorption only. The R² value calculated for the Redlich-peterson isotherm was found to be 0.995, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The β value as calculated from this isotherm was 0.401 The Dubinin-Kaganer-Radushkevich (DKR) model was adopted to describe the single-solute adsorption isotherms. The R² value calculated for the DKR isotherm was found to be 0.8019, indicating that the experimental data can be explained by the DKR isotherm poorly. The β value as calculated from this isotherm was 0.987. The values of desorption constant, β , in the Redlich-Peterson and the Dubinin-Kaganer-Radushkevich isotherms is a measure of the desorption constant. Its values are less than 1, indicating favourable adsorption. The sorption energy ϵ in the DKR isotherm is a valuable parameter to distinguish between physisorption and chemisorptions. Lower values suggest physisorption is more.

$$C_e/X=1/K^*K_L+Ce/K$$
 (3.1)
 $K_L=b^*q_0$

Ce is the equilibrium concentration of the adsorbate (mg/L), X is the amount of adsorbate adsorbed (mg/g), K_L indicates monolayer adsorption capacity (mg/g), K is the Langmuir equation constant (L/mg) ,Where b is Langmuir constant known as **adsorption energy**, in dm³ /mg. A plot of Ce/q_e vs. C_e gives a straight line with a slope = 1/ q₀ and intercept = 1/K_L.

$logq_e = logK_F + 1/nlogC_e$ (3.2)

 K_F and 1/n are constants for a given adsorbate and adsorbent at a particular temperature, A plot of log q_e vs log C_e will be a straight line and K_F and n can be obtained from the intercept and the slope respectively. Freundlich constant, n is a measure of the deviation from linearity of the adsorption.

The Redlich-Peterson Isotherm can be expressed as equation

 $q_e = K_R Ce / (1+b_R Ce\beta)$ ----- (3.3)

where $b_R K_{R}$ and β are Redlich-Peterson constants and can be obtained by plotting log C_e/q_e vs. log C_e .

The Dubinin-Kaganer-Radushkevich (DKR) isotherm can be expressed as equation

 $\log qe = \log Xm - \beta \epsilon^2 / 2.303 - (3.4)$

Where The constant, β in DKR isotherm equation gives an idea about the mean free energy (E) of sorption per molecule of the substrate. Xm is maximum sorption capacity. ϵ (the sorption potential) = RT ln (1 + 1/Ce), qe is the amount of ion adsorbed per unit weight of adsorbent(mg/g).

3.8 FT-IR Study

Fourier Transform Infra-Red (FTIR) spectra of *Lawsonia inermis*, before and after adsorption of As (V) ions, were recorded in order to determine the functional groups present on the surface of the adsorbent. The spectra were

taken within the wave number range of 400 -4000 cm⁻¹ and are shown in figures 10 and 11. The action of oxidizing Oxygen on the surface of the carbonaceous precursor causes formation of surface oxides .Their structure have not been investigated completely because of the greater number of possible surface groups .The most common Oxygen groups on the surface are carboxylic, lactonic and phenolic .These groups have acidic character, which can be relatively easily determined by titration methods that are based on titrations using bases of different strengths. The method of Boehm has been followed to find the density of functional groups present on the carbon surface.FT-IR (JASCO FTIR-3500)spectra of the activated carbon samples before and after adsorptions are shown in the figures (10 & 11) respectively. The spectra provide the evidences for the presence of surface groups on the adsorbent's surface. Notable differences among them are the peak carbons have intensities. The marked differences in the intensities of nearly all the absorption bands, reflecting that the density of corresponding functional groups differ a lot. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed absence of formation of new compounds shown in the fig 4.7.11. As can be inferred from the figures, the adsorption frequencies are almost the same and it is presumed that the functional groups were not affected due to adsorption. which only endorses that only physisorption has taken place. The intense broad band between 3100 and 4000 cm⁻¹ are connected with v(O-H). The O-H groups are likely associated by means of hydrogen bonds. The band of non bonded hydroxyl groupings ,besides being a sharp band is usually located above 3500 cm⁻¹ .The band in the range below 3700 cm⁻¹ was assigned by Zawadzki to Hydrogen bonds of type $(H_2O - H - OH_2)^+$ with protons of acidic groups. Intense bands at 2301.71 cm⁻¹ indicates C-H stretching from CH₂ groups. The bands around 1700 cm⁻¹ are ascribable to v(C=0)vibration in configurations such as lactones, quinone and COOH groups their intensity denotes a low concentration of surface C=O groups in adsorbent. According to correlation charts, Bands at 1416.27 and 1602.61 cm⁻¹ are due to asymmetric and symmetric v (COO-) vibrations are skeletal C=C aromatic vibrations .The band at 1112.38cm-1 is associated with phenolic OH groups and to OH groups in aliphatic carbons respectively. It could also be due to -SO₃H groups because of sulphuric acid

treatment. The bands at 665.94 and 582.48cm⁻¹ are due to COO and C-O-H groups respectively. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed absence of formation of new compounds.

3.9 SEM analysis

The surface morphology of *Lawsonia inermis* was examined using Scanning Electron Microscopy (SEM), before and after adsorption and the corresponding SEM micrographs were obtained at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000× magnification and are presented in figures 12 a and 13. At such magnification, the *Lawsonia inermis* particles showed rough areas of surface within which micropores were clearly identifiable.

3.10 XRD Study

The X-ray Diffraction Studies of the adsorbent *Lawsonia inermis*, before and after

adsorption of Chromium (VI) ions, were carried out using, Philips xperto X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III. The diffraction patterns are shows in figure 14 and 15. It is evident from the figures that there is no appreciable change in the spectra of adsorbent before and after adsorption. This may be due to the fact that adsorption does not alter the chemical nature of the surface of the adsorbent i.ess. The adsorption is governed by weak Van der Waals forces and is physical in nature.

3.11 Kinetics of adsorption

The percentage adsorption of metal ion/dye was determined at various time intervals, namely 10, 20, 30, 40, 50 and 60 min. The data were fed into four different kinetics models and the equilibrium absorption capacities and other useful parameters were calculated.

- a. Lagergren's pseudo-first order kinetics
- b. Pseudo-second order kinetics.
- c. The Elovich kinetics
- d. The intra-particle diffusion model.

The best fit model was selected based on both linear regression correlation coefficient and on the precision between the calculated values of adsorption capacity (qe) and rate constant (k). The Lagergren equation for pseudo-first order kinetics is shown in equation 3.5,

$log(q_e-q_t) = loq_e-k_1t/2.303$ (3.5)

Where q_e and q_t are the amounts of ion/dye adsorbed (mg g⁻¹) at equilibrium and at time t,

and k_1 is the Lagergren's first order rate constant (in min⁻¹). Values of k_1 and q_{e_r} calculated from the slope and y- intercept, respectively, of the plot of log (q_e - q_t) against t. The pseudo-second order kinetics can be expressed by the rate equation 3.6.

$t/q_t = 1/k_2 \cdot q_e^2 + t/q_e$ (3.6)

Where qe and qt are the amounts of ion/dye adsorbed (mg g⁻¹) at equilibrium and at time t; k_2 is the second order rate constant (gm g⁻¹min⁻¹).Values of k_2 and q_{e_i} calculated from plots of t/qt against t. The Elovich model can be expressed as equation 3.7.

$q_t = 1/\beta \ln \alpha \beta + 1/\beta \ln t$ (3.7)

Where α refers to initial adsorption rate and β is the desorption constant. Both α and β can be calculated from the slope and y-intercept of the plot of q_t verses log t.

The intra particle diffusion model of kinetics can be stated as the rate equation 3.8,

$$q_t = k_p \cdot t^{1/2}$$
 (3.8)

Where k_p is the rate constant for the diffusion process and c is a constant.

The kinetics parameters are given in Fig. 16-19. Analysis of the kinetics parameters shows that there is no correlation between theoretical and experimental qe values for the Lagergren's first order kinetics and hence the adsorption process is not likely to be of the first order. The R² values for the second order kinetics shows high precision suggesting that second order kinetics is a best fit.

3.12 Thermodynamics of the adsorption process

Four important thermodynamic parameters were deduced for the adsorption process, namely the change in Gibbs free energy (Δ G), change in Enthalpy (Δ H), energy of activation (Ea) and the change in Entropy (Δ S).From the percentage adsorption, the thermodynamic equilibrium constant, K_c was calculated. Δ G for the process was determined from K_c. Changes in enthalpy, entropy and activation energy was determined from the effect of temperature on the adsorption process. Van't Hoff equation in the following form,

$\Delta G = -RTInKc = \Delta H - T\Delta S$ (3.9)

was used to calculate the thermodynamic parameters such as Gibb's free energy change (Δ G), enthalpy change (Δ H) and entropy change

(Δ S), where Kc is the equilibrium constant for the adsorption process, T is the temperature in Kelvin and R, the gas constant. Rearranging equation 3.9,

$InKc = -\Delta H/RT + \Delta S/R \qquad (3.10)$

A plot of In Kc vs 1/T gives a straight line with a slope equal to - Δ H/ R and y-intercept, Δ S/ R. Van't Hoff plot was constructed for the adsorption process and Δ H and Δ S were calculated from the slope and intercept of the plot respectively. Δ G was calculated from the value of Kc, from equation 3.10.

Activation energies for adsorption of ion/dye on adsorbent was calculated using the Arrhenius equation (eq 3.11) , The activation energy obtained in this case , indicate that physical forces are involved in the sorption mechanism and sorption feasibility. A plot of log K vs log A gives a straight line with a slope equal to log A and y-intercept, Ea.

$logK = logA - (E_a/2.303RT) ------ (3.11)$

The thermodynamic parameters for the adsorption of As (V) ions on Lawsonia inermis are given in table 2. For the adsorption of As (V) on Lawsonia inermis, the free energy values are all negative confirming that the process is spontaneous even at room temperature. The entropy change is positive and explains the increase in randomness of the process. The endothermic nature of the adsorption process is evident from the positive values of enthalpy change. Presumably, the randomness factor $(T\Delta S)$ overcomes the energy factor (ΔH) and makes the overall process spontaneous (ΔG negative). Activation energies for adsorption of As (V) on adsorbent was calculated using the Arrhenius equation (eq 3.11), plotted in Fig 20 and tabulated in table 3. The activation energy obtained in this case , indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

4. CONCLUSIONS

Arsenic is present in water as a result of both natural and anthropogenic activities. Drinking water poses the greatest threat to public health from arsenic. Arsenic dissolved in water is acutely toxic and can lead to a number of health problems. At the present study, the adsorption ability of the *Lawsonia inermis* carbon (30°C) is evaluated for As(V) as an adsorbate. Batch adsorption tests demonstrate that the adsorption is affected by various conditions such as initial pH, adsorbent dosage, contact time, and initial As(V) concentration. From the present study, it can be seen that *Lawsonia inermis* carbon can be used effectively for the removal of As(V) from aqueous solutions. This adsorbent was able to remove up to 91% of As(V) from solutions whose initial concentration varied between 10 and $60 \mu g/L$. In addition, final concentration of As(V) reached lower than $10 \mu g/L$ as a maximum contaminant level in drinking water. The removal of As(V) from aqueous solutions is induced by adsorption on surface sites of the solid for low As(V)

concentration while both adsorption and internal exchange take place for high concentrations.

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Fig. 4: Effect of adsorbent dose on As(V) removal (the initial As(V) 25 $\mu g/L$, , and contact time of 180 min for carbon at 30°C)



Fig. 5: Effect of initial As(V) concentration for the adsorption of As(V) onto adsorbent in optimum condition







Fig. 7: The Langmuir isotherm for adsorption of As(V) onto *Lawsonia inermis* carbon 30°C



Fig. 8: The Redlich peterson isotherm for adsorption of As(V) onto *Lawsonia inermis* carbon 30°C

DKR isotherm









Fig. 11: FTIR after Adsorption



V 100 000 x 9.0 mm etc mode -----Fig. 12: SEM before Adsorption





Fig. 14: XRD before Adsorption











Fig. 17:











Fig. 20:

Langmuir parameters	K _L =2.95858	q0 = 25.0	b _L = 0.1183	
Freundlich parameter	K _F = 3.155	n =1.6		
Dubinin-kaganer-Radushkevich parameters	β = 0.8019	b =0.261	q0 =1.06194	
Redlich peterson parameters	β= 0.401	K _R = 1.5520	b _R =0.811052	

Table 1.

	Table 2:					
ΔG0	ΔΗΟ	Δ\$0	Log 10 Ka	1/T		
-1427.37	19.14714	57.44143	0.245953	0.003299		
-1887.58			0.314867	0.003193		
-2668.27			0.43132	0.003095		
-3242.5			0.508411	0.003002		

Table 3:				
Ea	Log A	R2		
16.94331	3.244	0.988		

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