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Removal of Arsenic from Aqueous Solution by Chemical Modification of Date Palm Bark

Furqan A. Khan[1], Fayaz A. Khan[2], M.T. Bashir[3]
[1, 2]*National Institute of Urban Infrastructure Planning, University of Engineering & Technology Peshawar, Pakistan*
[1, 3]*Department of Civil Engineering, Qurtuba University of Science & IT Dera Ismail Khan, Pakistan*

Abstract: ***Arsenic is sizeable contaminants in consuming water sources in world wise locations consisting of Pakistan. Date Palm (DP) Bark are available in abundance in Dera Ismail Khan, Pakistan as an agricultural waste that can be modified into a water treatment adsorbent through improving its affinity to remove anions and cations. This study evaluated the viability of the usage of modified DP Bark as a water purification medium to take away these contaminants. The assessment concerned identifying the sorption capacity, mechanics of contaminant removal and the sensible acceptance of this material. Eco-friendly and economical adsorbents were prepared by chemically modified or mercerized DP Bark. The resulting adsorbents, named "mercerized Bark based adsorbent" (MBA), were prepared in a one-step process. In this study, ground DP Barks were exposed to hydroxyl pre-treatment (mercerization) using sodium hydroxide to remove impurities and make the particles porous. Batch studies were conducted to determine the adsorption of Arsenic on MBA, varying contaminant concentrations, adsorbent doses, and pH. Subsequently, the experimental data were simulated using conventional isotherm models, including the Langmuir and Freundlich models as well as kinetics models. At initial Arsenic (As) concentration of 0.1 mg/L (100 µg/L, an adsorption capacity for Arsenic on MBA were 0.0875 mg/g (87.5µg/g) at pH 6. Based on the goodness of fit of a pseudo-second order model and pseudo-first order model, the adsorption process was classified as physiochemical adsorption.***
Keywords: Arsenic Removal, Adsorption, Date Palm Bark, Isotherm Modelling, Kinetics Modelling

I. INTRODUCTION

Arsenic is a chemical factor abbreviated by means of the symbol (As). Arsenic happens in many minerals; Arsenic consists of about 1.5 ppm of earth crust and is the 53rd most plentiful component [2]. Arsenic possesses numerous results such as long-term publicity in consuming water purpose fitness outcomes consisting of blood, skin, and lung cancer; soluble inorganic Arsenic can have immediately poisonous consequences such as vomiting, disturbance of blood circulations, damage in the worried system, and subsequently death. For an instant, in Taiwan, Arsenic in potable water brought about black foot disease that severely damages the blood vessels in decrease limbs [32]. Many techniques for elimination of Arsenic from potable water are mentioned in the literature. Eliminate Arsenic from consuming water by using activated carbons which have been extracted from olive pulp, and olive stone [4]. The researcher produced olive pulp and olive stone via chemical activation (K2CO3, HNO3) and physical activation. The result of this research suggests that olive pulp and olive stone are the excellent adsorbents for removal of Arsenic from drinking water. The most removal used to be discovered and the adsorption capability of olive pulp and olive stone is 11.42 and 9.85umol/g, respectively [4]. contamination in Bangladesh at a very scale. They removed Arsenic from drinking water by means of the use of bio adsorbents organized from jute stick powder, jute leaf powder, sugarcane powder, and lily leaf powder and egg shell maintaining in view the economy of remedial science that was appropriate for the humans of Bangladesh. Adsorption capacities of jute stick powder, jute leaf powder, sugarcane powder, and egg skull are mentioned as $6.64x10^{-5}$ kg/kg, $5.21x10^{-5}$ kg/kg, $7.79x10^{-6}$ kg/kg and $4.74x10^{-5}$ kg/kg, respectively [17].

The research work performed through [23], showed that Arsenic can be eliminated from drinking water by means of zeolite, betonies, sepiolite, and pyrolusite and limonite, these all are inexpensive and typically available [17]. According to lookup through [1], Arsenic can be removed from drinking water via the usage of date palm fibres and orange peel and observed greater affectivity of the absorbent organized from the orange peel in contrast to date palm fibres [1]. In any other recent research for elimination of Arsenic, the researchers determined that activated carbon is a pricey technique to remove Arsenic, so they used date palm fibre to get rid of Arsenic from drinking water took place [31]. This research shows that it is a more reasonable procedure compared to other methods.

In this research, Date Palm Bark was examined for its suitability to remove Arsenic from water over a broad range of temperature, pH, Arsenic concentration and adsorbent dosage without using a catalyst.

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II. MATERIAL AND METHODOLOGY

A. Chemical Reagents

The detail of chemicals and reagents used in the education of adsorbent and experimentation are Arsenic Solution, Sodium Hydroxide (NaOH), Acetic Acid (CH3COOH) and HCL. The chemical substances and reagents were used in all experiments except similarly purification. Material and Safety Data Sheet of all chemicals and reagents had been reviewed and understood prior to experimentation.

B. Material and Synthesis of Adsorbent

The adsorbents such as mercerized Bark based (MBA) were prepared by surface modification of DP Barks on method and procedure reported in the literature with significant modifications [3]. Raw Date Palm Barks were acquired from local areas of Dera Ismail Khan, Pakistan. Two kilograms of raw date palm Bark was cleaned and washed using hot water and dish washing liquid. The date palm Barks were then dried and ground into small particles with an effective diameter of approximately 0.125–2 mm. The drying process was carried out at 105 °C to ensure the complete removal of extrinsic moisture.

C. Preparation of Adsorbates

Arsenic stock solution used to be received from Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories having concentration of 1g/L. Solutions of required Arsenic concentrations (0.1–0.6 mg/L) had been bought through diluting the Arsenic stock solution with DI water (Milli-Q Water). The Arsenic concentrations had been measured the use of an Arsenic kit (QUANTOFIX®). All the diluted solution had been prepared using mass balance equation (3.1) while micropipette was once used for all measurements.

$$M_1 V_1 = M_2 V_2 \qquad (3.1)$$

D. Static Study for Arsenic Adsorption

Batch experiments of Arsenic have been carried out at 28 ± 2 ° C (room temperature) to study the effects of parameters such as contact time, pH, preliminary Arsenic attention and adsorbent dose of MBA (0.1-0.6 g). The preliminary Arsenic awareness is 0.1 - 0.6 mg / L (100 µg / L - 600 µg / L). The batch check used to be carried out with the aid of putting a 100 mL sample in a 250 ml Erlenmeyer flask, and then the combination was stirred at 110 ± 2 ° C for 2 hours the usage of an incubator shaker at one hundred ten rpm. Each take a look at was carried out in triplicate to limit experimental error. The adsorption capacity at the time of saturation was calculated by Equation 3.2.

$$q_e = \frac{V(Ci - Ce)}{m} \qquad (3.2)$$

Here, 'q_e' is maximum adsorption of Arsenic at equilibrium (mg/g), V is volume of adsorbate in the flask, 'C_i' and 'C_e' are initial, and equilibrium concentrations (mg/L) respectively and m is mass of the MBA (g).

E. Kinetic Modelling of Arsenic Adsorption

The kinetics of Arsenic removal by MBA were investigated by exposing both adsorbents (0.4 g) to a 0.1-mg/L Arsenic solution (100 ml) for various durations, and measuring the quantity of Arsenic removed from solution at each time interval. To more precisely define the dynamic aspect of Arsenic removal by MBA, pseudo-first-order models and pseudo-second-order models are used to describe the kinetic data. According to [24], the pseudo first-order langrenen equation can be used in the form of Equation 3.3, and the pseudo second order can be used by using the equation (3.4) described by [12], In Equations 3.3 and 3.4, q_t and q_e are the amount of Arsenic absorbed (mg/g) at time 'and equilibrium, respectively, and K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are coefficient.

$$\ln (q_e - q_t) = \ln qe - k_1 t \qquad (3.3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (3.4)$$

$$h = \frac{1}{K_2 q_e^2} \qquad (3.5)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (3.6)$$

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F. Adsorption Isotherms

Among the many models that can be used to study the behaviour and suitability of adsorption processes, the Langmuir and Freundlich isotherms are often used to investigate the effectiveness of adsorption. The linearized form of the Langmuir mannequin (Equations 3.7-3.9) used to be used to study the adsorption of Arsenic with the aid of MBA [6]. The Langmuir isotherm model cites a process that considers single layer adsorption barring lateral interaction.

$$q_e = \frac{Q_0 * b * C_e}{1 + b * C_e} \qquad (3.7)$$

$$\frac{1}{q_e} = \frac{1}{Q_0 * b * C_e} + \frac{1}{Q_0} \qquad (3.8)$$

$$R_L - \frac{1}{1 + K_L * C_i} \qquad (3.9)$$

The linearized form of the Freundlich isotherm model (Equation 3.10) was employed to investigate adsorption data. Freundlich isotherm model considers multilayer adsorption in which stronger binding sites are occupied at first [6] linear form of Freundlich model can be written as equation 3.10

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3.10)$$

In the above equations, 'C_i', 'C_e' and 'q_e' represent the initial and equilibrium concentration of Arsenic (mg/L), and quantity of solute adsorbed (mg/g), respectively. In addition, m is the mass (g) of adsorbent utilized, Q_0 represents the maximum monolayer adsorption capability (mg/g), b is the Langmuir isotherm model constant, and R_L is the separation factor. The constants 'K_f' and '1/n' are the adsorbent capacity and the adsorbent intensity, respectively, in the Freundlich model.

G. Characterization of Raw Material and Adsorbent

The bodily and chemical characteristics of the adsorbent and precursors are decided by means of quite a number characterization method. The starting substances DP Barks have different and complicated properties and this is taken into account in the instruction of the adsorbent. By advantage of this variance in nature, some vital exams have to be performed to ensure the characterization of the raw materials and subsequent MBA.

The surface morphology of the authentic DP Bark, MBA and depleted MBA have been examined using a scanning electron microscope (SEM) (S-3400N, Hitachi) geared up with an electron dispersion X-ray analyser (EDX) to provide an elemental analysis of the samples. Brunauer Emmett Teller (BET) was conducted to determine the surface area, a pore volume of the organized adsorbent, and pore diameter, exceptionally précised and exceptional automated fuel sorption structures (Gemini Analyzer, Micrometric USA).

III. RESULTS AND DISCUSSIONS

A. Effect of pH

The effect of pH on Arsenic adsorption by the mercerized Bark based adsorbent (MBA) was examined at a pH range of 2.0 to 9.0 at an adsorbent dose of 0.1mg/100. The pH affects DP Bark adsorption because the formation of anions as well as the surface charges on the adsorbent [26]. Arsenic removal efficiencies were observed to be 97, 96.4, 95, 90, 80, 78, 74, and 70 % at pH values of 2, 3, 4, 5, 6, 7, 8 and 9 respectively.

The elimination of Arsenic by means of a bio adsorbent is rather based on the pH of the aqueous segment [6]. Biomass-based bio adsorbents contain bio macromolecules such as amino, thiol, phenol and carboxyl groups. In addition, the system of bio sorption genuinely relies upon on the protonation and deprotonating of the purposeful groups [1]. It is imperative to consider that acidic pH resulted in higher Arsenic adsorption than did simple pH.

This is because, in the acidic region, the total cost on the bio adsorbent may be wonderful (or largely positive), prompting the negatively charged Arsenic ions to bind readily. These consequences exhibit that DP Barks adsorption occurs in a wide vary of pH. The low Arsenic elimination affectivity that was once observed at the pH price of eight might also be related with the response of Arsenic.

This phenomenon is also pronounced by means of [1]. In contrast, the susceptible adsorption of Arsenic at pH 9 was once due to unfavourable alkaline conditions and electrostatic repulsion between anions.

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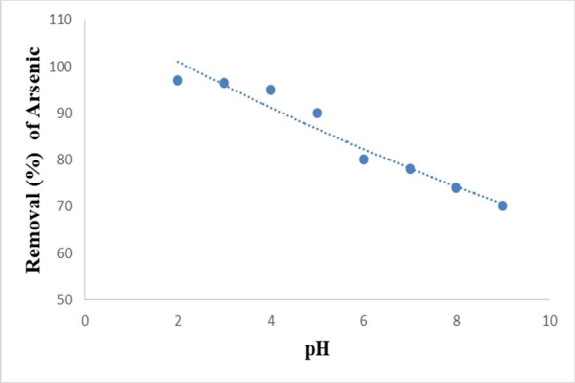

Fig. 1 Effect of pH on arsenic removal by MBA

B. Effect of Initial Arsenic Concentration

The effect of initial Arsenic concentrations on Arsenic removal efficiency was investigated using 0.4 g of mercerized Bark based adsorbent (MBA) at a range of initial Arsenic concentrations (0.1 - 0.6 mg/L) or (100 - 600 µg/L) at pH 6. Fig. 3 shows that Arsenic removal efficiency decreased from 80% to 71.5% when the initial Arsenic concentration increased from 100 µg/L to 600 µg/L (0.1 mg/L to 0.6mg/L). The amount of adsorbed Arsenic increased from 0.01 to 0.0875 mg/g at pH 6 when the initial Arsenic concentration increased from 100 µg/L to 500 µg/L (0.1 mg/L to 0.5mg/L) because of the Arsenic mass transfer that occurs between the liquid and solid phases [21].

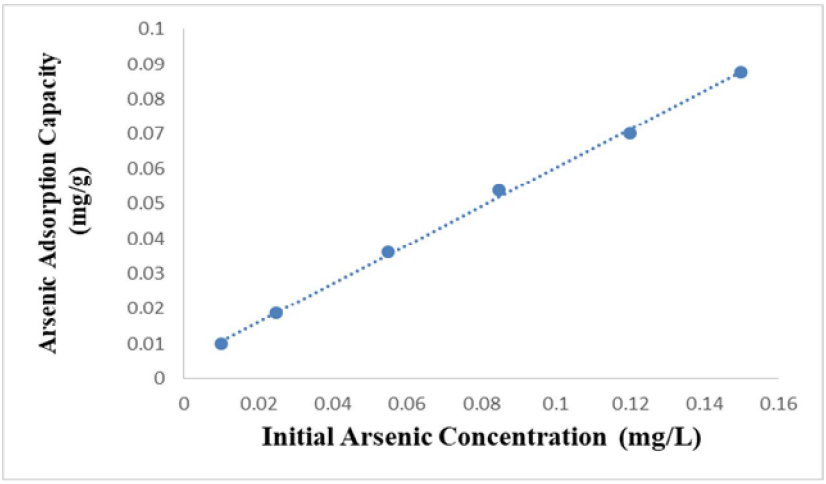

Fig. 2 Effect of initial arsenic concentration (mg/g) on arsenic adsorption capacity (mg/g) of MBA

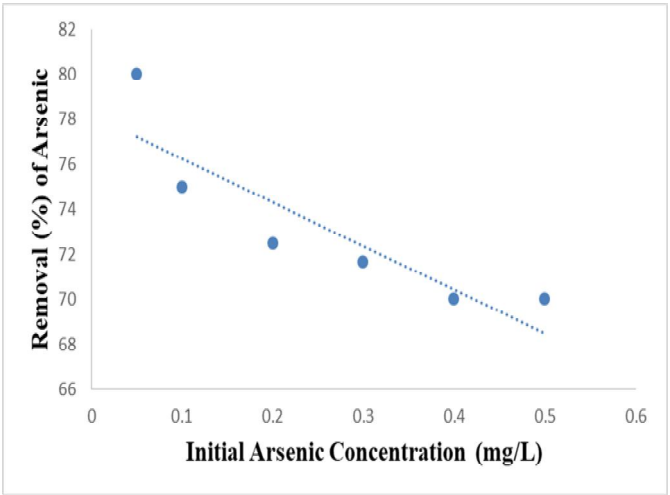

Fig. 3 Effect of initial arsenic concentration (mg/g) at pH 6 on arsenic removal by MBA

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C. Effect of Date Palm Bark Dosage

The impact of MBA dosage on Arsenic adsorption was further investigated at pH 6. As expected, Arsenic removal decreased as the dosage of adsorbent decreased, but the loss in Arsenic removal were only remarkable to a dosage of approximately 0.4 g (Fig. 3). Although adsorbent doses lesser than 0.4 g also decreased Arsenic removal, so therefore decreases were slight. A similar trend in the effect of adsorbent dosage on anions removal was reported previously for other chemically modified biomaterials such as wheat straw, sawdust, and rice husk [29], [24].

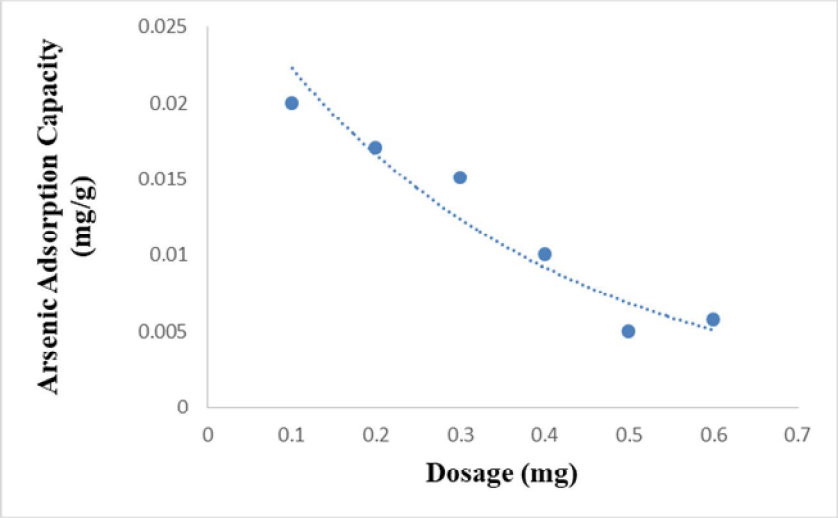

Fig. 4 Arsenic removals at different dosages of MBA

D. Effect of Contact Time

The kinetics of Arsenic removal by MBA were investigated by exposing MBA (0.4 g) on a (0.1 mg/L - 0.6 mg/L) with Arsenic solution of 100 ml for various durations and measuring the quantity of Arsenic removed from solution at each time interval. As shown in Fig. 4 the maximum rate of Arsenic adsorption occurred within the 5 minutes and reached a steady-state (at approximately 82% removal) after 60 minutes.

The phenomena observed in kinetic study shows that nature of the reaction is partially spontaneous and strong electrostatic attraction exist between respective anions and MBA. Primarily, three significant phases were observed in the overall process of Arsenic removal (Fig. 4). The first phase occurred when the adsorbent took up Arsenic at a very high rate. During the second phase, adsorption was much slower than in the first phase, indicating the near-consumption of all active sites throughout the surface of the adsorbent and signalling the onset of the equilibrium phase. The third phase was essentially one of adsorption equilibrium and was observable after a contact time of app.60 min for Arsenic adsorption.

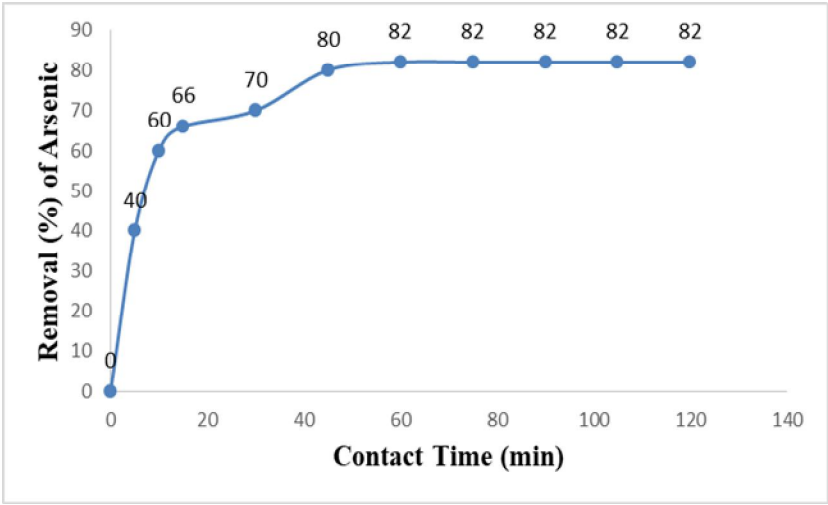

Fig. 5 Arsenic removal (%) by MBA as a function of time at pH 6

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E. Langmuir and Freundlich Isotherms Analysis for Date Palm Bark

1) Langmuir Isotherm Model: Among the several fashions handy to look at the behaviour and applicability of adsorption processes, the Langmuir isotherm mannequins are often used to evaluate the effectiveness of adsorption. Hence, the linearized form of the Langmuir mannequin established by [6] (Equations 3.10-3.11) was once employed to check out the adsorption of Arsenic through DP Bark. Moreover, the linearized form of the Langmuir isotherm model was once employed to investigate adsorption information

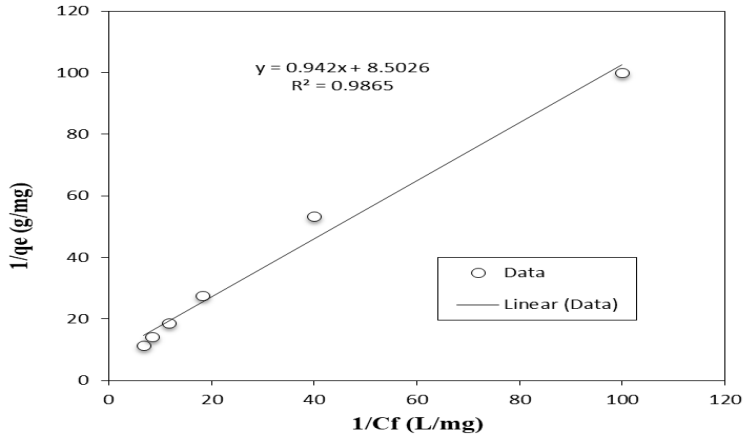

Fig. 6 Linearized form of Langmuir isotherm model for adsorption on MBA at pH 6

2) Freundlich Isotherm Model: The linearized form of the Freundlich Isotherm Model (Equation 3.13) did none ideally confirm the goodness of fit based on value of R^2 (R^2 = 0.9975) at pH value of 6. Moreover, the values of $\frac{1}{n}$ is between 0 and 1($\frac{1}{n}$ = 0.8052). These parameters of Freundlich Isotherm Model, indicating moderate heterogeneity and applicability of multilayer adsorption [11].

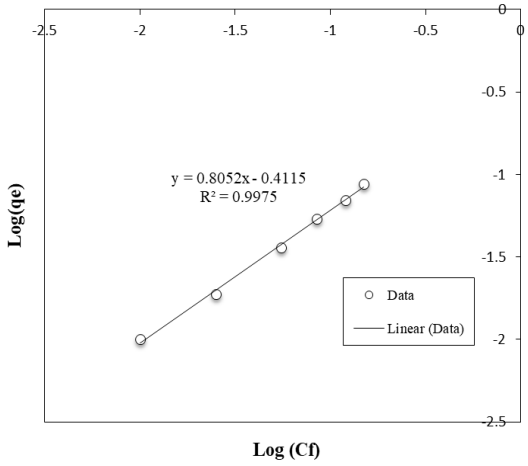

Fig. 7 Linearized form Freundlich isotherm model for adsorption on MBA at pH 6

Langmuir and Freundlich Isotherms assessed data obtained in static studies for Arsenic. The 'R_L' value resulting from the application of the Langmuir isotherm model (R_L< 1) suggested that Arsenic removal by DP Barks occurred by monolayer adsorption. This is because nature of adsorption is considered unfavourable, linear, favourable and irreversible corresponding to values of R_L (R_L>1, R_L=1, 0 <R_L<1 and R_L=0 respectively) [6]**.** According to Langmuir (1918), the phenomena of adsorption occur at particular sites without interaction of adsorb ate ions. At equilibrium, the surface of adsorbent is considered covered with monolayers. In this study, the Langmuir correlation co-efficient was almost close to unity for Arsenic adsorption (R^2 = 0.98) and presented in Table 1.Based on these values, it is depicted that Arsenic adsorption is fit for Langmuir isotherm.

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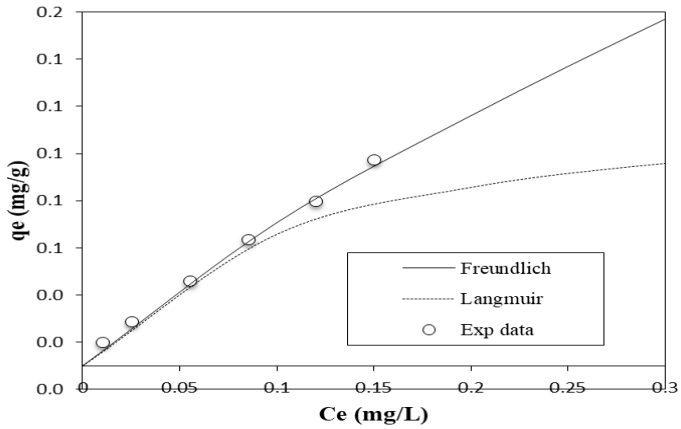

Fig. 8 Langmuir Freundlich isotherm model for adsorption on MBA at pH 6

TABLE I
Langmuir and Freundlich Parameters for Arsenic Adsorption on MBA

Isotherm	pH	Parameters	Arsenic Adsorption
Langmuir	6	Q_0 (mg/g)	0.117
		b (L/mg)	9.026
		R^2	0.986
Freundlich	6	K_f (mg/g)	0.3877
		1/n	0.8051
		n	1.2419
		R^2	0.998

F. Kinetic of Arsenic Adsorption onto MBA

The kinetic rates of Arsenic adsorption on DP Bark for the pseudo-first and second order models were calculated to be 0.016 /min and 19.61 g/ (mg. min) at pH 6 respectively in Table 2. The correlation coefficients (R^2) between experimental data and model predictions were 0.999 and 0.741 for the pseudo-second and first order models, respectively. This indicates that the pseudo-second order model proved a good representation of this particular Arsenic bio sorption process. On another hand, the pseudo first order model did not be observed in agreement particularly at pH value of 6 (R^2 = 0.741) (Fig. 10 and 11). The q_e value obtained from the pseudo second order model was 0.0107 mg/g. Unlikely; pseudo first order could not depict the adsorption capacity at equilibrium.

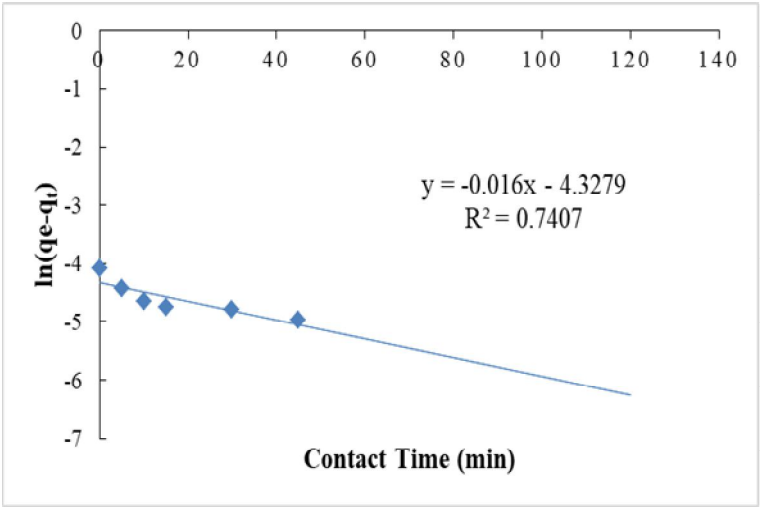

Fig. 9 Pseudo-first order model of arsenic adsorption by the MBA at pH 6

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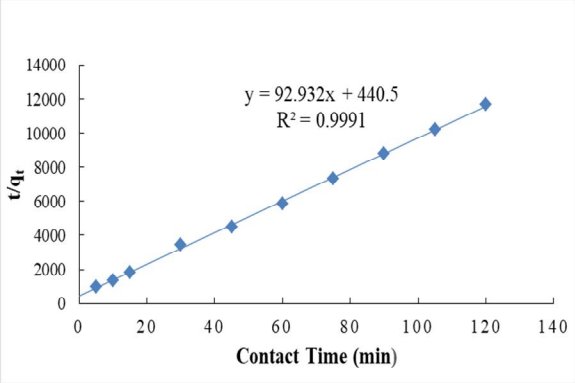

Fig. 10 Pseudo-second-order model of arsenic adsorption by MBA at pH 6

TABLE II
Summary of Pseudo-First Order and Pseudo-Second-Order Kinetic Model Parameters for Arsenic Adsorption on Date Palm Bark

pH	q_e (mg/g)	Pseudo First Order Model			Pseudo Second Order Model		
	Exp.	K_1 (min^{-1})	qe (mg/g)	R^2	K_2 (g/mg-min)	q_e (mg/g	R^2
6	0.0102	0.016	-	0.741	19.61	0.0107	0.999

IV. CONCLUSION

The Arsenic adsorption on MBA is favorable in range of 2 to 6 with slight variation in removal efficiency. Based on data generated for the adsorbents MBA has a slight more affinity for the adsorption of Arsenic. The Arsenic removal through adsorption on MBA ranged from (80% – 71.5%). The Arsenic adsorption capacity on MBA was 0.0875 mg/g or 87.5µg/g. The results illustrated the successful application of MBA hybrid adsorbent for the adsorption of Arsenic and other heavy metal ions and confirmed the possibility of using these agricultural wastes as adsorbing materials in individual as well as hybrid forms. Here the chemical activation of bio sorbents, in contrast is not favorable because it will make the technology less eco-friendly and costlier so there is need of improvement in DP adsorption potential. It is concluded that both isotherms models confirms the effective adsorption capability of MBA but Langmuir is superior to Freundlich. Pseudo-second order model explained the kinetic phenomena of the Arsenic adsorption somewhat better than a pseudo-first order model. This study recommends column study for MBA to remove Arsenic from water to attain better results. Decision makers can also utilize findings and cure solution in assisting investments on recommended technological know-how for elimination of high Arsenic ranges in consuming water. Based on the research results, filtration devices can be developed for domestic and business use to increase the countrywide industry and reduce the agricultural waste problems. Further research can be conducted on the amendment of the DP wastes considering phenomena concerned in mercerization.

V. ACKNOWLEDGMENT

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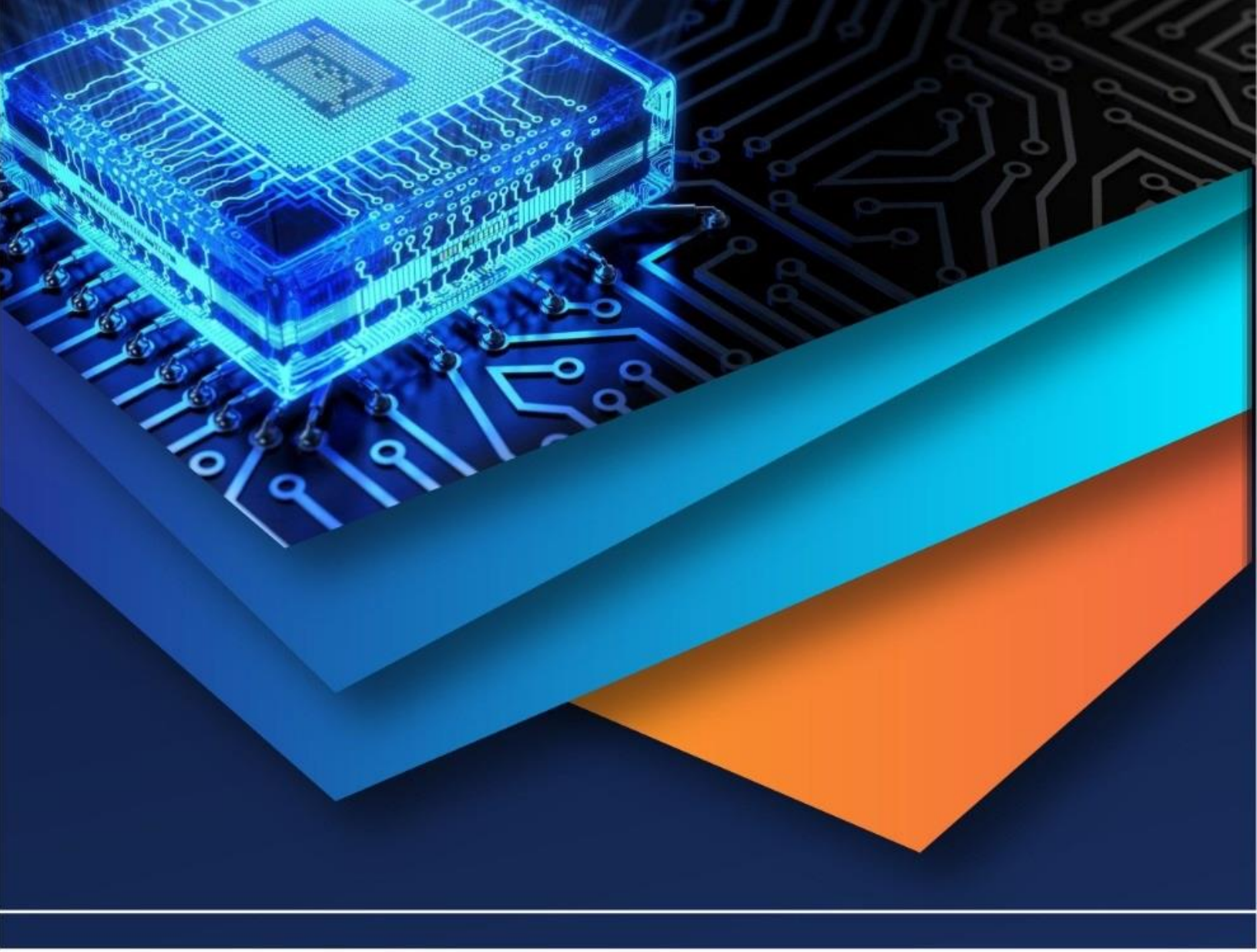

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