

OPTIMIZATION OF ARSENIC ADSORPTION ONTO ACTIVATED CARBON OF POTATO PEEL USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT:

The present study was designed to optimize the adsorption of arsenic onto potato peel derived activated carbon (MPP-AC) by employing response surface method and central composite design. Adsorbent of cheap and locally available potato residue was produced based on chemical activation with H_3PO_4 subsequently carbonization to produce the porous activated carbon. The individual and interactive effects of five variables including initial arsenic concentration, temperature, time, dosage amount and pH of the medium were investigated. Based on the statistical analysis (ANOVA), the quadratic model was developed associating the adsorption capacity (q_e). The optimum conditions were obtained of 9.98 mg L^{-1} of initial As (V) concentration, $28 \text{ }^\circ\text{C}$ of temperature, 39.7 min of time, 0.97 g of adsorbent dose and 7.3 of pH. The maximum adsorption capacity was 0.27 mg g^{-1} and 76.5% removal efficiency. The equilibrium isotherms and kinetic studies for estimating the mechanism of process demonstrated a good fit to Langmuir model and the pseudo-second order, respectively. The results of this study showed that the feasibility of central composite design (CCD) to control adsorption process and indicated the use of activated carbon of potato residue have important implications for As (V) removal.

KEYWORDS: Activated Carbon, Potato Peel, Adsorption, Heavy Metal, Central Composite Design.

1. INTRODUCTION

Wastewaters contaminated with high levels of toxics even at low concentrations heavy metals is a world-wide environmental issue (Babarinde and Onyiaocha, 2016; Genç-Fuhrman *et al.*, 2008). Among the various heavy metal ions, arsenic is one of great importance heavy metal contaminants in the wastewater. Arsenic (As) is classified in the top of concern list of hazardous elements for its carcinogenic effects to humans (Agency for Toxic Substances and Disease Registry) (ATSDR, 2017). Releasing of arsenic into environments involves mainly two effective ways, anthropogenic activities and human activities (Bibi *et al.*, 2015). Exposure to higher level of As causes hematological, gastrointestinal as well as other tangential neuropathic effects (Brown and Ross, 2002). Acute effects result in digestive system problems, specifically vomiting or stomach pain, which can cause a possible unconsciousness or death. While chronic effects result in different kinds of cancers (Bibi *et al.*, 2017). World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) suggested the maximum permitted limit of As concentration is 0.01 mg L^{-1} in drinking water (Jain and Ali, 2000; Pandey *et al.*, 2009).

Wastewaters contaminated with high levels of arsenic should be treated to avoid a discharge into environment and subsequently drinking waters. Different technologies have been employed in order to remove arsenic from wastewater including chemical precipitations, reverse osmosis, ion exchange, lime softening and microbial transformation (Bibi *et al.*, 2015; Genç-Fuhrman *et al.*, 2008; Hasanzadeh *et al.*, 2015; Lescano *et al.*, 2015; Zhang *et al.*, 2002). Recently, adsorption is extensively utilized for removing heavy metals from contaminated water sources. Adsorbents derived from

agricultural wastes have been much considered as these materials that have a good surface area and rich of the functional groups. Adsorption by agricultural wastes have several advantages comparing to other techniques mainly selectivity for specific contaminants, low cost, no minor toxic compounds and high metal binding efficiency (Yadanaparathi *et al.*, 2009). Adsorption of arsenic has been studied using several agriculture wastes as adsorbent such as tea waste (Hossain *et al.*, 2016), lemon peel (Nodoushan *et al.*, 2017), heated laterite (Saadon *et al.*, 2018) and Cucumis pubescens (Kazi *et al.*, 2018).

Potato is the most produced and consumed carbohydrate worldwide. During 2013, the world production was around 376 million tons of this crop (Bernardo *et al.*, 2016). Potato residue mainly consists of cellulose, starch and hemicelluloses (Zhang *et al.*, 2015). The utilization of available materials like agricultural waste has become the focus of research for using in wastewater treatment. Among this activated carbon, it has been widely used for treatment of industrial wastewaters as this material has significant low cost and environmentally friendly. The objective of this study is to optimize the adsorption of arsenic onto modified activated carbon derived from potato peel using statistical approaches response surface methodology (RSM) and to study the relationship between independent and the dependent variables.

2. METHOD AND MATIRALS

2.1 Preparation of Adsorbent

Potato peel (PP) was obtained from restaurant (Duhok/Kurdistan Region-Iraq). Biomass was washed thoroughly tap water several times to remove dusts and then it was cut into small pieces before subjected to washing with distilled water to remove dust, colour and other impurities. Chemical activation of the PP was carried

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out using phosphoric acid (H_3PO_4) as an activating agent in which PP was mixed with 0.1 mol L^{-1} of H_3PO_4 in a ratio of (1:1 w/v) and allowed to soak for 6 hrs at room temperature. Activated carbon yields of chemical activation can improve the pore development in the carbon structure due to the effect of different chemicals that is by dehydration and oxidation reactions of the chemicals (Sudaryanto *et al.*, 2006). The activated carbon was obtained by burning the sample in a muffle furnace at $650 \text{ }^\circ\text{C}$, $5^\circ\text{C}/\text{min}$ for about 2:30 hrs, the high temperature, >300 , deposition of tarry substances takes place when volatile components from carbon matrix diffuse out of the pore structure into the gas main stream (Arampatzidou and Deliyanni, 2016; Wereko-Brobby and Hagan, 1996). The sample was washed with distilled water several times until pH become neutral and then dried in an electric oven at 100°C for 1-2 h to reduce the moisture content. Activated carbon was ground and sieved of ($< 45\mu\text{m}$) particle size and stored in a desiccator prior to use in adsorption experiments and named as MPP-AC.

2.2 Preparation of Stock Solutions:

Stock solution of 100 mg L^{-1} of arsenic (V) ion was prepared from atomic absorption standard (Perkins Elmer, USA). Working standard solutions were prepared by serial dilution of stock in distilled water.

2.3 Adsorption Study

The batch study was accomplished with the rapid uptake of As (V) from aqueous solution. Adsorption experiments were performed in 100 mL volumetric flasks in the pH range (2–12). Both 0.01 N HCl and 0.01 N NaOH was used for solutions pH adjustment. A predestinate amount of adsorbent ($0.5\text{--}1.5 \text{ g}$) was mixed with 50 mL of heavy metals solution with various concentrations ($2\text{--}10 \text{ mg L}^{-1}$) and the suspensions were shaken at various temperatures ($20\text{--}40 \text{ }^\circ\text{C}$) using a shaking water bath. The agitation speed of shaker was fixed at 250 rpm for all experiments and time was studied in the range of ($5\text{--}40 \text{ min}$). The samples were centrifuged for 10 min at 3000 rpm and then filtered by using a syringe and filter discs ($0.20 \mu\text{m}$). The concentration of unadsorbed As (V) in residual solutions was determined by a graphite atomic absorption spectrophotometer (Shimadzu AA700 atomic absorption spectrophotometer). The removal efficiency (R%) and adsorbed As (V) amount were determined according to the following equations:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

Where C_o , C_e (mg L^{-1}) were the initial and equilibrium concentration of As (V), respectively. R% is removal percent of heavy metal. (q_e) was amount of As (V) uptake (mg g^{-1}). V solutions volume of adsorbate and m (g) refer to dosage amount of MPP-AC (Alswat *et al.*, 2016).

2.4 Response Surface Methodology

The experimental design is generally used to efficiently optimize the affecting variables in a process to improve the performance characteristics and minimize experimental error. Response surface methodology (RSM) includes a set of useful statistical and mathematical methods in designing the tests for determining the main and mutual effects between the effective parameters of the process. Among RSM designs CCD is the trendiest design can be applied to investigate the effect of different parameters. Applying this method can reduce the number of experimental trials required for each studied parameter and its interactions, also more environmental friendly by consuming less quantity of substances. The purpose of RSM is to optimize the response that is affected through a variety of parameters of the system. Commonly, the major steps of RSM are as involves: the

choosing of independent variables which are representing major effects on the process, the choice of the experimental design and accordingly conducting the experiments, the mathematic statistical management of the achieved experimental data throughout the fitting of a polynomial function, the valuation of the model's and finally the resolve of the optimum values (Nwabueze, 2010; Zhang *et al.*, 2016).

For optimization the adsorption process, an experimental design can be carried out with five independent parameters including the initial concentration (A), temperature (B), contact time (C), the amount of adsorbent (D) and pH (E). The optimization is in a randomized approach with the aim of minimize the effects of the uncontrolled factors using CCD of Design Expert software 11 (trial version) according to Table 1. In the optimization process, the responses (q_e) are determined using the corresponding regression equations as given below in Eq:3

$$y = \beta_o + \sum_{i=1}^5 \beta_i x_i + \sum_{i=1}^5 \beta_{ii} x_i^2 + \sum_{i=1}^5 \sum_{j=i+1}^5 \beta_{ij} x_i x_j \quad (3)$$

(y) is the predicted response (q_e), the x_i variables refer to the independent factors that are known for each experimental run, $\beta_o, \beta_i, \beta_{ii}, \beta_{ij}$ are the model constant, linear coefficient, the quadratic coefficient and interaction coefficient, respectively (Mazaheri *et al.*, 2017; Van Thuan *et al.*, 2017). Statistical significance of model variables is evaluated using analysis of variance (ANOVA). The lack of fit, F-values (Fisher variation ratio), coefficient of determination (R^2) and probability level ($p < 0.05$).

Table 1. the studied parameters and test design levels for each parameter.

Variables	Levels				
	+ α	1	0	1	- α
Initial concentration	1.5	2	6	10	10.5
Temperature	18.75	20	30	40	41.25
Contact time	2.8125	5	22.5	40	42.1875
Adsorbent dosage	0.4375	0.5	1	1.5	1.5625
pH	1.375	2	7	12	12.625

3. RESULTS AND DISCUSSION

3.1 Fitting of Process Models and Statistical Analysis

In order to optimize five parameters of the study, thirty-two experiments were designed by the software. Table 2, demonstrates the experimental design suggested by test CCD. The adsorption capacity (mg g^{-1}) of As (V) was calculated using polynomial regression equation in which the most significant, interaction and quadratic possessions of the individual variables were modelled. Expressed quadratic model afforded via CCD was illustrated below:

$$Y = + 0.0744 + 0.0834 A - 0.0095 B + 0.0185 C + 0.0041 D + 0.0096 E + 0.0140 AB + 0.0095 AC + 0.0017 AD - 0.0063 BE + 0.0114 CD + 0.0436 A^2 - 0.0226 B^2 + 0.0466 C^2 + 0.0198 D^2 - 0.0324 E^2 \quad (4)$$

Where, Y is amount of As (V) uptake onto MPP-AC (mg g^{-1}). The analysis of variance (ANOVA) demonstrates that fitted to the quadratic model as seem in Table 3. Significance and accuracy of the models were confirmed by coefficient of determination (R^2), F, P values and the results of lack of fit test values. Coefficient of determination R^2 was 0.98 which is close to 1. F and P-values were 61.31 and <0.0001 , respectively. The higher F-value and lower P-value demonstrate significant the model fits data well. Additional, the values for looking of fit test including F and P-value were 2.0100 and 0.2287, respectively, which recommend that the statistical significance of the model for As (V) uptake onto MPP-AC.

The actual values for adsorption of arsenic onto MPP-AC can be compared with predicted ones of 32 experimental. Figure 1, showed the correlation between predicted and actual values which provides evidence that the observed values are in good agreement with the predicted of the empirical model ones.

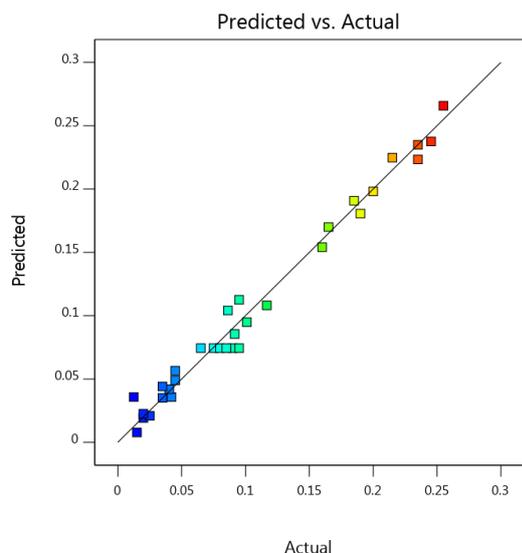


Figure 1. actual against predicted values

3.2 Effect of Influential Factors

3.2.1 Effect of Initial Concentration

Figure 2, represents 3-D simultaneous effects of As (V) concentration and time on adsorption capacity (q_e) at the fixed temperature, MPP-AC dosage and time. It is apparent that q_e increase from (0.0125 mg g⁻¹ - 0.255 mg g⁻¹) as the concentration rising from (2 - 10 mg L⁻¹). This behaviour can be attributed to the raise in the driving force of As (V) ions concentration between the MPP-AC and the aqueous medium that overcomes the mass transfer resistances

(Bhatnagar *et al.*, 2009). Previous studies have been reported that adsorption of arsenic in aqueous medium using different adsorbents is affected by initial concentration, when the latter is increasing the adsorption capacity increased (Jaiswal *et al.*, 2018; Saadon *et al.*, 2018).

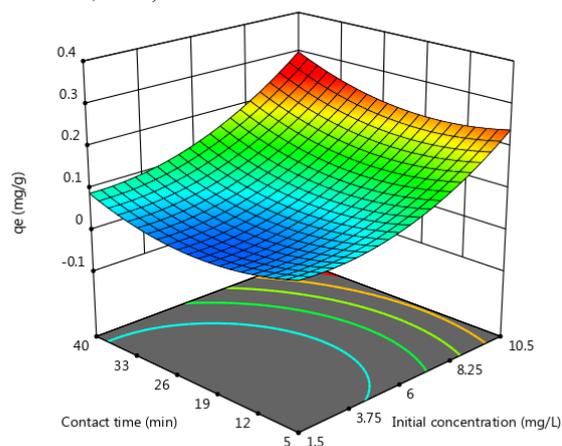


Figure 2. Response surface 3D plots indicating the effect of interaction between initial concentration and contact time on As (V) uptake.

3.2.2 Effect of pH

For the sake of investigation, the impact of pH on the As (V) adsorption, the pH for adsorption experiments was ranged between 2 to 12. The results in Figure 3, show that the removal capacity (q_e) of arsenic onto MPP-AC was increased as the pH increase from 2 to 8, although; a decrease was observed in removal capacity with above pH 8.

Table 2. CCD results for As (V) adsorption onto MPP-AC.

Run	A: Concentration mg L ⁻¹	B: Temperature C	C: Time min	D: Dosage g	E: pH	q _e mg g ⁻¹
1	6	18.75	22.5	1	7	0.045
2	6	30	22.5	0.4375	7	0.1010
3	10	40	40	1.5	12	0.2550
4	10	40	5	0.5	12	0.2000
5	6	30	42.1875	1	7	0.1600
6	10	40	5	1.5	2	0.1900
7	10	20	40	0.5	12	0.2350
8	6	30	22.5	1	7	0.0650
9	6	30	22.5	1	12.625	0.0350
10	10	40	40	0.5	2	0.2150
11	6	30	22.5	1	7	0.0900
12	2	40	5	1.5	12	0.0150
13	6	30	22.5	1	7	0.0800
14	6	30	22.5	1	7	0.0750
15	2	40	40	1.5	2	0.0403
16	2	20	40	1.5	12	0.1167
17	1.5	30	22.5	1	7	0.0125
18	10	20	5	0.5	2	0.1650
19	6	30	22.5	1.5625	7	0.0862
20	10	20	40	1.5	2	0.2453
21	6	30	2.8125	1	7	0.0950
22	6	41.25	22.5	1	7	0.0350
23	6	30	22.5	1	7	0.0850
24	10	20	5	1.5	12	0.1850
25	2	20	5	0.5	12	0.0915
26	2	40	5	0.5	2	0.0200
27	2	20	40	0.5	2	0.0450
28	2	20	5	1.5	2	0.0420
29	2	40	40	0.5	12	0.0250
30	10.5	30	22.5	1	7	0.2350
31	6	30	22.5	1	1.375	0.0200
32	6	30	22.5	1	7	0.0950

Table 3. analyses of difference variable (ANOVA) for As (V) uptake onto MPP-AC

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	0.1815	15	0.0121	61.31	< 0.0001	Significant
A-Concentration	0.1288	1	0.1288	653.01	< 0.0001	
B-Temperature	0.0017	1	0.0017	8.51	0.0101	
C-Contact time	0.0063	1	0.0063	31.98	< 0.0001	
D-Dosage	0.0003	1	0.0003	1.59	0.2257	
E-pH	0.0017	1	0.0017	8.61	0.0097	
AB	0.0032	1	0.0032	15.97	0.001	
AC	0.0014	1	0.0014	7.3	0.0157	
BE	0.0006	1	0.0006	3.24	0.0906	
CD	0.0021	1	0.0021	10.47	0.0052	
A ²	0.0074	1	0.0074	37.6	< 0.0001	
B ²	0.002	1	0.002	10.05	0.0059	
C ²	0.0085	1	0.0085	42.88	< 0.0001	
D ²	0.0015	1	0.0015	7.77	0.0132	
E ²	0.0041	1	0.0041	20.78	0.0003	
Residual	0.0032	16	0.0002			
Lack of Fit	0.0026	11	0.0002	2.01	0.2287	not significant
Pure Error	0.0006	5	0.0001			
Cor Total	0.1846	31				

At lower pH, proton ions and arsenic compete for binding activated sites on wall of MPP-AC which results in low uptake adsorption capacity due to competition binding sites (Aman *et al.*, 2008). A noteworthy enhancement in adsorption is recorded as the acidity decrease, As (V) existed as (HAsO_4^{2-}) in the solution with pH ranged from 7 to 10 which may be have strongly attracted towards active sites. However, the removal capacity of As reduced with increasing the pH above 8 due to competition between (HAsO_4^{2-}) and OH^- (Chaudhry *et al.*, 2017). The optimum condition of pH for arsenic uptake was ranging from 7 to 8 and arsenic adsorption capacity decreased trend in pH value <5 and >9.

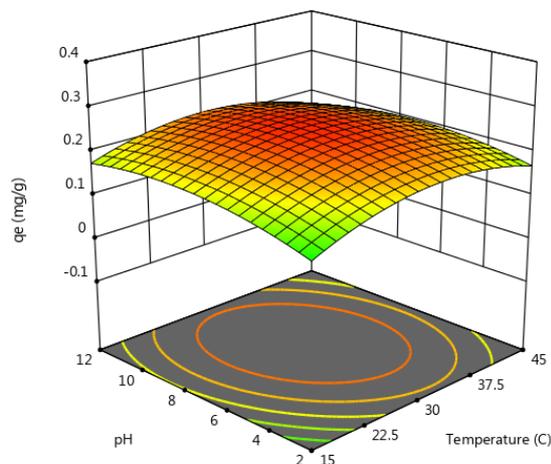


Figure 3. Response surface 3D plots indicating the effect of interaction between pH and temperature on As (V) uptake.

3.2.3 Effect of Temperature

The effect of temperature showed an increase in As adsorption with increasing temperature from 20 °C to 30 °C and approximately reached a maximum around 30 °C Figure 4. As the temperature increases, the rate of diffusion of the arsenic can increase crossways the outside boundary layer and within the vacant sites of MPP-AC. This could be achieved by decreasing the viscosity of solution. Additionally, the equilibrium capacity of adsorbent will change as the temperature changed (Khezami and Capart, 2005; Yoon *et al.*, 2017). However, the adsorption capacity of arsenic slightly decreases with temperature increasing over 35°C, sharply decreasing at 40 °C. The reasons of this decreasing may be due to the disruption of equilibrium of

ions in solution or destruction of active binding sites in the adsorbent or increasing tendency to desorb metal ions from interface of the solution. Moreover, the mobility of arsenic may increase with temperature increasing, thus could result a decrease of surface precipitation. Furthermore, as the temperature increases the stability of the bonds between the active sites of arsenic and MPP-AC decreases (Gaur *et al.*, 2018; Nodoushan *et al.*, 2017).

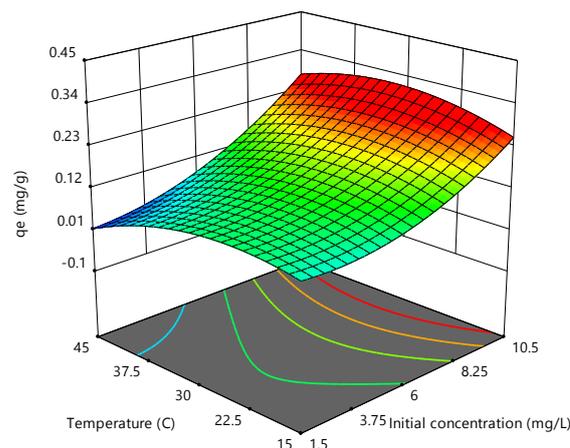


Figure 4. Response surface 3D plots indicating the effect of interaction between temperature and initial concentration on As (V) uptake.

3.2.4 Effect of Adsorbent Dose

The effect of adsorbent dose was studied as shown in Figure 5, by selecting adsorbent amounts from 0.5 to 1.5 g. The results showed that as MPP-AC dosage increased adsorption capacity (q_e) increased. This may due to more activated sites are available resulting in more arsenic being attracted and attached to the surface of MPP-AC (Alswat *et al.*, 2016), the adsorption capacity increases slowly due to an unsaturation of some activated side and strong limitation on adsorbate mobility (Aryal *et al.*, 2010). Additional, arsenic adsorption had two stages at first formation of mono layer and following through slow plateau stage (Mondal *et al.*, 2008).

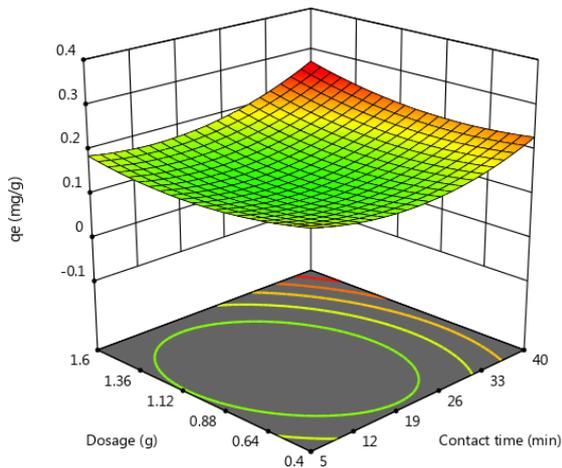


Figure 5. Response surface 3D plots indicating the effect of interaction between contact time and adsorbent dosage on As (V) uptake.

3.2.5 Effect of Time

The contact time effect on adsorption capacity was examined. It can be seen that adsorption capacity of arsenic increased corresponding to time as shown in Figure 2, the adsorption capacity was slightly increased at the beginning then increased as contact time increasing from 25-40 min. Based on Figure 5, the value did not significantly change with the contact time.

According to the obtained results, the operation conditions were to obtain maximum adsorption capacity were predicted and presented in Table 4. In the all experiments for model confirmation, the adsorption capacity suggested by the RSM derived optimum conditions was (0.27 mg g⁻¹) which is close to the actual value, indicating the accuracy and suitability of the models.

Table 4. optimum condition for adsorption of As (V) onto MPP-AC

Factors	A	B	C	D	E	Qe
Units	mg L ⁻¹	°C	min	gm		mg g ⁻¹
Values	9.98	28	39.7	0.97	7.3	0.27

3.3 Adsorption Isotherms

Several isotherm models were always utilized for analysis the experimental result to inspect the association between the adsorbent and adsorbate amount at equilibrium. In order to explain the experimental data the Langmuir, Freundlich and Elovich kinetic models were investigated. The main Langmuir assumption is the monolayer formation (homogenous) of adsorbate species on the surface of adsorbent in the solution at equilibrium without interaction between the solute molecules (Xiyili *et al.*, 2017). Isotherm equation is expressed in the bellow:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \quad (5)$$

Where q_e and q_{max} (mg g⁻¹) are the adsorption capacity at equilibrium and maximum, respectively. K_L is the Langmuir constant (L mg⁻¹) that is refer to the heat of adsorption. Both K_L and q_{max} can be computed from the slope and the intercept, respectively. The Langmuir parameters which are essential characteristic used to predict affinity between adsorbent and adsorbate applying of the dimensionless separation factor (R_L), which is represented as follow:

$$R_L = \frac{1}{1 + K_L C_e} \quad (6)$$

Where K_L (L mg⁻¹), C_e (mg L⁻¹), Langmuir constant and the equilibrium concentration of adsorbate, respectively. The value of R_L point out the type of isotherm which is ranged from (0-1), it is favorable in case of R_L between (0-1),

however unfavorable if R_L greater then 1, and irreversible if R_L equal (0). (Eloussaief *et al.*, 2013; Samadi *et al.*, 2014). Figure 6, shows a plot of C_e/q_e versus C_e . The q_{max} and K_L values were obtained to be 0.2455 mg g⁻¹ and 1.247 L mg⁻¹, respectively. While R_L value was calculated and found to be 0.074, which reveal that the process was favorable. The coefficient of determination (R^2) was 0.97, which recommended good fitting of As (V) adsorption onto MPP-AC.

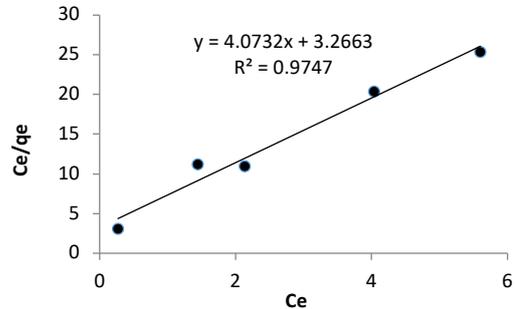


Figure 6. the Regression line plot of Langmuir isotherm

In the other hand, the Freundlich adsorption isotherm is widely valid for multilayer adsorption on a heterogeneous surface of the adsorbent with non-uniform energy distribution (Wang *et al.*, 2015). The linearized form can be expressed by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

Where q_e (mg g⁻¹) and C_e (mg L⁻¹) uptake amount on the adsorbent and concentration of adsorbate in the solution at equilibrium, respectively, K_f (L g⁻¹) constant and $1/n$, ranging from 0-1 is an empirical parameter show the adsorption intensity or surface heterogeneity. $\ln q_e$ was plotted vs. $\ln C_e$ as shown in Figure 7. The values of K_f and $1/n$ were found to be 0.13 L g⁻¹ and 0.317 respectively. The coefficient of determination line was 0.92 suggesting poor linearity comparing to Langmuir isotherm.

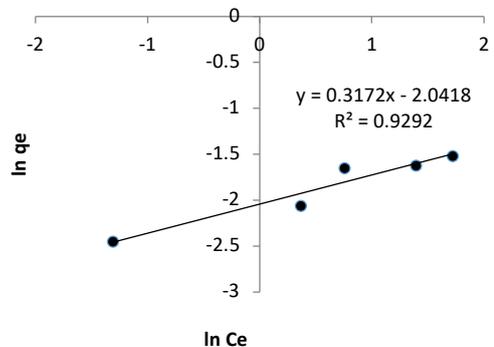


Figure 7. linear plot of Freundlich isotherm

However, Dubinin-Radushkevich, (D-R), isotherm was employed for consideration the nature of adsorption whether adsorption process take place by a physical or chemical process (Günay *et al.*, 2007). The general forms given bellow:

$$\ln q_e = \ln q_{D-R} - \beta \epsilon^2 \quad (8)$$

Where, q_{D-R} and q_e (mg g⁻¹), are theoretical Dubinin-Radushkevich adsorption capacity and at equilibrium, respectively. β and q_{D-R} can be calculated from slop and intercept of plotting $\ln q_e$ versus ϵ^2 , respectively. β (mol²/J²) is D-R constant which is associated to the free energy of adsorption. ϵ is a term of Polanyi prospective related to the equilibrium concentration (C_e) which can be computed as the following:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

$$E = \frac{1}{\sqrt{-2\beta}} \quad (10)$$

Where, T, R are absolute temperature in Kelvin, and gas constant (8.314 J K⁻¹ mol⁻¹), respectively. E is the mean energy of adsorption which is related to a mole of molecules started transferred from solution to the surface of adsorbent. The magnitude of E is useful for estimation the kind of adsorption. If its value between 8 to 16 kJ/mol, this means that the adsorption mechanism is controlled by an ion exchange process (chemisorptions) (Kumar *et al.*, 2018). However, in case of E<8 kJ/mol, that is meant that physisorption adsorption progression considering and driven via the pore filling mechanism. The magnitude of E value greater than 16 kJ/mol particle diffusion mechanism is considering being occurred (Pandiarajan *et al.*, 2018). Figure 8, demonstrate straight line with coefficient of determination (R²) of 0.9. The value of q_{D-R} to be 0.21 (mg g⁻¹) and E value was 2.35 kJ/mol which may suggest that the adsorption process was involved physical adsorption, (Pandiarajan *et al.*, 2018; Şahan and Öztürk, 2013). The results are given in Table 5, showed various constant values from isotherm models which indicated that Langmuir isotherm is more fitted for As (V) adsorption onto MPP-AC.

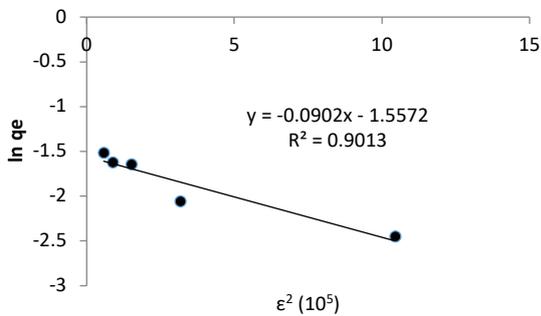


Figure 8. liner plot of the Dubinin–Radushkevich (D-R) isotherm model

3.4 Kinetic Study of Adsorption

Kinetic parameters were studied to establish the efficiency and mechanism of As (V) adsorption onto MPP-AC. Three kinetic models were studied including pseudo-first and second order kinetic as well as Elovich kinetic model. The pseudo-first-order (1st) kinetic model, applied to the study of adsorption in liquid-solid system, was expressed by Lagergren and custom-made by Ho (Robati *et al.*, 2016). The generally equation given below:

$$\ln(q_e - q_t) = \ln q_{\max} - k_1 t \quad (11)$$

Where, q_e and q_t (mg g⁻¹) are the amount of uptake at equilibrium and time, respectively. k₁ (min⁻¹) is pseudo-first order rate constant for adsorption process. q_{max} and k₁ were calculated from the intercept and slope respectively, by plotting of ln(q_e-q_t) vs. t time (min) (Chaudhry *et al.*, 2017; Pandiarajan *et al.*, 2018). The values of q_e and k₁ were determined to be 0.18 (mg g⁻¹) and 0.032 (min⁻¹), respectively as shown in Figure 9. Actually, the theoretical value of q_e was about 70 % less than practical value, in addition the coefficient of determination of plot was slightly poor (0.88). Consequently, the adsorption of As (V) onto MPP-AC was not fitted to first order kinetic model.

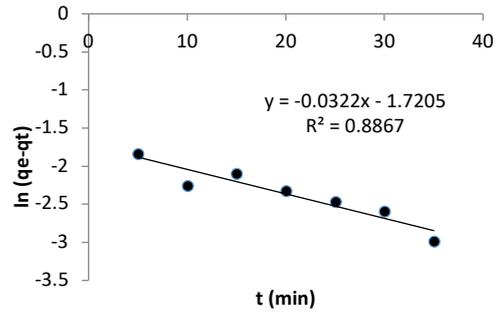


Figure 9. liner plot of pseudo-first order kinetic

The pseudo-second order (2nd) kinetics model recommends that the adsorbent surface activated sites and the number of adsorbate in the solution simultaneously determine the kinetics (Mashhadi *et al.*, 2016). Linearized mathematical model of pseudo second order kinetic is expressed as the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

Where, q_t and q_e (mg g⁻¹) are the amounts of As (V) ion adsorbed at t (min) and equilibrium, respectively. (k₂) rate constants in (g mg⁻¹ min⁻¹) of the pseudo-second-order (Chaudhry *et al.*, 2017). Figure 10, shown q_e and k₂ were determined to be 0.27 (mg g⁻¹) and 0.6 (g mg⁻¹ min⁻¹), respectively. The coefficient of determination value was 0.97 meaning that adsorption process is more fitted with pseudo-second order.

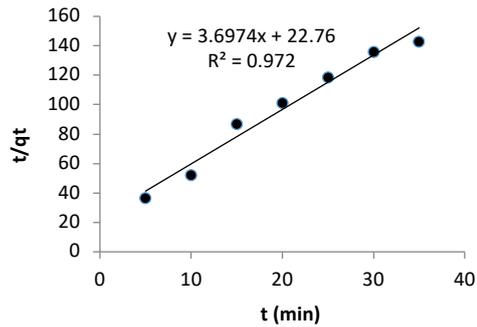


Figure 10. liner plot of pseudo second order model for As (V) uptake onto MPP-AC

Though, the Elovich model is another equation explained the rate of adsorption/desorption that takes place between the adsorbate (arsenic) and adsorbent (MPP-AC). Linearized model of Elovich which can be expressed as the following equation

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (13)$$

Where q_t (mg g⁻¹) metal uptake amount at t time (min). α and β are known as the Elovich coefficients. α (mg g⁻¹ min⁻¹) and β (mg g⁻¹) are adsorption and desorption rate, respectively where computed from intercept and slope of liner plot between q_t vs. ln t (Lasheen *et al.*, 2012). Figure 11, shown the higher value of α (72.4 mg g⁻¹ min⁻¹) comparing to β (20.8 mg g⁻¹) which can explain that initial adsorption rate is higher than desorption of As (V) onto MPP-AC. Table 6, summarizes kinetic parameters.

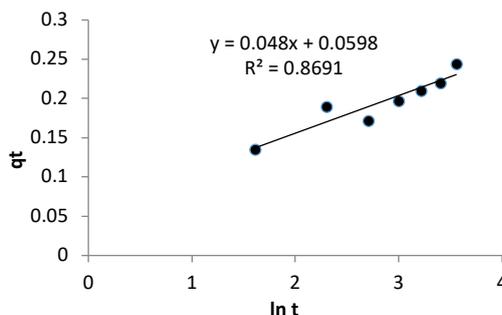


Figure 11. plot of Elovich kinetic model for As adsorption

Table 5. isotherm parameters and results

Langmuir				Freundlich			D-R		
q _{max}	K _L	R _L	R ²	K _f	1/n	R ²	q _{D-R}	E	R ²
0.2455	1.247	0.074	0.97	0.13	0.317	0.92	0.21	2.35	0.9

Table 6. values of Kinetic parameters

first order model			second order model			Elovich kinetic model		
q _e	k ₁	R ²	q _{max}	k ₂	R ²	α	β	R ²
0.18	0.032	0.88	0.27	0.6	0.97	72.4	20.8	0.87

4. CONCLUSION

This research was carried out to remove of As (V) from aqueous solutions by the modified activated carbon derived from potato peel. The response surface method involve (CCD) was successfully applied for optimization of process parameters and to examine the effect of independent variables, including initial arsenic concentration, MPP-AC amount, temperature, pH and contact time. The quadratic equation developed to model of adsorption process was proved statistically significant. Furthermore, the actual values were founded in a good agreement with the predicted data by model. Accordingly, the maximum adsorption capacity was obtained at (0.27 mg g⁻¹). The adsorption isotherms data were in a good fitted well with Langmuir. In addition, the kinetic study showed that the adsorption was followed to the pseudo-second- order model. The obtained results proved a great potential to use of MPP-AC for As (V) removal and is effectiveness, simplicity, environmentally friendly, economically attractive.

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