JPIChE 48 (2) 2020: 17-30

PAKISTAN INSTITUTE OF CHEMICAL ENGINEERS
Since 1969

Journal of Pakistan Institute of Chemical Engineers

journal homepage: www.piche.org.pk/journal

Mathematical Model and Experimental Study To Optimize Rates Constants of Desorption And Adsorption of The Waste Water Using Palm Fronds

A.S. Ibrahim[*,1], T.S. Mohammed[1], A.A. Jabri[1], H.A. Breiki[1]*

Submitted: 28/10/2020, Accepted: 20/01/2021, Online: 15/02/2021

Abstract

Physical, mechanical and multi step chemical treatments on the adsorptivity of palm fronds adsorbent for the removal of 5 waste metal components from wastewater was studied and estimated in this paper. Three techniques are used for palm frond to produce modified activated carbon as adsorbents. Physical treatment is represented in the furnace at 600 oC. Mechanical treatment is established more suitable surface area from 300μm2 to 500 μm2 to increase efficiency of adsorbent. Chemical treatment of palm fronds used Acetone ethanol - methanol treated palm fronds. The fixed bed column study was achieved under multi layered fixed bed columns. It was discovered that, the adsorption of 5 metals were expressively increased in the following order: Acetone ethanol Methanol treated palm fronds. The highest percentage reduction of the area under the curve was represented by chemical treatment for palm fronds reached 98.74%. Derived mathematical model to describe the system and compared it with experimental results in active accuracy. Proposed model includes the most significant variables like partial pressure and concentration of waste metal acts on rates of adsorption and desorption. Newton Raphson is a mathematical optimization technique used to determine the optimal values of rate constants adsorption and desorption of the waste of palm fronds for Cu, Cd, Zn, Ni and K to increase the ability of mathematical model. The freshness of this study is used to assess the carrying into action of bio waste to get rid of waste metals due to utilize more than one technique to compute the rate constants of adsorption and desorption. However, further studies are asked to emphasize with the results of this survey using this active technique.

***Keywords**:* Palm fronds; Wastewater treatment; Mathematical model; Adsorption;Desorption;Multi metals.

1. Introduction:

Wastewater is any water that has been un favorably affected in its quality. Water may be polluted by industrial and agricultural wastes containing waste metals, and a wide range of possibility contaminants and concentrations may be caused by toxic metals like aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni), and zinc (Zn), that normally find their ways to the industries as metal plating industries, nickel batteries, pigments, and as stabilizers of alloys [1,2].

It's regrettable that waste metals can be absorbed by living organisms because of their high solubility in the water and large concentrations of them may accumulate in the human body, the time they enter the food series. As a consequence, serious health disorders may be caused if the consumed metals are

[1] *Chemical Engineering Department, Dhofar University,211 Salalah Oman*
Corresponding Author: ahmadsaadi47@yahoo.com

further than the permitted concentration [3]. Due to this, metal contaminated wastewater is necessarily treated before to its removal to the environment. Some treatment processes such as, ion exchange, and electrochemical removal, are used to remove these waste metals. These processes, however, are not efficient and reported to produce high toxic sludge, requiring high-energy requirements, and do not offer complete removal [4]. In recent research, several approaches are proposed to develop inexpensive and more functional technologies, which intends to both reduce the pollutants concentration in the water and to get better the its quality after treatments. Among the modern alternative treatments is adsorption, which includes physico-chemical treatment processes establish to be active in the removing waste metals from aqueous solutions. Searches for economic cost adsorbents that have metal-binding abilities has recently increased [5]. Materials from which adsorbents may be found include mineral, polymeric, organic, industrial byproducts, agricultural wastes, and biomass [6].

Inexpensive adsorbents may be obtained from some easily available natural materials, or sure waste products from agricultural activities. Cost effective techniques are therefore achieved using such economic cost, adsorbent materials that may be found abundant in nature and only require little processing. Examples of such natural materials have appeared on the preparation of rice husk and its ash [7], and coconut shell carbon [8]. Further examples of agricultural by-products which have been evaluated for this objective contain palm fronds, peat, wood, pine bark [9], cotton seed hulls [10], peanut shells [11], hazel nut shell [12], saw dust, wool, orange peel [13], and maize cobs [14].

It is reported that Oman, as a middle eastern country, produces 3 million tons of palm leafs annually [15]. This quantity makes the palm fronds as an important commercial crop in the Gulf states and in Oman in particular.

Many published research have used palm fronds as an adsorbent, where in [16], El Shafey et al proposed date palm leaflets as a chemical adsorbent of ciprofloxacin (CIP) from aqueous solution. In [17], Kaakani M. has used the palm tree leaves as an adsorbent together with many other natural types.

With many of the published researches in the area, the focus was on the removal of individual waste metals. For example, in [18], Daifullah et al. studied the removal of iron, manganese, cupper, cadmium and lead individually from waste water. Chockalingam and Subramanian, have also reached to similar results used different techniques [19].

Instead of targeting the removal of individual waste metals, this paper, is using a natural inexpensive material, which is the palm fronds as adsorbent and studied the potential of this material for the removal of multi metal elements from polluted water. In addition to deriving a mathematical model with novel features, this paper focuses on determining the adsorption of waste metals in multi layered fixed bed columns and evaluating the effects of physical, mechanical and multi step chemical treatments of palm fronds on its adsorptive.

2. Methodology:

2.1 Preparation Of Palm Fronds For Modified Activated Carbon:

The palm fronds abundant material is applied for polluted metal adsorption from wastewater. The palm fronds are carbonized at 600°C in furnace for 4 hours. Following to that, three treatments to prepare the modified activated carbon are applied; namely physical, mechanical and chemical.

1. Physical treatment: It is the first treatment to burn it to modify active carbon at 600°C.

2. Mechanical treatment is the second treatment used to reduce the size and sieve to a desired mesh size in a range size from 300 to 500μm to be used as adsorbent.

3. Mechanical treatment, where outcomes of modified activated carbon go through this treatment by mixing all the modified activated carbon with acetone for a day, followed by treatment with ethanol for 1 day then followed by added methanol for 1 day. The solvents were all carbonaceous solvents that will deposit on the surface to control the pore size and the

characteristics were shown in Table 1. All the modified carbon was purified, washed and dried at 100°C after each chemical treatment to remove chemical residue.

Table 1: Characteristics of solvents used for chemical treatment

Solvent	Type of solvent	Dielectric Constant	Solubility in water (g/100g)	Dipole moment (statcoulomb -centimetre)
Acetone	Polar aprotic	21	Miscible	2.88
ethanol	Nonpolar	2.1	0.15	0
Methanol	Polar protic	33	Miscible	0

2.2 Characterization Of Activated Carbon:

The main properties were represented by specific surface area and the pore distribution of adsorbent were estimated with a Micromeritics ASAP-2010 surface area measurement instrument (Micromeritics Instrument, Norcros, USA) following BET method. Elemental analysis for carbon, hydrogen, nitrogen, oxygen and sulphur was specified by CHNO/S Analyzer 2400, Perkin Elmer.

2.3 Hypothetical T-shirt Pore Model:

Modification of carbonized palm fronds into high performance adsorbent by treatment using multi types solvent is hypothetically producing a t-shirt size pore. The mechanism of t-shirt pore model formation is presented in Figure 1. The Figure illustrates a normal single pore assume in cylindrical shape. However, the mechanism is hardly proven by current existing instrumentation, due to the size factor of adsorbent. Therefore, it is hypothetically proven with result of metal adsorptions by adsorbent [22].

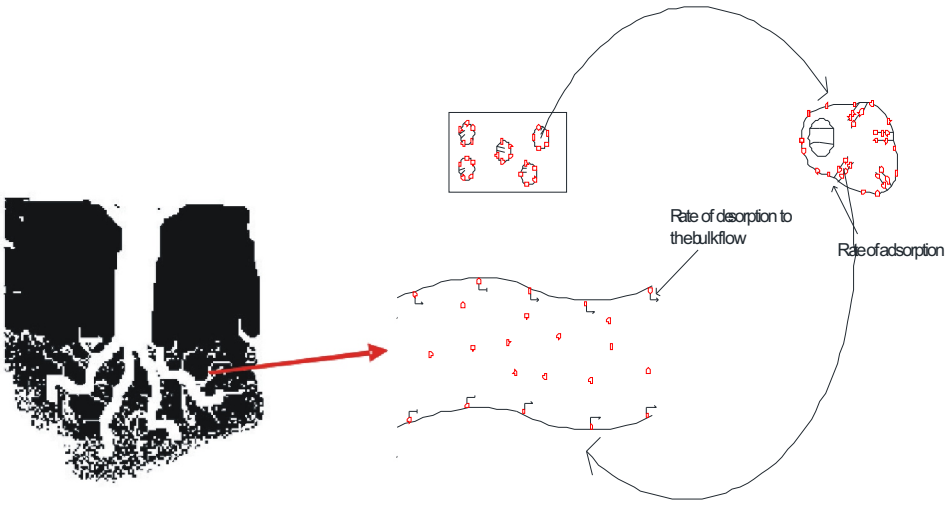

Figure 1: Explain the mechanism of adsorption and desorption

2.4 Elaboration of wastewater solution:

The wastewater applied for adsorption includes different metals which are Copper, Cadmium, Zinc, Nickel and Potassium due to these metals are represented toxic to the surroundings. These metals are designed by the reducation of 1g chemicals of each metal in 1 liter of distilled water. The adsorption of adsorbates was studied due to its harmful and it is absorbed by several adsorbents preferentially to a very good extent. The concentration of elements in wastewater solution is determined by ICP-OES. The initial concentration of each element is 1gm/ liter and is classified with high toxicity [21,22].

2.5 Fixed bed adsorption study:

Adsorption characteristics of metals onto palm fronds modified activated carbon in fixed-bed column were employed using mixed treat with acetone, ethanol and methanol. All the adsorption experiments were processed in continuous downward flow mode. 15g modified activated carbon is occupied in each filter paper, with the top opened in the column to block modified activated carbon dropped to the bottom of column. Amount of activated carbon is 5g for each three levels. The flow of feed solution is steady. The treated wastewater solution was collected at regular duration time for 360 minutes and the concentration is estimated by ICP-OES. The assumption of mathematical model can be represented in Table 2.

Table 2. List of proposed mathematical model assumptions

1. Phases of the system are represented liquid and solid Phase
2. No, chemical modified activate carbonation happens in the system.
3. Temperature and concentration changes are ignored in the radial direction.
4. Adsorption happens to adsorbent solid particles inside the surfaces of holes of modified activated carbon
5. Mass transfer happens for the molecules of waste solids from inside holes to the surface of modified activate Carbon.
6. Desorption is represented by diffusion of molecules of waste metals from surface of modified activate carbon to the bulk flow.
7. Rates of adsorption and desorption at the surface of modified activate carbon are considered the dynamics study.
8. Each fixed bed inside considered as CSTR system
9. The heat transfer is ignored in proposed model.

3. Derivation mathematical model:

Adsorption, desorption states and mass balance are applied to derive a mathematical model. These steps are represented active mechanism for the process as shown in Figure 1 and can be derived as follow;

3.1. Study adsorption state:

Molecules of waste metals are diffusion and adsorption on the catalyst surface of modified activated carbon depend on the variance in the concentrations and partial pressure of the waste metals, concentration of vacant catalyst surface of modified activate carbon and partial pressure of molecules to activate rate constant absorption of forward direction as indicated in equations (1-5).

$$HM_1 + Sr \rightleftharpoons_{K^-_{ads,1}}^{K^+_{ads,1}} HM_1 . Sr \quad (1)$$

$$r_{ad} = K^+_{ads,1} [P_{HM} C_V - K^-_{ads,1} C_{HM_1.Sr}] \quad (2)$$

$$r_{ad} = K^{+}_{ads,1}\left[P_{HM}\,C_V - \frac{C_{HM_1.sr}}{\frac{K^{+}_{ads,1}}{K^{-}_{ads,1}}}\right] \quad (3)$$

$$K^{*}_{ads} = K^{+}_{ads,1} \Big/ K^{-}_{ads,1} \quad (4)$$

Substitute (4) in (3)

$$r_{ad} = K^{+}_{ads,1}\left[P_{HM_1}\,C_V - \frac{C_{HM_1.Sr}}{K^{*}_{ads}}\right] \quad (5)$$

3.2 Study Desorption State:

When the concentrations and partial pressure of waste metals increase due to the effect of adsorption on the catalyst surface of modified activated carbon compare to the surrounding will produce inverse diffusion of mass transfer of molecules of waste metals from the surface of the modified activated carbon to the bulk flow due to increase the rate constant disruption of reverse direction as explained in equations (6-10).

$$HM_1.Sr \underset{K^{-}_{Srp,1}}{\overset{K^{+}_{Srp,1}}{\rightleftharpoons}} HM_1 + Sr \quad (6)$$

$$r_d = K^{+}_{Srp,1}\,C_{HM_1.Sr} - K^{-}_{Srp,1}\,P_{HM_1}C_V \quad (7)$$

$$r_d = K^{+}_{Srp,1}\left[C_{HM_1.S}\frac{P_{HM_1}C_v}{\frac{K^{+}_{Srp,1}}{K^{-}_{Srp,1}}}\right] \quad (8)$$

Let

$$K^{*}_{Srp} = \frac{K^{+}_{Srp,1}}{K^{-}_{Srp,1}} \quad (9)$$

Let

$$r_d = K^{+}_{Srp,1}\left[C_{HM_1.Sr} - \frac{P_{A_1}C_V}{K^{*}_{Srp}}\right] \quad (10)$$

Rate of desorption will reach to the zero due to the activity of the rate adsorption be controlled all the state of the process. So, the main assumption . From equation (10)

$$C_{HM_1.Sr} = \frac{P_{HM_1}\,C_V}{K^{*}_{srp}} \quad (11)$$

Substitute (11) in (5)

$$r_{ad} = K^{+}_{ads,1}\left[P_{HM_1}\,C_V - \frac{P_{HM_1}C_V}{K^{*}_{srp}\,K^{*}_{ads}}\right] \quad (12)$$

$$C_T = C_{HM.Sr} = \frac{P_{HM_1}\,C_V}{K^{*}_{srp}} \quad (13)$$

$$C_V = \frac{C_T\,K^{*}_{sr}}{P_{HM_1}} \quad (14)$$

Substitute (14) in (12)

$$r_{ad} = K^{+}_{ads,1}\left[C_T\,K^{*}_{srp} - C_T \Big/ K^{*}_{ads}\right]$$

$$r_{ad} = K^{+}_{ads,1}\,C_T\,K^{*}_{srp} - C_T K^{-}_{ads,1} \quad (15)$$

Represent the system as CSTR process

$$\frac{V_i}{V}\left[C_{HMi} - C_{HM_1}\right] + r_{HM} = \frac{dC_{HM_1}}{dt} \quad (16)$$

Volumetric flow rate compare to the volume of the system is very limited so,

$$\frac{V_i}{V} = 0 \quad (17)$$

So, equation (16) will be

$$r_a = \frac{dc}{dt} \quad (18)$$

Rate of remodified activate carbontion represent,

$$r_a = -r_{ad} = \frac{dc_{HMI}}{dt} \quad (19)$$

Substitute equation (15) in (19)

$$-\left[K^{+}_{ads,1}\,C_T\,K^{*}_{srp} - C_T K^{-}_{ads,1}\right] = \frac{dc_{HM_1}}{dt} \quad (20)$$

Solve equation (20)

$$C_{HM_1} = -\left[K^{+}_{ads,1}\,C_T\,K^{*}_{srp} - C_T K^{-}_{ads,1}\right]t + \text{constant} \quad (21)$$

Boundary conduction

$$\text{At} \quad t=0 \;,\; C_{HM_1} = C_{HMi} \;,\; constant = C_{HMi} \quad (22)$$

Substitute in (21)

$$C_{HM_1} = -\left[K^{+}_{ads,1}\,C_T\,K^{*}_{srp} - C_T K^{-}_{ads,1}\right]t + C_{HMi} \quad (23)$$

$C_{HMI} = C_{HMi} - mt$

Where $m = -C_T\left[K^{+}_{ads,1}\,K^{*}_{srp} - K^{-}_{ads,1}\right]$

The mathematical model is represented in equation (23) and assumptions of mathematical model can be represented in Table 2.

4. Result and Discussion

4.1 Adsorption Of Cadmium (cd) By Modified Activated Carbon Of Palm Fronds:

At the beginning the concentration of Cadmium is 1.8 ppm and its represented high level of risk [21]. This value is progressively decreasing through the time. After 1.5 hrs, the concentration of Cadmium zero. Cadmium is strongly adsorbed by modified activated carbon of using palm fronds Adsorbents in multi layered bed as shown in Figure 2. Besides that, 100% adsorption of Cadmium by modified activated carbon of coconut occurred at contact time of 90 minutes. Accordingly, Figure 2 shows area under the graph for adsorption of Cadmium.

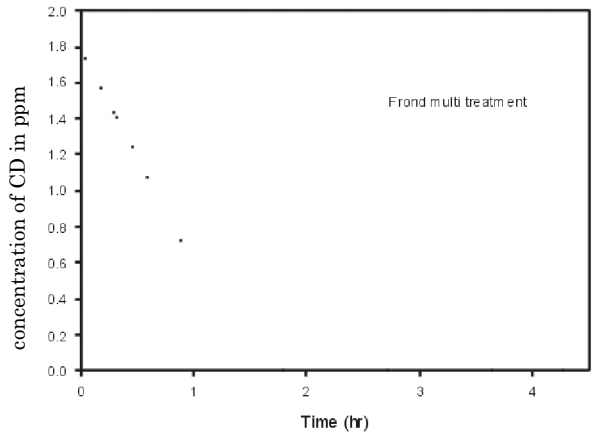

Figure 2: *Adsorption of Cadmium using palm fronds Adsorbents*

4.2 Adsorption Of Nickel (ni) By Modified Activated Carbon Of Coconut:

At the beginning the concentration of Nickel is 1.5 ppm and its represented high level of risk [21]. This value is progressively decreasing through the time. After 1.5 hrs, the concentration of Nickel 0.02 ppm then increased to 0.2 ppm at 4.5 hrs. Nickel is strongly adsorbed by modified activated carbon of palm fronds in multi layered bed. Besides that, 96.66% adsorption of Nickel by modified activated carbon of coconut occurred at contact time of 90 minutes then desorption will effect to reduce percentage of adsorption 86.66% at 270 minutes. Accordingly, Figure 3 shows area under the graph for adsorption of Nickel.

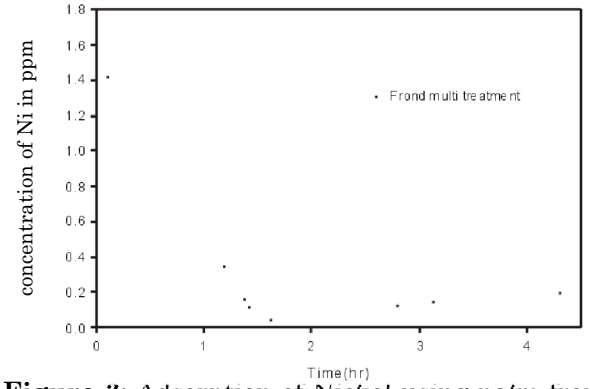

Figure 3: Adsorption of Nickel using palm fronds Adsorbents.

4.3 Adsorption Of Copper (cu) By Modified Activated Carbon Of Palm Fronds:

At the beginning the concentration of Copper is 1.3 ppm and its represented high level of risk [21]. This value is progressively decreasing through the time. After 1.5 hrs, the concentration of Copper 0.45 ppm then slightly reduced to 0.43 ppm as steady state. Copper is strongly adsorbed by modified activated carbon of palm fronds in multi layered bed. Besides that, 65.38% adsorption of Copper by modified activated carbon of palm fronds occurred at contact time of 94 minutes and adsorption will be quietly increased about 66.92% at 285 minutes. Accordingly, Figure 4 shows area under the graph for adsorption of Copper.

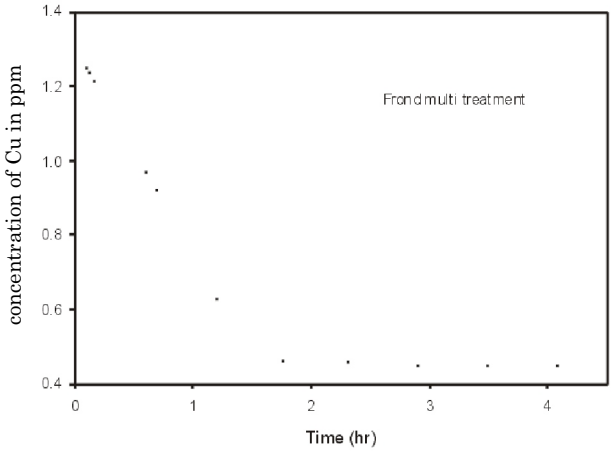

Figure 4: Adsorption of Copper using palm fronds Adsorbents.

4.4 Adsorption Of Potassium (k) By Modified Activated Carbon Of Palm Fronds:

At the beginning the concentration of Potassium is 0.52 ppm and its represented high level of risk [21]. This value is progressively decreasing through the time. After 1.5 hrs, the concentration of Potassium zero. Potassium is strongly adsorbed by modified activated carbon of palm fronds in multi layered bed. Besides that, 100% adsorption of potassium by modified activated carbon of palm fronds occurred at contact time of 90 minutes. Accordingly, Figure 5 shows area under the graph for adsorption of potassium.

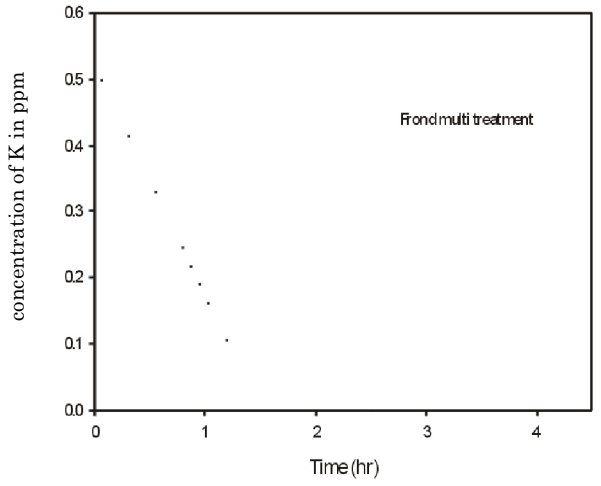

Figure 5: Adsorption of Potassium using palm fronds Adsorbents.

4.5 Adsorption Of Zinc (zn) By Modified Activated Carbon Of Palm Fronds:

At the beginning the concentration of Zinc is 1.75 ppm and its represented high level of risk [21]. This value is progressively decreasing through the time. After 1.5 hrs, the concentration of Zinc zero. Zinc is strongly adsorbed by modified activated carbon of palm fronds in multi layered bed. Besides that, 100% adsorption of Zinc by modified activated carbon of palm fronds occurred at contact time of 90 minutes. Accordingly, Figure 6 shows area under the graph for adsorption of Zinc.

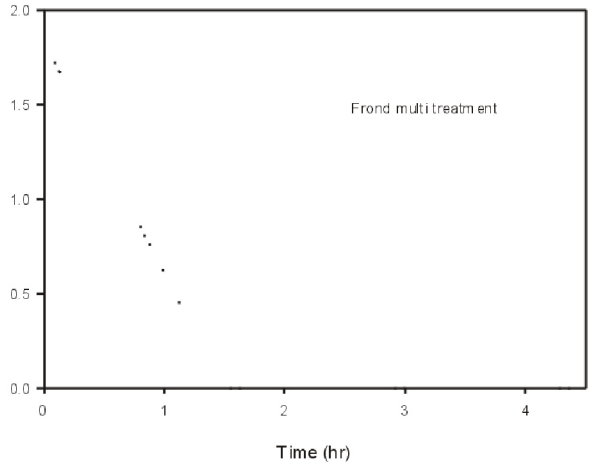

Figure 6: Adsorption of Zinc using palm fronds Adsorbents.

4.6 Validity Of The Mathematical Model:

Experimental results merge with proposed mathematical model were presented in the previous sections as shown in this work. With respect to many published models; such as Langmuir, and Freundlich models [20], the proposed model has proved to be more universal. In table 3, five different functions that are considered in our proposed model, are compared as to how far they are considered in three other models. For instance, all the three models are considering liquid phase only, while liquid, gas and solid phases are considered in our model. Additionally, the functions of desorption and energy transfer are only considered in our model, and among the three models, two are not considering the calculation of mass transfer. With this coverage, our model can be considered superior to the three compared models. Validity of the proposed model is moreover certified, where the dynamic behaviour of the model is found to be very close to the actual experiment results, as shown in Figure 7 (a-e). This accuracy depends on the exact values of rate constants of adsorption and desorption due to derive it from actual experiment data (see equation (23)) and these results can be illustrated in Table 4.

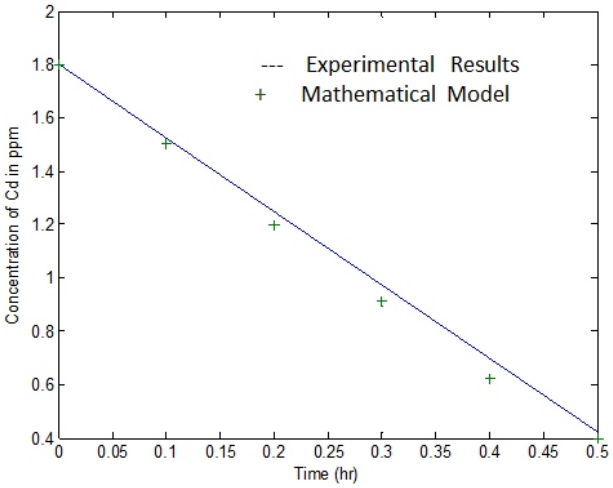

Figure 7: (a) Experimental results of Cd versus model.

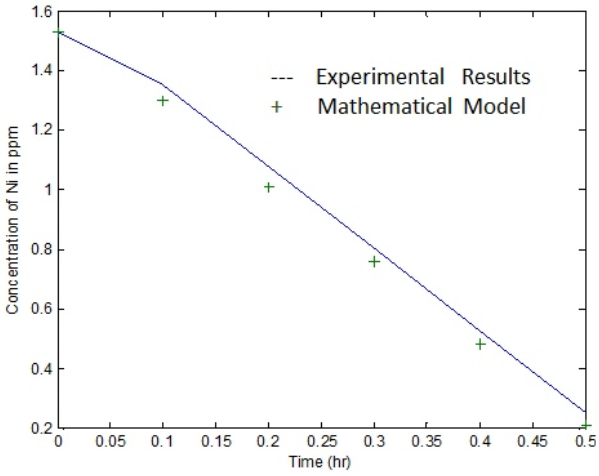

Figure 7: (b) Experimental results of Ni versus model.

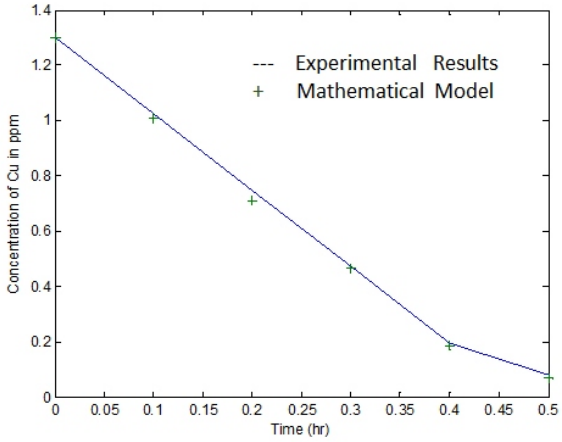

Figure7:(c) Experimental results of Cu versus model.

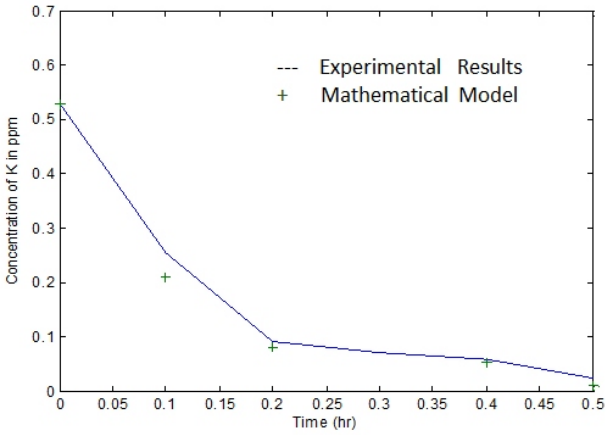

Figure 7: (d) Experimental results of K versus model.

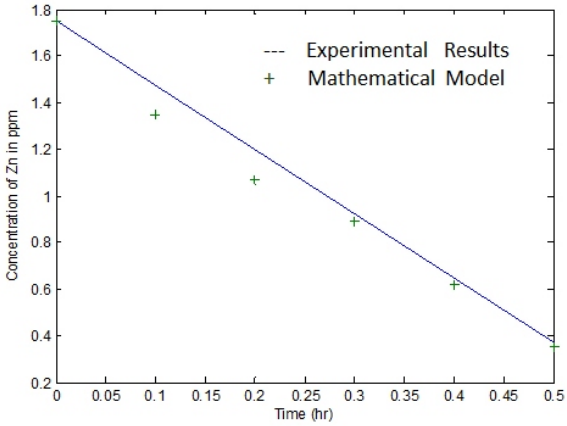

Figure 7: (e) Experimental results of Zn versus model.

Table 3: Derived mathematical model compared with different published models.

No	Functions	Proposed Mathematical model	Langmuir model[18]	Freundlich isotherm model[18]	Pseudo-first-order model [18]
1	Phases	Liquid , gas and solid phase	Liquid phase	Liquid phase	Liquid phase
2	Mass transfer	Calculated without chemical re modified activate carbonation	Not estimated	Not estimated	Estimated without chemical re modified activate carbonation
3 4	Adsorption	Diffusion of molecules of waste metals from surf modified activate carbon to the entrails holes of modified activate carbon without chemical	Considered	Considered	Considered
5	Desorption	Diffusion of molecules of waste metal from entrails holes of modified activated carbon to the surface activate carbon without chemical	Not take into account	Not take into account	Not take into account
	Energy transfer	Considered	Not take into account	Not take into account	Not take into account

Table 4: Explains rate constants of desorption and adsorption.

Metals	$K_{ad,1}^{+}\, K_{sr}^{*} - K_{ad}^{-}$
Cadmium	0.174
Nickel	0.143
Copper	0.123
Potassium	0.05
Zinc	0.169

4.7 Optimize Of Proposed Mathematical Model:

The main aim of this paper is to reduce the percentage of variation between experimental and theoretical outcomes for proposed model. To be more accurate require to optimize two variables $K_{ad,1}^{+}$, K_{sr}^{*} and K_{ad}^{-} of Cd, Ni, Cu, K and Zn using **Newton Raphson method**. Tables 5, 6, 7,8 and 9 are appearing the most active solution to decrease the percentage of errors of proposed model for Cd, Ni, Cu, K and Zn. Depend on the main planning of **Newton Raphson** method the objective function is represented by proposed model to make fixed step

changes for the K_{ad}^{-} and $K_{ad,1}^{+}$ K_{sr}^{*} and to attain to the better values. The optimum outcomes of rates constants of desorption and adsorption are rising the efficiency of proposed model and let it describe the dynamic behaviour of modified activated carbon of palm fronds very well. The specific modulation of this work are expounded in the interaction of experimental, mathematical model and optimization are providing optimum outcomes to calculate the rate constants of K_{ad} and $K_{ad,1}$ K_{sr} for any absorbent. A lot of researches are required to study and employ the results of this study to specify the actual and optimize values of adsorption and desorption for any adsorbent.

Table 5: Explains comparison results of optimization K_{ad}^{-} and $K_{ad,1}^{+}$ K_{sr}^{*} of Cd.

K_{ad}^{-}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize K_{ad}^{-}	Error %
0.001	15.09		
0.002	17.47	0.00014	9.73
0.003	17.55		
0.004	19.53		
$K_{ad,1}^{+}$ K_{sr}^{*}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}	Error %
0.001	15.28		
0.002	17.99	0.0023	8.02
0.003	15.98		
0.004	20.01		

Table 6: Comparison results of optimization K_{ad} and $K_{ad,1}^{-}$ K_{sr} of Ni.

K_{ad}^{-}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize K_{ad}^{-}	Error %
0.001	17.22		
0.002	19.78	0.00017	7.05
0.003	19.04		
0.004	20.34		
$K_{ad,1}^{+}$ K_{sr}^{*}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}

0.001¤	13.76¤	¤	¤
0.002¤	15.22¤	0.0027¤	6.66¤
0.003¤	17.07¤	¤	¤
0.004¤	17.888¤	¤	¤

Table 7: Comparison results of optimization K_{ad}^{-} and $K_{ad,1}^{+}$ K_{sr}^{*} of Cu.

K_{ad}^{-}¤	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$¤	Optimize K_{ad}^{-}¤	Error·%¤
0.001¤	20.41¤	¤	¤
0.002¤	22.81¤	0.0003¤	9.71¤
0.003¤	21.22¤	¤	¤
0.004¤	22.36¤	¤	¤
$K_{ad,1}^{+}$ K_{sr}^{*}¤	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$¤	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}¤	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}¤
0.001¤	16.23¤	¤	¤
0.002¤	15.91¤	0.0024¤	8.24¤
0.003¤	14.39¤	¤	¤
0.004¤	16.75¤	¤	¤

Table 8: Comparison results of optimization K_{ad}^{-} and $K_{ad,1}^{+}$ K_{sr}^{*} of K.

K_{ad}^{-}¤	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$¤	Optimize K_{ad}^{-}¤	Error·%¤
0.001¤	20.77¤	¤	¤
0.002¤	22.56¤	0.00017¤	12.33¤
0.003¤	22.13¤	¤	¤
0.004¤	23.47¤	¤	¤
$K_{ad,1}^{+}$ K_{sr}^{*}¤	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$¤	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}¤	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}¤
0.001¤	20.54¤	¤	¤
0.002¤	21.72¤	0.0025¤	11.57¤
0.003¤	20.08¤	¤	¤
0.004¤	23.02¤	¤	¤

Table 9: Comparison results of optimization K_{ad}^{-} and $K_{ad,1}^{+}$ K_{sr}^{*} of Zn.

K_{ad}^{-}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize K_{ad}^{-}	Error %
0.001	23.34		
0.002	20.07	0.00019	10.21
0.003	21.66		
0.004	22.72		
$K_{ad,1}^{+}$ K_{sr}^{*}	$Error = \frac{C_{exp} - C_{theoritical}}{C_{exp}} \times 100\%$	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}	Optimize $K_{ad,1}^{+}$ K_{sr}^{*}
0.001	18.03		
0.002	15.77	0.0032	8.19
0.003	14.99		
0.004	17.29		

5. Conclusions:

More than one technique is utilized to make high quality modified activated carbon to rise the ability of adsorption for five waste metals from the waste water with the suggested mathematical model has the power to estimate dynamic desorption and adsorption for modified activate carbon to make an obvious viewpoint about the mechanism of the arrangement because it included all the kinds of the rates desorption and adsorption with the effected partial pressure of fluid along the system compared to the other examples. Cadmium has higher value of rate constant adsorption of forward direction and rate constant desorption of reverse direction. Potassium has lower value of rate constant adsorption of forward direction and the higher value of rate constant adsorption of reverse direction. Optimize technique is employed to optimize the rate constants of desorption and adsorption to raise mathematical model performance.

References:

1. R. Verma and P. Dwivedi, "Heavy metal water pollution- A case study", *Recent Research in Science and Technology*, 5(5): 98-99, 2013.
2. M. A. Barakat, "New trends in removing waste metals from industrial wastewater", *Arabian Journal of Chemistry*, 4, 361377, 2011.
3. S. Babel and T. A. Kurniawan, "Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan", *Chemosphere*, 54 (7), 951967, 2004.

[4] H. Eccles, "Treatment of metal-contaminated wastes: why select a biological process?", *Trends Biotechnology*, 17, 462465, 1999.

5. W. C. Leung, M. F. Wong, H. Chua, W. Lo and C. K. Leung, " Removal and recovery of waste metals by bacteria isolated from activated sludge treating industrial effluents and municipal wastewater", *Water Sci. Technol.* 41 (12), pp.233240, 2000.

6. T. A. Kurniawan, G. Y. S. Chan, W. H. Lo and S. Babel, "Comparisons of low-cost adsorbents for treating wastewaters laden with waste metals", *Science. Total Environ.*, 366 (23), pp. 409426, 2005.

7. M. Ahmaruzzaman and V. K. Gupta, "Rice Husk and Its Ash as Low-Cost Adsorbents in Water and Wastewater Treatment", *Ind. Eng. Chem. Res.*, 50 (24), pp 1358913613, 2011.

8. P. C. Okafor, P. U. Okon, E. F. Daniel and E. E. Ebenso, "Adsorption Capacity of Coconut (Cocos nucifera L.) Shell for Lead, Copper, Cadmium and Arsenic from Aqueous Solutions", *Int. Journal of Electrochemical . Science.*, 7, 12354 12369, 2012.

9. L. Cutillas-Barreiro, L. Ansias-Manso, D. Fernández-Calviño, M. Arias-Estévez, J. C. Nóvoa-Muñoz, M. J. Fernández-Sanjurjo and E. Álvarez-Rodríguez, "Pine bark as bio-adsorbent for Cd, Cu, Ni, Pb and Zn: Batch-type and stirred flow chamber experiments", *Journal of Environmental Management*, Volume 144, 1 November, Pages 258-264, 2014.

10. **E.** W. Marshall and E. T. Champagne. "Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater", ***J.*** *of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology*, Vol. 30, Issue 2, pp 241-261, 1995.

11. Z. Yang et al., "Preparation and modification of peanut shells and their application for heavy metals adsorption", *Bulgarian Chemical Communications*, Vol. 48, No.3, pp. 535 542. 2016.

12. M. Zhu, R. Lium, H. Chai, Y. Chen and Z. Yi, "Hazelnut shell activated carbon: a potential adsorbent material for the decontamination of uranium(VI) from aqueous solutions", *J. of Radioanalytical and Nuclear Chemistry*, Dec., Vol. 310, Issue 3, pp 11471154, 2016.

13. A. Habi, N. Islam, A. Islam and A. M. Shafiqul Alam, "Removal of Copper from Aqueous Solution Using Orange Peel, Sawdust and Bagasse", *Pak. J. Anal. Environ. Chem.* Vol. 8, No. 1 & 2, pp.21- 25, 2007.

14. J. C. Igwe, D. N. Ogunewe and A. A. Abia, "Competitive adsorption of Zn (II) Cd and Pb (II) ions from aqueous and non-aqueous solution by maize cob and husk", *African Journal of Biotechnology*, 4 (10): 1113-1116, 2005.

15. R. Al-Yahyai and S. Al-Khanjari, "Biodiversity of date palm in the sultanate of Oman",

African Journal of Agricultural Research, 3, pp. 389-395, 2008.

16. E. I. I. El-Shafey, H. Al-Lawati and A. S. Al-Sumri, "Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets", *J. of Environmental Sciences*, September, pp 1579-1586, 2012.

17. M. Kaakani, "Heavy metal removal from wastewater using novel adsorbent", *Ms. Thesis, American University of Al Sharja, UAE*, 2012.

18. A. A. M. Daifullah, B. S. Girgis and H. M. H. Gad, "Utilization of agro-residues (rice husk) in 17small waste water treatment plans", *Materials Letters*, vol. 57, pp. 1723 1731, 2000.

19. E. Chockalingam and S. Subramanian, "Studies on removal of metal ions and sulphate reduction using rice husk and Desulfotomaculum nigrificans with reference to remediation of acid mine drainage", *Chemosphere*, vol. 62, pp. 699 708, 2005.

20. K. Y. Foo and B. H. Hameed, "Insights into the modeling of adsorption isotherm systems",

Chemical Engineering Journal, 156, 210, 2010.

21. *World Health Organization.Conference inGeneva in 23-25 May*, 2017.

22 NurAzreenBtFuadi, Ahmmed Saadi Ibrahim, Kamriah Nor Ismail , "Hypothetical T-shirt Model Pore for Waste Water Treatment by Using Modified Activated Carbon", Wulfina Journal Vol 19,2012, pp.10 33.

Nomenclature

Symbols	**Function**
HM	Waste metals
$K_{ads,1}$	Rate constant adsorption of forward direction.
$C_{HM1.Sr}$	*Concentration of polluted of adsorption surf modified activate Carbone.*
C_{HM1}	Concentration of polluted of adsorption.
C_{HMi}	Initial concentration of polluted of adsorption.
C_V	*Concentration of vacant catalyst surface of modified activate carbon.*
$K^{-}_{ads,1}$	Rate constant adsorption of reverse direction.
$K^{-}_{Srp,1}$	Rate constant desorption of reverse direction.
$K^{+}_{Srp,1}$	Rate constant desorption of forward direction.
P_{HM}	*Partial pressure* of waste metals
r_{ad}	
r_d	Rate of desorption.
Sr	Surface of modified activate carbon.
Vi	Volumetric flow rate
V	Volume
t	Time (s).