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Chemical Pre-Treatments of Oil Palm Frond for Improvement in the Removal of Zn and Cu from Wastewater by Sorption Process

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Abstract

As a result of industrialization, Environmental pollution is becoming more and more serious. Heavy metals are often present industrial wastewaters and need to be removed before discharge. Adsorption is a commonly used method for heavy metal removal from aqueous solutions. Despite of the good efficiencies for heavy metal removal still the process can be improved by chemical or physical improvement of the sorbent material. The effects of different pre-treatments on oil palm frond (OPF) with the objectives of improving the sorption of Zn and Cu have been investigated. Acid, base, steam and reactive dye treatment were investigated for improvement in the sorption process. Base treatment resulted in the highest improvement in the heavy metals sorption capacity of the sorbent (64%). In this study the sorption process was fitted with the Langmuir and Freundlich isotherm lines which resulted in high fitting with $R^2 \geq 0.99$. The response surface methodology was employed in order to optimize the conditions of the base pre-treatment of OPF. It resulted in two quadratic models, one for Zn and one For Cu, demonstrating the less effect of time of treatment against the high effect of the base solution concentration. The conditions for the optimized process were soaking the sorbent in a 1.0 M solution of NaOH for 45 min under normal room temperature of 25 °C.

Key words: low cost, pretreatment, adsorption, heavy metal, oil palm frond

1.0 Introduction

The presence of heavy metals in aqueous waste streams has become a problem due to its harmful effects on human health and the fauna and flora of receiving water bodies. It is known that legal standards on environment control are strict and, as a result, the discharge of heavy metals into aquatic bodies and sources of potable water should be properly controlled [1].

Different methods have been investigated for removal of heavy metals from wastewaters. The most widely used methods are such as membrane filtration, chemical precipitation, ion exchange, reverse osmosis and solvent extraction, liquid extraction, electro-dialysis, settling as settleable metal hydroxides, activated carbon adsorption, evaporation, biological methods, electrochemical treatment and membrane separation process [2-5].

Different low-cost materials are reported to have ability for heavy metal sorption. Removal of Cr (III), Cu (II) and Zn with carrot residues [6], Cu (II) removal using wheat shell [4],

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sorption of Pb on peat [7] and rice husk for uptake of Zn [8] and Pb [2] are some examples of low-cost removals for heavy metals. Although the sorption capacities are considered to be good, but they can still be further improved by chemical or physical modification.

Response surface methodology (RSM) is a mathematical/statistical based technique which is useful for analyzing the effects of several independent variables on the response, [9]. In Most RSM applications, the relationship between the response and the independent variables is unknown. Therefore, the first step in RSM is to approximate the function (f). Usually, this process employs a low-order polynomial in some region of the independent variables. If the response is well-modeled by a linear function of the independent variables, then the approximating function is a first-order model. If there is curvature in the system or in the region of the optimum, then a polynomial of higher degree must be used to approximate the response. This is to analyze and locate the optimum, i.e. the set of independent variables such that the partial derivatives of the model response with respect to the individual independent variables that is equal to zero. The eventual objective of RSM is to determine the optimum operating conditions for the system, or to determine the region, which satisfies the operating specifications. Almost all RSM problems utilize one or both of these approximating polynomials [10-12].

RSM has an important application in the process design and optimization as well as the improvement of existing design. This methodology is more practical compared to the approaches mentioned above as it arises from experimental methodology which includes interactive effects among the variables and, eventually, it depicts the overall effects of the parameters on the process [13].The design of adsorption column is often carried out based on the kinetic and mass transfer coefficients determined by isotherm models or the general practice of determining the optimal operating conditions while keeping the others at a constant level or one-variable-at-a-time technique. Therefore, the steady state models are basically able to predict the parameters which have been considered in mass balance relations but are unable to estimate other interrelated effluent quality parameters (responses) [14].

In this study the sorption capacity of Zn and Cu on OPF pretreated with different methods including treatment with acid, base, steam using auto clave and reactive die will be discussed. Response surface methodology is employed to optimize the best treatment method. The sorption isotherms, Langmuir and Freundlich will also be discussed in this text to check on the fitting of the sorption process.

2.0 Materials and Methods

2.1 Stock Solutions

Stock solution for Zn was prepared by dissolving zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, BDH) into distilled water while for Cu, copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Merck) was used [15]. The initial solution was made at a concentration of 100 mg/l and diluted to the desired concentrations using distilled water if required. The nitrate salts were of analytical grade.

2.2 Measurements

The Zn concentration was measured with a HANNA zinc meter (model HI93731), while that of Cu was measured using a HANNA copper meter (model HI93702). The solution pH was measured using a WTW pH meter (model pH330i 2A2O-1012). The COD test was done using spectrophotometer (CICIL brand CE1010) following Standard Method no. 5220 D (close reflux, colorimetric method).

2.3 Biomass Preparation

Oil palm frond (OPF) was obtained from the palm oil trees in Universiti Sains Malaysia. The biomass was ground with a blender (model Epicson Eb-321) for 1 min, washed thoroughly with distilled water and then dried in an oven at 70°C for 12 h to reach constant weight. The dried biomass was then treated with different methods including, acid, base, steam with autoclave and reactive dyes treatments.

2.3.1 Base Treatment

For the preparation of alkaline treated sorbent material, 2 g of biomass was treated for 172 min in a 250 ml of 0.6 M NaOH solution at room temperature of 25 °C. It was then thoroughly washed with distilled water until the constant pH of the washing water. Subsequently it was then dried for 12 h in an oven of 70 °C until constant weight.

2.3.2 Acid Treatment

The biomass was soaked into a 250 ml of 0.6 M H_2NO_3 solution for 172 min at normal room temperature of 25 °C. After the desired time, the biomass was washed thoroughly with distilled water to reach the constant pH of the washing water. The sorbent was then oven-dried for 12 h at 70°C.

2.3.3 Treatment with Steam Using Autoclave

Without usage of any chemical, 2.5 g of OPF was placed in a 250 ml conical flask and the flask was then put inside an autoclave (Selecta, Autester-E). The temperature was settled at 122ºC for 44 min. after cooling down the auto clave the samples was oven dried in an oven of 70 °C until constant weight in order to remove any moisture from the biomass.

2.3.4 Treatment Using Reactive Dye

Methylene blue was used in this study as a dye for biomass modification. The dye solution for the treatment was prepared at a concentration of 125 ppm. OPF was treated with dye before using as a sorbent for the sorption process of heavy metal in either presence of Glauber's salt to improve dye uptake by the OPF. 1 g of dried untreated biomass was added to 40 ml of dye solution at 40 °C and was heated up to 85 °C under constant stirring using a hot plate stirrer (Favorite brand) for 30 min. For the treatment using glauber's salt, after 10 min 16.25 g/l glauber's salt was added in a two lot of 10 min interval for enhancing the dye's uptake by the biomass. After that, the biomass was washed until constant colour of washing water. The treated biomass was then oven dried at 70 °C overnight before being used in the sorption process [16].

2.4 Batch Sorption Studies

In a typical experiment, the mixture for sorption study consisted of 1 g of OPF pre-treated biomass in 250ml of 100 mg/l concentration of heavy metal solution and was agitated at 150 rpm 240 min under normal room temperature of 25°C. The sorbent solution mixture was then filtered and the filtrate was analyzed for heavy metal concentration.

2.5 RSM Design

Central composite design modified with $\alpha=1.25$ was used for the optimization of the best pretreatment process. For a full rotatable design, α is equal to $\sqrt{k}$, for this design with k=2 the distance from the center α should be equal to 1.41421. For this design as the low value of the design would become negative the amount of α should be reduced. It has been chosen as 1.25 because the higher number of α would lead to a lower range of the axial point which is neither effective and nor reachable in actual. This design with two factors consisted of a 2^k factorial points coded as ± 1 augmented by $2k$ axial points ($\pm\alpha$) and n_c center points coded as 0 where k is the number of variables and α is the distance from the center of design to an axial point. The coded and actual values of variables of the design are shown in Table 1. The same design was used for both Zn and Cu sorption process.

Table 1 Coded and actual values of variables of the design for biomass pre-treatment

Factor		Coded levels of variables		
		-1.00	0	1.00
Time, min	A	45	172.5	300
Solution concentration, M	B	0.2	0.6	1

Optimization process was carried out by using the same range of independent variables and responses. Table 2 indicates the actual experiment design carried out for developing the model for optimizing the pre-treatment of the biomass for Zn and Cu sorption process.

A second order polynomial equation (Equation 1) was fitted to the experimental data obtained, based on the above design, in order to generate the response surface model.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j + \varepsilon$$

(1)

where

Y = response calculated by model (dependent variables)
β_0 = constant coefficient
β_i = coefficients for the linear effect
β_{ii} = coefficients for the quadratic effect
β_{ij} = coefficients for the cross-product effect
X_i, X_j = variables corresponding to factors (independent variables)
ε = error

Table 2. Experimental Matrix for Central Composite Design (CCD) for Biomass Pre-treatment

Run No.	Point type	Factors A	Factors B
1	Fact	45.00	0.2
2	Fact	300.00	0.2
3	Fact	45.00	1.0
4	Fact	300.00	1.0
5	Axial	13.13	0.6
6	Axial	331.88	0.6
7	Axial	172.50	0.1
8	Axial	172.50	1.1
9	Center	172.50	0.6
10	Center	172.50	0.6
11	Center	172.50	0.6
12	Center	172.50	0.6
13	Center	172.50	0.6

3.0 Result and Discussion

3.1 Effect of Different Treatment Methods

The results using different biomass for removal of heavy metals showed the sharpest uptake in the first 10 min for both Zn and Cu removals. After that, the concentration of the heavy metal in the solution remains constant. Figure 1 demonstrates the sorption of zinc on different pretreated biomass while Figure 2 shows he amount of Cu sorption on the same pretreated biomass.

For both Zn and Cu removals treatment with base is found to be the most effective way to improve the sorption capacity of the biomass. Nagase et al. [17] has reported NaOH to show the highest percentage in heavy metal removal. The highest removal for NaOH treated biomass was found to be 52 % (13 mg/g) and 57 % (14.25 mg/g) for Zn and Cu removal, respectively before the optimization. The lowest improvement was obtained with acid treated OPF for sorption of both Zn and Cu on the treated biomass.

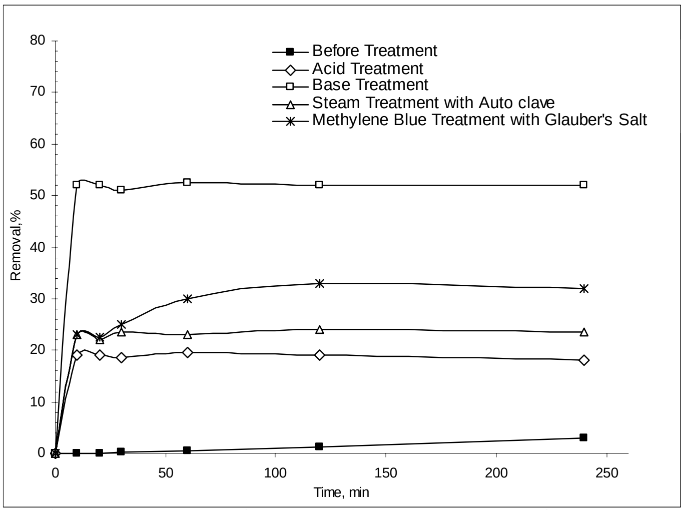

Figure 1 Zinc Sorption on Pretreated OPF Biomass

Comparing the similar treatments between Zn and Cu sorption reveals the higher uptake for treatments with NaOH, H_2NO_3 and steam, while the improvement with methylene blue treating shows nearly the same amount of sorption of 22.5% (5.5 mg/g) for both heavy metals. The treatment using methylene blue without using the glauber's salt shows better improvement in Zn removal reaching the highest uptake of 35% (9.0 mg/g) while only removed only 24% (6.0 mg/g) of Cu was removed by this treatment.

COD test was carried out to check whether any secondary pollutants being introduced to the solution from the biomass. This is important to make sure the quality of the stock solution is free from other pollutions prior to discharge. The COD test didn't show any significant inorganic mater introduced to the water.

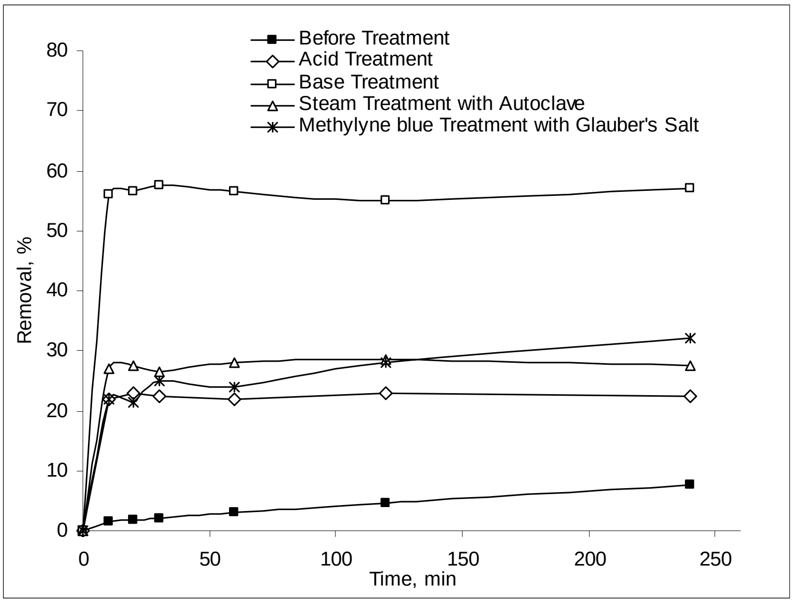

Figure 2 Copper Sorption on Pretreated OPF Biomass

3.2 *Sorption Isotherms*

Two important operational aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the sorption and the kinetics. Equilibrium studies give sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium [18] Two different isotherm lines have been mostly studied for the adsorption behavior of the biomass: Langmuir and Freundlich [19-21]

3.2.1 *Langmuir Isotherm*

The Langmuir adsorption isotherm is often expressed as:

$$\frac{x}{m} = \frac{bQ_0C_e}{1 + bC_e} \tag{2}$$

Where:
x = amount of material adsorbed (mg or g)
m = weight of adsorbent (mg or g)

C_e =concentration of material remaining in solution after adsorption is complete
Q_0 and b = constants

Taking the reciprocal of both sides of equation yields:

$$\frac{1}{x/m} = \left(\frac{1}{Q_0}\right) + \left(\frac{1}{Q_0 b C_e}\right) \tag{3}$$

For adsorption that follows the Langmuir isotherm, a linear trace should result when the quantity $\frac{1}{x/m}$ is plotted against $\frac{1}{C_e}$. Values of the constants Q_0 and b can be determined from the linear graph [20]:

$\frac{1}{Q_0 b}$ = the slope of the graph

$\frac{1}{Q_0}$ = the intercept of the graph

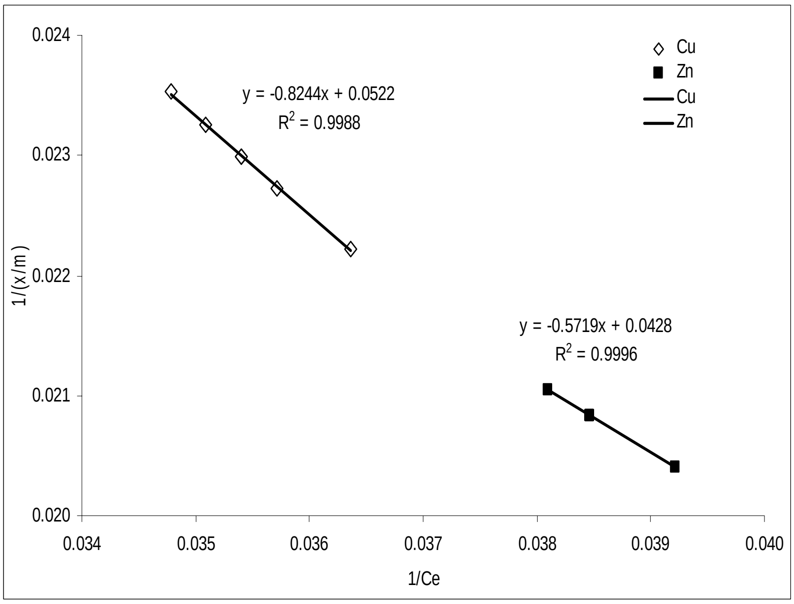

Figure 3 Langmuir Isotherm Fitting the Cu and Zn Removal Using OPF Pre-treated with NaOH

3.2.2 Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$\frac{x}{m} = K_f \cdot C_e^{1/n} \tag{4}$$

where:
x = amount of material adsorbed (mg or g)
m = weight of adsorbent (mg or g)
C_e = concentration of material remaining in solution after adsorption is complete

K_f and n = constants that must be evaluated for each solute and temperature

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$ln(\frac{x}{m}) = lnK_f + (\frac{1}{n})lnC_e \tag{5}$$

A plot of $ln\left(\frac{x}{m}\right)$ against $ln\ C_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. Values of the constants n and K_f can be determined from the linear graph:

$1/n$ = the slope of the graph
$ln\ K_f$ = the intercept of the graph

The related parameters for the fitting of Langmuir and Freundlich equations at 25 °C along with correlation coefficients using OPF biomass treated with different methods are summarized in Table 3. The results show that all the correlation coefficients suggested high fitting with the values near to 1.

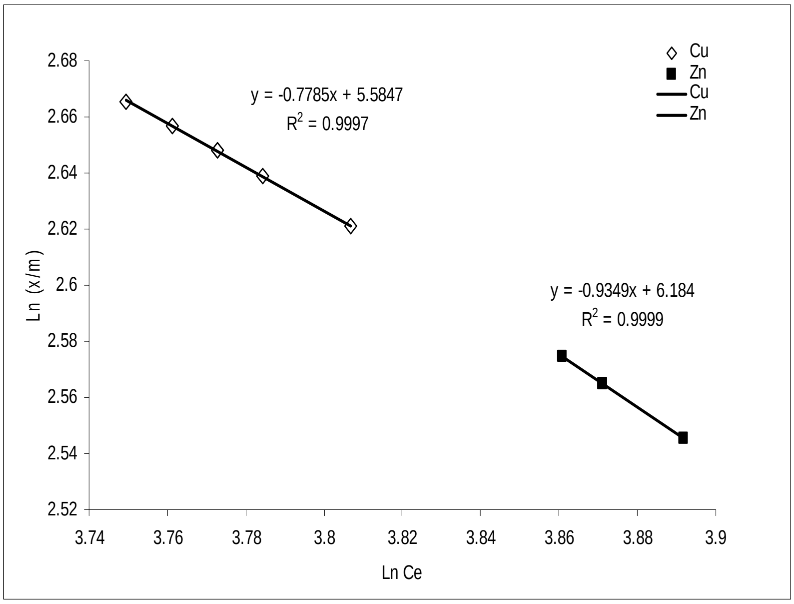

Figure 4 Freundlich Isotherm Fitting the Cu and Zn Removal Using OPF Pre-treated with NaOH

Figure 3 and Figure 4 respectively demonstrate the Langmuir and Freundlich isotherm fitting the Cu and Zn removal using OPF pre-treated with NaOH to represent the biomass with the highest sorption capacity.

Table 3 – R^2 and isotherm constants for Langmuir and Freundlich Isotherms in the sorption of Zn and Cu on various pretreated OPF

Heavy metal	Treatment	Isotherm	R^2	Langmuir constants		Freundlich constants	
				b	Q_0	n	K_f
Zn	NaOH	Langmuir	0.9996	0.0733	23.0	-	-
		Freundlich	0.9998	-	-	1.083	4.84×10^2
	H_2SO_4	Langmuir	0.9986	0.590	66.2	-	-
		Freundlich	0.9890	-	-	0.230	9.26×10^8
	steam	Langmuir	0.9967	0.379	59.5	-	-
		Freundlich	0.9999	-	-	0.298	1.23×10^7
	Methylene blue	Langmuir	0.9997	0.271	52.4	-	-
		Freundlich	0.9996	-	-	0.379	2.44×10^5
Cu	NaOH	Langmuir	0.9988	0.063	19.2	-	-
		Freundlich	0.9997	-	-	1.285	2.66×10^2
	H_2SO_4	Langmuir	0.9989	0.394	60.2	-	-
		Freundlich	0.9750	-	-	0.290	1.81×10^7
	Autoclave	Langmuir	0.9989	0.265	52.6	-	-
		Freundlich	0.9997	-	-	0.379	5.53×10^5
	Methylene blue	Langmuir	0.9999	0.293	54.1	-	-
		Freundlich	0.9997	-	-	0.361	9.70×10^5

3.3 Response Surface Methodology

Table 4 demonstrates the values of each point used for the experimental design for Zn and Cu. By using coded values from the estimation of data a linear regression model was developed. The model for removal of Zn is given in Equation 6 while the model for Cu removal in Equation 7.

$$\text{Zn Removal, \%} = + 50.71 + 11.09\,B - 2.69\,B^2 \quad (6)$$

$$\text{Cu Removal, \%} = +49.00 + 2.12A + 10.86\,B \quad (7)$$

The above model indicates that term A as a factor of time was not effective in the prediction of this process for Zn removal, while the Cu removal followed a linear equation which only the first order with respect to A and B. The concentration of the NaOH solution shows significant effect for first order and second order with term B for Zn removal. The significance of each coefficient in the Equations 6 and 7 was determined by Student *t*-test and *p*-values [3].

The ANOVA for Zn removal model used to estimate the responses as a function of NaOH solution and time is shown in Table 5, while, Table 6 presents ANOVA for Cu removal model for estimating the responses as the function of the same factors.

The regression was highly significant at 99 % of confidence level for both Zn and Cu removal. The coefficient of determination, R^2 was found to be equal to 0.9081 and 0.9401 for Zn and Cu removal, respectively and were reasonably good which suggested 59.1 % for Zn removal and 57.7% for Cu removal were explained by the variation in the variables. The remaining (60.9% and 42.3% for Zn and Cu removal, respectively) were therefore, explained by the residues.

Table 4- Experimental design and results for Zn and Cu removals with OPF treated with NaOH

	Coded values		Zn Removal, %		Cu Removal, %	
Run	A	B	Observed	Predicted	Observed	Predicted
1	-1	-1	34.50	36.93	34.00	37.52
2	1	-1	35.00	36.93	36.50	37.52
3	-1	1	57.50	59.10	57.00	59.24
4	1	1	63.50	59.10	64.00	59.24
5	-1.25	0	50.00	50.71	48.00	49.75
6	1.25	0	51.00	50.71	52.50	49.75
7	0	-1.25	36.00	32.64	37.50	34.03
8	0	1.25	58.00	60.36	59.00	61.18
9	0	0	52.00	50.71	52.00	49.75
10	0	0	49.00	50.71	50.50	49.75
11	0	0	47.50	50.71	49.00	49.75
12	0	0	50.00	50.71	48.00	49.75
13	0	0	56.00	50.71	49.00	49.75

The model F-value of 49.4 and 78.4 for Zn and Cu removal, respectively implies that the model is significant and there is only a 0.01 % chance that a "Model F-Value" could occur due to noise. The "Lack of Fit F-value" of 0.76 implies the Lack of Fit is not significantly relative to the pure error. There is a 63.8 % chance that a "Lack of Fit F-value" of this level could occur due to noise for Zn removal. Non-significant lack of fit is considered good and is desired the model to fit. Also the "Lack of Fit F-value" of 3.12 implies the Lack of Fit is not significant relative to the pure error for Cu removal. There is only a chance of 14.5 % that a "Lack of Fit F-value" this large could occur due to noise.

Table 5- Analysis of variance for the Quadratic Model for Zn removal by OPF treated with NaOH

	Source	Sum of Squares	DF[a]	Mean Square	F Value	Prob. > F
Removal, %	Model	911.97	2	455.99	49.38	< 0.0001
	Residual	92.34	10	9.23		
	Lack of Fit	49.14	6	8.19	0.76	0.6378
	Pure Error	43.20	4	10.80		
	Total	1004.31	12			

R^2= 0.9081, CV[b]= 6.17%

[a] DF= Degree of freedom
[b] CV= Coefficient of variation

The significance of the model terms were proved by the small value of "Prob.>F" (less than 0.05). The non-significant value of lack of fit above 0.05 for all the models demonstrated that the quadratic models were valid for the present study [1].

Table 6- Analysis of variance for the quadratic model for Cu removal by OPF treated with NaOH

	Source	Sum of Squares	DF[a]	Mean Square	F Value	Prob. > F
Removal, %	Model	872.37	2	436.19	78.41	< 0.0001
	Residual	55.63	10	5.56		
	Lack of Fit	45.83	6	7.64	3.12	0.1454
	Pure Error	9.80	4	2.45		
	Total	928.00	12			

R^2= 0.9401, CV[b]= 4.81%

[a] DF= Degree of freedom
[b] CV= Coefficient of variation

3.3.1 Graph-based Overall Discussion

Figure 5 and Figure 6 demonstrate the response surface 3D plot for the effect of interaction between NaOH concentration and time for Zn and Cu removals on NaOH pre-treated OPF, respectively. As obvious in these figures the effect of time was not very essential in improving the sorption capacity of the sorbent, while the concentration showed a very high effect on the sorbent capacity. This could also be observed in the modified quadratic model derived in which the term A (time, min) was considered not significant.

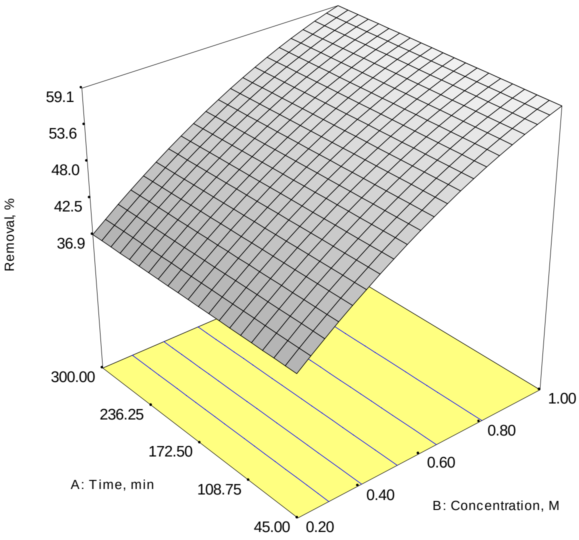

Figure 5 Response surface 3D plot indicating the effect of interaction between NaOH concentration and

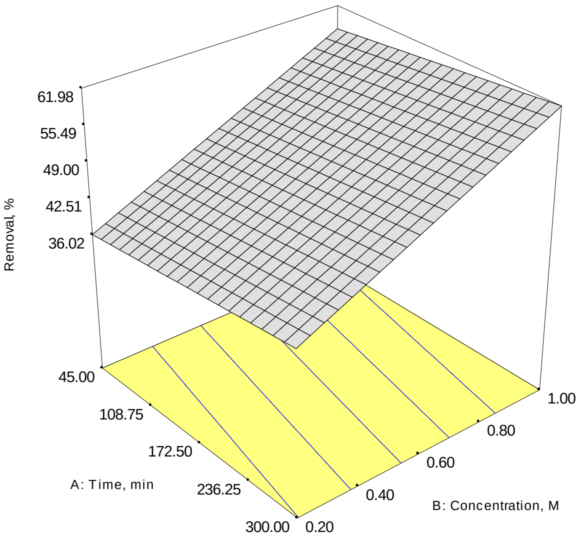

Figure 6 Response surface 3D plot indicating the effect of interaction between NaOH concentration and time for Cu

It is observed from the graphs that by using the time at it's lowest value and by increasing the NaOH solution concentration up o 1.0 M the best sorption capacity could be achieved. A set of solution was given by the software for the optimum conditions of the NaOH treatment of OPF which are summrized in Table 7.

Table 7. Optimum conditions found by the Design Expert software for pretreatment of OPF for Zn and Cu sorption process

				Removal, %			
Metal	Run	A	B	Obtained	Predicted	Error	S.D.*
Zn	1	45	1.0	61.5	59.1	2.4	1.69
Cu	1	45	1.0	64	57.74	6.26	4.43

* S.D. = Standard Deviation

As shown in Table 7 the best optimum conditions for pretreatment for both Zn and Cu removal are the same vis., by using 1.0 M of NaOH solution treated for 45 min to achieve the highest sorption capacity in normal room temperature of 25 °C. These conditions led to a removal of 61.5 % and 64.0 % for Zn and Cu, respectively using the NaOH treated biomass.

4.0 Conclusion

In this study, the treatment with NaOH was the most effective way of treating the OPF biomass in order to be used as a sorbent for heavy metals. Although this method could improve this capacity even up to 61% and 64% for Zn and Cu removal repectively but still the sorption process needs to be improved by optimizing the sorption operation parameters such as initial concentration of heavy metal, pH, temprature and the amount of biomass loading. Both the isotherm models of langmuir and frendlich showed high fitting with $R^2 \geq 0.99$. the RSM design suggested the condition of 1.0 M solution concentration in order to treat the sorbent for 45 min can give the highest efficiancy for the treatment process. With the obtained solutions based on RSM removals of 61.5 % and 64 % were achieved for Zn and Cu removals, respectively.

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