Bioadsorption of 2,6-Dichlorophenol from Aqueous Solution onto Plantain and Pineapple Peels Mixture Used as Adsorbent: Optimization Studies Based on Taguchi Method, Batch Equilibrium, and Kinetic Modelling

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Abstract
The feasibility of using pineapple/plantain peels mixture to remove 2, 6-dichlorophenol (2,6-DCP) from its aqueous solutions was investigated under batch mode. The effects of factors such as pH, initial 2, 6-DCP concentration, temperature and pineapple/plantain peels adsorbent ratio on the removal process were evaluated. Four factors and three levels according to Taguchi's (L9) orthogonal array were used to assess and optimize the bioadsorption behaviour of pineapple/plantain peels mixture. Analysis of variance was applied to determine the significant factors that affect bioadsorption. The levels of significant factors were optimized using Signal to Noise ratio. The results showed that bioadsorption of 2, 6-DCP was dependent on these factors. However, pH was the major factor that affects the percentage (%) removal of 2,6-DCP with its % contribution of 52.23. An optimum parameter combination for the maximum percentage removal of 2,6-DCP was obtained using the analysis of Signal to Noise (S/N) ratio. The best conditions for bioadsorption of 2,6-DCP were determined by the Taguchi method and desirability approach as pH = 7, initial 2,6-DCP concentration of 300 mg/l, temperature 50 °C, and pineapple/plantain adsorbent ratio of 2:1. The equilibrium bioadsorption data were analyzed by Langmuir and Freundlich isotherm models. The Freundlich isotherm model provided the best fit (R^2 = 0.9980) to the experimental data. The maximum monolayer bioadsorption capacity ($Q_{\max}$) was found to be 76.92 mg/g. The bioadsorption kinetics data of 2, 6-DCP were analyzed by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The pseudo-second order kinetic model gave the best fit. Therefore, pineapple/plantain peel adsorbent mixture has potential for application as an effective bioadsorbent for 2, 6-DCP removal from aqueous solution.
Keywords: Bioadsorption; Bioadsorption isotherms; Kinetics; Pineapple-Plantain peel mixture; 2, 6-Dichlorophenol; Taguchi method.

1.0 Introduction

Chlorophenols constitute an important class of pollutants because of their wide use in the production of wood preservers, pesticides and biocides (Bae *et al.*, 2002; Agarry *et al.*, 2012). These compounds are present in the wastewater generated from industrial activities such as petrochemical, pharmaceutical, wood preserving, plastic, rubber proofing, pesticide, iron steel, textile, and paper and cellulose bleaching industries (Fattahi *et al.*, 2007; Hamad *et al.*, 2010). Chlorophenols as environmental pollutants are highly toxic and carcinogenic with strong odour emission, not readily biodegradable and persistent in the environment and thus poses a serious ecological problem and public health risk causing problems with the human respiratory and nervous system (ATSDR, 1999; Tan *et al.*, 2009).

Therefore, removing chlorophenols from aqueous solution is important prior to discharging wastewater into the environment. Consequently, many treatment processes have been applied for the removal of chlorophenols from waste waters. Some of these processes include: adsorption (Hamad *et al.*, 2011; Agarry *et al.*, 2013a), photo-fenten degradation (Poulopoulos *et al.*, 2008), catalytic wet oxidation (Chaliha and Bhattacharyya, 2008), photocatalytic degradation (Devipriya and Yesodharan, 2010), and biodegradation (ElKarmi *et al.*, 2009). Liquid-phase adsorption has been shown to be an effective way for removing suspended solids, odors, organic matter, and oil from aqueous solutions (Annadurai *et al.*, 2002). Activated carbon is most widely used as adsorbent in the removal of heavy metals, hydrocarbons and other hazardous chemicals (Hameed, 2009) which may be found in waste waters because of its high adsorptive capacity, but its high cost and difficulty in regeneration limits its commercial application in large-scale waste water treatment (Popuri *et al.*, 2007).

This has led to research for cheaper substitutes. One of these cheaper substitutes is the use of agricultural byproducts which is an ubiquitous green waste which may cause some serious environmental pollution. Some of the agricultural waste products that has been developed as adsorbents with varying success for the removal of contaminants include, orange peels (Owabor and Audu, 2010, Agarry and Aremu, 2012), banana peels (Achak *et al.*, 2009), banana stalk (Ogunleye *et al.*, 2014), spent tea leaves (Hameed, 2009; Agarry *et al.*, 2013a), peanut husk (Hu *et al.*, 2011) and pineapple peels (Agarry and Aremu, 2012; Solidum, 2013). More and more interests are focused on developing these agricultural wastes as adsorbent for wastewater treatment due to their relative high sorption affinity, ubiquitous presence in the environment, and the ease of being modified to materials with higher efficiency (Chen *et al.*, 2011; Agarry and Aremu, 2012).

The classical method of varying the level of one factor at a time over a certain range and holding the rest of the test factors constant in order to determine their effects as well as to optimize these factors is a time and labor consuming work. However, the use of statistical experimental design and the Taguchi method (SureshKumar *et al.*, 2008; Rajan *et al.*, 2010; Kumar *et al.*, 2013) are of recent gaining popularity as it can determine the effect of the factors on characteristic properties and the optimal conditions of factors. It is an efficient and less time consuming method. Taguchi method is a combination of mathematical and statistical techniques used in an empirical study. It is economical for characterizing a complicated process. It uses fewer experiments in order to study all levels of all input parameters, and filters out some effects due to statistical variation. The Taguchi's design can further simplify by expending the application of the traditional experimental designs to the use of orthogonal array. This method is a simple, efficient and systematic approach to optimize designs for performance, quality and cost. Recently, Kumar *et al.* (2013) and Zolghamein *et al.* (2013) used Taguchi methodology to optimize process parameters involved in the adsorption of Cu (II) and Cd (II) heavy metals onto neem leaves and Carpinus betulus tree leaves, respectively. Nevertheless, the use of Taguchi method in studying the effects and optimization of process parameters in adsorption process is still very limited. Agarry *et al.* (2013b) have made use of plantain peel as adsorbent for the adsorption of 2,6-dichlorophenol from aqueous solution and the use of pineapple peels as a low cost adsorbent in immobilizing Pseudomonas aeruginosa for phenol removal has been reported (Agarry and Aremu, 2012). However, the mixture of two or more agricultural wastes to be used as adsorbent in the removal of organic chemicals or hydrocarbon pollutants has rarely been reported in the literature.

Therefore, the purpose of this work is to investigate the possibility and potential of using the mixture of cellulose-based waste, plantain peel and pineapple peel as a non-conventional low cost adsorbent for bioadsorption of 2, 6-dichlorophenol (2,6-DCP) from aqueous solution. The main effects of physical parameters such as initial 2,6-DCP concentration, pH, temperature, and mixture ratio of adsorbent on the bioadsorption process were investigated using Taguchi method. More also, the bioadsorption equilibrium isotherms and kinetic parameters were determined and evaluated.

2.0 Materials and Methods

2.1 Preparation of synthetic wastewater sample

All the reagents used for the current investigation were of analytical grade from E. Merck Ltd., India. A stock solution was prepared by dissolving 1 g of 2,6-DCP (Sigma Aldrich) in 1 L of sterilized de-ionized water. From this original stock solution, five test working solutions with various concentrations (100, 200, 300, 400, and 500 mg/L) were prepared by dilution with de-ionized water. Before mixing the adsorbent, the pH of each 2,6-DCP solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution.

2.2 Plantain and pineapple peel collection and bioadsorbent preparation

Plantain peels used in this study were collected from local food sellers, restaurants and eateries located in Ogbomoso while pineapple peels, a waste product of pineapple pulp were obtained from pineapple fruits bought from a local market in Ogbomoso, Nigeria. The plantain and pineapple peels were washed and sundried for 10 days. The respective dried plantain and pineapple peels were then reduced to small-sized particles by grinding using a serrated disk grinder. The powdered particles were sieved to obtain a desired average particle size of 1.68 mm. The plantain peel powdered particles and the pineapple peel powdered particles were separately washed thoroughly with sterilized de-ionized water and dried in the oven for 2 – 3 h at 60^{o}C, after which they were stored in sterilized closed glass bottles prior to use as a bioadsorbent. Both the powdered plantain and pineapple peels were differently pretreated with chemical solvent to increase the 2, 6-dichlorophenol uptake efficiency. For this purpose, 100 g of each powdered peels were treated with 1000 ml of 1M H_3PO_3 for 24 h and then kept on water bath (70^{o}C) for 30 min. It was later cooled and neutralized with 500 ml of 1M NaOH. The filtrates were separated and dried in the oven at 60^{o}C for 4 – 5 h. The pretreated powdered plantain and pineapple peels were used as mixed bioadsorbent for the study.

2.3 Characterization of plantain and pineapple peel

The plantain and pineapple peel was each characterized for surface functional groups by Fourier Transform Infra Red Spectroscopy (FT-IR) method using a Perkin–Elmer 2000 infrared spectrometer. The spectrum of the biosorbent was recorded in 400−4000 cm^{-1}.

2.4 Batch equilibrium bioadsorption studies

The batch biosorption tests were carried out in a glass-stoppered 250 ml Erlenmeyer conical flask with 100 ml of working volume and an initial concentration of 100 mg/L of 2,6-DCP having a solution pH of 7. A weighed amount (2.0 g) of bioadsorbent (mixture of plantain and pineapple peels) was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 150 min in a temperature controlled – water bath shaker at 30^{o}C. Different initial 2,6-DCP concentration (100, 200, 300, 400, 500 mg/L) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals of 30 min for analyzing the residual 2,6-DCP concentration in the solution. Prior to analysis, samples were centrifuged to separate bioadsorbent from the adsorbate and minimize interferences. At time t = 0 and equilibrium, the 2,6-DCP concentrations were determined using UV-spectrophotometer at an absorbance wavelength of 340 nm. The amount of bioadsorption at equilibrium, q_e (mg/g) was calculated according to Eq. (1) (Crisafully *et al.*, 2008):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

Where C_o and C_e (mg/l) are the initial and final (equilibrium) concentrations of 2,6-DCP in waste water. V (ml) is the volume of the waste water and W (g) is the mass of dry bioadsorbent used.

2.5 Batch bioadsorption kinetic studies

The procedures of kinetic studies were basically identical to those of batch equilibrium studies.

The amount of 2,6-DCP sorbed at time t, q_t was calculated according to Eq. (2) (Xun *et al.*, 2007):

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

Where C_t is the concentration of 2,6-DCP in waste water at time t. The percentage of 2,6-DCP removal was calculated using Eq. (3) (Hamad *et al.*, 2011):

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (3)$$

2.6 Optimization studies

The selected experimental design parameters are as given in Table 1.

Table 1: Process parameters and their levels

Symbol	Factors	Levels		
		1	2	3
A	pH	4	7	10
B	Initial Concentration (mg/l)	100	300	500
C	Temperature (^{o}C)	30	40	50
D	Pineapple: Plantain adsorbent Ratio	1:1	1:2	2:1

Table 1 shows four factors and three levels used in the experiment. If three levels were assigned to each of these factors and a factorial experimental design was employed using each of these values, number of permutations would be 64. The fractional factorial design reduced the number of experiments to nine. The pH (A), initial 2,6-DCP concentration (B), temperature (C) and plantain/pineapple biosorbent ratio (D) were assigned to the 1st, 2nd, 3rd and 4th column of L9 array respectively. The orthogonal array of L9 type was used and is represented in Table 2. This design requires nine experiments with three parameters at each of these three levels. The interaction between main factors was neglected. The S/N ratios were computed for percentage (%) 2,6-DCP removal in each of the 9 trial conditions and their values are as given in Table 2.

Table 2: Experimental layout using an L_9 (3^4) orthogonal array and the experimental results

Run	Main Factors				% 2,6-DCP Removal			Average	S/N Ratio (dB)
	A	B	C	D	1	2	3		
L1	1	1	1	1	94.50	94.52	94.56	94.53	11.58
L2	1	2	2	2	95.0	95.20	95.40	95.20	11.60
L3	1	3	3	3	97.85	97.80	98.05	97.90	11.68
L4	2	1	2	3	98.70	98.65	98.68	98.67	11.70
L5	2	2	3	1	99.74	99.79	99.82	99.78	11.74
L6	2	3	1	2	96.70	96.80	97.10	96.87	11.65
L7	3	1	3	2	93.40	93.25	93.10	93.25	11.54
L8	3	2	1	3	96.25	96.38	96.47	96.37	11.64
L9	3	3	2	1	95.90	95.84	95.88	95.87	11.62

2.4 Data Analysis

Analysis of Variance (ANOVA) was used to determine the significance of each factor while signal to noise ratio (S/N) was used in deciding the optimum levels of the factors. ANOVA is a statistically based objective decision making tool for detecting any differences in average performance of groups of tested items. It thus determines the effects of the different factor – level combination through an analysis of their variability. The final outcome of the ANOVA table is the determination of F-value. The F- value is a measure of how statistically significant a particular factor is to the overall experiment. It is the ratio of the variance due to the factors and the variance due to the error. The F-value for each factor from the experiment is compared with the values from existing tables which are generated for different levels of 'confidence'. If the F- value of the experimental factor is much larger than that of the standard value, in the F examination, then this factor bears an important effect in the experiment. Signal to Noise (S/N) ratio is a performance measure designed by Taguchi and it selects the factor levels that maximize this ratio. The term signal represents the quality characteristic while noise is a measure of the variability (as measured by the variance) of the characteristics. The S/N equation depends on the criterion for the quality characteristics to be optimized. There are three forms of S/N ratios, smallest -is - best, nominal- is - best and highest-is - best quality characteristics, which are generally applicable in contamination, strength and dimension, respectively.

1. Lowest -is-best

$$S/N = \frac{-10\log(\sum_{i=1}^{n} y_{i,n})}{n} \quad (4)$$

n = number of tests in a trial

2. Nominal -is - best

$$S/N = -10\log V \text{ (variance only)} \quad (5)$$

3. Highest -is-best

$$S/N = \frac{-10\log(\sum_{i=1}^{n} 1/y_{i,n})}{n} \quad (6)$$

Whatever is the type of characteristic, the transformations are such that the S/N ratio is always interpreted in the same way, the larger the S/N ratio better the result.

3.0 Results and Discussion

3.1 Characterization of plantain and pineapple peels

FT-IR spectrum of plantain and pineapple peels were obtained in order to identify the functional groups like -OH, -CO, -CHO, N-H, - CONH, -C=C- and -COOH present in these peels that can be involved in bonding with 2,6-DCP during bioadsorption.. Table 3 shows the FT-IR spectrum elucidation of dried plantain and pineapple peels structure with a particle size of 1.68 mm.

Table 3: FT-IR spectrum elucidation of dried plantain peel and pineapple peel structure

Adsorbent	Absorption Peak Number (cm^{-1})	Suspected Functional Groups
Plantain peel	766.06	C-H (bend), C=C (out of plane)
	1033.95	C-O (alcohol), C-H (in plane), C=N (bend)
	1395.85	C-H (bend), C-O (alcohol), C-N, OH (carboxylic acid)
	1620.98	C-H (alkane), C=C, C=O (stretch)
	3445.71	C-H (stretch), OH (stretch), OH (non-bonding), N-H (stretch)
Pineapple peel		
	576	C-H (bend), C=C (out of plane)
	1053.00	C-O (alcohol), C-H (in plane), N-H (amine group)
	1395.85 - 1253.36	C-H (bend), C-O (alcohol), C-N, OH (carboxylic acid)
	1641.24	C-H (alkane), C=C, C=O (stretch)
	2925.71	C-H, CH_2 and CH_3 (alkane), COOH (carboxylic acid)
	3435.00	C-H (stretch), OH (stretch), OH (non-bonding), N-H (stretch)

For the plantain peel, the bands in the region of 3445.71 cm^{-1} were assigned to OH stretch (alcohol and carboxylic acid), OH non-bonding, those at 1620.98 cm^{-1} to C-H (alkane), C=C (aromatic) and C=O stretch and the bands appearing at 1395.85 cm^{-1} to C-H bend, C-O (alcohol), C-N, and OH (carboxylic acid). The absorption peaks (bands) at 1033.95 cm^{-1} were attributed to C-O (alcohol), C-H and C=N bend (nitriles). The weak band in the region of 776 cm^{-1} was assigned to C-H bend and C=C which are out of plane. For the pineapple peel, the bands in the region of 3435.00 cm^{-1} were assigned to OH stretch (alcohol and carboxylic acid), OH non-bonding, those at 2925.71 cm^{-1} to C-H, CH_2, CH_3 (alkanes) and COOH (carboxylic acid) and the bands appearing at 1641.24 cm^{-1} to C-H (alkane), C=C (aromatic) and C=O stretch. The absorption peaks (bands) at 1395.85-1253.36 cm^{-1} were attributed to C-H bend, C-O (alcohol), C-N, and OH (carboxylic acid) and that at 1053.00 cm^{-1} to C-O (alcohol), C-H and C=N bend (nitriles). The weak band in the region of 576 cm^{-1} was assigned to C-H bend and C=C which are out of plane. The FT-IR spectra showed that carboxyl, carbonyl and hydroxyl groups were very prominent functional groups on the surface of both the plantain and pineapple peels which could play major role in 2,6-DCP bioadsorption.

3.2 Taguchi's analysis of 2,6-DCP Bioadsorption

Nine different set of experiments were performed using the design factor combinations in the specified orthogonal array table. Three replicates were carried out for each of the factor combinations. The completed response table for these data appears in Table 4. In order to estimate the effect of factor A (pH of the solution) on the average value of response variable, sum of the average three observed response at level 1 of factor A was divided by 3 to obtain the average response at level 1 of factor A. The average responses at level 2 and 3 were obtained in a similar manner. The estimated effects are presented Table and shown graphically in Fig. 1.

Table 4. Estimated individual factor effects on percentage removal of 2,6-DCP by pineapple/plantain peels mixture

Factors	Levels		
	1	2	3
pH (A)	95.88	98.44*	95.16
Initial 2,6-DCP Concentration (B)	95.48	97.12*	96.88
Temperature (C)	95.92	96.58	96.98*
Plantain: Pineapple peels sorbent Ratio (D)	96.73	95.11	97.65*

*Optimum level

The estimated individual factor's effect on % removal of 2,6-DCP from aqueous solution is shown in Fig. 1.

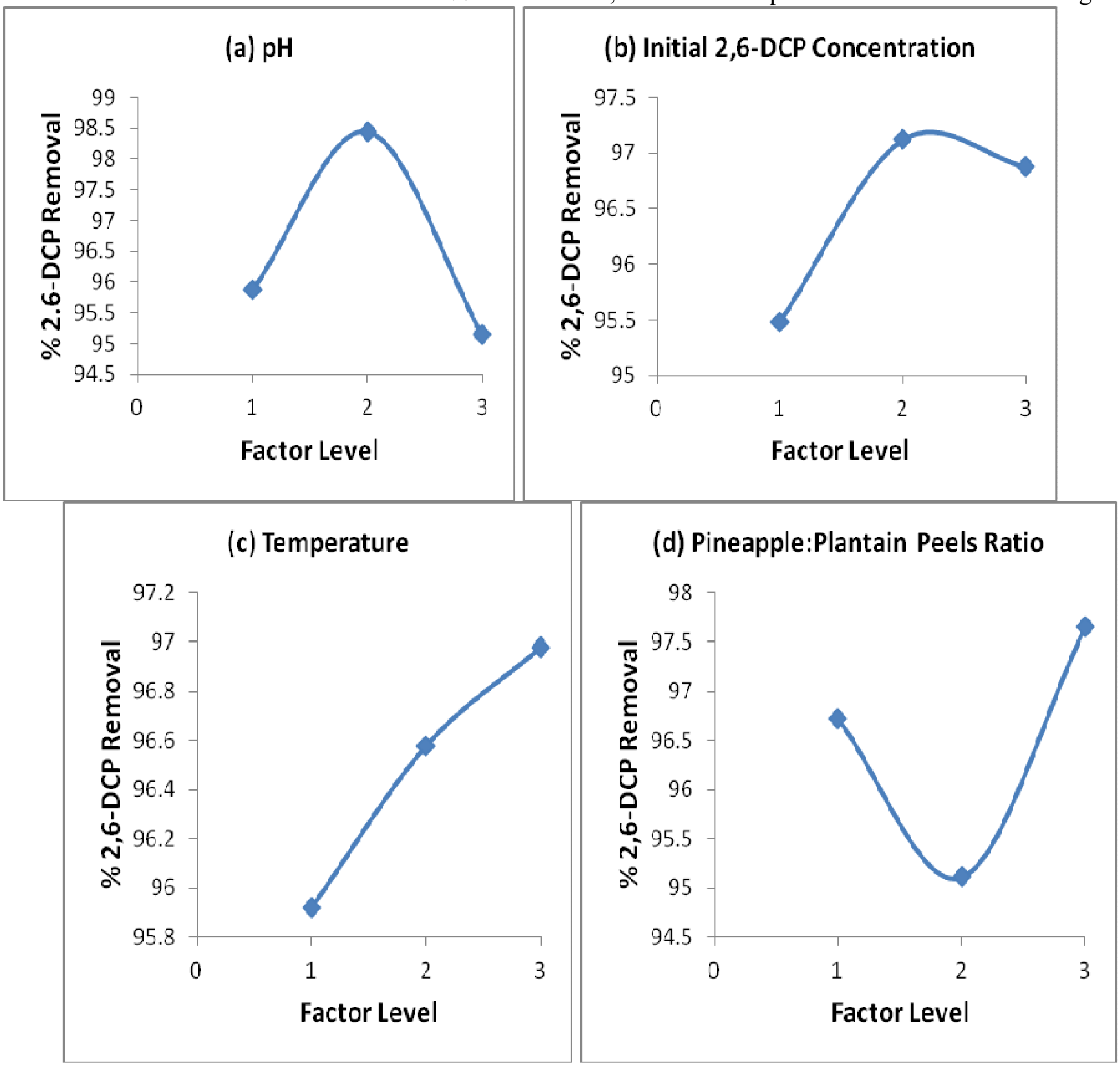

Fig. 1. Estimated individual factor effects at different factor level on percentage removal of 2,6-DCP by pineapple/plantain peels mixture (a) pH (b) Initial 2,6-DCP concentration (c) temperature (d) pineapple/plantain peels adsorbent ratio

Fig. 1(a) shows the effects of pH on the adsorption of 2,6-DCP by mixture of plantain and pineapple peels. pH of the solution is an important operational parameter that governs the adsorption process of organic chemicals or metals in solution. This is because it affects the solubility of the chemical ions concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of adsorbate during reaction (Agarry *et al.*, 2013b). At the range of pH 4 to 10, the % 2,6-DCP removal increased from 95.88% at pH 4 to 98.44% at pH 7 and decreased to 95.16% at pH 10. The seemingly high adsorption of 2,6-DCP at lower pH was due to high electrostatic attraction between the negatively charged 2,6-DCP molecules and positively charged adsorption sites. As the pH increased, there were fewer H+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated decreased 2,6-DCP removal due to electrostatic repulsion. The effects of initial 2,6-DCP concentration on its adsorption is shown in Fig. 1 (b). The percentage removal of 2,6-DCP generally increased with increase in the initial concentration of 2,6-DCP. However, the maximum percentage removal was obtained using 300 mg/L and above this value it decreased. This observation is in contrast to our earlier report (Agarry *et al.*, 2013) when modified plantain peels alone was used for 2,6-DCP adsorption from aqueous solution. This observation indicates that the rate of bioadsorption was high at moderate to high sorbate concentration which resulted in higher percentage removal of 2,6-DCP as compared to lower concentration. This may be due to decreased concentration gradient which acts as increased driving force to overcome the resistances to mass transfer of 2,6-DCP between the aqueous phase and the solid phase (Baek *et al.*, 2010; Agarry *et al.*, 2013). Fig. 1 (c) shows the effects of temperature on 2,6-DCP bioadsorption onto pineapple and plantain peels mixture. It could be observed that the percentage removal of 2,6-DCP from aqueous solution generally increased with increment of the solution temperature. This observation is in agreement with our earlier report (Agarry *et al.*, 2013) when modified plantain peels alone was used for 2,6-DCP adsorption from aqueous solution. This observation suggests that bioadsorption of 2,6-DCP onto pineapple/plantain peel mixture was an endothermic process.

The effects of pineapple/plantain peels adsorbent ratio on the bioadsorption of 2,6-DCP from aqueous solution is as shown in Fig. 1 (d). It is seen that the mixing ratio of pineapple and plantain peels affects the rate of 2,6-DCP bioadsorption. The pineapple/plantain peels adsorbent ratio of 2:1 (i.e. the mixture having a larger pineapple peels component) relatively elicited greater 2,6-DCP bioadsorption than those with 1:1 and 1:2 pineapple/plantain peels adsorbent ratio, respectively. However, the pineapple/plantain peels adsorbent ratio of 1:1 (i.e. equal mixture of pineapple and plantain peels) relatively performed better (with 96.73% 2,6-DCP removal) than pineapple/plantain peels adsorbent ratio of 1:2 (i.e. the mixture having a larger plantain peels component) having a 95.12% of 2,6-DCP removal. Table 3 suggests that the optimum condition for the maximum % of 2,6-DCP removal is the combination of A2B2C3D3 levels of the respective control factors. It is evident from Fig. 1 that pH (Factor A) has the greatest increasing effect on the % of removal rate.

3.3 ANOVA and Signal to Noise Ratio Analysis for Percentage Removal Rate of 2,6-DCP

The pH, initial concentration, temperature and plantain/pineapple adsorption ratio were studied for their effects on % removal of 2,6-DCP from aqueous solution. From Table 2 the ANOVA for % removal of 2,6-DCP and % contribution of each factor are found and are presented in Table 5. From Table 5, it is seen that the F-calculated value for pH, initial concentration, temperature and plantain/pineapple adsorption ratio time are infinity while the F-table value is 10.9, which indicates that all the factors studied have a significant effect on the % removal rate of 2,6-DCP. The percent contributions of the factors are shown in Table 5. Percent contribution indicates the relative power of a factor to reduce variation (Esme, 2009). For a factor with a high percent contribution, a small variation will have a great influence on the performance. According to Table 3, pH was found to be the major factor affecting the % removal rate of 2,6-DCP (52.23%), whereas pineapple: plantain peel adsorbent ratio was found to be the second ranking factor (29.09%) and relatively followed by initial 2,6-DCP concentration. The percent contribution of temperature is much lower, being 4.98%.

Table 5: ANOVA results for percentage removal of 2,6-DCP by pineapple/plantain peels mixture

Factor	SS	DF	MS	F-value	% Contribution
pH (A)	17.82	2	8.91	∞	52.23
Initial 2,6-DCP Concentration (B)	4.67	2	2.34	∞	13.70
Temperature (C)	1.70	2	0.85	∞	4.98
Pineapple: Plantain Peels Adsorbent Ratio (D)	9.92	2	4.96	∞	29.09
Error	0	0	0		
Total		8			

The effect of each factor on the S/N ratio at different levels can be separated out because the experimental design is orthogonal. It was found from Table 2 that the combination of the levels A 2, B 2, C 3, and D 1 gives higher % removal rate of 2,6-DCP than the levels A 1, B 3, C 3, D3 (Experiment 3) and A 2, B 3, C1, D 2 (Experiment 6). However, according to the mean Signal to Noise (S/N) ratio which has been determined for each level of the significant factors using the formula highest-is–best (Table 6), levels A 2, B 2, C 3, and D 3 are chosen as the optimum set of levels for the factors considered to maximize the percentage removal rate of 2,6-DCP. In order to verify the optimum process conditions selected, confirmatory experiments were performed.

Table 6: Mean S/N ratio (dB) response for the bioadsorption of 2,6-DCP by pineapple/plantain peels

Factors	Levels			Maximum – Minimum
	1	2	3	
pH (A)	11.62	11.70	11.60	0.10
Initial 2,6-DCP Concentration (B)	11.61	11.66	11.65	0.05
Temperature (C)	11.62	11.64	11.65	0.02
Plantain: Pineapple peels adsorbent Ratio (D)	11.65	11.60	11.67	0.07

Total mean (S/N) $\bar{\eta}$ = 34.92

Fig. 2 shows the S/N ratio plot where the dashed line is the value of the total mean of the S/N ratio.

Basically, the larger the S/N ratio, the better is the percentage removal rate.

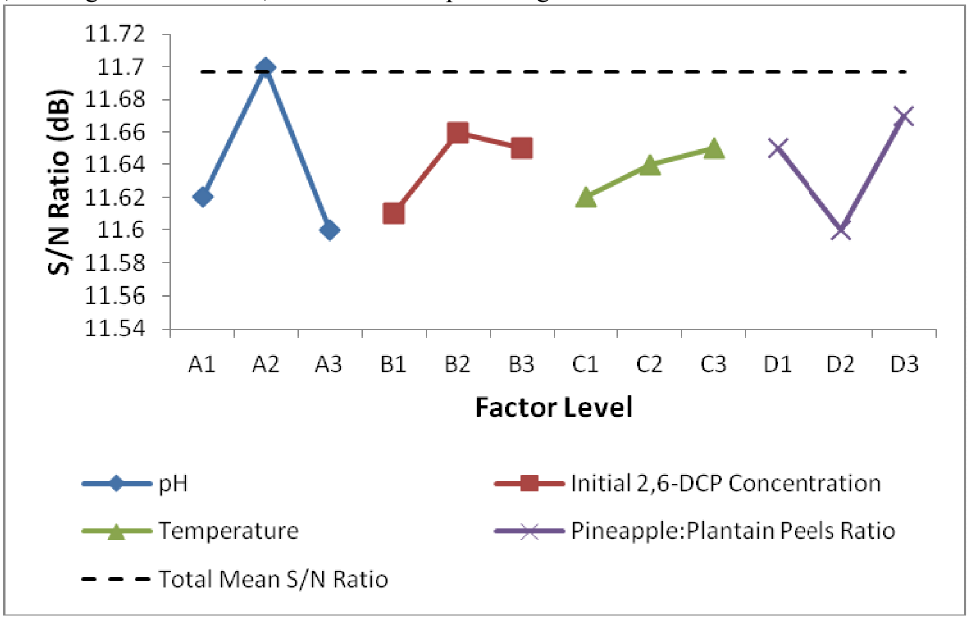

Fig. 2. S/N ratio plot for percentage removal of 2,6-DCP at different factor level

3.4. Confirmation Test

In this study, after determining the optimum conditions and predicting the response under these conditions, a new experiment was designed and conducted with the optimum levels of the factors considered. The result is presented in Table 7.

Table 7: Results of confirmation experiment

	Optimal Process Parameters	
	Experimental	Predicted
Level	A2B2C3D3	A2B2C3D2
% 2,6-DCP Removal	96.20	96.49
S/N (dB)	11.58	11.54

3.5 Bioadsorption isotherms

A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir and Freundlich isotherm models were used to describe the equilibrium data. The Langmuir isotherm model (Langmuir, 1918) was used to describe observed bioadsorption phenomena. The Langmuir model is as given in Eq. (7):

$$q_e = \frac{Q_{\max} a C_e}{1 + a C_e} \quad (7)$$

Where $Q_{\max}$ and a are isotherm constants. The $Q_{\max}$ and a can be determined from the linear plot of $1/q_e$ vs. $1/C_e$ as shown in Fig. 3(a).

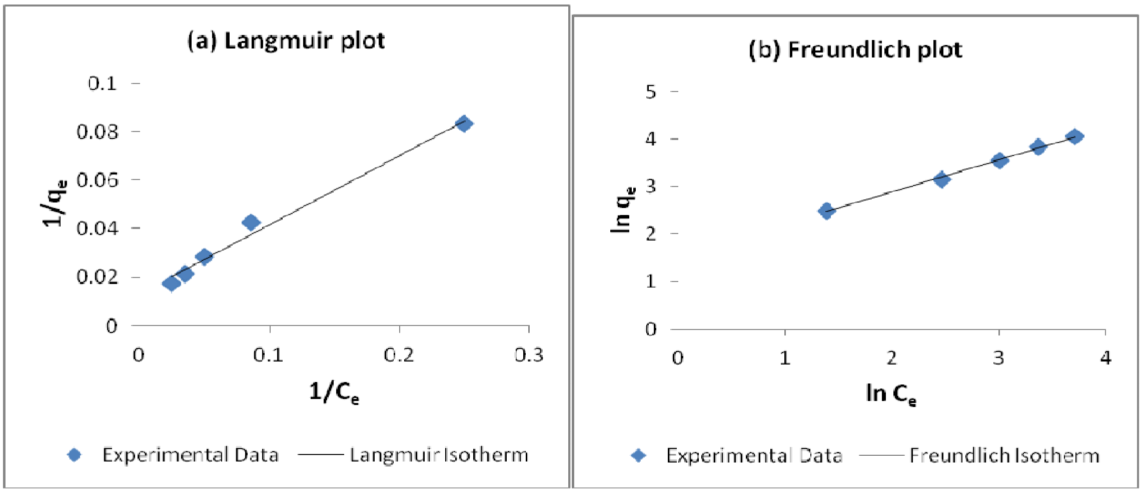

Fig. 3. Linear regression fitting of bioadsorption isotherms to the batch equilibrium data of 2,6-DCP bioadsorption by pineapple/plantain peels mixture (a) Langmuir isotherm (b) Freundlich isotherm

Langmuir equation is valid for monolayer sorption unto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface (Popuri *et al.*, 2007). The estimated constants from the linear plot of ($1/q_e$ vs. $1/C_e$) (Fig. 3a) are given in Table 8. It can be explained apparently that when a > 0, sorption system is favorable (Chen *et al.*, 2008). In this study, a is 0.0456 L/mg and the maximum monolayer bioadsorption capacity ($Q_{\max}$) was obtained to be 76.92 mg/g. Sathishkumar *et al.* (2009) obtained 17.94 mg/g as the maximum monolayer adsorption capacity of maize cob carbon for the adsorption of 2,4-DCP while Agarry *et al.* (2013) obtained 14.25 mg/g g as the maximum monolayer adsorption capacity of modified plantain peels for the adsorption of 2,6-DCP.

The Freundlich isotherm model (Freundlich, 1906) is given in Eq. (8):

$$q_e = K_f C_e^{1/n} \qquad (8)$$

Where K_f and n are Freundlich constants. K_f is roughly an indicator of the adsorption capacity (mg/g) and n is the adsorption intensity. The K_f and $1/n$ can be determined from the linear plot of $\log q_e$ vs. $\log C_e$ as shown in Fig. 3(b). The evaluated constants are given in Table 8.

Table 8: Bioadsorption isotherm parameters and correlation coefficients for the bioadsorption of 2, 6-dichlorophenol by pineapple/plantain peels mixture

Isotherm Models	Isotherm Constant Parameters		Correlation Coefficient
	Name	Value	R^2
Langmuir Isotherm	$q_{\max}$ (mg/g)	76.92	0.9870
	a (L/mg)	0.0456	
Freundlich Isotherm	K_f (mg/g)(L/mg)	4.58	0.9980
	$1/n$	0.68	

Generally, the tested isotherm models fitted well to the equilibrium bioadsorption experimental data with high correlation coefficient, however, the Freundlich isotherm model provided the best fit with a higher correlation coefficient ($R^2 = 0.9980$) to describe the bioadsorption process. A similar observation has been reported for the adsorption of 2,6-DCP onto modified plantain peels (Agarry *et al.*, 2013b), adsorption of 2, 4-DCP onto activated bamboo charcoal (Ma *et al.*, 2010) and the adsorption of 2,4,6-trichlorophenol (TCP) onto coir pith carbon (Namasivayam and Kavitha, 2004) and coconut shell carbon (Radhika and Palanivelu, 2006). In this study, K_f and $1/n$ were found to be 4.58 mg/g (L/mg) $^{1/n}$ and 1.47, respectively. Agarry *et al.* (2013b) obtained K_f and n of 2.79 and 3.03 for the adsorption of 2,6-DCP onto modified plantain peels. Achak *et al.* (2009) obtained K_f and n of 0.13 and 1.13 for the adsorption of phenolic compounds from olive mill wastewater onto banana peel; while Namasivayam and Kavitha (2004) and Radhika and Palanivelu (2006) correspondingly obtained a K_f : n value of 1.2: 0.7 and 2.05:1.5 for the adsorption of 2,4,6-TCP onto coir pith carbon and coconut shell activated carbon, respectively.

3.6 Bioadsorption kinetics modelling

In order to analyze the rate of bioadsorption and possible adsorption mechanism of 2, 6-DCP onto pineapple/plantain peel adsorbent mixture, the Lagergren pseudo first- order (Mckay and Ho, 1999), pseudo second-order (Ho and Mckay, 2000) and intraparticle diffusion (Weber and Morris, 1963) were applied to bioadsorption data.

The Lagergren pseudo first-order kinetic model equation (Mckay and Ho, 1999) is represented in an integral form as given in Eq. (9):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (9)$$

Where, q_e is the calculated maximum equilibrium biosorption capacity (mg/g) and k_1 is the biosorption rate constant (min^{-1}). The values of q_e and k_1 at different concentrations were calculated from the slope and intercept of the linear plots of $\ln(q_e - q_t)$ vs t (Fig. 4a).

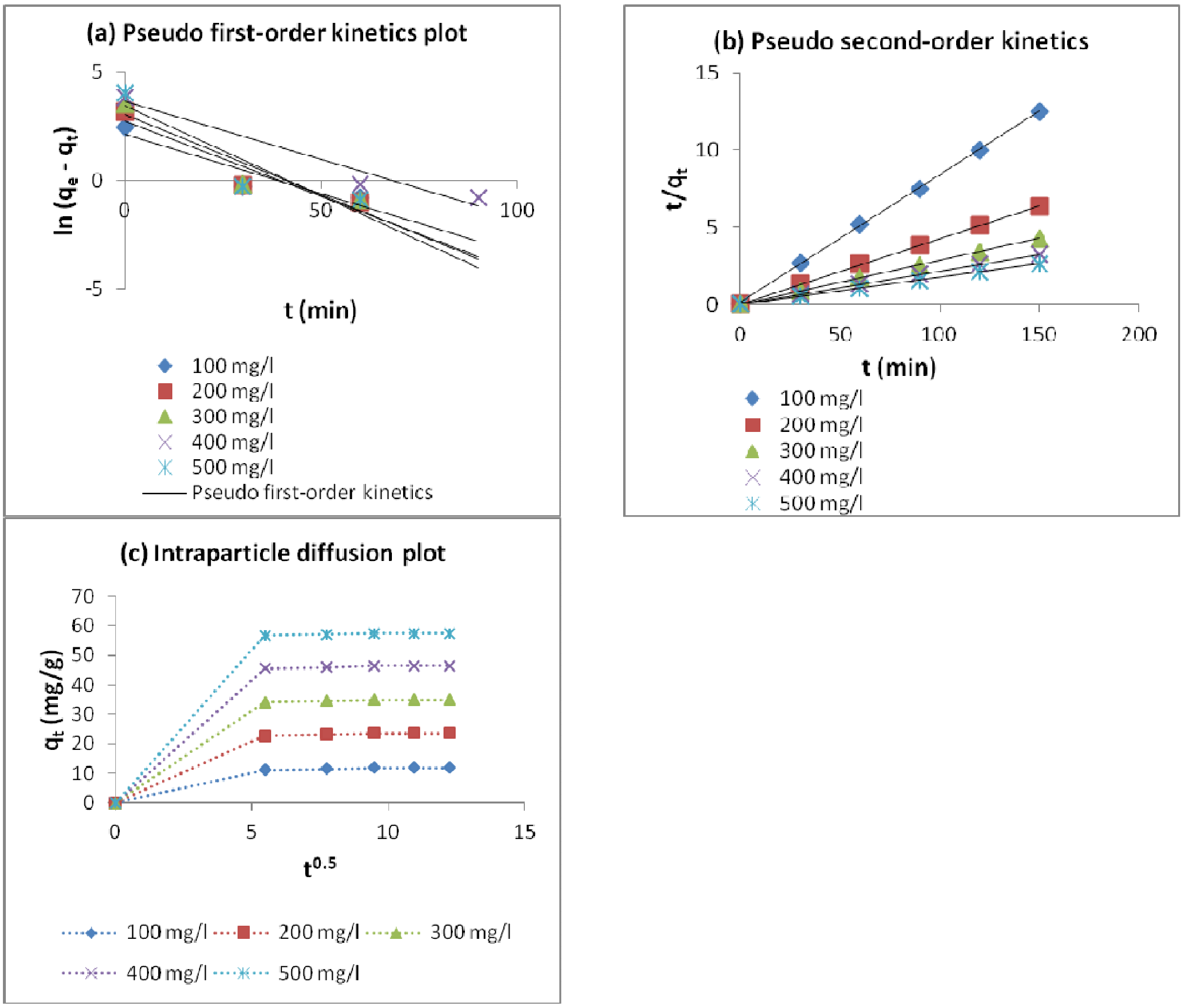

Fig. 4. Kinetic model fitted to the batch kinetic data of 2,6-DCP bioadsorption by pineapple/plantain peels mixture at different initial 2,6-DCP concentration (a) Pseudo first-order kinetics (b) Pseudo second-order kinetics, (c) Intraparticle diffusion

The respective values are given in Table 9. It is seen that the bioadsorption rate constant (k_1) generally increased with increased initial 2,6-DCP concentration.

The pseudo-second- order kinetic model which is based on the assumption that chemisorption is the rate-determining step and can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

Where k_2 is the rate constant of second order bioadsorption (g/mg/min). The initial bioadsorption rate, h (mg g^{-1} min^{-1}) is represented as in Eq. (11) (Sari *et al.*, 2010):

$$h = k_{ad_2} q_e^2 \qquad (11)$$

Values of k_2 and q_e were calculated from the plots of t/q_t vs. t (Fig. 4b) for different initial concentration. The respective constant values are given in Table 6. It is observed that the rate constant k_2 generally increase with increased initial 2,6-DCP concentration. Also, as evident from Table 9, the initial adsorption rate, h, increased with increase in initial 2,6-DCP concentration suggesting that bioadsorption of 2,6-DCP by pineapple/plantain peel adsorbent mixture was favorable at higher concentration. The increase in initial biosorption rate with increase in 2,6-DCP concentration may be due to increased concentration gradient which acts as increased driving force to overcome the resistances to mass transfer of 2,6-DCP between the aqueous phase and the solid phase (Baek *et al.*, 2010).

Table 9: Pseudo first-order, pseudo second-order and intraparticle diffusion kinetic parameters and correlation coefficients obtained for the bioadsorption of 2, 6-dichlorophenol by pineapple/plantain peels mixture

Kinetic Model		Initial concentration (mg/L)				
		100	200	300	400	500
Pseudo first-order	k_1	0.054	0.065	0.065	0.063	0.072
	q_e (theo.)	8.31	15.23	21.12	38.24	31.06
	q_e (exp)	12.00	23.54	34.97	46.39	57.40
	R^2	0.867	0.883	0.871	0.958	0.843
Pseudo second-order						
	k_2	0.059	0.065	0.065	0.063	0.072
	q_e (theo.)	12.20	23.81	35.71	47.62	58.82
	h	8.78	36.85	82.89	142.9	249.1
	R^2	0.999	0.999	1.000	1.000	1.000
Intraparticle diffusion						
	K_p	0.124	0.123	0.132	0.134	0.121
	C	10.60	22.17	33.49	44.89	56.05
	R^2	0.865	0.854	0.856	0.862	0.863

a= min^{-1}, b = mg/g, c = g/(mg.min), d = mg $g^{-1}min^{-1}$, e = mg/g.min, f = g/mg

The intra particle diffusion kinetic model (Weber and Morris, 1963) can be written as presented in Eq. (12):

$$q_t = K_p t^{1/2} + C \qquad (12)$$

Where K_p is the intra particle diffusion rate constant (mg/g $min^{-½}$) and C is the intercept. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. Intra particle diffusion is the sole rate-limiting step if the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin (Weber and Morris, 1963). In fact, the linear plots at each concentration (Fig. 4c) did not pass through the origin. This deviation from the origin is due to difference in the rate of mass transfer in the initial and final stages of the bioadsorption. This indicated the existence of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step. The calculated diffusion coefficient K_p values are listed in Table 9. The K_p values shows no trend with increase in initial 2,6-DCP concentration.

Generally, all the tested bioadsorption kinetic models fitted well to the bioadsorption kinetic data with high correlation coefficient at different initial 2,6-DCP concentration, however, the pseudo second-order kinetic model gave the best fit with higher correlation coefficient to describe the bioadsorption behaviour of 2,6-DCP onto pineapple/plantain peels adsorbent mixture. Similar observations have been reported for the adsorption of chlorophenols onto other single adsorbents (Wang *et al.*, 2011; Agarry *et al.*, 2013).

4. Conclusions

In this study, pineapple/plantain peel adsorbent mixture was tested and evaluated as a possible bioadsorbent for removal of 2,6-DCP from its aqueous solution using batch bioadsorption technique. The Taguchi method was applied to investigate the effects of pH, initial 2,6-DCP concentration, temperature and pineapple/plantain peels adsorbent ratio on percentage removal of 2,6-DCP by pineapple/plantain peels adsorbent mixture. The level of importance of the factors considered was determined using ANOVA. Based on the ANOVA method, it was found that all the four factors, pH, initial 2,6-DCP concentration, temperature and pineapple/plantain peels adsorbent ratio have profound influence on the percentage removal of 2,6-DCP from aqueous solution. The solution pH is the major factor that affects the percentage (%) removal of 2,6-DCP with its % contribution of 52.23% and is relatively followed by pineapple/plantain peels adsorbent ratio (29.09%) and initial 2,6-DCP concentration (13.70%). An optimum parameter combination for the maximum percentage removal of 2,6-DCP was obtained by using the analysis of signal-to-noise (S/N) ratio. The optimum test condition at which the maximum percentage removal of 2,6-DCP was obtained has been determined to be A2B2C3D3 levels. The experimental results confirmed the validity of the used Taguchi method for optimizing the parameters in bioadsorption operations. Bioadsorption equilibrium data fitted very well to both the Langmuir and Freundlich isotherm equation. Nevertheless, Freundlich isotherm equation gave the best fit, confirming the non-ideal heterogeneous adsorption capacity of 2,6-DCP onto pineapple/plantain peel adsorbent mixture with a bioadsorption capacity (K_f) of 4.58 mg/g and bioadsorption intensity ($1/n$) of 0.68 at 30°C. The maximum monolayer bioadsorption capacity ($Q_{\max}$) was found to be 76.92 mg/g. The bioadsorption kinetics followed pseudo-second-order kinetic model with a very good correlation coefficient. Intra-particle diffusion was not the sole rate controlling factor.

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