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Modeling of the continuous copper and zinc removal by sorption onto sodium hydroxide-modified oil palm frond in a fixed-bed column

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ABSTRACT

In this study, the sorption of Cu and Zn onto NaOH-treated oil palm frond (OPF) in a fixed-bed up flow column operated in continuous mode at hydraulic retention times (HRTs) of 6, 12 and 18 min was investigated. The column was operated at room temperature and fed with 100 mg/l of heavy metal solution. The data confirmed high ability of sorption in continuous mode (>90% removal) and breakthrough occurred after 216 min. The whole continuous sorption process was simulated using an empirical model and the parameters were estimated. The fitting of experimental data to different models such as Adams-Bohart, Wolborska, Thomas and Yoon and Nelson Models was also tested for comparison. The best fitting was generally obtained with Adams-Bohart model which showed high degree of fitting within this HRT range. The software used the experimental data to fit a model to simulate the behaviour of the continuous system and was based on the concentration of the effluent and time as the main variables. A high accuracy ($R^2 > 0.96$) was achieved and the model was modified to be used for the heavy metal sorption system.

1. Introduction

Due to its special physical and chemical properties, water is consumed in many industries and has consequently been polluted with different pollutants, depending on the industrial process involved [1]. Heavy metals can be introduced into the water by various industries. The heavy metal-containing water is one of the most toxic industrial wastes. Nowadays, with the exponential increase in population, the measure towards controlling heavy metal emissions into the environment is essential. This is best done right at the source of such emissions, before toxic metals even enter the complex ecosystem [2].

Cu, which is widely used in wire, other electrical conductors, metal plating, alloys and coins can cause muscle ache, hemolytic and heart failure. Meanwhile, Zn that is widely used in alloy, galvanized metal, fluorescence components, paint pigments, sunscreens, fast-setting dental cements, deodorants, embalming and fireproofing lumber, can cause mucous membrane damage, diarrhea and dizziness [3]. Thus it is necessary to remove these heavy metals from wastewater before they can be safely discharged into the sewage system or into the aquatic environment.

There are several existing methods for heavy metal removal from wastewater. The most widely used methods are 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 [4–8]. However, most of these methods are often ineffective, uneconomical or very technically complicated, especially when the heavy metal concentration is in the range of 10–100 mg/l [9]. On that basis, efforts for finding an economical way for the removal of heavy metals from low concentration liquid streams should be intensified.

Continuous sorption processes behave in much the same way as ion exchange process in its operation [10]. When wastewater is introduced at the top of a clean bed of sorbent, most solute removal initially occurs in a rather narrow band at the top of the column, referred as the sorption zone. The performance of packed beds sorption process is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of a sorption column. The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration and flow rate. The breakthrough curve would be a step function for favorable separations, i.e., there would be an instantaneous jump in the effluent concentration from zero to the feed concentration once the column capacity is reached [11,12].

Oil palm industry is known to produce abundance supply of biomass of different types and the possible utilization of those

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Nomenclature

A	sorption rate (mg/g min)
b	constant term (mg^{-1})
C	effluent heavy metal concentration (mg/l)
C_0	inlet or initial heavy metal concentration (mg/l)
C_1	first outlet concentration at the steady-state condition (mg/l)
C_b	bulk heavy metal concentration in the column (mg/l)
D	axial diffusion or dispersion coefficient (cm^2/min)
k_{AB}	kinetic constant in Adams-Bohart model ((mg min)$^{-1}$)
k_{Th}	kinetic constant in Thomas model (ml/mg min)
k_{YN}	kinetic constant in the Yoon–Nelson model (min^{-1})
m	weight of sorbent (mg or g)
N_0	saturation concentration in the Adams-Bohart model (mg/l)
q	heavy metal concentration in the column at any time (mg/l)
q_0	maximum solid-phase concentration of the solute (mg/g)
Q	flow rate (ml/min)
R^2	coefficient of determination
t	time (min or h)
t_{total}	total flow time (min)
U_0	superficial velocity (cm/min)
V_{eff}	effluent volume (ml)
x	constant term
X	amount of material sorbed (mg or g)
Z	height of the column (cm)
Greek letters	
β_0	external mass transfer coefficient
β_a	kinetic coefficient of the external mass transfer in the wolborska model (min^{-1})
τ	time required for 50% adsorbate breakthrough (min)
ν	migration rate (cm/min)

biomasses is an active research area. However, until recently, literature reports on the use of oil palm biomasses as a sorbent material for Zn and Cu in continuous mode are hardly found. In the meantime, other types of biomass have been intensively investigated for this application. Copper removal using *Turbinaria ornata* in column was successfully demonstrated by Vijayaraghavan et al. [13]. Aksu et al. [14] investigated copper removal on Ca-alginate, agarose and immobilized *C. vulgaris* in a continuous packed-bed column fed with various flow rates and inlet metal ion concentrations [14]. Lower Cu removals and early saturation were reported at higher flow rates. Al-Asheh et al. [15] reported the use of spent animal bones in a packed-bed column for sorption of Cu.

The continuous sorption process was essential to study its characteristics behaviour of such process in a real heavy metal sorption application. The results obtained from batch studies were useful in providing information on the validity and effectiveness of the heavy metal sorption on NaOH pre-treated OPF [16]. Although data from batch studies were tried to be applied to a continuous sorption process, only certain parameters were able to be carried out with the present experimental setup. For Zn and Cu, the pH of the sorption was set at the optimum pH value of 5.5 and 4.5, respectively, at a room temperature of 25 °C. The initial concentration of the biomass was set at 100 mg/l. The experimental data were fitted to several models to estimate the parameters and subsequently the accuracy of these models to fit the experimental data.

2. Material and methods

2.1. Preparation of sorbent material

The oil palm frond biomass (OPF) was collected from oil palm trees in Universiti Sains Malaysia. They were then ground with a blender (Epicson Eb-321) for 1 min. In this study, the uniformity of the quality of the OPF used was obtained by using the biomass of the same batch throughout the study. Besides, the duration of the grinding process was accurately set at 1 min and the same equipment was used for this purpose. Thus, it was expected that the OPF sorbent to be of uniform quality and characteristics. As a rough measurement, the blended OPF particles were in the range of 4–6 mm in length. It was then washed thoroughly with distilled water in order to clean it and subsequently oven-dried at 70 °C for 12 h to reach constant weight. The purpose of the washing step was to remove any silt and dirt on the OPF sorbent as their presence could affect the sorption process. Basically, other water soluble substances on the surface could be removed as well. After the NaOH modification process, the sorbent was washed for at least three times and the pH of the wash water was determined.

2.2. Modification of the sorbents

Generally, oil palm frond (OPF) has fair affinity towards heavy metal sorption. However, it has been modified with NaOH treatment to further improve its heavy metal sorption capacity [16,17]. However, these works merely focused on the batch sorption process of Cu and Zn. Therefore, it is of great interest to further extend the work to continuous treatment process which is generally used in the actual operation of the heavy metal removal processes.

The chemical modification of OPF was performed by using 250 ml 0.1 M sodium hydroxide (NaOH) to treat 2.5 g of the biomass in a conical flask at room temperature (25 °C). The biomass was then dried for 12 h in an oven of 70 °C and the dried biomass were stored in airtight storage containers for later use. The treatment was made because of low ability of adsorption by the fresh OPF [18] and an optimization using Design Experts Software by response surface methodology (RSM) was carried out for the optimization of the treatment conditions [16].

2.3. Continuous sorption study

2.3.1. Stock solutions

The stock solution for Zn and Cu were prepared at a concentration of 100 mg/l by dissolving the desired quantity of zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$) and copper nitrate ($Cu(NO_3)_2\cdot 3H_2O$) in deionized water as used by Nasernejad et al. [19]. For other concentrations, the stock solutions were diluted with deionized water to obtain the concentration needed. The salts were of analytical grade.

In this study, nitrate salts of Cu and Zn were used based on the fact that they show complete dissociation at pH 4.5 and 5.5 which were determined earlier as the optimum value for Cu and Zn sorption, respectively [16]. Other possible salts such as acetate and chloride could subject to incomplete dissolution or having significant effect on the solution pH that lead to erroneous results. However, despite having the ability to influence the result, the effect of solution pH was not studied in the present work as particular focus was given on the fitting of experimental data to various models when the system was operated at three different hydraulic retention times (HRTs).

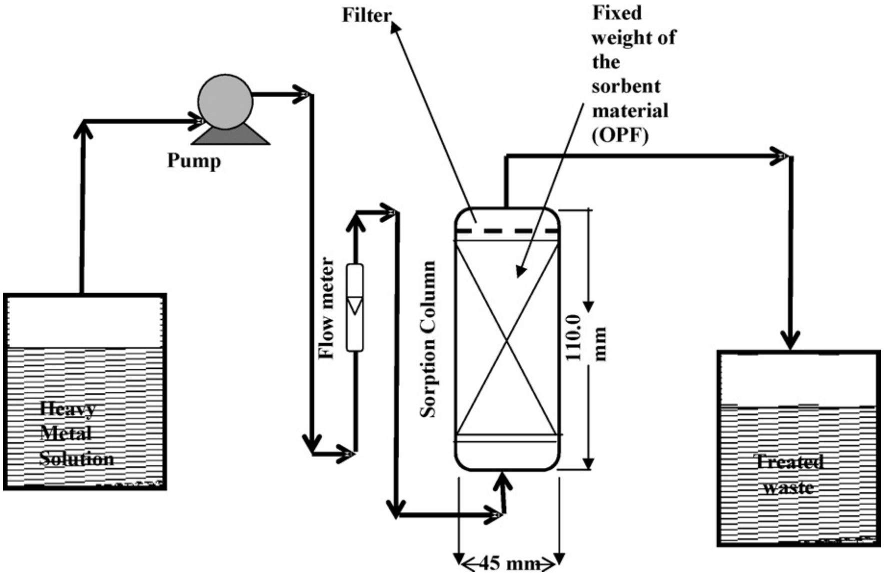

Fig. 1. Experimental setup for continuous sorption study.

2.3.2. *Experimental setup*

Fig. 1 shows schematic diagram of the setup for the continuous sorption study. The study was carried out in a perspex up-flow column with an inner diameter of 45.0 mm and a height of 110.0 mm and filled with a fixed weight 20 g of OPF pre-treated with NaOH. A pump was used in order to pump the stock solution of Zn and Cu at a concentration of 100 mg/l into the column. The flow rate of the inlet was controlled using a flow meter.

2.3.3. *Continuous sorption process conditions*

The samples obtained at a hydraulic retention time of 6, 12 and 18 min were analyzed for heavy metal concentration. The initial concentration, pH, temperature and bed depth were fixed during the experiments. The experimental runs were carried out at 25 °C and the optimum pH of 5.5 and 4.5 for Zn and Cu, respectively. The feed metal concentration was 100 mg/l for both metals. This concentration was found in our earlier work to be the most suitable to enable the breakthrough curves to be obtained within a reasonable length of process time with the amount of sorbent used (20 g). This concentration also well within the normal range of heavy metal concentrations encountered in heavy metal removal units of many industrial wastewaters.

The outlet sample was analyzed for the heavy metal concentration every 6 min. All the outlet samples were passed through a Whatman filter paper (110 mm) in order to remove any suspended solid before being tested for heavy metal concentration. In this study, the concentration measurements were performed in triplicate and the average values are shown in the figures. In the breakthrough analysis, particular focus was given on the overall trends of the breakthrough curves and not on the accuracy of individual data points. However, the degree of fitting was also evaluated on the basis of the R^2 values.

In this study, the Cu and Zn solutions were prepared using distilled deionized water while the sorbent material was cleaned thoroughly before treatment with NaOH and used for the sorption study. Therefore, the initial microbial population in the sorption system was very small to cause significant effect on the result. Furthermore, the sorption process was performed for up to only 330 min, during which significant growth of microbial population was not likely considering the absence of essential nutrients for the growth in the solution. A blank run without the sorbent was also carried out in this study to the confirmation of the absence of heavy metal removal mechanisms other than the sorption process. During the sorption process, a COD test was also conducted on the effluent to confirm the absence of water soluble organics.

2.3.4. *Heavy metal measurements*

The Zn concentration in the aqueous solution was measured using a zinc meter (HANNA, model HI93731), while that of Cu was measured using a copper meter (HANNA, model HI93702). A pH-meter (WTW, pH330i 2A2O-1012) was used to measure the pH of the solution while the COD test was performed using spectrophotometer (CICIL brand CE1010) following Standard Method no. 5220 D (close reflux, colorimetric method). The determination of Cu and Zn using their respective meters is a rapid method, yet providing sufficiently accurate measurements. In fact, the results have been compared with those obtained using atomic absorption spectrometer and the deviation was found to be only less than 1%.

2.4. *Modeling of continuous sorption process*

Suitable suggested models for heavy metal sorption including Adams-Bohart, Wolborska, Thomas and Yool–Nelson models were employed in order to predict the sorption behaviour. These models were linearized with the experimental data obtained from the continuous studies at different HRTs. In order to predict the behaviour of the existing system, the data were also fit to a mathematical model using SigmaPlot 2000 version 6.0 software and all the model parameters were estimated. This model was based on the concentration of the effluent and time, and properly modified to be used as a prediction model for the process.

3. Results and discussion

3.1. *Effects of flow rate*

The column studies were carried out at three different flow rates viz. 24.7, 12.3 and 8.2 ml/min to achieve corresponding retention times of 6, 12 and 18 min, respectively. At steady-state conditions, the highest amount of sorption was observed as shown as initial flat lines in Figs. 2 and 3 for both Zn and Cu removals. The highest

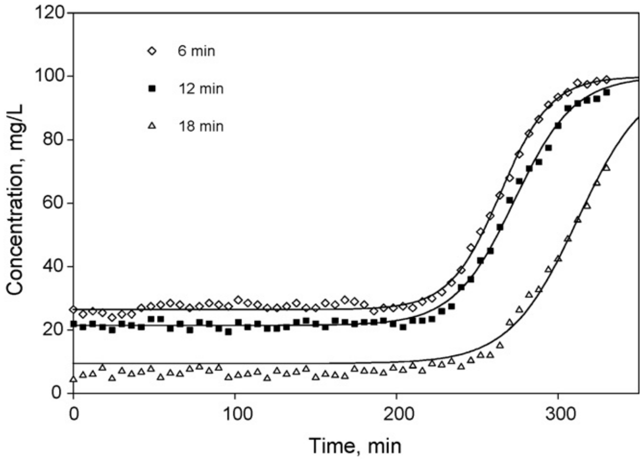

Fig. 2. Experimental data from Zn removal using NaOH-treated OPF fitted with the model at various HRTs.

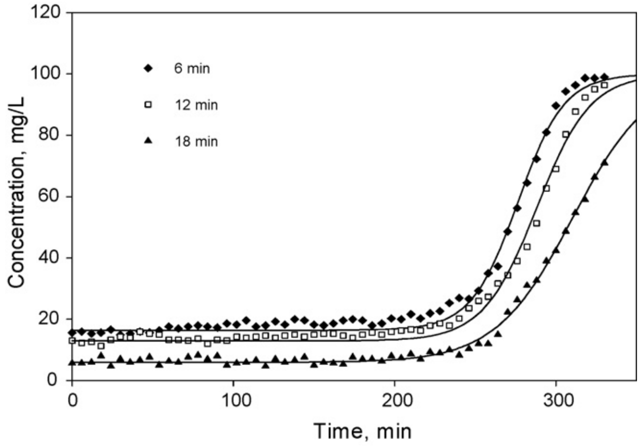

Fig. 3. Experimental data from Cu removal using NaOH-treated OPF fitted with the model at various HRTs.

amount of uptake for different HRTs and the saturation time are tabulated in Table 1.

With an increase in the HRT, the amount sorbed also showed a corresponding increases. This observation was attributed to the higher contact time between the sorbent material and the solution so that the heavy metals had more opportunity to sorb on the biomass. Higher removal was observed in Cu removal compared to that of Zn removal. This observation was in agreement with the results for batch studies in which the OPF showed a better ability of sorption for Cu (91%) compared to Zn (80.5%) [16].

Figs. 2 and 3 also show that after a certain contact time of around 250 min, the breakthrough occurred where the amount of sorption decreased sharply, attributed to the partial saturation of heavy metal binding sites in the biomass. Corresponding increase in the saturation time was observed when the HRT of the system was increased (by decreasing the flow rate). The effluent concentration continued to increase until a complete saturation where the process was said to have reached its equilibrium. A comparison between different HRTs showed that when the HRT increased, a higher sorption was achieved. This observation was mainly due to longer contact time between heavy metals in the solution and the binding sites in the biomass. This observation was in agreement with that reported by other researchers [13,14]. This conclusion was valid for both Zn and Cu sorption processes as they showed similar behaviour under the same experimental conditions. Complete removal was not achieved with this system and this was attributed to an incomplete contact between metal ions and metal binding sites in the sorbent due to high flow rate. This was supported by the figures that generally show higher uptake rate at lower flow rates (or higher HRTs).

Table 1
The highest Zn and Cu removals, saturation time and sorption rate for the continuous sorption study at different HRTs

Heavy metal	HRT (min)	Highest removal (%)	Saturation time (min)	Removal rate at time = 0
Zn	6	73.5	216	90.77
	12	78.5	240	47.97
	18	91	258	37.11
Cu	6	83.5	252	104.15
	12	87	264	53.51
	18	94	270	38.68

During the initial stage of the sorption process, active metal binding sites were abundantly available to cause immediate capture of Cu and Zn ions. At the breakthrough, partial saturation of the binding sites occurred and the extent which was clearly governed by the HRT of the system. However, it should be noted that the system was yet to reach its equilibrium at this particular stage as active net sorption process still took place. By increasing the HRT, corresponding increase in the contact time between the sorbent and the sorbate increased. Consequently, the metal ions could have better opportunity to diffuse to the active sites within the sorbent which were not easily reached. This led to the better sorption efficiency and correspondingly better later saturation time of the system. However, with this desired effect could be offset by the external transfer rate of the metal ions to the binding sites. Therefore, the saturation times occurred within a narrow range of about 40 or 20 min for Cu and Zn, respectively.

As evident in Table 1, the saturation time increased with an increase in the HRT. This was because when the flow rate was higher, the time (or opportunity) for the contact between the binding sites and heavy metals decreased. Also, weak attachment between the metal and the binding sites in the biomass could detach at high flow rate. The biomass took longer time to saturate for Cu removal than in Zn removal while showing better removal compared to Zn. This was in agreement with the result of the batch studies where a better capacity for Cu was observed by the NaOH-treated OPF.

3.2. *Empirical model for simulation of sorption process*

In order to predict the behaviour of the continuous sorption process, the data were fitted to a mathematical model using SigmaPlot 2000 version 6.0 software. The software used the experimental data to fit a model to simulate the behaviour of the continuous system. This model was based on the concentration of the effluent and time as the main variables and was modified to be used for the heavy metal sorption system. The model derived was a sigmoidal equation with four parameters. After deriving the parameters, Eq. (1) was obtained. In this model, the bed depth and biomass loading were fixed at 110.0 mm and 20 g, respectively. The steady-state condition was achieved at the time when the system reached its highest uptake:

$$C = C_1 + \frac{C_0 - C_1}{1 + e^{-(t-x/b)}} \tag{1}$$

where C is the concentration of the effluent (mg/l), C_0 the initial concentration (mg/l), C_1 the first outlet concentration at the steady-state (mg/l), t the time (min), x, b is the constants.

Table 2
Constants of the fitted equation and the correlation coefficients

Heavy metal	HRT (min)	C_0	C_1	x	b	R^2
Zn	6	100	26.5	264.5	15.61	0.9973
	12	100	21.5	273.0	18.63	0.9964
	18	100	9.5	312.1	21.08	0.9671
Cu	6	100	16.5	276.3	14.41	0.9922
	12	100	13	288.1	16.61	0.9898
	18	100	6	310.3	23.84	0.9939

The sorption rate was calculated by the following equation:

$$A = \frac{Q(C_0 - C)}{m} \tag{2}$$

where A stands for the sorption rate (mg/g min), Q is the inlet flow rate (l/min), while m represents the amount of the sorbent (g).

By including Eq. (1) in Eq. (2) instead of the concentration, the sorption rate at any time can be predicted by the following equation:

$$A = \frac{Q(C_0 - [C_1 + (C_0 - C_1)/(1 + \mathrm{e}^{-(t-x/b)})]}{m} \tag{3}$$

The sorption rate was calculated in order to estimate the characteristic of column such as flow rate, void volume, and biomass loading for later sorption column designs. This model showed a high fitting to the experimental data as shown in Figs. 2 and 3 for Zn and Cu sorption processes, respectively. The trends show a high degree of fitting with the experimental results with $R^2 \geq 0.96$. The constants of the equation and the definition coefficient are summarized in Table 2.

It is evident in Table 2 that the value of C_1 decreased with an increase in the retention time. This was attributed to the sufficient contact time between the binding sites of the biomass and the heavy metal [11]. The value of constant x increased with the increase in HRT. As this constant was related to the time in the equation, by evaluating the real obtained values from Table 2, this term could represent the saturation time of the biomass. This suggested that by an increase in HRT, the saturation time of the biomass also increased. The saturation time value for Cu was slightly higher than that of Zn, which was related to the higher desirability of Cu to be sorbed on the surface of the biomass.

3.3. Other suggested models for continuous sorption studies

The data obtained from the continuous sorption studies were also fitting with other models reported for continuous sorption process. These models include the Thomas, Adams-Bohart, Wolborska and Yoon–Nelson models. However, these models are suitable only for the breakthrough curve and not for the whole sorption process [10]. For simplicity the breakthrough curves were all plotted starting from the lowest obtained saturation time observed at 216 min for both Zn and Cu sorption process.

3.3.1. Adams-bohart and the wolborska models

The Adams-Bohart (or Wolborska) sorption model was applied to the experimental data in order to describe the breakthrough curve. The maximum sorption capacity (N_0, mg/l) and kinetic constant k_{AB} for the Adams-Bohart model and the kinetic coefficient of the external mass transfer (β_a) from Wolborska model were estimated through this breakthrough curve. The Adams-Bohart model is used for the description of the initial part of the breakthrough curve. The mass transfer rates obey the following equations:

$$\frac{\partial q}{\partial t} = -k_{AB} q C_b \tag{4}$$

$$\frac{\partial C_b}{\partial Z} = -\frac{k_{AB}}{U_0} q C_b \tag{5}$$

where k_{AB} is the kinetic constant (mg min)$^{-1}$, U_0 is the superficial velocity (cm/min), while q is heavy metal concentration in the solid-phase in the column at any time (mg/l), Z is the height of the column (cm). In the above equations t stands for the flow time (min), while, C_b is the bulk heavy metal concentration in the solution in the column (mg/l). By assuming that: (i) the concentration field is low, e.g. effluent concentration $C < 0.15C_0$, (ii) for $t \to \infty$, $q \to N_0$ (where N_0 is the saturation concentration) [10] the following equation is obtained (with parameters k_{AB} and N_0) when the differential equations are solved:

$$\ln\frac{C}{C_0} = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \tag{6}$$

where C_0 and C are the inlet and effluent heavy metal concentrations (mg/l), respectively. From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of $\ln C/C_0$ against t at a given bed height and flow rate [10,20].

A method of the fixed-bed adsorption on activated carbon was used in the removal of *p*-nitrophenol from water by Ref. [20]. The range of low concentrations of a breakthrough curve was analyzed. On the basis of a three-stage model of the process the equations describing the initial stage of the adsorption dynamics and concentration distribution in the bed at low concentrations of the breakthrough curve were derived. The equations were used to determine the effective kinetic coefficient and to evaluate the effect of axial diffusion on the process kinetics in Wolborska's study. A method for determination of the time for protective action of the sorbent layer was proposed [20].

The Wolborska model in the fixed-bed sorption is described by the following equations with some assumptions previously described by Wolborska [20]:

$$\ln\frac{C}{C_0} = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a Z}{U_0} \tag{7}$$

while

$$\beta_a = \frac{U_0^2}{2D}\left(\sqrt{1 + \frac{4\beta_0 D}{U_0^1}} - 1\right) \tag{8}$$

where β_0 is the *external* mass transfer coefficient with a negligible axial dispersion coefficient (D). It is also observed that in short beds or at high flow rates of solution through the bed, the axial diffusion is negligible and $\beta_a = \beta_0$. The migration velocity of the steady-state front satisfies the relation, known as Wicke's law [10,20]:

$$\nu = \frac{U_0 C_0}{N_0 + C_0} \tag{9}$$

The expression of the Wolborska solution is equivalent to the Adams–Bohart relation if the coefficient k_{AB} is equal to β_a/N_0.

Table 3
Estimated parameters values for Adams-Bohart and Wolborska models for the sorption process of Zn and Cu on NaOH-treated OPF

Heavy metal	HRT (min)	Adams-Bohart model		Wolborska model	R^2
		k_{AB} ((mg min)$^{-1}$)	N_0 (mg/l)	β_a (min^{-1})	
Zn	6	1.22×10^{-4}	5171.3	0.631	0.930
	12	1.39×10^{-4}	2652.2	0.369	0.949
	18	1.89×10^{-4}	1906.4	0.360	0.934
Cu	6	1.66×10^{-4}	5262.6	0.874	0.960
	12	1.78×10^{-4}	2705.2	0.482	0.982
	18	2.2×10^{-4}	1895.7	0.417	0.968

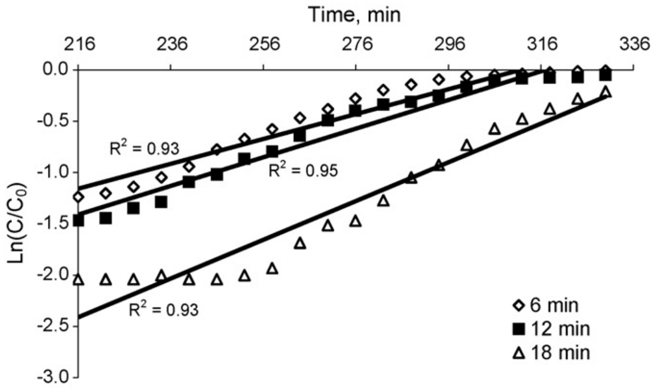

Fig. 4. Experimental and Adams-Bohart (or Wolborska) predicted values for the breakthrough in Zn removal by NaOH-treated OPF at different HRTs.

Therefore, the drawing of $\ln C/C_0$ vs. t would also give information on this model [20,21].

The Adams-Bohart and Wolborska models have been discussed under the same section due to the same linear relationship between them and also the direct relation between their constants. A linear relationship between $\ln(C/C_0)$ and time for varying flow rates were obtained using the experimental data. For all breakthrough curves, the R^2 values were found to be above 0.92. Respective values of N_0, k_{AB} and β_a calculated from the $\ln(C/C_0)$ vs. t plots for all flow rates are presented in Table 3 together with corresponding correlation coefficients. The values of the parameters were influenced by the changes in HRT. Adams-Bohart constant increased by the increase in the HRT while the other parameters showed different behaviour and decreased by increasing the retention time. This result showed that the overall system kinetics was dominated by external mass transfer in the initial part of sorption column [10] also found the same results with the sorption of phenol on activated sludge in a continuous packed bed treatment system.

The high accuracy of the Adams-Bohart (or Wolborska) model for both Cu and Zn sorption could be attributed to the incorporation of all critical parameters governing the sorption process, i.e., sorption capacity, external mass transfer coefficient, superficial velocity and kinetic constant. Impressive result using this model has also been reported for the continuous sorption of Cr(VI) onto chitin [22]. Although better fitting model was demonstrated by the Adams-Bohart (or Wolborska) model, the rest of the models (Yoon–Nelson and Thomas) are also capable of showing acceptable fitting. The R^2 and constants calculated for this model are shown in Table 3. Predicted and experimental breakthrough curves with respect to the HRT are shown in Figs. 4 and 5 for Zn and Cu, respectively.

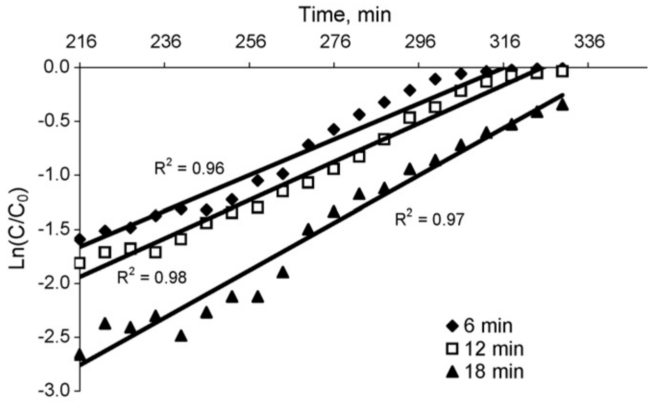

Fig. 5. Experimental and Adams-Bohart (or Wolborska) predicted values for the breakthrough in Cu removal by NaOH-treated OPF at different HRTs.

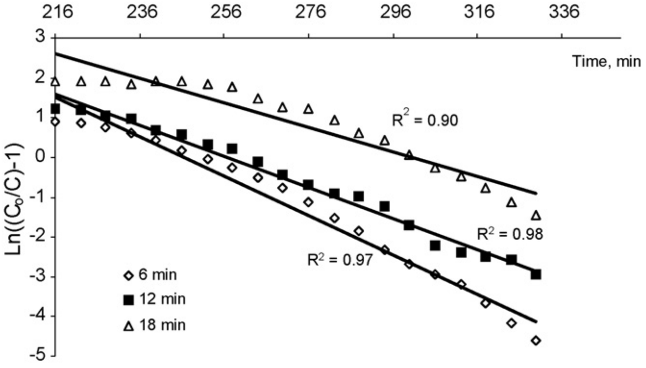

Fig. 6. Experimental and Thomas model predicted values for the breakthrough in Zn removal by NaOH-treated OPF at different HRTs.

3.3.2. *Thomas model*

Thomas model was used to fit the experimental data in order to determine the rate constant (k_{Th}) and also the maximum solid-phase concentration (q_0). Successful design of a column sorption process requires the prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum sorption capacity of a sorbent is also needed in design. Traditionally, the Thomas model is used to fulfill the purpose. The model is expressed as the following form:

$$\frac{C}{C_0} = \frac{1}{1 + \exp((k_{Th}/Q)(q_0 X - C_0 V_{eff}))} \tag{10}$$

where k_{Th} is the Thomas rate constant (ml/min mg) and q_0 is the maximum solid-phase concentration of the solute (mg/g). X stands for the amount of sorbent in the column (g), while V_{eff} is the effluent volume (ml). V_{eff} can be calculated by the following equation:

$$V_{eff} = Q t_{total} \tag{11}$$

where Q is flow rate (ml/min) and t_{total} stands for total flow time (min). This model was fitted to the C/C_0 ratios at the times above 216 min. A linear regression was used to determine the coefficients. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th} q_0 X}{Q} - \frac{k_{Th} C_0}{Q} V_{eff} \tag{12}$$

The kinetic coefficient k_{Th} and the sorption capacity of the bed q_0 can be determined from a plot of $\ln[(C_0/C) - 1]$ against t at a given flow rate. Figs. 6 and 7 exhibit the predicted and experimental data

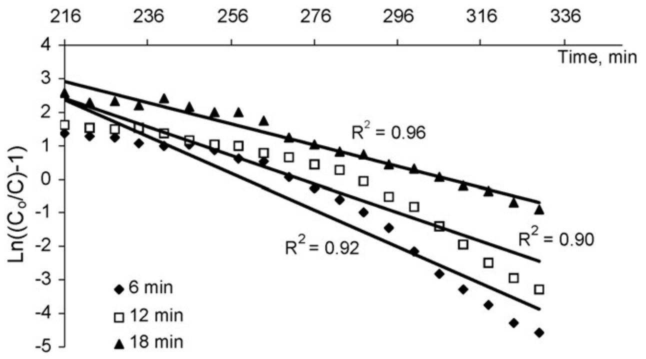

Fig. 7. Experimental and Thomas model predicted values for the breakthrough in Cu removal by NaOH-treated OPF at different HRTs.

Table 4
Estimated parameters values for Thomas model for the sorption process of Zn and Cu on NaOH-treated OPF

Heavy metal	HRT (min)	k_{Th} (ml/mg min)	q_0 (mg/g)	R^2
Zn	6	3.030	0.0203	0.9738
	12	1.241	0.194	0.9841
	18	0.757	0.0166	0.8979
Cu	6	3.580	0.0193	0.9092
	12	1.434	0.0184	0.8988
	18	0.797	0.0162	0.9633

for the Thomas linear fitting, $\ln[(C_0/C) - 1]$ vs. time, for both Zn and Cu removal processes. The trends show a fair fitting of experimental data and Thomas model for both Cu and Zn sorption process at various HRTs.

The regressed lines showed that they were all fitted with linear regression coefficients ranging from 0.8979 to 0.9841 (Table 4). The values of k_{Th} and q_0 calculated are also presented in the table. As the HRT increased, the values of k_{Th} and Q_0 decreased. The values obtained for k_{Th} in Cu removal with a negligible difference were larger than those in Zn removal. For q_0, the larger values were obtained in Zn removal at the same HRT.

Thomas model is more suitable for sorption processes where the external and internal diffusions are not the limiting step [10]. Although the Thomas model showed a high fit to the experimental data, a comparison between Thomas model and, Adams-Bohart and Wolborska models suggested that, Adams-Bohart and Wolborska model showed slightly better fitting.

3.3.3. Yoon and nelson model

Yoon and Nelson model is a simple theoretical model which was applied to investigate the breakthrough behaviour of Zn and Cu on NaOH pre-treated OPF. The Yoon and Nelson equation concerning a single component system is usually expressed as

$$\ln \frac{C}{C_0 - C} = k_{YN}t - \tau k_{YN} \qquad (13)$$

where k_{YN} is the rate constant (min^{-1}); τ the time required for 50% sorbate breakthrough (min), t is the breakthrough (sampling) time (min).

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k_{YN} and τ for the sorbate. By plotting the experimental data of $\ln C/(C_0 - C)$ vs. sampling time (t) according to Eq. (13). If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with slope of k_{YN} and intercept τk_{YN} [23,24].

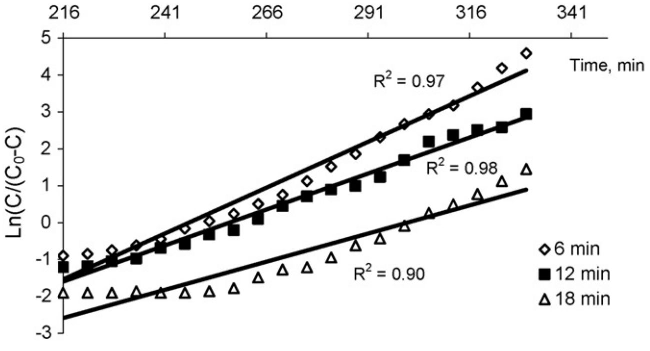

Fig. 8. Experimental and Yoon–Nelson model predicted values for the breakthrough in Zn removal by NaOH-treated OPF at different HRTs.

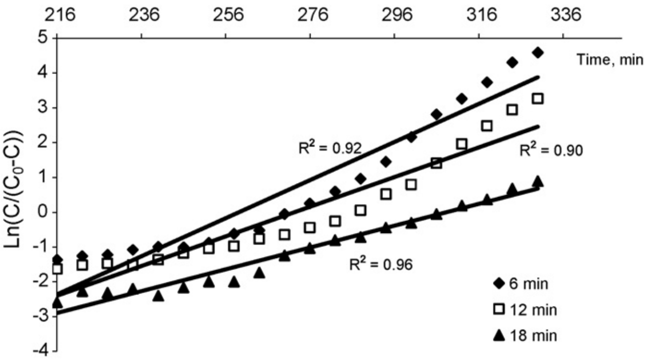

Fig. 9. Experimental and Yoon–Nelson model predicted values for the breakthrough in Cu removal by NaOH-treated OPF at different HRTs.

Table 5
Estimated parameters values for Yoon–Nelson model for the sorption process of Zn and Cu on NaOH-treated OPF.

Heavy metal	HRT (min)	k_{YN} (min^{-1})	τ (min)	R^2
Zn	6	0.0496	246.79	0.974
	12	0.0390	257.21	0.984
	18	0.0305	300.79	0.898
Cu	6	0.0559	258.78	0.909
	12	0.0426	272.04	0.899
	18	0.0313	308.75	0.963

By plotting $\ln(C/(C_0 - C))$ against time for various HRTs, the values of k_{YN} as a rate constant and τ as the time required for 50% sorbate breakthrough were determined. The theoretical curves were compared with the corresponding experimental data in Figs. 8 and 9 for Zn and Cu sorption processes, respectively. The figures show an acceptable fitting to the experimental data for all breakthrough curves. By comparing Figs. 8 and 9 with Figs. 6 and 7, respectively, it is observed that the graphs show exactly a mirror image of their corresponding figures. The values of the k_{YN} and τ and the respective correlation coefficient are listed in Table 5.

Data in Table 5 suggested that with the increase in HRT, the k_{YN} constant was found to decrease while the 50% breakthrough time increased. This observation was consistent with the behaviour of phenol sorption on immobilized activated sludge sorption [10]. The experimental data were close to those predicted by Yoon–Nelson Model according to the coefficient of determination.

4. Conclusions

In this study, several models were developed and tested for the accuracy and applicability in the simulation of the sorption process. Sufficient degree of accuracy has been demonstrated by these models. The advantage of these models is that it is able to simulate the sorption data before and after the breakthrough occurred. The main conclusions that can be made from this study are:

(1) The Adam-Bohart (or Wolborska), the Thomas and the Yool–Nelson models were successfully applied to the experimental data obtained from the continuous sorption studies performed to predict the breakthrough curves and to determine the sorption kinetic parameters.
(2) The best fitting model for the experimental data was obtained with the Adams-Bohart (or Wolborska) model and the results showed that the models were in a reasonably good agreement with the experimental data with reliable value of parameters.
(3) A new mathematical model was also established to accurately predict the sorption behaviour in a continuous system with the

determination coefficients of $\geq$0.96. The constants calculated from the models can be used for the scale up processes.

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