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Short Communication

Test of the Randomness of Residuals for the Pseudo-1st Order Kinetic Modelling of Adsorption of the Brominated Flame Retardant 4-bromodiphenyl Ether onto Biochar-immobilized *Sphingomonas* sp.

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ABSTRACT

Numerous papers fail to conduct statistical diagnostics of the nonlinear model that was used, and the data may be non-random, which is a need for all parametric statistical evaluation procedures that rely on random data. Whenever the diagnostic tests find that the residuals reflect a pattern, there is a range of treatments available, such as nonparametric analysis or transferring to a different model, which should resolve the issue. To ensure that randomization is satisfied, we conduct the Wald–Wolfowitz runs test statistical diagnosis tests. It was decided to conduct this study because it was necessary to assess the randomness of the residual for the pseudo-1st order kinetic model in the adsorption of the brominated flame retardant 4-bromodiphenyl ether onto biochar-immobilized *Sphingomonas* sp. was carried out using the Wald–Wolfowitz runs test. the number of runs was 15, and the predicted number of runs under the premise of randomness was 8.20, initially suggesting that the residual series had enough runs. The z-value indicates how many normal errors the number of runs discovered exceeds the anticipated number of runs, and the p-value indicates how severe this z-value is. The significance is the same as with the other data on p-values. The null hypothesis that the residuals are random can be rejected if the p-value is less than 0.05. However, because the p-value was smaller than 0.05, the null hypothesis was dismissed, implying that there is strong evidence of non-randomness of the residues and further remedy is needed.

INTRODUCTION

As a result of their fire-retardant properties, polybrominated diphenyl ethers (PBDEs) are commonly used in the industrial business. PBDEs are utilised as additives in several sectors, including plastics and textiles, where they are mixed with polymers to create a new product. Despite this, because they are not chemically bonded to the surfaces of plastics or textile goods, they have the potential to leach off the surfaces of these items and into the environment. PBDEs are widely dispersed in several environmental media, including soils, groundwater, groundwater sediments, and even the atmosphere, as a result of this discovery. A significant health danger to humans arises from the high lipotropy of polybrominated diphenyl ethers (PBDEs), which can biomagnify in food webs, providing a significant threat to human health. Furthermore, due to their aromatic structures and bromide substituent groups, some PBDEs are harmful to human health and the environment and remain in the environment [1–11]. It is necessary to treat industrial wastewaters before releasing them into the environment to protect human health and the environment from pollution caused by polybrominated diphenyl ethers (PBDEs). This is necessary to protect both human health and the environment from pollution caused by these compounds. Adsorption has been the most widely used method of pollutant removal from industrial wastewater in comparison to other existing treatment methods. This is owing to the various advantages it offers, such as its simplicity, high efficiency, and ease of application. One of the most major challenges in the field of adsorption is the selection of efficient and cost-effective adsorbents, and many different materials have been studied in prior research initiatives to solve this problem. At now, researchers are concentrating their attention on biochar (a type of charcoal created by biomass pyrolysis) as a possible low-cost adsorbent for sequestering pollutants and restricting the spread of contaminants [11–21].

With the capacity to restrict biological uptake, storage, and absorption of organic pollutants, biochar can reduce the threat to an ecosystem's well-being. Four brominated flame retardants (BFRs), such as 4-Bromophenyl phenyl ether (4-BE), have been used in a variety of consumer and commercial items for many years, including apparel and furniture. In recent years, they have risen to the rank of a top-priority environmental contaminant on a worldwide scale, and they have been found in the tissues of nearly everyone who has been examined thus far [22–29].In various areas of the world, the chemical 4-Bromophenyl phenyl ether has been discovered in raw drinking water, mineral water, and river water. The United States Environmental Protection Agency (USEPA) advises that the absolute maximum allowable level to preserve freshwater aquatic life be 6.2 ug/L to protect aquatic life in freshwater. When tested on the aquatic creature Daphnia magna (Water flea), it was discovered that the concentration that produces 50 per cent mortality (LC50) is 0.36 mg/L/48 hours at which the organism dies [30]. Research utilising activated sludge microorganisms revealed that it should not be decreased in any way; nevertheless, a second investigation under aerobic conditions revealed that it degrades at extremely low concentrations.

It is important to accurately assign the kinetics and isotherms of 4-BDE biosorption to have a complete understanding of the process of biosorption. This is especially true when it comes to the research of endocrine-disrupting substances. When linearization is used to smooth out a nonlinear curve, the error structure of the data is disturbed, as is the case in this example. As a result, evaluating the uncertainty of the kinetic parameters, which are often given as a 95 per cent confidence interval range, becomes more difficult. In addition, the linearization method leads to the introduction of error into the independent variable as a result of the linearization procedure [31–36]. Additionally, changes in the weights assigned to each data point can occur, which typically results in differences in the fitted parameter values between the linear and nonlinear versions of the kinetics model when compared to the linear version.

It is important, however, that the residuals of the curve be naturally distributed in nonlinear regression, as opposed to the typical least square's technique, which requires the residues to be normally distributed in linear regression. More significantly, the residuals must be random and have identical variance (homoscedastic distribution). The Wald–Wolfowitz runs test is used to determine whether or not randomization has been achieved [37] statistical diagnosis tests. The subject of this study is to test for the randomness of the residual for

MATERIALS AND METHODS

Residual data were acquired from a previously published work [38].

Residuals

Residuals are very important in assessing the health of a curve from a particular used model. Mathematically, residual for the i^{th} observation in a given data set can be defined as follows (**Eqn. 1**);

$$e_i = y_i - f\left(x_i; \hat{\beta}\right) \qquad \textbf{(Eqn. 1)}$$

where yi denotes the i^{th} response from a given data set while x_i is the vector of explanatory variables to each set at the i^{th} observation corresponding values in the data set.

Runs test

The runs test [39] was applied to the regression residuals to detect nonrandomness. In a given model, it is feasible to create an ordered variance of the curve that is either above or below the estimate. The run test contrasts a compound's typically negative and optimistic sequence of residues to determine if it is hazardous. A noteworthy result is often characterised by a shift or mixture of shifts or combinations of shifts between the negative and positive residual values. The greatest possible percentage is frequently used to denote the number of signs runs. The running test evaluates if a big number of sign passes are likely, or an insufficient number of sign passes are likely. A disproportionate number of run signs may suggest a negative serial relationship, but a disproportionate number of runs may indicate that residues are connected with the same sign or that systemic biases exist.

The test statistic is

H_0= the sequence was produced randomly
H_a= the sequence was not produced randomly

$$Z = \frac{R - \bar{R}}{sR} \qquad \textbf{(Eqn. 2)}$$

Where Z is the test statistic, $\bar{R}$ is the expected number of runs, R is the observed number of runs and sR is the standard deviation of the runs. The computation of the values of $\bar{R}$ and sR (n_1 is positive while n_2 is negative signs) is as follows;

$$\bar{R} = \frac{2n_1.n_2}{n_1+n_2} + 1 \qquad \textbf{(Eqn. 3)}$$

$$s^2R = \frac{2n_1.n_2\left(2n_1.n_2 - n_1 - n_2\right)}{\left(n_1+n_2\right)^2\left(n_1+n_2-1\right)} \qquad \textbf{(Eqn. 4)}$$

As an example
Test statistic: $Z = 3.0$
Significance level: $\alpha = 0.05$
Critical value (upper tail): $Z_{1-\alpha/2} = 1.96$
Critical region: Reject H_0 if $|Z| > 1.96$
If the test statistical value (Z) is greater than the critical value, then the dismissal of the null hypothesis at the significance stage of 0.05 implies that the sequence was generated in a non-random manner.

RESULTS AND DISCUSSION

From **Table 1**, the number of runs was 15, and the predicted number of runs under the premise of randomness was 8.20, initially suggesting that the residual series had enough runs. The z-value indicates how many normal errors the number of runs discovered exceeds the anticipated number of runs, and the p-value indicates how severe this z-value is. The significance is the same as with the other data on p-values. The null hypothesis that the residuals are random can be rejected if the p-value is less than 0.05. However, because the p-value was smaller than 0.05, the null hypothesis was dismissed, implying that there is strong evidence of non-randomness of the residues and further remedy is needed.

Table 1. Runs test data from the pseudo-1st order Kinetic modelling of adsorption of the brominated flame retardant 4-bromodiphenyl ether onto biochar-immobilized *Sphingomonas* sp.

Runs test	Residual data set
R=	5
n0=	6
n1=	9
n=	15
E(R)=	8.20
Var(R)=	3.19
StDev(R)=	1.79
Z=	-1.79
p-value=	0.037

The fitting of a mathematical model may be precisely diagnosed scientifically by using residual measurements. Residuals are the differences between a mathematical model's anticipated and actual quantity values. The main idea is that a poor model would show a bigger difference between predicted and actual values. The run technique is frequently used in time-series regression models to test for the presence of autocorrelation. Specifically, Monte Carlo simulation experiments have revealed that the run-time test causes strikingly asymmetrical error rates in the two tails, implying that the use of run-time autocorrelation research may not be stable and that the Durbin-Watson approach will be the preferred method for measuring autocorrelation [40].

Previous similar studies based on looking at the randomness of the residuals justify the method used in this study. For instance the use of the Baranyi-Roberts model in fitting an algae growth curve which shows adequacy in the statistics [41], the Buchanan-three-phase model used in fitting the growth of *Paracoccus* sp. SKG on acetonitrile [42], and *Moraxella* sp. B on monobromoacetic acid (MBA) [43]. The runs tests on the residuals for the Sips and Freundlich models for lead (II) absorption by alginate gel bead were found to be sufficient in biosorption [44]. There are other examples of the use of the runs test of residual in the literature in assessing the health of the nonlinear regression [45–49].

CONCLUSION

In this study, a test for the randomness of the residual for the data from the pseudo-1st order Kinetic modelling of adsorption of the brominated flame retardant 4-bromodiphenyl ether onto biochar-immobilized *Sphingomonas* sp. was carried out using the Wald–Wolfowitz runs test. The number of runs was 15, and the expected number of runs under the premise of randomness was 8.20, implying that the residual series had sufficient runs. The z-value represents how many normal mistakes were detected when the number of runs discovered exceeded the expected number of runs, and the p-value indicates how severe this z-value is. The significance is the same as with the other p-value data. If the p-value is less than 0.05, the null hypothesis that the residuals are truly random can be rejected. However, because the p-value was less than 0.05, the null hypothesis was rejected, suggesting that there is significant evidence of non-randomness of the residues and that more intervention is required such as the detection of potential outliers.

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