Modelling Metribuzin Removal Efficiency Through Adsorption Using Activated Carbon of Olive-waste Cake

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Abstract A simple mathematical model is developed for the prediction of Metribuzin removal efficiency through adsorption using activated carbon of olive-waste cake for any combination of input conditions. Based on earlier experimental results, factors from three independent variables (pH, initial Metribuzin concentration and adsorbent dose concentration) were incorporated in the model. All the factors are multiplied to derive a combined diminishing factor, which is multiplied with maximum achievable removal efficiency. It is found that although the model results are having good correlation (0.92) with the experimental results, those are slightly away from the ideal line. Through the introduction of an adjustment factor, model predictions are closely matching with the measured values having a correlation coefficient of 0.96. The primary model predicted results are having standard errors as RMSE = 6.34, MAE = 5.99 and RAE = 0.07, whereas the same error statistics of the adjusted model are 1.97, 1.71 and 0.01, respectively. Such modelling technique will predict removal efficiency for any combination of input parameters, which at times are required to be changed for other constraints.

1 Introduction

To maximise agricultural productions, different types of pesticides are being used, some of which might have adverse impacts on the environment. One of the effective herbicides in controlling the weed is metribuzin, which has been widely used during the last decade. This recalcitrant component can move and reach to the groundwater and can potentially contaminate the water storage (Honório et al., 2013). The destructive impacts of metribuzin on the environment has been reported by several researchers such as Yang et al. (2019), Ara et al. (2013), Cara et al. (2021), Mehdizadeh et al. (2019) and Kumar et al. (2017). Adsorption techniques have been in use for the removal of different pollutants from aqueous solutions (Alam & Anwar, 2020; Harmayani & Anwar, 2016; Khan & Imteaz, 2020; Khan & Imteaz, 2021). The deleterious implications of metribuzin have

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compelled the researchers to explore different adsorption methods for its removal such as using granular carbon (Kumar et al., 2017), mesoporous carbon (Cara et al., 2021) and corn cob (Ara et al., 2013). Some researchers investigated other techniques such as ozonation (Honório et al., 2013) and a PbO$_2$/WO$_3$ composite anode (Yang et al., 2019). Among the effective adsorbents, the olive-waste cake is a material that has been used in several studies for the removal of pollutants. The efficiency of olive-waste cake activated carbon in removing metribuzin from aqueous solution has been reported by Angin and Ilci (2021), Peña et al. (2016) and Pineiro et al. (2013). Which distinguishes olive-waste cake activated carbon from others is its low initial cost, efficiency, capacity and large-scale applicability (Angin & Ilci, 2021). More importantly, activated carbon materials are capable of adsorbing various organic compounds for a long time (Angin & Ilci, 2021).

Despite the successful performance of the adsorbents in removing metribuzin from aqueous solutions, it is undoubtedly a laborious effort, which are often time-consuming and costly. In addition, achieving good efficiency requires an optimum level of internal and external conditions (Honório et al., 2013), which confirms the challenge of the successful implementation of such a process. Therefore, to avoid predominantly higher costs of conducting experiments, researchers have been exploring alternate options with the aim of minimising experimental measurements. With the emerging techniques and tools, mathematical modelling has become a popular and cost-effective option for analysing efficient input parameters for any such treatment or production. Mathematical models can reduce the number of required measurements, which leads to reduced time and material use, and consequently the cost (Dąbek et al., 2020). Due to this fact, the application of mathematical models in the simulation of removal processes has been studied in a variety of investigations (Anusha & Murugadoss, 2014; Dąbek et al., 2020; Kitous et al., 2014; Sivaprakasam & Venugopal, 2019). Dąbek et al. (2020), in their study, has concluded that practical application of mathematical models will optimise the pollutant removal process and thus reduce the process costs. The high accuracy of a mathematical model in the prediction of methylene blue removal efficiency through adsorption has been reported by Imteaz et al. (2021). Anusha and

Murugadoss (2015) developed a mathematical model for simulating the adsorption of nickel and lead from wastewater. In the study of Sivaprakasam and Venugopal (2019), the performance of the developed mathematical model was overwhelming in predicting the removal efficiency with a high correlation coefficient. Kitous et al. (2014) presented a mathematical model for simulating the adsorption of metribuzin pesticides onto electro-activated granular carbon. The application of the PEARL model has been evaluated by Kolupaeva et al. (2006) for assessing the migration of metribuzin in soil.

The above-mentioned articles emphasise the need of using mathematical models as an appropriate and efficient tool, which in a cheaper way can replicate the situation associated with an intricate process such as pollutant removal (Imteaz et al., 2020; Imteaz et al., 2021). Recently, with the emerging technique of artificial intelligence (AI), several authors proposed AI and ANN (artificial neural networks) based models for wastewater treatment or pollutant removal (Manu & Thalla, 2017; Pakrou et al., 2015; Razvarz & Jafari, 2017; Sutherland et al., 2019; Zhao et al., 2020). However, being a black box type model, which does not explain the underlying physical process within the system, artificial intelligence models are disliked by many stakeholders. Moreover, some stakeholders avoid complex models due to difficulties in frequent use. As such, simple, physically based simulation models are often preferred by the users. Despite the importance of modelling on contaminant removal processes through adsorption, there is a lack of study on the simulation of the removal of metribuzin through effective activated carbon of different products. Therefore, this study attempts to fill in the knowledge gap. The methodology can be replicated for other pollutants, as well as for other adsorbents. Based on a recent experimental study (Angin & Ilci, 2021), this paper presents the development of a simple mathematical model for the prediction of metribuzin adsorption from aqueous solutions using olive-waste-derived activated carbon.

2 Methodology

The methodology employed for the development of mathematical models is to derive generalised equations for metribuzin removal efficiency based on

several independent variables, which were established through rigorous experimental measurements conducted in the study of Angin and Ilci (2021). In their study, the studied activated carbon (AC) was produced by chemical activation ($ZnCl_2$) of olive-waste cake collected from the local olive-oil industry in Manisa (Turkey). In addition to presenting detailed physical characteristics of the produced AC, they have provided detailed results on the metribuzin removal efficiencies through the studied AC under different experimental conditions. The experimental variables used are initial pH values: 2, 3, 5, 7, 9.20, 11 and 12; adsorbent amount: 0.1–0.8g (per 100 ml metribuzin solution); solution temperature: 298 K, 308 K and 3018 K; time: 1–420 min.; and initial solution concentration: 50 mgL^{-1}, 100 mgL^{-1}, 150 mgL^{-1}, 200 mgL^{-1}, 250 mgL^{-1} and 300 mgL^{-1}. The measurements were taken in two phases: (i) post-equilibrium phase and (ii) pre-equilibrium phase. It was demonstrated that the adsorption of metribuzin on activated carbon can be well explained by the pseudo-second-order kinetic model. Also, the adsorption process can be defined as homogeneous and monolayer in accordance with the Langmuir isotherm model.

The following sections provide detailed descriptions of the adopted methodology and subsequent mathematical formulations for the mentioned phases.

2.1 Model for Post-equilibrium Phase

Angin and Ilci (2021) reported that the metribuzin removal efficiency using olive-waste is significantly affected by initial pollutant concentration, pH and adsorbent dose concentration. Through observing the relationships of individual parameters on the removal efficiencies (described later), after the adsorption has reached to its equilibrium, the removal efficiency can be represented by the following equation:

$$RE = f(pH) \times f(IC) \times f(D) \times MRE \qquad (1)$$

where RE is the percentage removal of metribuzin, $f(pH)$ is the pH factor affecting removal efficiency, $f(IC)$ is the initial concentration factor affecting removal efficiency, $f(D)$ is the dose concentration factor affecting removal efficiency and MRE is the maximum achievable removal efficiency.

$f(pH), f(IC), f(D)$ are calculated from the individual relationship between the individual parameter and the corresponding metribuzin removal efficiency as obtained through the experimental measurements reported by Angin and Ilci (2021). For the current study, the relationships between individual parameters and metribuzin removal efficiencies were drawn from the experimental measurements mentioned above. For each relationship, a best-fit trendline was drawn and a best-fit equation is proposed. From the derived best-fit trendlines, the following expressions of $f(pH)$, $f(IC)$ and $f(D)$ are deduced (the developments of the expressions are described in the 'Results and Discussions' section):

$$f(pH) = \frac{\left(M_{pH} \times pH + C_{pH}\right)}{RE_{max}^{pH}} \qquad (2)$$

$$f(IC) = \frac{\left(M_{IC} \times IC + C_{IC}\right)}{RE_{max}^{IC}} \qquad (3)$$

$$f(D) = \frac{\left(M_D \times \ln(D) + C_D\right)}{RE_{max}^{D}} \qquad (4)$$

where RE_{max}^{pH}, RE_{max}^{IC} and RE_{max}^{D} are the maximum metribuzin removal efficiencies from experiments for varying pH, initial concentration and dose concentration, respectively. M_D and C_D are the slope and constant of the logarithmic best-fit line for the experimental results on metribuzin removal efficiency with varying dose values. Similarly, M_{IC} and C_{IC} are the slope and constant of the best-fit line for varying initial concentrations. M_{pH} and C_{pH} are the slope and constant of the best-fit line for varying pH values. 'IC' is the initial concentration, and 'D' is the dose concentration (per 100 mL of solution).

Potential metribuzin removal efficiencies for different combinations of independent parameters (pH, initial concentration and dose concentration) were calculated using Eq. (1). In the equation, the maximum removal efficiency (*MRE*) was unknown. For the selected experimental results, the MRE was assumed to be 100% as in most of the cases, very high (above 90%) removal efficiencies were achieved. The 'Results and Discussions' section describes detailed derivations of $f(pH)$, $f(IC)$ and $f(D)$ for the experimental measurements presented in Angin and Ilci (2021).

2.2 Model for Pre-equilibrium Phase

In the experimental study of Angin and Ilci (2021), the post-equilibrium experiments were conducted under constant temperature at 298 K. However, the pre-equilibrium behaviour of the selected adsorbent was studied under three different temperatures (298 K, 308 K and 318 K) for varying contact time up to 425 min. As such, a generalised equation of removal efficiency was derived, having temperature and contact time as independent variables. It was observed that for a particular temperature, the removal efficiency is varying with contact time following the power function as shown below:

$$RE = a \times (CT)^b \qquad (5)$$

where 'CT' is the contact time in minutes, and 'a' and 'b' are the coefficient and exponent, respectively. From the best-fit lines of the measured values, three different 'a' and 'b' values were extracted for three different temperatures. It is found that all the 'a' and 'b' values can be correlated with temperature as per the following linear pattern:

$$a, b = m \times T + c \qquad (6)$$

where 'T' is the temperature (K), and 'm' and 'c' are the slope and intercept of the linear line, respectively. Eventually, replacing these linear equations into Eq. (5) yields a single generalised equation as follows:

$$RE = \left(m_1 \times T + c_1 \right) \times CT^{\left(m_2 \times T + c_2 \right)} \qquad (7)$$

The following section describes the final development of the model equations and comparisons with the corresponding measured data.

3 Results and Discussions

3.1 Post-equilibrium Model

3.1.1 Derivation of Factors

For the measurements with varying pH, the pH values were varied from 2 to 12, while the initial metribuzin concentration was 100 mg/L, the adsorbent dose was 0.2 g (per 100 mL solution) and the contact time was 24 h (which was beyond equilibrium time). Figure 1 shows the relationship plot of pH and metribuzin removal efficiency, which provides the following best-fit equation with a coefficient of determination value of '0.84':

$$RE_{pH} = -0.21 \times pH + 97.639 \qquad (8)$$

where RE_{pH} is the removal efficiency under varying pH values.

Fig. 1 Relationship between pH and metribuzin removal efficiency

y = -0.21x + 97.639
R² = 0.8419
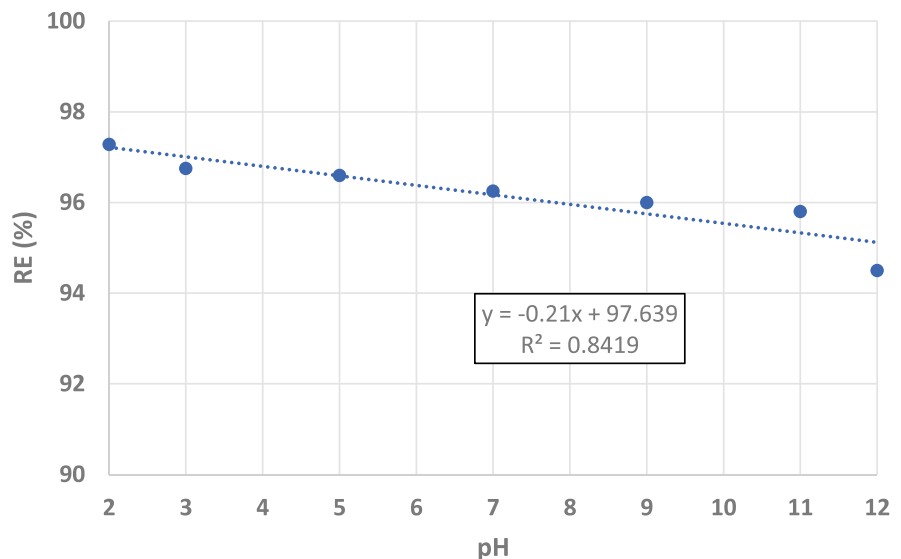
For the measurements with varying initial concentrations, the initial metribuzin concentrations were varied from 50 to 300 mg/L under a constant adsorbent dose of 0.2 g/100 mL, pH 9.2 and contact time of 24 h. Figure 2 shows the relationship plot of initial concentration and removal efficiency, which provides the following two best-fit equations with a coefficient of determination value of '0.96':

$$RE_{IC} = -0.0943 \times IC + 102.17 \qquad (9)$$

where RE_{IC} is the removal efficiency under varying initial concentration values.

For the measurements with varying dose concentrations, the dose concentrations were varied from 0.1 to 0.8 g per 100 mL of solution, with a constant initial concentration of 100 mg/L, contact time of 24 h and pH value of 9.2. Figure 3 shows the relationship plot of dose concentration and metribuzin removal efficiency, which provides the following best-fit equation with a coefficient of determination value of '0.665':
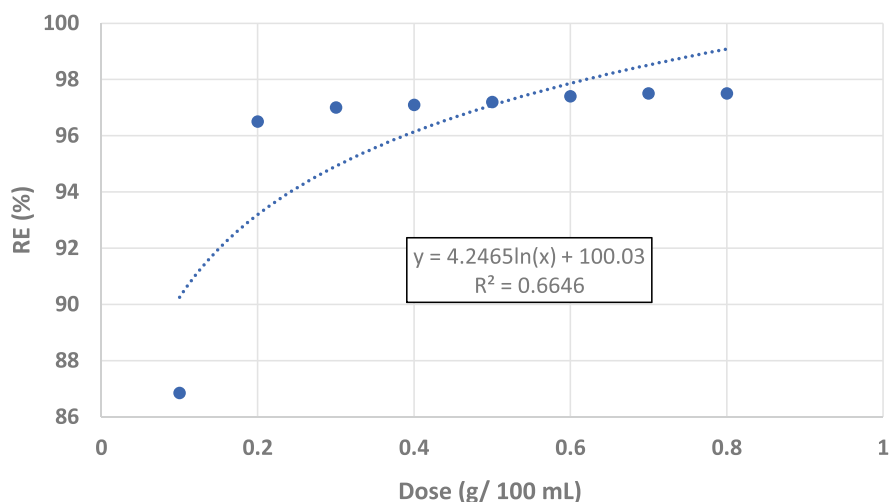
$$RE_D = 4.2465 \times \ln(D) + 100.03 \qquad (10)$$

where RE_D is the removal efficiency under varying dose concentrations.

Fig. 2 Relationship between initial metribuzin concentration and metribuzin removal efficiency
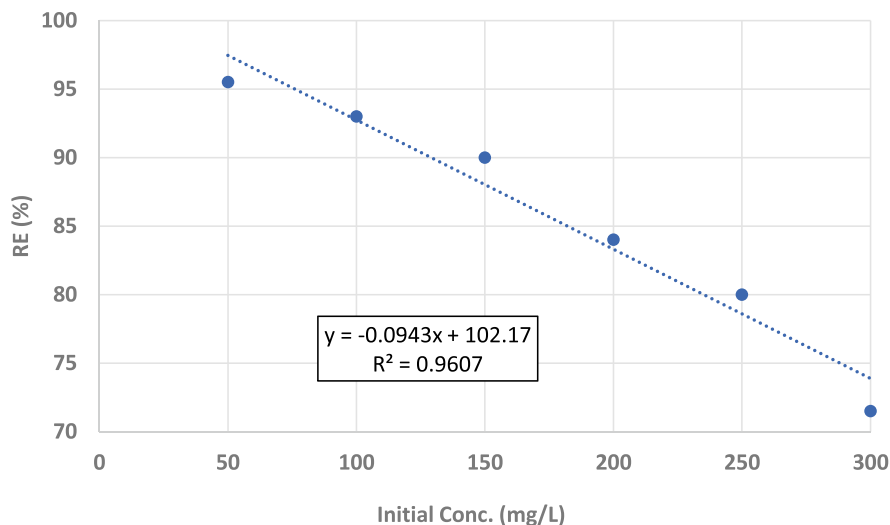
Fig. 3 Relationship between adsorbent dose concentration and metribuzin removal efficiency

For the available twenty-one measurements, replacing all the values of RE_{pH}, RE_{IC} and RE_D into Eqs. (2)–(4), the values of $f(pH)$, $f(IC)$ and $f(D)$ were calculated. Then replacing these values into Eq. (1), the expected removal efficiencies were calculated, while assuming the value of *MRE* (maximum removal efficiency) to be 100%.

3.2 Comparison of Model Results

Table 1 shows the calculated $f(pH)$, $f(IC)$ and $f(D)$ values for different combinations of independent variables: *pH*, *IC* and *D*. The table also shows the corresponding values of the model calculated removal efficiency for each set of experimental conditions. Figure 4 shows the comparison between model calculated values and the measured values of removal efficiencies. Figure 4 also presents the best-fit line showing the relationship between the measured values with the model predicted values, along with an ideal line which is expected to be followed by the best model. From the figure, it is clear

that the model slightly underestimates the removal efficiencies compared to the measured values. However, the model predicted values follow the same trend as the measured values, which rendered a correlation coefficient of 0.96. To evaluate the errors of the model calculated values, the root mean squared error (RMSE), mean absolute error (MAE) and relative absolute error (RAE) values were calculated. It is found that the model calculated values are having an RMSE value of '6.34', MAE value of '5.99' and RAE value of '0.07'.

The slight discrepancies of the model results from the measured values are not unlikely as not all the factors' best-fit equations are closely matching with the measured data. Especially, the measured RE values for varying dose concentrations were not closely matching with the defined best-fit curve, which is logarithmic and that is the best option to fit the measured values. However, as the skewed pattern shows a clear trend, it is possible to adjust the model predictions through applying an adjustment, which can be derived from the best-fit line shown in the

Table 1 Calculated factors based on individual relationship, model predicted and experimental values of metribuzin removal efficiencies

pH	Initial conc. (mg/L)	Dose(g/100 mL)	f(pH)	f(IC)	f(D)	RE (%)model	RE (%)measured
2	100	0.20	1.00	0.95	0.94	89.26	97.28
3	100	0.20	1.00	0.95	0.94	89.07	96.75
5	100	0.20	0.99	0.95	0.94	88.68	96.60
7	100	0.20	0.99	0.95	0.94	88.30	96.25
9	100	0.20	0.98	0.95	0.94	87.91	96.00
11	100	0.20	0.98	0.95	0.94	87.53	95.80
12	100	0.20	0.98	0.95	0.94	87.33	94.50
9.20	50	0.20	0.98	1.00	0.94	92.34	95.50
9.20	100	0.20	0.98	0.95	0.94	87.87	93.00
9.20	150	0.20	0.98	0.90	0.94	83.41	90.00
9.20	200	0.20	0.98	0.85	0.94	78.94	84.00
9.20	250	0.20	0.98	0.81	0.94	74.47	80.00
9.20	300	0.20	0.98	0.76	0.94	70.00	71.50
9.20	100	0.10	0.98	0.95	0.91	85.10	86.85
9.20	100	0.20	0.98	0.95	0.94	87.87	96.50
9.20	100	0.30	0.98	0.95	0.96	89.50	97.00
9.20	100	0.40	0.98	0.95	0.97	90.65	97.10
9.20	100	0.50	0.98	0.95	0.98	91.54	97.20
9.20	100	0.60	0.98	0.95	0.99	92.27	97.40
9.20	100	0.70	0.98	0.95	0.99	92.89	97.50
9.20	100	0.80	0.98	0.95	1.00	93.42	97.50

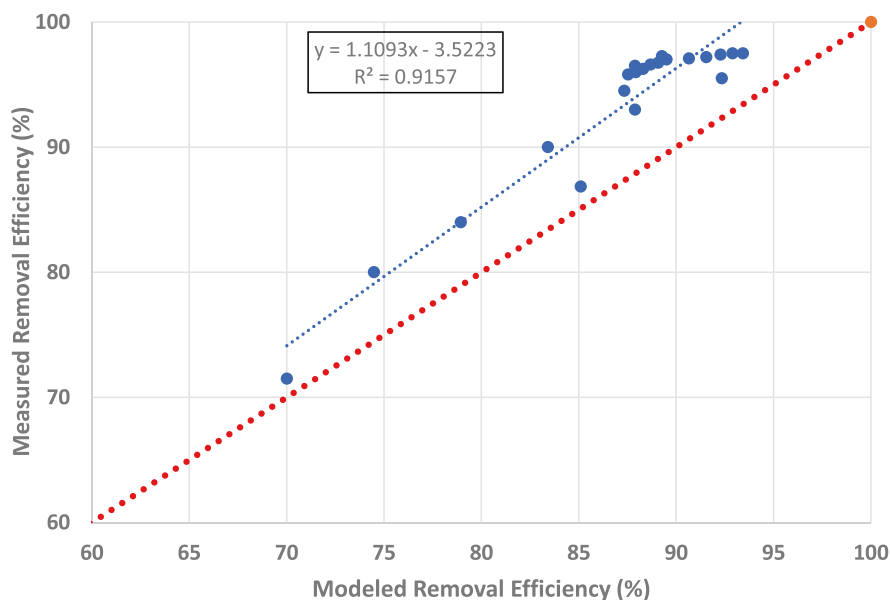**Fig. 4** Comparison of model results with the experimental measurements

figure. From the current results, it is found that the adjusted model would follow the following pattern:

$$ARE = 1.1093 \times RE - 3.5223 \qquad (11)$$

where '*ARE*' is the adjusted removal efficiency, and '*RE*' is the predicted removal efficiency calculated using Eq. (1). Figure 5 shows the comparison of measured results with the predictions through the adjusted model. From the figure, it is clear that the adjusted model can accurately predict the measured

values having RMSE, MAE and RAE values of 1.97, 1.71 and 0.01, respectively. The improvements through such adjustment are RMSE reduced to 31%, MAE reduced to 29% and RAE reduced to 14%.

3.3 Pre-equilibrium Model

Metribuzin removal efficiency significantly varies with the contact time and solution temperature until the equilibrium of adsorption and desorption processes is

Fig. 5 Comparison of adjusted model results with the experimental measurements
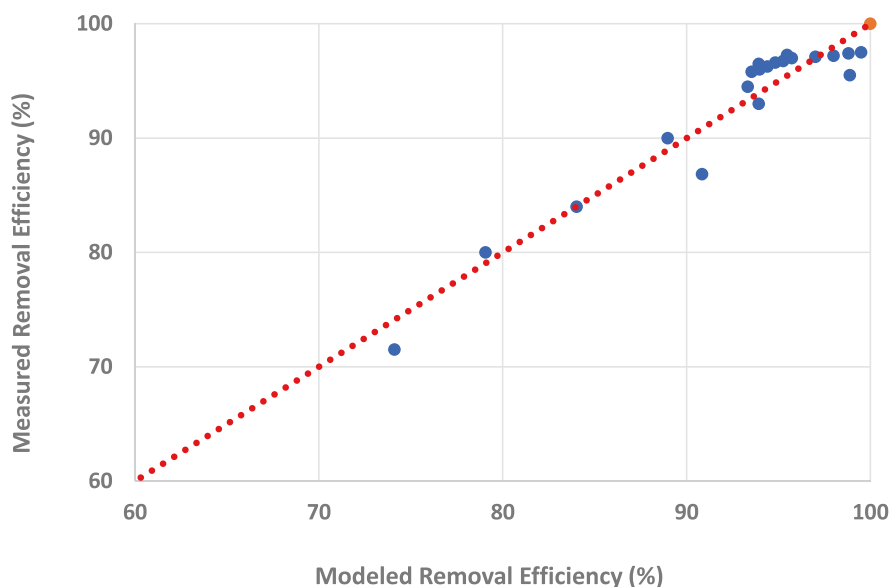
reached. In the study of Angin and Ilci (2021), this phenomenon was investigated through measuring metribuzin removal efficiencies at different times up to 420 min under three different temperatures (298 K, 308 K and 318 K). Figure 6 shows the relationships of removal efficiency with the contact time under selected temperatures. All three investigations follow the same pattern, which can be replicated by a power function as stated in Eq. (5). From the best-fit lines drawn through the measured values under varying temperatures yield Eqs. (12), (13) and (14) for the solution temperatures of 298 K, 308 K and 318 K, respectively, as shown below.

$$RE = 20.05 \times CT^{0.223} \tag{12}$$

$$RE = 21.21 \times CT^{0.244} \tag{13}$$

$$RE = 21.50 \times CT^{0.247} \tag{14}$$

R^2 values of the derived best-fit equations are 0.996, 0.9955 and 0.984 for Eqs. (12), (13) and (14), respectively.

It is found that the coefficients (20.05, 21.21, 21.5) and exponents (0.223, 0.244, 0.247) of Eqs. (12)–(14) can be correlated with the temperature as follows:

$$For\ coefficients,\ a = 0.0725 \times T - 1.41 \tag{15}$$

$$For\ exponents,\ b = 0.0012 \times T - 0.1316 \tag{16}$$

R^2 values of the derived Eqs. (15) and (16) are 0.893 and 0.842, respectively.

Replacing Eqs. (15) and (16) into Eq. (5) yields the final generalised equation for metribuzin removal efficiency for any contact time under any temperature. The final derived equation is

$$RE = (0.0725 \times T - 1.41) \times CT^{(0.0012 \times T - 0.1316)} \tag{17}$$

Equation calculated results are compared with the original measured values. Figure 7 shows the comparison of the results along with the ideal line. From the figure, it is clear that the developed equation can accurately predict the experimental values with a correlation coefficient of 0.99 between the measured and calculated values. Also, the RMSE, MAE and RAE values of the predicted values are 3.49, 2.71 and 0.05, respectively. The error statistics are quite low, which ascertains accurate estimations by the derived equation.

This is a pioneer attempt at developing a parametric mathematical model for predicting metribuzin removal efficiency using olive-waste AC based on different experimental conditions. Such kind of mathematical model is likely to serve as a useful tool for decision makers, who would be able to take decisions on the required levels input parameters for their

Fig. 6 Time-varying metribuzin removal efficiencies under different temperatures
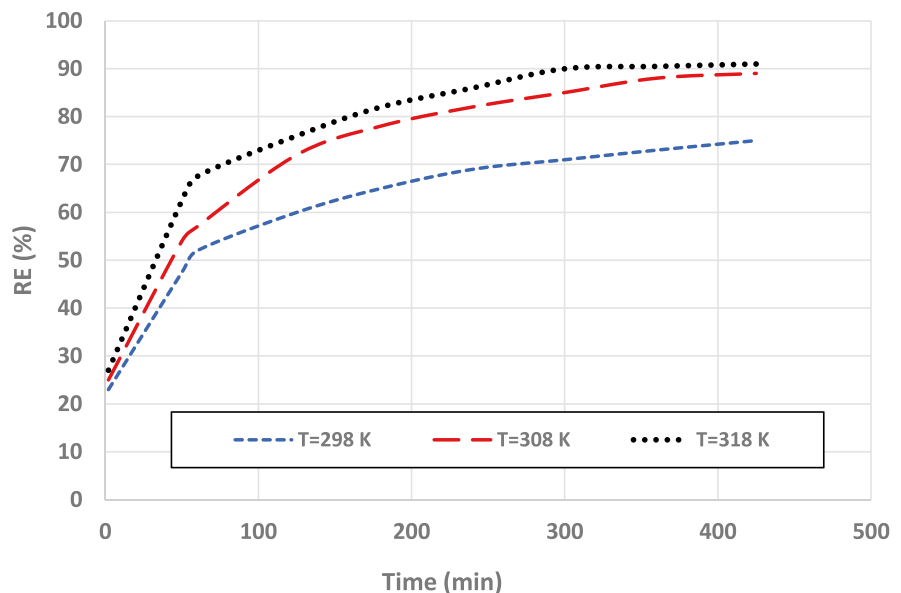
Fig. 7 Comparisons of time-varying, temperature-dependent model results with the experimental measurements
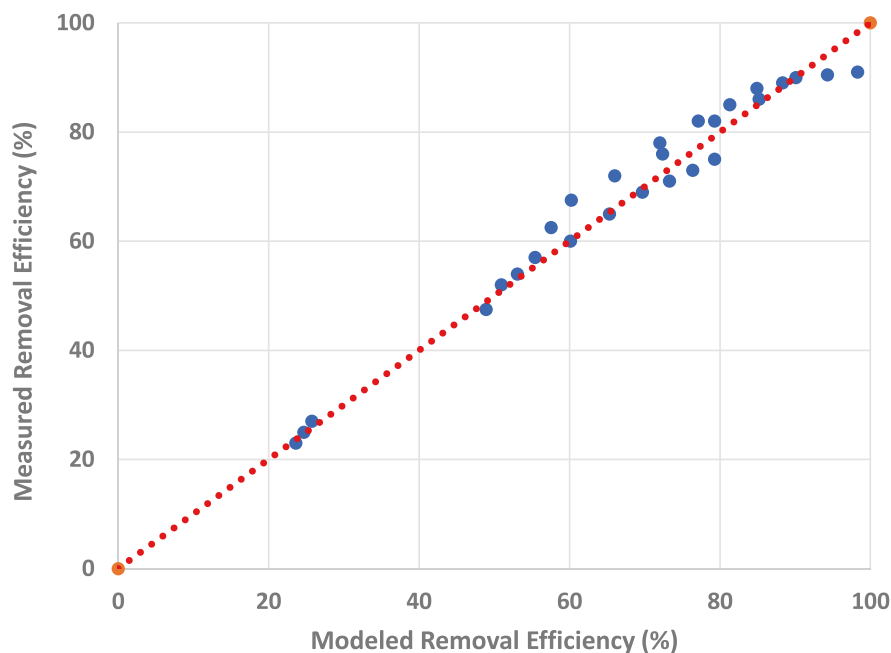
desired target(s). For any industrial-scale implementation of such a pollutant removal process, often, it is necessary to optimise the input variables with the aim of minimising the cost while fulfilling the requirements of relevant regulatory authorities.

4 Conclusions

With the aim of assessing the efficiency of metribuzin removal from aqueous solutions using activated carbon made from olive-waste cake under any input condition, a simple mathematical model was developed. The model was developed with the experimental data reported in an earlier study on metribuzin removal using adsorbent derived from olive-waste. As the earlier study used three dominating variables such as pH, initial metribuzin concentration and dose concentration, the developed model is also based on the same variables. Based on the earlier experimental data, a contributing factor was derived for each selected variable. Finally, all the selected factors were multiplied together to evaluate a single diminishing factor towards maximum achievable removal efficiency, which will render the potential removal efficiency under the specific input parameters. Model calculated results for a set of input parameters were compared with the experimental measurements. It is shown that

the model predicted results are close to the measured values reported in the earlier study. However, to improve the developed model's accuracy, an adjustment factor on the originally derived model equation was proposed and with the application of such adjustment factor model's predictions were improved significantly. With the pre-adjusted model, the simulated values rendered the following standard errors: RMSE = 6.34, MAE = 5.99 and RAE = 0.07. Whereas, after the application of the adjustment factor, the RMSE, MAE and RAE values were reduced to 1.97, 1.71 and 0.01, respectively.

It was found that prior to reaching the equilibrium, removal efficiency is significantly affected by reaction time and temperature. The experimental data had several time-dependent removal efficiency measurements under three different temperatures. It is shown that all the experimental data follow some definite trends, which can be generalised. From the pre-equilibrium experimental data, a combined generalised equation was derived, which includes both the temperature and time. The accuracy of the developed generalised equation is high, having a correlation coefficient of 0.99. Also, the standard errors of the predictions are RMSE = 3.49, MAE = 2.71 and RAE = 0.05.

It is to be noted that the model presented in this paper was developed for the metribuzin removal using

olive-waste cake as adsorbent, as such not likely to be valid for other pollutants/adsorbents. However, a similar methodology can be applied for the development of an appropriate modelling framework for other pollutants and/or adsorbents.

Declarations

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