

PACKAGE DEVELOPMENT FOR ADSORPTION KINETIC CONSTANT DETERMINATION

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CSC 421

2022-09-07

Abstract

The use of adsorption technologies to purify waste water streams of pollutants and toxins is a subject of great scientific interest, with a vast number of studies on various adsorbates present in literature. However, these studies often utilise mathematic kinetic models which are simplified, linearised forms of the more accurate, and widely applicable, differential equations.

A Python programme was developed using a differential equation to model the kinetics of an adsorption system, while incorporating both ad- and desorption. This programme was then tested using 38 independent adsorption data sets to determine its accuracy and reproducibility.

This programme is capable of reading user defined Excel spreadsheets, and is fully automatic apart from a few specific user inputs in terms of generating the adsorption constant k_{ad} through means of a best fit algorithm, as well as the system's Q_{max} , ΔS° and ΔH° , or k_L , whichever is applicable.

Upon the completion of the analysis, 32 % of the data sets were modelled with a high degree of accuracy, with a further 34 % proving inconsistent with the isothermal one surface Langmuir model used. The remaining 34 % were a mixed array of experimental flaws, function errors in terms of convergence, and statistical anomalies. However, given accurate experimental data in some of these, the function was able to produce results with a high degree of accuracy.

The programme's success in certain cases provide a strong motivation for further investigation in this topic, and bolster the use case argument for the more sophisticated differential equations in future experiments and analysis.

Keywords: Python, adsorption constant, differential equation, isotherm, kinetics, adsorption, use case

Contents

Abstract.....	ii
Nomenclature	vi
1 Introduction.....	1
2 Literature Review	2
2.1 General Background.....	2
2.2 Kinetics, Modelling and Shortcomings	4
3 Development and Methods.....	7
3.1 Initial Fitting.....	7
3.1.1 Isotherm Fitting.....	7
3.1.2 Kinetics Modelling.....	8
3.2 Initial Parameter Determination	9
3.2.1 Isotherm Initialisation	9
3.2.3 Kinetics Initialisation	10
3.3 Simultaneous Fitting	11
3.3.1 Initial Trials.....	11
3.3.2 Secondary Trials	11
3.3.3 Tertiary Trials	12
3.4 Automation.....	13
3.4.1 Loop Numbering.....	13
3.4.2 Special Inputs.....	13
3.4.2.1 Temperature Variance.....	13
3.4.2.2 Tolerance.....	14
3.4.2.3 Kinetics Time Arrays	15
3.4.3 Data Retrieval	15
3.4.4 Curve Plotting	16
3.4.5 ‘Goodness of Fit’ Parameters.....	16

3.5	Spreadsheet Format	17
3.6	User Inputs and Returns	18
4	Data Analysis.....	19
4.1	Reformatting.....	19
4.2	Data Analysis and Storage	20
5	Results and Discussion.....	22
5.1	Initial System.....	22
5.2	Extremely Fast Kinetics	24
5.3	Good Fits	25
5.4	Poor Kinetic Fits.....	27
5.4.1	Poor Isotherm Fits.....	27
5.4.1	Good Isotherm Fits	28
6	Conclusions and Recommendations.....	30
6.1	Conclusions	30
6.2	Recommendations	31
6.2.1	Programme Improvements.....	31
6.2.2	Graphical User Interface	32
7	References.....	33
8	Appendices.....	37
Appendix A	User Instruction Document.....	37

Figures

Figure 1:	Experimental v Predicted Isotherms for Muedi et al. (2021)	23
Figure 2:	Experimental v Predicted Kinetics (Muedi et al, 2021)	23
Figure 3:	Comparison between Wei et al. (2014) guess values.....	24
Figure 4:	Experimental v Predicted Isotherms for Wei et al. (2014).....	25
Figure 5:	Experimental v Predicted Kinetics (Bhaumik et al, 2012), (Bulut et al, 2007)	25
Figure 6:	Raji and Pakizeh (2013) Isotherm and Kinetics Experimental v Predicted curves.	26

Figure 7: Fadzil et al. (2016) Experimental v Predicted Isotherm and Kinetics curves	27
Figure 8: Gupta et al. (2012) Experimental v Predicted Isotherm and Kinetics curves	27
Figure 9: Shadbad et al. (2011) Experimental v Predicted Isotherm and Kinetics curves	28
Figure 10: Zabihi et al. (2009) Experimental v Predicted Isotherm and Kinetics curves.....	29
Figure 11: Lu et al. (2005) Experimental v Predicted Isotherm and Kinetics curves.....	29
Figure 12: Python Options Menu.....	37
Figure 13: Kernel Menu.....	37
Figure 14: Cell Menu.....	38
Figure 15: Dialogue Box.....	38

Tables

Table 1: Function Outputs based on 'no_Tvar' Assignment	13
Table 2: Naming Conventions for Spreadsheet Data Headings.....	17
Table 3: Required User Inputs	18
Table 4: Data Set Categories.....	21
Table 5: Results Spreadsheets Names.....	21
Table 6: Isotherm Best Fit Parameters for Muedi et al. (2021)	22
Table 7: Parameters for Muedi et al, (2021)	23
Table 8: Kinetic Parameters for Bhaumik et al. (2012) and Bulut et al. (2007)	25
Table 9: Equilibrium comparisons of kinetic and isothermal data	29

Nomenclature

Q_t	Adsorption capacity at time 't'	mg/g
k_L	Equilibrium adsorption constant	L/mg
Q_{max}	Maximum adsorption capacity	mg/g
C_e	Equilibrium adsorbate concentration	mg/L
Q_e	Equilibrium adsorbent adsorption capacity	mg/g
k_1	Pseudo first order constant	1/(min)
k_2	Pseudo second order constant	g/(min·mg)
t	Time	min
k_{ad}	Adsorption kinetic constant	L/(g·min)
k_{de}	Desorption kinetic constant	mg/(g·min)
C_a	Adsorbate concentration of species 'a'	mg/L
C_{a0}	Initial adsorbate concentration of species 'a'	mg/L
m	Mass of adsorbent in solution	g
V	Volume of adsorbate solution	L
R	Universal gas constant	J/(mol·K)
T	Temperature	K
ΔS°	Standard entropy change	J/K
ΔH°	Standard enthalpy change	J/mol

1 Introduction

The use of adsorption technology as an environmentally friendly and highly efficient means of waste water treatment and system purification (de Namor et al., 2017), is one that has been widely explored and investigated in literature (Largitte and Pasquier, 2016b). Various adsorbents, some highly engineered (Ozcan et al., 2004), and others from basic natural and food wastes (Bulut et al., 2007) have been explored for their ability to remove toxic and harmful substances in liquid media. In order for these adsorbent materials to be readily comparable, means of quantification of the magnitudes of adsorbates removed, as well as the speeds of this process have been developed, and are used frequently in similar forms throughout literature.

Various equations and models have been proposed to model both the adsorption isotherms (magnitude of removal) and kinetics (rate of removal), as will be described in the review of relevant literature, with some of the most frequently applied and consistently accurate models the Langmuir isotherm (or equilibrium) (Langmuir, 1918).

$$Q_e = \frac{k_L Q_{max} C_e}{1 + K_L C_e} \quad (1)$$

the pseudo first order (Lagergren, 1898),

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (2)$$

and the pseudo second order models (Lagergren, 1898)

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (3)$$

The above Langmuir model represents an isotherm model, which predicts the equilibrium adsorbent adsorption capacity at varying equilibrium concentrations of adsorbate, while the pseudo first and pseudo second order equations are kinetic equations, which model the rate of adsorption of the adsorbate into the adsorbent.

However, the majority of available literature concerning the processes of adsorption technologies focus rather on the discovery of new adsorbent materials, as described above, than the improvement of the mathematics, specifically the kinetics and thus rate relations, used to model and quantify the results of the experiments conducted. The pseudo first- and second-order models currently widely do not provide constants with which extrapolation provides any degree of accuracy, and models of the purer differential form have not received adequate testing

or trials to verify their accuracy, and thus allow their acceptance into the current adsorption meta.

The following equation has been proposed by Muedi et al. (2021):

$$\frac{dQ}{dt} = k_{ad}C_a \left(1 - \frac{Q_t}{Q_{max}}\right) - k_{de}\left(\frac{Q_t}{Q_{max}}\right) \quad (4)$$

with

$$C_a = C_{a0} - Q_t \frac{m}{V} \quad (5)$$

which accounts for the simultaneous and equilibrating processes of ad- and desorption, as well as allows for the determination of constants which are able to be extrapolated across varying initial concentrations of adsorbate.

Thus, the fundamental objective of the project was to create a package, on Python, or in application form, which includes some form of user interface capable of receiving bulk adsorption data and returning the isothermal and kinetic constants, applicable over any range of initial concentration data, as well as assistance in plotting this data, and the curves generated by the calculated constants.

The package developed is capable of, with minimal user inputs, automatically generating ‘guess’ or initial values for the constants based on linearized models, and passing these constants into fitting functions, which generate global best fit parameters for the data, as well as plotting the data, returning the generated data points at the experimental time values, and providing ‘goodness of fit’ parameters.

This package is integrated with the excel interface, in that excel documents specifically formatted in terms of naming conventions, will be able to be read and the data extracted into the Python interface for more sophisticated curve fitting that is available through excel, with minimal user input.

2 Literature Review

2.1 General Background

The Langmuir isotherm, as depicted in equation 1, is the most common and widely used isotherm which describes adsorption onto homogeneous adsorbent surfaces (Sircar, 1991a), or

active adsorption sites (Puziy et al., 2001). The term ‘adsorption’ is also broadly used to describe two discrete types, or forms, of adsorption, including physical and chemical adsorption (often termed physisorption and chemisorption).

Physical adsorption is a phenomenon usually encountered at low temperatures, or mild conditions (typically between 0 and 100 K) (Vidali et al., 1991), between gas or vapour and solid mixtures. The molecules of the adsorbate are weakly attracted to, and held onto the surface of the adsorbent by van der Waals forces (Thommes and Cychosz, 2014), and are thus easily desorbed (Webb, 2003). Thus, in the current study, the most prominent means of adsorption is chemisorption, as the temperatures are sufficiently high that the contributions by physical adsorption can be considered negligible.

Chemical adsorption is the chemical bonding of adsorbate particles, involving the sharing of electrons, with the atoms of the adsorbent surface, indicating a much stronger bond, and thus one more difficult to break (Webb, 2003). Chemical adsorption only occurs on so called ‘active sites on the surface of the adsorbent, which are the sites at which the potential energy between the adsorbate molecule, and the adsorbent, is at its lowest (Sircar and Myers, 1988). Chemisorption is further broken down into reversible and irreversible adsorption, with the former describing the weakest, and the latter the strongest, bonding of the adsorbate to the active sites of the adsorbent molecule (Webb, 2003).

The Langmuir isotherm thus, as described in Webb (2003) as accurate in most cases, and as described above, is modelled on the transfer of particles to and from the adsorbent surface, accounting for both ad- and desorption as continuous processes (Puziy et al., 2001). However, the Langmuir isotherm, as described by the results obtained in Zhang et al. (2008) models homogeneous surfaces ideally, but falls short at accurately modelling heterogeneous surfaces. As described in Sircar (1984), homogeneous surfaces are those at which the potential energy remains constant between the molecules and the adsorbent across the entire surface, whereas those surfaces with varying energies across each site are termed heterogeneous.

The heterogeneity of the active sites on an adsorbent surface is derived from either structural or chemical characteristics, or a combination of both (Moon and Tien, 1988). Thus, the structure of the surface, as well as the varying chemical groups present on the structure are strong determinants in the specific molecules which will be best adsorbed onto the surface, and held irreversibly (Sircar and Myers, 1988).

Heterogeneity has also historically been modelled as an amalgamation of homogeneous sites, with the use of the Langmuir isotherm to describe ‘local’ sites, or individual sites of equal energies, of which there exists a large range across the surface of a heterogeneous surface (Sircar, 1991b). Thus, the development of new, or multi-site isotherms, including multi-site (Kumar et al., 2021) or ‘two surface’ models for the Langmuir isotherm has also become a topic of research to better model these interactions.

Finally, in addition to the adsorption into the active sites themselves, Tan and Hameed (2017) as well as Wang and Guo (2020) further describe the process as containing three steps, namely external diffusion through the substrate towards the adsorbent, internal diffusion into the pores of the adsorbent, and finally the adsorption into the active sites of the adsorbent.

2.2 Kinetics, Modelling and Shortcomings

Given the inability of the Langmuir isotherm to effectively model the effect of heterogeneity (multiple sites) in adsorption, the popular Freundlich isotherm, as described in Ayawei et al. (2017) was developed, which does account for the surface heterogeneity of surfaces, but is a highly empirical equation, with limitations on its applications at broader ranges of pressure, concentration and saturation, and also does not model homogeneous surfaces accurately (Kumar et al., 2021).

Thus, in the following study, the Langmuir isotherm is used as the modelling of the equilibrium between the adsorbate concentration and the equilibrium adsorption capacity of the adsorbent, with consideration therefore given to the fact that there may potentially be discrepancies in the modelling of the isotherm data, but not necessarily in the modelling of the kinetic data. The kinetic equation, equation 4, as suggested by Muedi et al. (2021) also simplifies to the Langmuir isothermal model at kinetic equilibrium (equation 1), provided that the Langmuir constant k_L , as classified in Ayawei et al. (2017) represents the ratio of the constant of adsorption over that of the constant of desorption, $k_{de} = k_{ad}/k$.

The most popular models in literature in terms of kinetic modelling, as mentioned previously, are the pseudo-first and pseudo-second order kinetic models, as used in Gupta et al. (2012), Ding et al. (2020) and Wang et al. (2014), amongst countless others. These models owe their popularity to their ease of use, being analytical rather than differential equations, allowing for their utilization with only a considerably basic knowledge of curve plotting and parameter fitting software.

Although existing in differential form,

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (6)$$

and

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (7)$$

(Muedi et al., 2022), (Zohra et al., 2008), these equations are often simplified to the linearized form represented in equation 2 and equation 3. In addition to this, these equations are also simplified to specific use case scenarios, only modelling the kinetics to a degree of accuracy at very low amounts of adsorbate adsorbed (Q). The order represents the assumed order of reaction Largette and Pasquier (2016a).

These models, due to their extreme simplification, are also unable to model the kinetics of surfaces which exhibit heterogeneity, as depicted in Azizian (2006). In order to improve their accuracy, various other terms accounting for the presence of multiple sites are introduced into the equations, complicating them further, and making them far more empirical, thus restricting their use-case and applicability.

As described in Tan and Hameed (2017), both of these models only contain a singular rate constant, which arbitrarily assumes a value covering a large range of potential adsorption phenomena, with Wang and Guo (2020) also specifying that both models are empirical in nature, and are not based off of the study of the physical activity and movement of particles onto or out of the active sites in the pores of the adsorbent molecules.

Both models also are highly restricted in their ranges of application, with the pseudo first order model only accurately describing the adsorption rate at very high initial adsorbate concentrations, where the regime is reaction rate controlled, often at the very beginning of the adsorption (Tan and Hameed, 2017); (Wang and Guo, 2020). Simonin (2016) however also argues against the complete use in the pseudo second order equation as accurate over the entire process regime, as this is often used when the adsorption process reaches equilibrium quickly, and thus provides an very good fit against essentially flat line data, when the adsorbate concentrations are low (Wang and Guo, 2020).

Revellame et al. (2020) further points to the fact that these equations are also used mainly in their linearized forms, with the pseudo first order becoming undefined close to equilibrium

adsorption capacities. Lima et al. (2021), upon analysis of 225 literature papers citing the use of these equations, proves that a roughly 50 % discrepancy exists in the best fit model to use, when alternating between the linearized and non-linearised forms of the two analysed models. Thus, both Lima et al. (2021) and Bujdák (2020) devote their papers to proving that the poor use of assumptions, and eagerness to obtain ‘better’ or ‘easier’ fits using the linearized versions of these popularized models is a significant shortcoming in the current analysis of adsorption kinetics, especially when the non-linear models exist, with sufficient computing software available to utilize these models efficiently.

Bujdák (2020) recommends using linearized models instead as methods to obtain better initial parameters, rather than using the models to model kinetics systems as a whole. This recommendation is applied in this report.

Further, as described in Largitte and Pasquier (2016b), these models have a number of additional shortcomings, including that they do not account for desorption of particles from the available adsorption sites, and thus account only for an ‘empty to fill’ use case, instead of considering a potential kinetic equilibrium in terms of the rates of ad- and desorption from the surface. In addition, as the models are empirical and analytical in nature, when fitted with experimental data, do not provide constants favorable for extrapolation (Muedi et al., 2021), due to dependence on the initial adsorbate concentration in the system.

Although a number of other models exist, which model the reaction, or adsorption step in the adsorption process (Qiu et al., 2009), none of these has found similar popularity and wide level of use as the pseudo first and pseudo second order equations.

Thus, a significant shortcoming of the model introduced as equation 4, is its lack of application currently, and thus does not have a strong, and well proven use-case implementation yet. Proving such could be the first step in applying this model more broadly in adsorption studies and could lead to better accuracy of quantification and therefore comparison between different adsorbent technologies, over ranges of initial adsorbate concentrations. In addition, the model does also not fully account for the mass transfer, or diffusion effects, of the adsorption process.

However, the model is nonlinear in nature, and is based on the physical processes of adsorption and desorption from the active sites, and the mathematical description of such (Muedi et al., 2021). Thus, the issue raised by Wang and Guo (2020), Lima et al. (2021) and Bujdák (2020) in terms of non-application of the purest form of these equations will be combated in this report.

The Langmuir isothermal model, as described in depth above, and, as first introduced along with its two-surface addition, was first presented by Langmuir (1918), and will be used alongside the kinetic model, as it provides adequate fits to most single-surface assumed adsorbent materials, and allows for the assumption of equilibrium, as well as integrating with the kinetic model deduced as described above. Its two-surface addition is also sufficient in modelling processes with which the one-surface model cannot accurately return well-fitting constants for.

3 Development and Methods

3.1 Initial Fitting

The investigation, and initial development of the package, was based on the data and results obtained by Muedi et al. (2021), which were used as a means of ensuring that the programme operated as desired, and returned the results obtain using the same equations, but a different software package.

3.1.1 Isotherm Fitting

In order to obtain the data required for the analysis, the *pandas* module in Python was used, specifically the *pandas.read_excel* functionality, which allows the user to define a file location of a saved Microsoft Excel (excel) spreadsheet, and have this data imported and read by the Python interface, which stores the data in a list of the same name of the column in excel under which it is presented. This was done crudely in the initial importation, with each name ‘hard coded’ or written out explicitly in the Python code. The data sets included the three isothermal runs, with the C_e and corresponding Q_e values presented for the temperatures of 298 K, 308 K, and 318 K.

Any ‘NAN’ or ‘no attribute’ values were sifted out from the lists (these values may be present in data lists in excel where no value is present in a particular cell), as Python cannot operate on these values, not reading them as 0. This was done using the *pandas.isnull* or the *numpy.isnan* functions.

A basic ‘isotherm’ function was then defined in Python, using equation 1 and equation:

$$k_L = e^{\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}} \quad (8)$$

with inputs defined as ‘S’ (ΔS°), ‘H’ (ΔH°) and ‘Qmax’ (Q_{\max}) as well as ‘t’ (time). This equation was then passed into the *scipy.optimize.curve_fit* function in Python, along with the

data for one temperature run, namely that at 298 K, to obtain the best fit parameters. These parameters were then compared to the result obtained by Muedi et al. (2021) in order to ascertain coding accuracy.

Initially, the best fit parameters obtained varied to an extreme extent based on the initial guess, or initialization values passed to the *curve_fit* function, but this was later eliminated when all data sets were simultaneously used in the fitting.

3.1.2 Kinetics Modelling

A similar approach was used in modelling the kinetics of the system as for the isothermal data, with the retrieval of the data ‘hard coded’ into the interface, and the lists extracted individually. The values obtained in Muedi et al. (2021) for ΔS° , ΔH° and Q_{\max} were again used, both directly into the differential equation 4, as well as in equation 7 for the temperature at which the kinetics trials were conducted, namely 298 K.

The data sets utilized include a common time array, and four Q_t data sets, each with a different initial concentration of adsorbate in the solution used in the experiment, C_{a0} .

Initially, a ‘inte’ function was defined, taking these values, as well as ‘t’ (time) as an input, with the output being the differential output, dQ_t/dt . This function was then integrated using the Python function *scipy.integrate.solve_ivp*, which takes the time array, the function and the initial Q_t value as inputs, with Q_t at time zero equivalent in magnitude to 0, as no adsorption would have occurred, and the available adsorption sites within the adsorbent are assumed to be completely empty at this stage.

This integration was also performed on each data set individually, with the k_{ad} value manually adjusted such as to allow for the continuous curve generated by the integrating function to best fit the experimental data, with this optimal fit being determined visually. This k_{ad} value then provided a good estimate as to whether the k_{ad} value obtained using the *curve_fit* function was accurate, or there was a persistent error in the function.

A separate ‘kinetics’ function was then defined, with the ‘inte’ function nested within this function, as well as the integrating procedure followed. The output of the function was thus a list of Q_t values, corresponding with the times present in the time array passed to the function. This function was then passed through the *curve_fit* function, with the output the value of k_{ad} determined.

3.2 Initial Parameter Determination

3.2.1 Isotherm Initialisation

The following linearized version of equation 1 was used (Subramanyan and Das, 2014):

$$\frac{1}{Q_e} = \frac{1}{bQ_{max}} \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (9)$$

Using the *numpy.polyfit* module, which returns the coefficients of a linear polynomial expression, with the function modelled as a first order ‘straight line graph’ with equation:

$$y = mx + c \quad (10)$$

The values for b and Q_{max} were obtained for each data set looped through the function, with

$$Q_{max} = \frac{1}{c} \text{ and } b = \frac{1}{Q_{max}m} \quad (11)$$

and the inverse of the arrays for Q_e and C_e the values of y and x respectively. The ‘ b ’ value in this case is analogous to the k_L value presented in equation 1, with the ‘ b ’ notation used in Subramanyan and Das (2014).

As this is a ‘guess’ value, the average of the Q_{max} value across all data sets was used as the input into the fitting function as an initial ‘guess’ parameter.

In cases where no temperature variation occurred, or single data sets were presented for isothermal data, the k_L ‘guess’ value was also calculated as the average of the ‘ b ’ values across all data sets, as determination of ΔS° and ΔH° values would not be possible.

For cases, such as in Muedi et al. (2021) where experiments at different temperatures were carried out, the following procedure was followed to obtain the values of ΔS° and ΔH° :

Firstly, a linearised version of equation 8 was used:

$$\ln(k_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

Which again is analogous to equation 8. Each ‘ b ’ value was thus used as the corresponding ‘ y ’ values passed to the *polyfit* function, with the corresponding temperature array inverted and passed as the ‘ x ’ values. Determination of ΔS° and ΔH° was then conducted as follows:

$$\Delta S^\circ = Rc \text{ and } \Delta H^\circ = -RTm \quad (13)$$

These parameters were then passed to the fitting function as the initial ‘guess’ values of ΔS° and ΔH° .

All of the magnitudes of the values described above were arrived at using very crude, linearized means, with the use of averaging and approximations. Thus, these values are not suitable for use as the final return parameters, but are useful in providing a good estimation to the fitting function as to the range in which to begin the iterations to obtain the final values. This process, owing to the ability to model the equations as a linear graph, is able to automated, using the *polyfit* function, and thus the initial ‘guess’ values do not require any user input or knowledge of the system whatsoever.

3.2.3 Kinetics Initialisation

At very low values of Q_t , desorption plays a negligible role in the determination of the uptake of adsorbate into the adsorbent, and thus the second term in equation 4 can be taken as negligible, as Q_t/Q_{max} tends to 0. The equation can then be written as follows (factoring out $1/Q_{max}$):

$$\frac{dQ}{dt} = \frac{k_{ad}C_a}{Q_{max}}(Q_{max} - Q_t) \quad (14)$$

This form thus resembles that of the pseudo first order, equation 5, and thus, at time 0, where $C_a = C_{a0}$, and $Q_t = 0$:

$$k_1 Q_e = \frac{k_{ad}C_{a0}}{Q_{max}}(Q_{max}) \quad (15)$$

This equation can then be approximated for small values of Q_t .

Taking the natural logarithm of equation 2 yields:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \quad (16)$$

Which is again analogous to equation 10. The value for Q_e at the specific temperature of operation is obtained using the isotherm function, and the values for the parameters, after the fitting function as been performed. This is simply taken as the maximum, or end, value of the Q_e data produced when equation 1 is used with the parameters obtained, over a similar range of C_e values as used in the isotherm investigations.

Thus, both the ‘y’ and ‘x’ arrays are composed of known values, and can be passed to the *polyfit* function, where:

$$k_1 = -m \quad (17)$$

Thus, an initial ‘guess’ value of k_{ad} can be solved for, using equation 15. This value is then passed into the fitting function for the kinetics data as the ‘guess’ parameter into the *curve_fit* function.

3.3 Simultaneous Fitting

In order to obtain global fitting parameters, all of the data sets provided need to be fitted simultaneously, with one parameter which best suits all of the data sets being output by the function. Thus, for both the isothermal data sets, in which temperature varies, and the kinetics data sets, in which the initial adsorbate concentration varies, the same conceptual coding practice could be used to fit the data.

3.3.1 Initial Trials

The code presented by Phillips (2018) for two data sets was used as a basis, into which the three initial isotherm data sets presented by Muedi et al. (2021) were ‘hard coded’ initially. In essence, the *curve_fit* function necessitates that input comparison, or experimental, data be a single list of values, and thus the three data sets had to be combined, for both ‘x’ and ‘y’ parameters (C_e and Q_e values). Thus, the combined data sets were passed to the function, wherein ‘hard coded’ isotherm functions were called, each coded for its own specific corresponding temperature, and the results of the three functions were appended together and returned by the function.

In order for the *curve_fit* function to operate, the return of the function passed into this function must also be in the form of a one dimensional array, which is why the scenario above was performed. Using this method, the three desired parameters, Q_{max} , ΔS° and ΔH° were obtained extremely accurately, with the function converging to these values reliably, as confirmed using extremely large and extremely small ‘guess’ values.

3.3.2 Secondary Trials

Thus, as the function could be proven to provide accurate results for the system at hand, secondary trials could commence, in order to make the function automatic, given that it was passed the combined, 1 dimensional data sets as required by the *curve_fit* function. These trials

consisted of attempts to loop through all of the values in the 'x' data (C_e), and append to a list the values of the 'y' (Q_e) data obtained using the isotherm function.

The temperatures used were appended to their own array, thus allowing for the calling of each into the isotherm function itself, using a separate index as the outer loop, as this looped through a much larger number of values, the total of each of the lengths of the data sets. These trials, however, proved unsuccessful, as the *curve_fit* function could not converge provided the appended lists, even when these lists were converted to *numpy* arrays.

Thus, the *numpy.append* functionality, as used by Phillips (2018) was then used for the remainder of the trials.

3.3.3 Tertiary Trials

In order to best replicate the results of the 'hard coded' function, which produced the desired results, the 'original' data sets, or those at each specific temperature, had to be extracted from the combined data set passed to the function, and then passed through the isotherm (nested) function to obtain the results, which then had to be appended together to again return a one dimensional array, to allow for the *curve_fit* function to converge.

Thus, each length of the original array had to be found, and the cumulative sum of the lengths appended to a new list, which could be called on inside the fitting function, in order to index the larger list for the extraction of the original lists. Thus, if two lists were passed, and combined, with lengths 6 and 5 respectively, the length array would contain the values [0, 6, 11]. This was achieved using two loops, one finding the lengths of each list and appending it a new list, and the following appending the cumulative sum to the final length list, with an initial value of 0 always appended first to this list.

This then allowed for each data set to be run through nested function within the fitting function, and the results to be obtained. These results then had to be appended to a new results list. This was made difficult due to the requirement of the *numpy.append* functionality of at least two input lists, one original list, and the new list. Thus, an empty list was passed initially, after which this empty list was redefined in each loop to be the new, appended results list. This was then passed to the function return.

Applying this functionality to the isotherm data sets yielded the desired results, and through further manipulation, this was applied to the kinetics data sets, with which the desired k_{ad} value was obtained. These results indicated the desired performance of the code.

3.4 Automation

3.4.1 Loop Numbering

Two of the required user inputs into the function are the temperatures and initial adsorbate concentrations, in the form of two arrays. In order for the code to function, each loop must be programmed to iterate for each data set, and thus the number of times these loops must be known and be a variable. Thus, the length of these two input arrays is determined automatically, the assigned to a variable name 'no', which is then used as the maximum range of the corresponding loops for the isotherm and kinetic analyses.

In further refinements of the code to allow for ease of use for inexperienced users, the number of isothermal or kinetic experimental runs, or data sets (data arrays) will need to be inserted manually by the user, to allow for the programme to automatically request an array of the temperatures used for the isothermal experiments, and the initial adsorbate concentrations used for the kinetics experiments. This is done automatically, with the user being requested to enter each temperature or concentration individually, with the programme appending this to an array for use in the code. This loop will request the exact number of variables as defined by the user into the manually entered number of variables input.

3.4.2 Special Inputs

A number of special inputs are required for the function to correctly retrieve the data, as will be described in the following sub-heading. These include the option of temperature variance in the isothermal data, the use of a tolerance value in the kinetic fitting for data sets which converge to their equilibrium values extremely quickly, and the option as to whether a single time array, or multiple time arrays were used for the kinetics experimental runs.

3.4.2.1 Temperature Variance

This input is automatically determined by the function, based on the length of the isothermal temperature array based to the function. If this array has a length of 1, then the function will set the variable 'no_Tvar' to a value of 1, which will be used in 'if' statements to determine the method of isothermal fitting. A value of 0 is assigned to this variable should the length of this array be greater than 1. The outputs of the isothermal fitting function are presented in the table below:

Table 1: Function Outputs based on 'no_Tvar' Assignment

'no_Tvar' Assignment	Function Outputs
-----------------------------	-------------------------

1	Q_{max}, k_L
0	$Q_{max}, \Delta S^\circ, \Delta H^\circ$

3.4.2.2 Tolerance

Initial trials were performed on a tolerance function within the code, which allowed the user, for data sets in which the convergence to the equilibrium adsorbent capacity for the kinetics experiments happened extremely quickly, to force the function to place a higher emphasis on the initial data points, further away from this final equilibrium value, to allow for a better fitting of the adsorption constant, which is a rate parameter.

This was done to avoid the potential situation where the function fails to accurately converge to the desired value, due to the abundance of equilibrium data points which essentially do not vary. Thus, the fit, in terms of the least squares, will always be very good, as the distance of the initial points from the predicted curve will have an insignificant impact on the fitting. Data sets like this usually converge to the guess, or initial guess value provided, as this provides a ‘good enough’ fit.

Thus, the tolerance code was designed to reduce the data sets to only those points prior to the initial ‘levelling off’ of the graph, or even those points a significant distance from this point. The fitting function would thus only be passed a smaller number of points on the more ‘curved’ section of the experimental run, thus forcing the function to fit to the initial part of the data, with only a few asymptotic points used. This would theoretically allow for a better fit to the overall shape of the data, and not just the relatively flat line displayed when equilibrium is achieved.

The tolerance value would be a user-defined input from 0 – 100, which would represent the percentage of the final equilibrium value, to be used in the code described.

The code was however excluded from the final programme presented, as it functioned relatively counter-intuitively, as the difference between each array value was determined, and compared to the tolerance value. Thus, a higher tolerance value excluded more data points from the final data set, as the closer the values to the final value, the smaller the difference, and this did not fit within the tolerance, as this was based on the final equilibrium adsorption capacity. This code thus requires reworking, such that a tighter tolerance implies a stricter appending of the final array, to allow the code to operate more logically for users unfamiliar with the code.

Convergence was also achieved with relatively good guess values, and once this could be achieved automatically, it was deemed acceptable to remove this feature until it was adequately optimized and tested.

3.4.2.3 Kinetics Time Arrays

In some data sets, universal time arrays existed for all of the kinetics experimental runs, regardless of the initial adsorbate concentration used. Thus, for these data sets, only one time array was recorded, with values for each adsorption capacity array returned at standard time intervals.

However, the adsorption capacity at each initial concentration for other data sets' experimental runs was recorded individually, and thus each adsorption capacity array had a corresponding time array specific to that initial concentration of adsorbate.

Thus, a functionality similar to that described in section 3.4.2.1 above was introduced, where, with a user input determining which type of experiments were conducted out of the two cases presented above, the 'No_Timevar' variable was assigned a value of 1 or 0, with 1 corresponding to the function searching for only one universal time array and applying it to all of the adsorption capacity arrays, and 0 corresponding to each adsorption capacity array being paired with its respective time array.

3.4.3 Data Retrieval

In order to automate the data retrieval process, the data sets had to be named in such a way that they could be retrieved, and have function and manipulations performed on them using looping. However, in Python variable names are fixed, with only string names able to be looped through and updated. However, strings cannot hold or store data, as these are not variables, and thus the data sets cannot be defined using string names.

Therefore, the *locals()* function was used, along with the *.format* functionality for strings. As long as the columns of data in excel were named in such a way that the difference between them was a numerical value, a looping function could be used to first change the name of a string, by formatting a numerical value into it, and then converting this name into a Python variable using the *locals()* function. This allowed for each data set to be pulled from excel, renamed and appended to a larger list, in order to allow for future operations to be more easily performed, as this larger list could be simply indexed to obtain the entire corresponding data set.

Using this functionality the data sets were also able to be combined into a singular array automatically, using a similar method as described in sub-heading 3.3.3, with the *numpy.append* functionality. These combined arrays could then be passed into the fitting functions, to allow for automatic global data fitting. The previous lists, containing the smaller data set lists in list form, could then also be used to obtain the cumulative length array required for the fitting function, as described in sub-heading 3.3.3.

3.4.4 Curve Plotting

The final curve fitting of the kinetics curves for the evaluation of the programme and the mathematics on which it is based, was done automatically, through a loop in which each data set was individually called, its continuous counterpart plotted using the 'inte' function, and then itself also plotted as a series of discrete points along the same graph. Thus, after each data set has been looped through, the final graph will contain all of the data sets and their plotted fitted responses.

The isotherm curves are also presented at the end of each data set run-through, and were programmed to be automatically generated in a similar manner. The 'isotherm_plot' function and its inputs are defined based on whether or not the system contains temperature variation in the isotherm trials, ie. whether the function accepts a k_L value, or both an ΔS° and a ΔH° value. A continuous 'x' (C_e) array is also developed using the *np.linspace* function, with the largest final value of C_e in all potential isotherm data sets used as the final value, as this array is used for each temperature, to model the function out with the fitted parameters as a continuous plot. Each data set is then again looped through a plotting 'for loop' and all of the isothermal data sets are plotted against their respective predicted function outputs using the best fit parameters determined.

3.4.5 'Goodness of Fit' Parameters

The 'goodness of fit' parameters returned by the programme for each data set, the 'R Squared' and standard error values, were determined using the *scipy.stats.linregress* function in Python, which, in a similar manner to the *np.polyfit* functionality, returns the constants associated with the best fit line generated based on an input of an x and y array. However, unlike the *polyfit* function, the *linregress* function only works for linearised data, but has the additional inbuilt functionality of returning the r , p and standard error values associated with the best fit line applied to the input data.

In order to allow for this function to operate, data at the exact experimental time points used are generated by a modified ‘kinetics’ function, with the added functionality of not only integrating the process, but appending to a new list the values of the adsorption capacity at the specific time intervals, for each initial concentration. The *np.append* function is again then applied to combined these values into a total list of predicted adsorption capacity values, similar to that required to be passed into the fitting functions, and as described in section 3.3.3. This array was named ‘Q_{tot_new}’ and was then passed as the *y* array into the *linregress* function, with the *x* array the original experimental adsorption capacity data. The slope and intercept were not required, but the output *r* value was squared to obtained the R^2 parameter, and the standard error was also returned.

3.5 Spreadsheet Format

In order for the programme to be able to read the spreadsheet and extract the data, the spreadsheet is required to firstly; be saved in the same folder as the Python .ipynb file, and secondly; have the data laid out in a particular manner, specifically in terms of the way the data is presented, and the column headings of this data.

The formatting requirements are summarised below:

- The isotherm data and kinetics data should be saved on separate sheets within the spreadsheet file.
- The data should be in column form, not rows.
- The data headings should be in row 1 of the sheet.
- The adsorbate concentration data should be in units of mg/L.
- The amount of adsorbate adsorbed data should be in units of mg/g.
- The time data can be in any units.

The naming conventions for the data headings are presented in the table below:

Table 2: Naming Conventions for Spreadsheet Data Headings

Data Type	Description	Naming Convention
Isotherms <i>x</i> data	Equilibrium adsorbate concentration (C_e)	Ce(no) – eg. Ce1

Isotherms y data	Equilibrium amount of adsorbate adsorbed (Q_e)	(Temperature)K – eg. 298K
Kinetics x data	Time	If one universal time: Experimental time If multiple individual times: Time(Concentration) – eg. Time10
Kinetics y data	Initial adsorbate concentration (C_0)	(Concentration) ppm

Notes:

- The naming conventions are case and spacing sensitive, if not input exactly correctly, Python will be unable to read them.
- If the concentrations are float values, or, in other words, contain any decimal point, all of the headings must contain a decimal point, including the ‘Time10.0’ headings, with decimal points being included even if these are 0.
- Although ‘ppm’ or parts per million is used as a naming convention, the units of the concentration used should be in mg/L, which in many cases can be approximated as ppm. However, the units of the experimental data should be converted to mg/L before being run through the code, as a part of the formatting.

3.6 User Inputs and Returns

The following table provides the inputs required by the programme from the user, in order to run the code:

Table 3: Required User Inputs

Input	Description	Unit
no1	Number of isothermal experimental data sets	1
no2	Number of kinetic experimental data sets	1
T_range	List of temperatures at which isotherm data was obtained	K

C_array	List of initial adsorbate concentrations used for kinetics study	mg/L
m	Mass of adsorbent dosed for kinetics experiments	g
V	Volume of adsorbate solution	L
T_kinetics	Temperature at which kinetics experiments were carried out	K
Spreadsheet_name	Name of the spreadsheet containing data	
Isotherms_name	Name of the sheet in the spreadsheet in which the isotherms data is presented	
Kinetics_name	Name of the sheet in the spreadsheet in which the kinetics data is presented	
Timevar	Is there an individual time array for each kinetics data set	'Yes'/'No'
Time_units	Units of the time array for the kinetics experimental data	

The function will then return the following:

- An isotherms graph comparing all experimental and predicted data
- A kinetics graph comparing all experimental and predicted data
- The 'goodness of fit' parameters
- The fitted best-fit parameters

4 Data Analysis

4.1 Reformatting

A spreadsheet titled 'Digitised data.xlsx' was provided with the project upon introduction, and contained the raw data from approximately over 100 papers, containing around 140 independent data sets. However, not all of these data sets contained both kinetic and isothermal

experimental data, and not all data sets facilitated the ease of reformatting into the required form, without empirical data manipulation.

Thus, approximately 50 papers were chosen and reformatted, of which 6 provided further errors in the reformatting procedure, with 44 papers ultimately being reformatted such that they were able to be passed through the function, described above. These papers contained 61 independent data sets, all containing sufficient kinetics and isothermal data for the function to operate as intended.

The reformatting procedure entailed the copying of the data onto a new spreadsheet, the renaming of the data column arrays in Excel, as well as the potential conversion of the data should it be necessary. The data was commonly presented as linearised arrays, or fractions of the initial adsorbate solution concentration. Unit conversion from mole or molar units was also often required, to maintain all of the analysis in the units of mg/g for Q , and mg/L for C for consistency. These units, upon analysis of sufficient papers and their data sets, seem to be the universally used units for adsorption experiments.

In addition to the reformatting of the data required, critical information was also required, namely the temperature(s) used for the isothermal experiments, the temperature used for the kinetics experiments, the initial adsorbate concentration of the kinetics solutions (C_0), the mass of adsorbent used in the kinetics experiments (m) and the volume of solution (V). The units of time used for the kinetics experimental study was also entered into the spreadsheet, so as to correctly return the units of the adsorption constant, and accurately plot the graphs.

The additional information was simply entered into the Excel spreadsheet, and was used as a part of the user defined inputs for the analyses of the systems.

The spreadsheet containing the reformatted data sets is provided alongside the submission of this report, and is named 'Reformatted.xlsx'.

4.2 Data Analysis and Storage

Out of the reformatted data sets, approximately 13 provided errors, usually regarding the guess value convergence, and thus did not allow for the entire data set to accurately be passed through the Python function. If these errors could not be manually rectified without significant effort, the data sets were flagged, and their results not returned. A further 10 data sets which similar, or in the same paper as those repeatedly being flagged, were not analysed, in order to place greater emphasis on experiments which provided data sets more conducive to analysis.

Thus, 38 data sets were ultimately passed through the Python functionality, of which selected data sets bearing similar results and characteristics were selected for discussion in the report.

Each of the data sets could be placed into one of four broad categories, as follows:

Table 4: Data Set Categories

Category	Description
1 - Variation in both kinetics and isotherms	The isotherm experiments were conducted at multiple temperatures (multiple isothermal data sets) and multiple initial adsorbate concentrations were used for the kinetics trials.
2 - No temperature variation in isotherms	Only one isotherm data set was provided, with kinetics trials done at multiple initial adsorbate concentrations.
3 - No concentration variation in kinetics	Multiple isotherm data sets provided, but with only one initial adsorbate concentration used in the kinetics experiments.
4 - No variation	Only one isotherm, and one kinetics experimental data set provided in the paper.

Once passed through the function, the best fit plots based on the parameters determined for the isothermal and kinetics data were returned, plotted against the experimental data. The ‘R Squared’ (R^2) and standard error of the data was also returned, as well as the magnitude of the determined parameters. For those data sets with only one isothermal data set, only the equilibrium constant, k_L , was returned, whereas for those with multiple experimental isothermal runs, at different temperatures, both the standard entropy (ΔS°) and standard enthalpy (ΔH°) changes for the adsorption process. The maximum adsorption capacity of the adsorbent (Q_{max}) and the adsorption constant (k_{ad}) were returned for all data sets.

The results were then pasted into four Excel documents corresponding to the category into which the data set fell, and are named as follows:

Table 5: Results Spreadsheets Names

Category	Spreadsheet name
1	‘Both var.xlsx’

2	‘No Tvar in Isotherms.xlsx’
3	‘Tvar no kinetics Conc var.xlsx’
4	‘No var.xlsx’

A detailed ‘user guide’ to running the code, using the ‘Reformatted.xlsx’ spreadsheet as an example, is presented in Appendix A, and gives further insight into the method of running each data set through the code, and the results generation.

5 Results and Discussion

5.1 Initial System

The isotherm graph, and best fit parameters determined using the isotherm fitting function, are presented below, for the original data analysed from Muedi et al. (2021).

Table 6: Isotherm Best Fit Parameters for Muedi et al. (2021)

Parameter	Value	Unit
Q_{max}	101.93	mg/g
ΔS°	15.5	J/(mol*K)
ΔH°	6344.8	J/(mol*K)

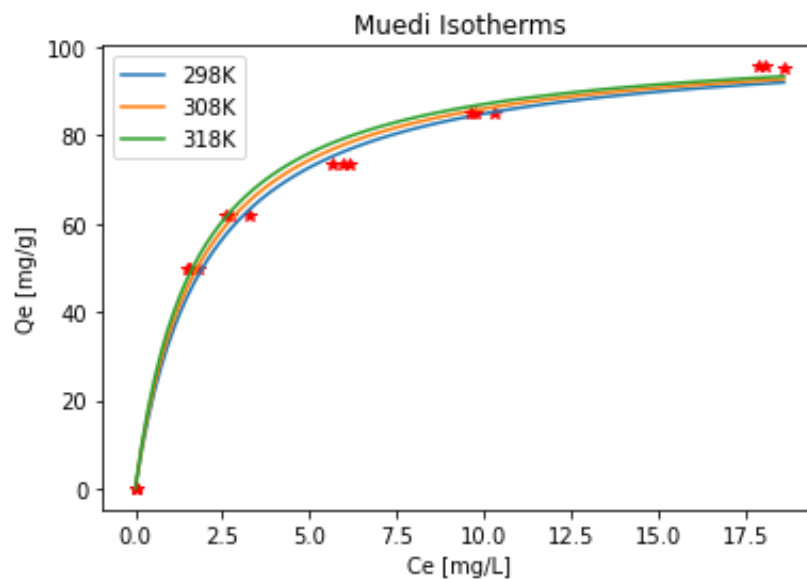


Figure 1: Experimental v Predicted Isotherms for Muedi et al. (2021)

The tabulated parameters match those reported in Muedi et al. (2021) extremely accurately.

The following kinetics graph was obtained for the analysis of the original data from Muedi et al. (2021), with the goodness of fit values, and k_{ad} tabulated below:

Table 7: Parameters for Muedi et al, (2021)

Parameter	Value	Unit
k_{ad}	0.02014	L/(g.min)
R^2	0.9959	
Standard error	0.0137	

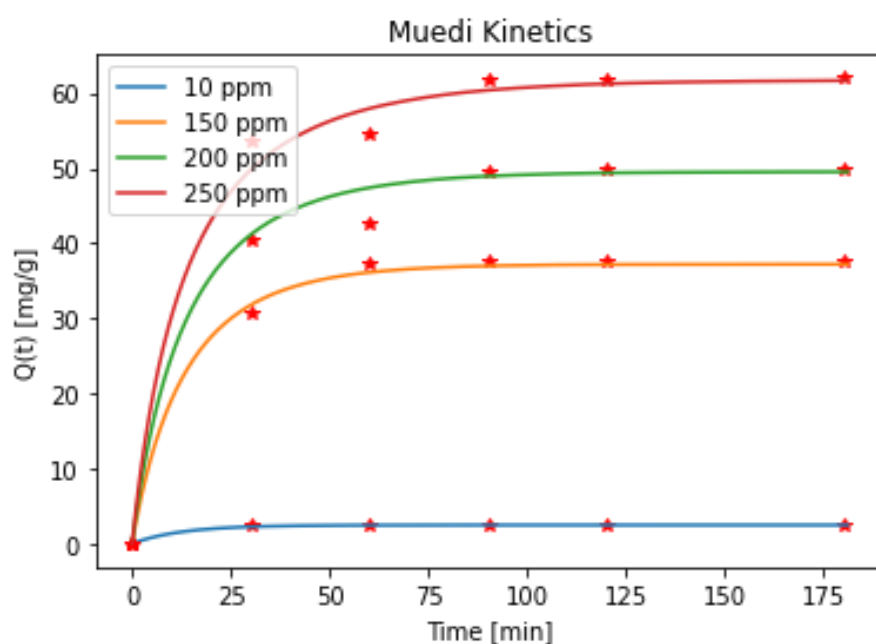


Figure 2: Experimental v Predicted Kinetics (Muedi et al, 2021)

The R^2 value of 0.9959 indicates a very good fit of the predicted data to the experimental data, indicating that the best fit parameter, k_{ad} , the adsorption constant, is accurate for this system. Thus, kinetic behaviour of the system would be predictable at various other initial adsorbate concentrations, and with varying amounts of adsorbent and solution added. Good estimations of the equilibrium amount of adsorbate that the adsorbent can adsorb would also be available at varying initial conditions.

Thus, the function is seen to function efficiently in this case, arriving at not only the same values reported in the original paper, but generating an extremely good final fit, and doing so automatically.

5.2 Extremely Fast Kinetics

The data collected by Wei et al. (2014), and the response generated indicates that systems with extremely fast kinetics, and insufficient early measurement, do not properly converge. When initially entered into the programme, the k_{ad} guess value did not properly converge, due to the second data points already being at equilibrium adsorption capacity. Manual guesses were entered, with a manual guess of 10 converging to a magnitude of 10.123, and a manual guess of 1 converging to a magnitude of 0.6066. The two kinetics graphs are presented below for each case:

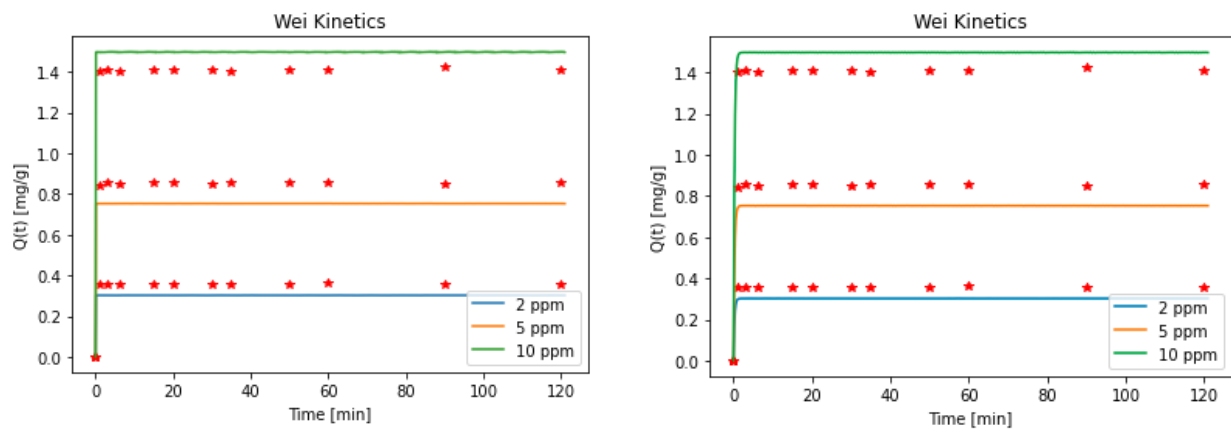


Figure 3: Comparison between Wei et al. (2014) guess values

The left graph displays the results for the guess value of magnitude 10, with the right graph displaying those for guess value with magnitude 1. The graphs are essentially identical, with a small curve visible in the slower system. The graphs also do not converge to the experimental equilibrium values, possibly a consequence of the relatively poor fit to the isothermal data, and the lack of sufficient isothermal data points in each experimental run, especially at high C_e values.

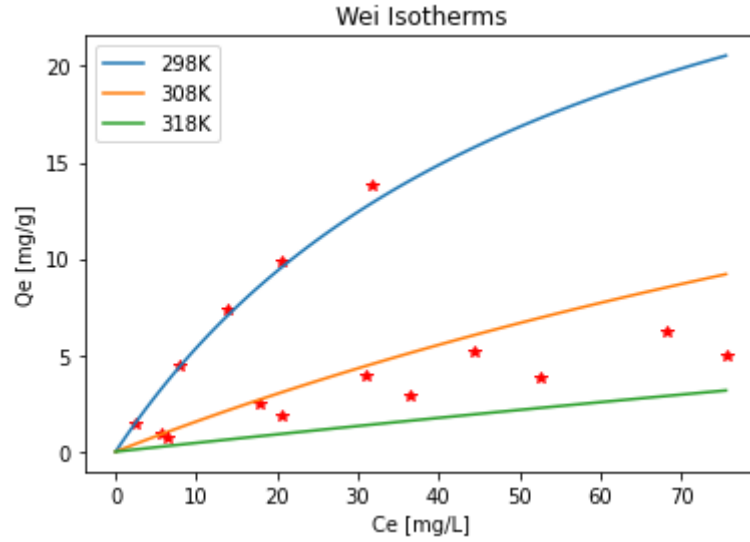


Figure 4: Experimental v Predicted Isotherms for Wei et al. (2014)

5.3 Good Fits

Upon analysis of the data sets, 11 data sets other than Muedi et al. (2021) exhibited good fits to both the isothermal and kinetics experimental results, indicating that 32 % of the data sets analysed provided reproducible and extendable results. The kinetics results for two of the data sets with both temperature variation in the isotherms, and initial adsorbate concentration variation for the kinetics are provided below:

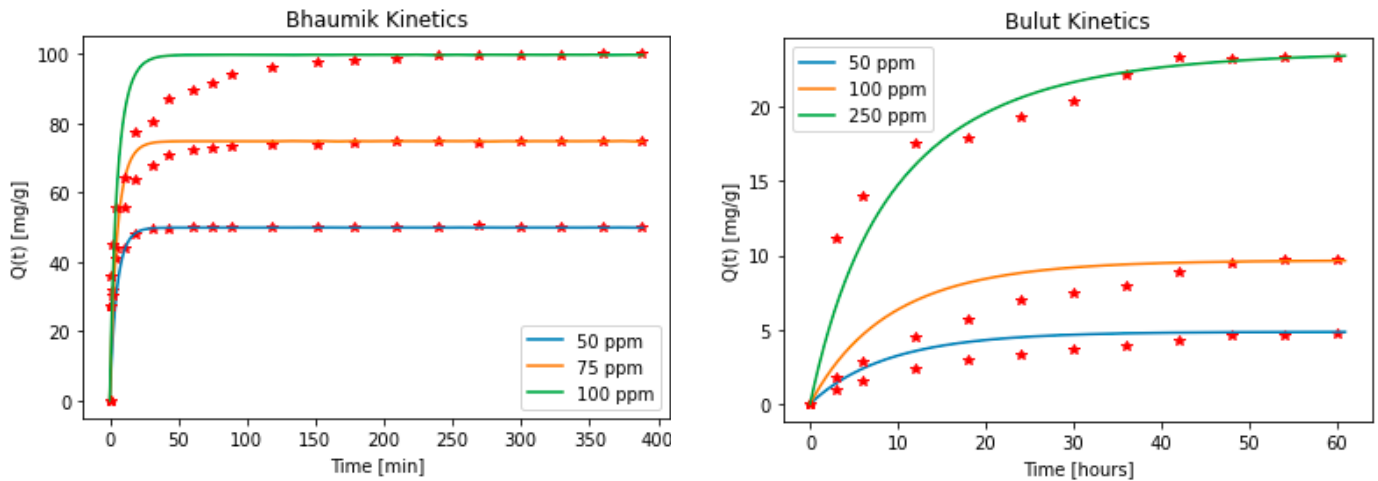


Figure 5: Experimental v Predicted Kinetics (Bhaumik et al, 2012), (Bulut et al, 2007)

The k_{ad} and R^2 values for each data set are presented in the table below:

Table 8: Kinetic Parameters for Bhaumik et al. (2012) and Bulut et al. (2007)

Paper	Parameter	Value	Unit
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Bhaumik et al. (2012)	k_{ad}	0.2155	L/(g.min)
	R^2	0.9546	
Bulut et al. (2007)	k_{ad}	0.0112	L/(g.hr)
	R^2	0.9713	

As can be seen from the above, the fits are not as ideal as that provided by Muedi et al. (2021), but are reasonably accurate, with both Bhaumik et al. (2012) and Bulut et al. (2007) converging to the final experimental values with a good accuracy.

An example of a fit using data with no temperature variation in the isotherm, but multiple initial concentration of adsorbate in the kinetics experiments, is shown below:

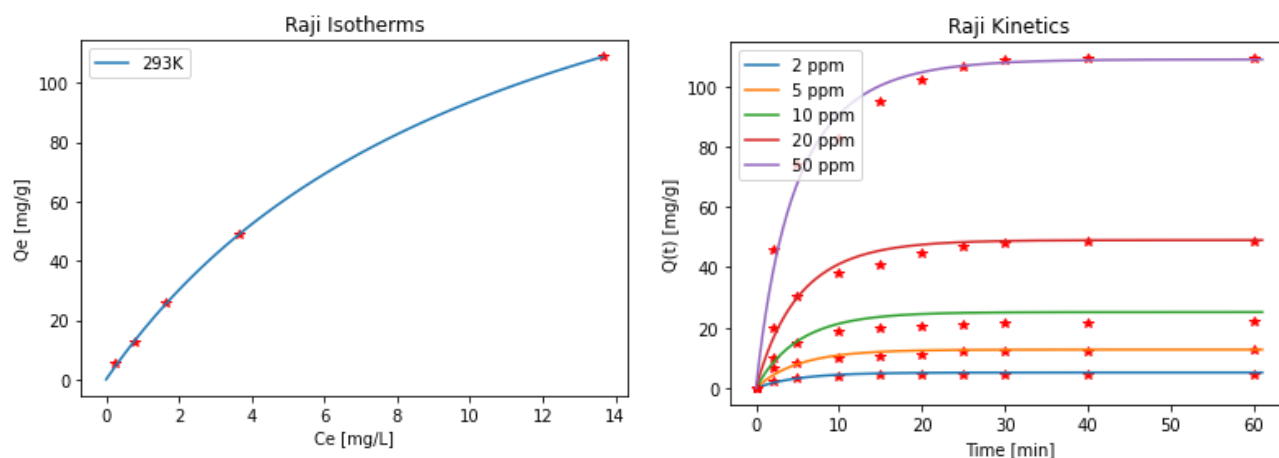


Figure 6: Raji and Pakizeh (2013) Isotherm and Kinetics Experimental v Predicted curves

The R^2 value for Raji and Pakizeh (2013) was 0.9941, almost equivalent to that achieved in the analysis of Muedi et al. (2021). Song et al. (2011) data achieved a fit with $R^2 = 0.995$, and Yu et al. (2017) data for As(III) achieved an $R^2 = 0.9699$.

All of the above kinetic fits exhibit some form of overshoot, but converge well towards the equilibrium concentration of the adsorption capacity. This is an indication that one of the shortcomings of the equation may be that it does not accurately consider the mass transfer effects (diffusion effects) occurring prior to the actual reaction, or adsorption process. As this

would influence the process of adsorption prior to the ‘reaction’ step, the model has not accounted for additional physical phenomena in the early stages of the process.

5.4 Poor Kinetic Fits

5.4.1 Poor Isotherm Fits

Of the analysed data sets, 13 could be placed into the category of poor isotherm fit, poor kinetics fit, which is 34 % of the data. However, this trend could be attributed to the isothermal data not being best suited to be analysed by the Langmuir isothermal model, as this is a one surface model, and does not account for surface heterogeneity, as the Freundlich model does (Ayawei et al., 2017). These fits could also potentially be better represented by the two surface Langmuir model, but analysis using this model is beyond the scope of this report and the programme under investigation and development.

Examples of the poor fits are depicted below:

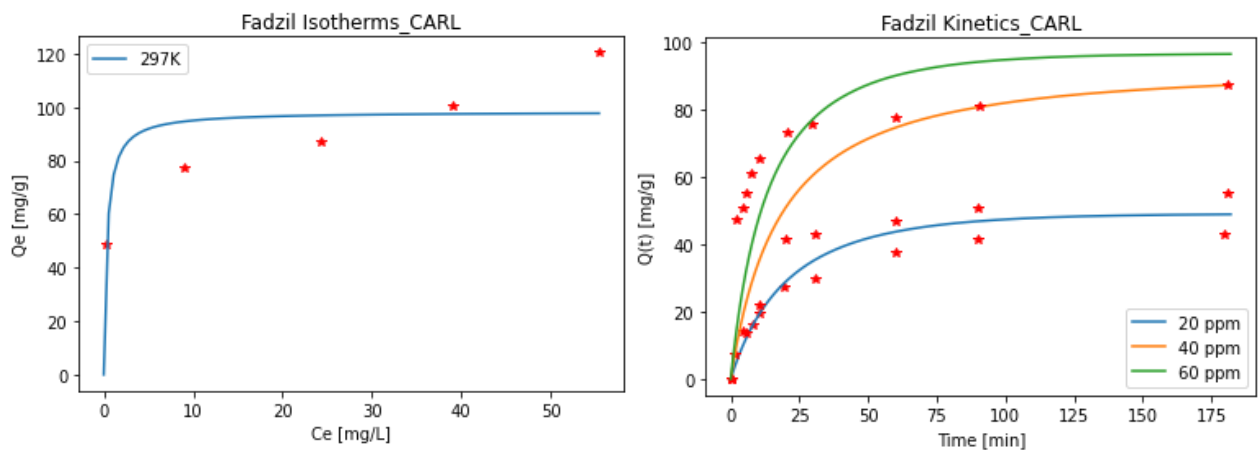


Figure 7: Fadzil et al. (2016) Experimental v Predicted Isotherm and Kinetics curves

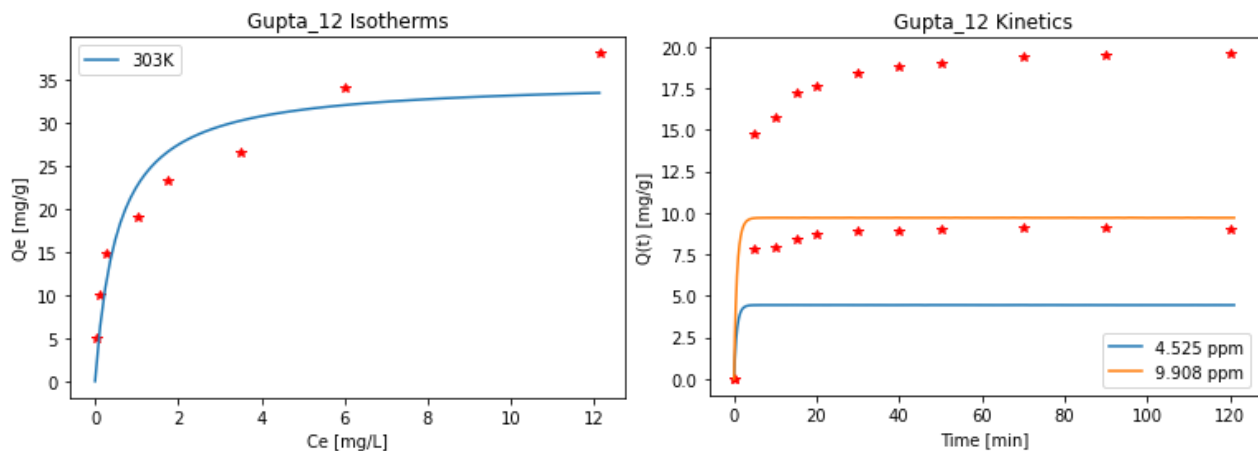


Figure 8: Gupta et al. (2012) Experimental v Predicted Isotherm and Kinetics curves

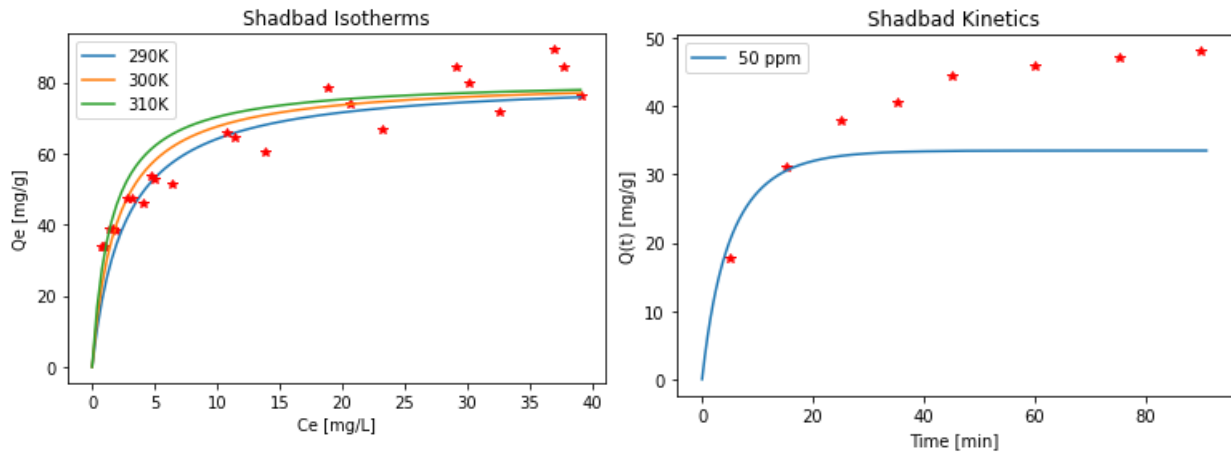


Figure 9: Shadbad et al. (2011) Experimental v Predicted Isotherm and Kinetics curves

Fadzil et al. (2016) and Gupta et al. (2012) show very steep variations in the isotherm data away from the converging predicted curve, with this trend slightly more subtle in Shadbad et al. (2011). However, with all of these data sets, the isothermal fit is not ideal, especially towards convergence, which results in the severe over-, or under prediction of the kinetics curves, despite their reasonable k_{ad} values.

This sharp, sudden steepness in the experimental results for the isothermal curves observed in all three cases gives an indication of the possibility of two surfaces, or surface heterogeneity, of the adsorbates, with the distinct equilibrium regions well visible through the experimental data. Thus, the Langmuir one surface model is inadequate in its prediction of these data sets, thus explaining why the isothermal constants determined would not lend toward a good kinetic fit, when applied into the kinetic function, as these do not adequately match the system type.

The analysis of the majority of the other systems which fall under this heading results in similar trends being observed, although slightly less obvious in most of the other cases, especially when insufficient time was allowed for the isothermal experiments to extend to high C_e and Q_e values.

5.4.1 Good Isotherm Fits

Of the remaining data sets, 12 exhibited good isotherm fits, but poor kinetic fits. This amounts to 32 % of the data.

The following two data sets were analysed, exhibiting similar responses:

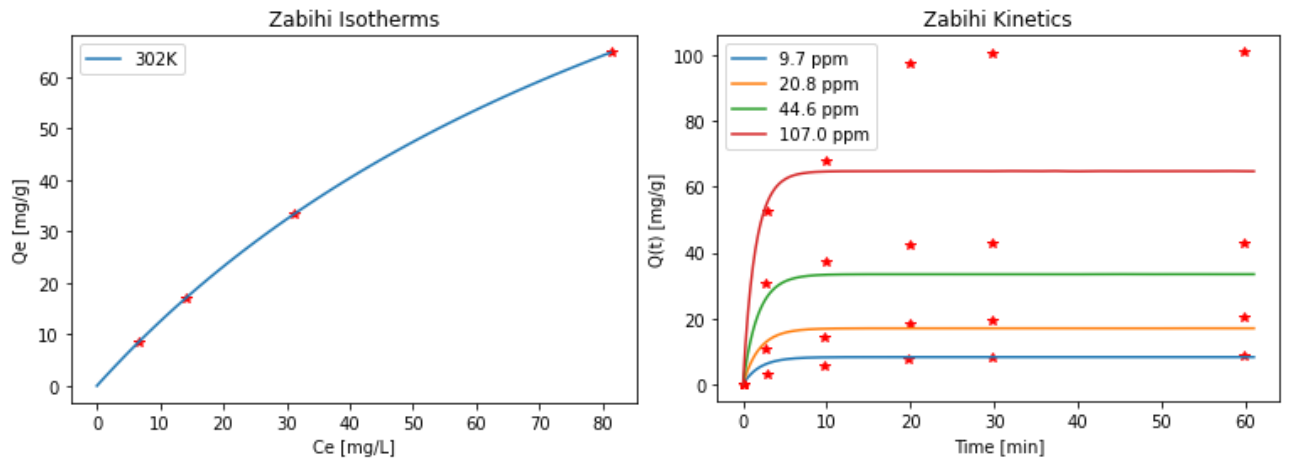


Figure 10: Zabihi et al. (2009) Experimental v Predicted Isotherm and Kinetics curves

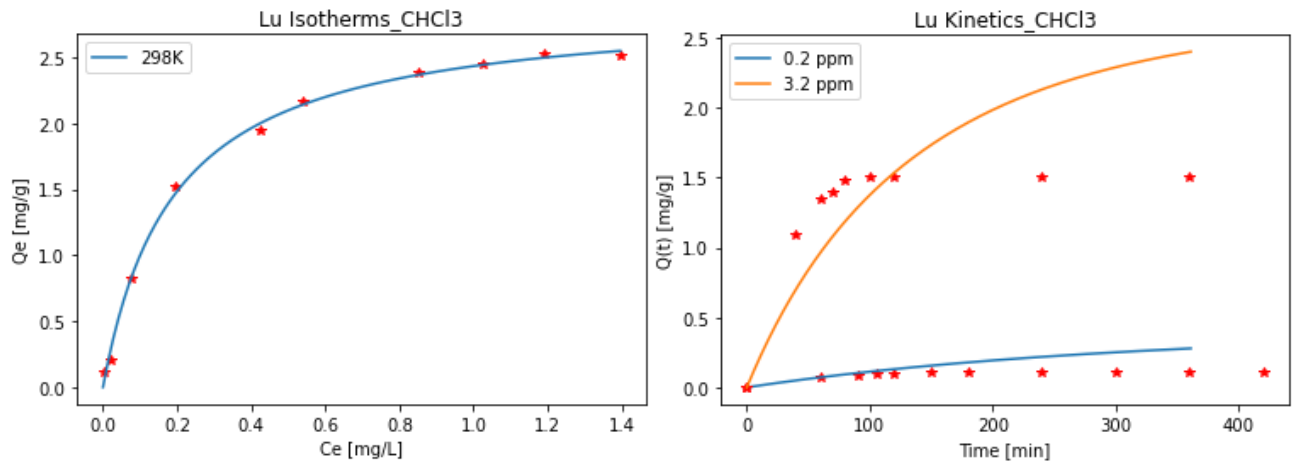


Figure 11: Lu et al. (2005) Experimental v Predicted Isotherm and Kinetics curves

As can be visibly seen on the two graphs, the isothermal data provides a very good fit, with the kinetics data, especially at higher initial adsorbate concentrations, providing a very poor fit.

The experimental kinetics data was analysed using equation 5, modified to use the equilibrium adsorption limit Q_e from the kinetics data, to calculate the corresponding equilibrium adsorbate concentration, C_e . This was done for the predicted and experimental curves. The results are presented in the table below:

Table 9: Equilibrium comparisons of kinetic and isothermal data

Paper	Type	Experimental Q_e [mg/g]	Calculated C_e [mg/L]
Zabihi et al. (2009)	Experimental	100	67
107 mg/L	Predicted	65	81

Lu et al. (2005)	Experimental	1.5	2.6
3.2 mg/L	Predicted	2.5	2.2

As can be seen on both graphs, using the C_e value as an x point, and the Q_e as a y point, neither of these points, as calculated using the experimental data, would occur on the isothermal curve. Thus, there exists a disconnect between the experimental data sets, with the isothermal curve not matching the kinetics equilibrium values. The predicted values, however, both fall perfectly onto the isothermal curve, as the basis relation for the fitting function was based off of this result.

6 Conclusions and Recommendations

6.1 Conclusions

Only 2 % of the data analysed, or 1 data set, did not fall within the three broad categories discussed in the results section. This paper exhibited a perfect kinetics fit, but a poor isothermal fit. However, this small percentage could be ruled down to experimental error in the paper or an anomaly for this specific system in the code, where it converges with a perfect mix of incorrect parameters, or a mistake in the reporting or recording of the exact values or data used in the experiments.

A pleasing statistic is the 32 % of the data sets which exhibited perfect or close to perfect fits for both the isothermal and kinetics data. In addition to this, the remaining data sets all exhibited some degree of variation which could be justified. Although not every non-conforming data set was analysed specifically, similar trends could be visually observed in the remainder of the graphs analysed.

It is difficult to properly quantify the performance of the programme while the data sets do not conform to the Langmuir one surface model, and thus a large portion of the non-conforming data do not conform based on their intrinsic physical properties. Further analysis using appropriate models on these systems is recommended, but is beyond the scope of this investigation. Further, the model should also potentially be altered to include the mass transfer effects occurring prior to the adsorption process itself, to better model the kinetics of the entire process.

In the two cases analysed for the third category of data sets, good isothermal fits but poor kinetics fits, the programme was observed to return results that fit the isothermal data high with a high degree of accuracy, indicating that had the isothermal and kinetics experimental data sets been a good reflection on one another, as they should in theory, the programme would provide a very good fit for the kinetics data set, with an accurate and reproducible k_{ad} value.

Ultimately, the data sets analysed show the use case of equation 4, as well as the use case of the programme developed in utilising equation 4 to produce accurate adsorption constants and parameters relating to adsorption. The analysis performed using the developed programme provides sufficient evidence to suggest that equation 4 is not only an accurate, but a usable equation, given modern society's available computing power.

Therefore, this investigation provides strong evidence for the further analysis of data using the programme developed, and the improvement of the programme developed to broader systems. Furthermore, by incorporating equation 4, the parameters produced and returned by this programme are able, with a high degree of accuracy, for conforming systems, to predict the behaviour of these systems at varying inlet specifications.

6.2 Recommendations

6.2.1 Programme Improvements

As seen in the results section, the isothermal parameters determined can have a significant impact on the accuracy of the kinetics fits, and thus incorrectly performed or mis-managed isothermal experiments, or even insufficient isothermal data gathered can have a large effect on the prediction of the kinetics of the adsorbent and the system.

Thus, in order to counteract this, a functionality will need to be built into the code to allow for the prediction of the equilibrium constant (k_L), the maximum amount of adsorbate adsorbed (Q_{max}) as well as the adsorption constant (k_{ad}) using just equation 4, and the kinetics fitting functionality. This would allow for the comparison with the results of the isothermal fitting with the Langmuir equation, to determine whether this model correctly predicts the equilibrium relationships of the system. This may also allow for potentially better kinetics prediction, without reliance on another data set, another experiment or another equation, all of which may contain errors, or may not be entirely accurate for the system at hand.

6.2.2 Graphical User Interface

After the requirements and recommendations of section 6.2.1 have been considered and met, the following should be considered.

Although the programme currently operates as desired, and is able to generate constants and graphical comparisons automatically, it still requires the user to have a basic understanding of the Python interface. The programme is also not free of potential convergence errors, which lead to the code halting, unable to proceed without certain specific parameters being defined. The average user, especially those unfamiliar with the detail of this report, will thus not be adequately equipped to utilise the system, especially if an error does occur.

In addition, the Python *pandas* module used in the programme requires that the specific file location of the Excel file be specified, or that the file be save in the same folder (file location) as the main programme file being used. This, to users unfamiliar with the technicalities of this module, this programme, or even the concept of file directories, presents a significant stumbling block in the ability of the programme to operate as desired, in terms of ease of access.

Thus, in order to provide a system which is as user friendly as possible, it is desired that the programme should incorporated into a graphical user interface, or GUI, such that this can be opened as a separate file, without having to run Jupyter Notebook or Google Collaborate to open Python, and have all the functionalities presented as scroll down menus, selectable options/buttons, or easy to understand dialogue boxes. It would also be ideal for the Excel file to be selected and read by the programme, from any file location, or have the data pasted into cell blocks within the GUI itself, doing away with any naming conventions.

The addition of a GUI has the potential to not only facilitate the ease of further analysis and correction to the current programme and the current adsorption analysis approach, but to allow for the breakthrough into the field of much more accurate and reproducible results being obtained on a more consistent basis. This will also allow for a focus shift back onto the adsorbent types, and experimental rigour, as the programme will facilitate the ease of prediction and analysis.

This is recommended as a basis for future projects on this topic.

7 References

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8 Appendices

Appendix A User Instruction Document

This documentation assumes a basic understanding of Excel, and thus focuses on the Python coding description which is more specific in nature. For more information on the Excel format, revisit section 3.5. For more information on the Python inputs, revisit section 3.6.

After the experimental runs have been performed, the data gathered should be stored in a spreadsheet, or Excel file. The isotherm and kinetics data sets should be stored on separate sheets of the file, with the column headings, in the correct units and in column format, as specified in section 3.5.

The file should then be saved in the same folder, or file directory, as the Python .ipynb file containing the programme, for ease of reading this file. Ensure that all changes have been saved, or Python will read the oldest file version.

The Python .ipynb file should then be opened. The following menu will be present at the top of the screen:



Figure 12: Python Options Menu

Select 'Kernel'. The following menu will appear:

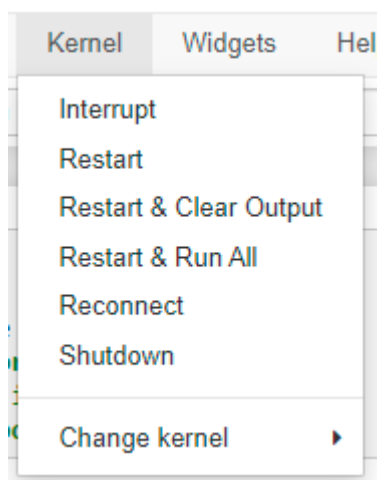


Figure 13: Kernel Menu

Select 'Restart and Clear Output'. This will ensure that all variable names are cleared, and that no previous runs will interfere with the current results, if a specification is omitted.

After a few seconds, the code will be ready. Select 'Cell', as indicated on Figure 12:

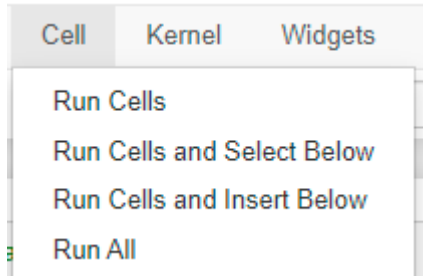


Figure 14: Cell Menu

Select 'Run All'. The code will redirect the user to the following dialogue box after a few seconds:

Enter name of the spreadsheet:

Figure 15: Dialogue Box

Enter the name of the spreadsheet, without inverted commas, or the file extension (.xlsx), as this will be added automatically. Press the 'Enter' key on the keyboard to run the cell. The code will then automatically take the user to the next dialogue box, and so forth. For numbers, enter the numerical magnitude as a number, not as a word.

The units required will be indicated by the instruction before the dialogue box. Follow these instructions until the last box is completed. The last dialogue box requests the units of time. These only effect printed results, and thus 'min', 'minutes' or any other variation is acceptable, the graph and final constants will be returned with these units.

Once the 'Enter' key is pressed after the time units are input into the code, the code will run to completion, and will automatically take the user to the bottom, or end, of the code, where the results graphs will be printed, and the constants and their units presented.