Imperial College London

Department of Earth Science and Engineering

MSc in Applied Computational Science and Engineering

Independent Research Project
Project Plan

Predicting Removal of Arsenic from Sorbents

by

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Abstract

1 Introduction and Objectives

Nowadays, while we make progress on the remediation of contaminated water, there are still many studies making efforts to improve the efficiency from different aspects, including but not limited to how the efficiencies related to the selection of adsorbent material(Arslan et al. 2022), and the novel materials in different fields(Linghu et al. 2017, Saka et al. 2012). Heavy metals such as arsenic have become an intractable environmental problem for a long time. The dangers of bioaccumulation and toxicity brought to life have been discussed (Dev et al. 2022). Moreover, more than one billion people are suffering from access to safe drinking water. This number will keep growing with the problems we are facing, such as population growth, urbanization, and climate change (Dev et al. 2022, Latif et al. 2020). To release the pressure, the improvement of efficiency in water treatment on heavy metals seems to be urgent.

According to recent studies, the water treatment capacity has boosted in this century due to the dramatic increase in population, followed by the significant growth of energy consumption(Smith & Liu 2017). However, the energy costs can take up 30% of the total operation cost for the water treatment plant(Biehl & Inman 2010). Thus, the accuracy of adsorption kinetics of the utilized adsorption model is crucial (Gibelhaus et al. 2022, Bullen et al. 2021) for both batch and column or continuous flow treatments (Bullen et al. 2021, Dichiara et al. 1900). An experiment from a laboratory is limited to operating under the condition of a certain adsorbent. In practice, the adsorbent(C_s) concentrations vary with the different concentrations of treated contaminants in the influent(C_0). Hence, the adsorption models ought to be sensitive to the operating conditions, making predictions possible (Bullen et al. 2021).

The pseudo-second-order (PSO) equation from Ho and McKay(Ho & McKay 1999) is a widely used adsorption kinetic model (Bullen et al. 2021), taking the form

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{1}$$

where t is the time (minutes), q_t is the amount of adsorbate adsorbed per mass of adsorbent at time t (mg g^{-1}), and q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}).

The concentration of aqueous adsorbate left at time t is

$$C_t = C_0 - C_s q_t \tag{2}$$

where C_t is the concentration of the aqueous adsorbate at time t (mg L^{-1}), C_0 is the initial adsorbate concentration at $t = 0$ (mg L^{-1}), and C_s is the concentration of the adsorbent (g L^{-1}).

According to Bullen, the PSO model has advantages in the following aspects: a)the simple mathematical form, b) adaptability for a wide range of reaction mechanisms, and c)able to be integrated and rearranged to provide linear equations so that the model parameters $k2$ and q_e can be obtained. However, the limitations, as mentioned above, are obvious to be the lack of the operation concentrations in the equations. The obtained parameters $k2$ and q_e can only be valid under the same condition as the experiment. As a result, the PSO model can not provide prediction to the adsorption kinetics with any given C_0 and C_s, of course, causing limited usefulness in practice. (Bullen et al. 2021)

To cover the shortage of the PSO model, Bullen published a revised PSO (rPSO) model which

includes the C_0 and C_s in the equation:

$$\frac{dq_t}{dt} = k'C_t(1 - \frac{q_t}{q_e})^2 \tag{3}$$

where the unit of rate constant k' is L $g^{-1}min^{-1}$.

However, usually, the kinetics are calculated via Excel, requiring to input data and equations manually. When it comes to numerous data sets, even the comparisons between the results from different experiments, the workload becomes heavy. This project aims to implement the original PSO with linear regression and nonlinear fitting, and Bullen's revised PSO into an executable python routine to obtain the adsorption kinetics and the visualized data to plots, allowing users to apply and process kinetic data easily. What's more, software for desktops will be developed via QT, which only requires users to enter the data obtained from the laboratory, and becomes friendly to all kinds of users.

2 Progress to Date

Dataset

The data as input used to running the program for trail is from (Manna et al. 2003).

```
C0 = 50.0
Cs = 4.0
Ct = C0-Cs*qt
t = np.array([0.,15.,30.,45.,60.,75.,90.,105.,120.,150.,180.,210.])
qt = np.array([0,2.022644346,4.609541933,6.399231094,7.236343423,8.474510454,
     9.392376354,9.933348215,10.24436494,10.87449072,11.34656137,11.62453718])
```

Mathematical Approaches for the Determination of Adsorption Kinetics

The first approach towards the adsorption kinetics uses the linearized form of the integrated PSO rate equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

which can be regarded as a form of $y = mx + c$. $\frac{t}{q_t}$ is plotted as a function of t, where m is the slope of the linear regression and c is the y-intercept. The linear regression was implement using the built-in function $LinearRegression()$ from $sklearn$ package, which minimising the residual sum of squares between the data points and the linear regression. Hence, the equilibrium adsorption parameter $q_e = \frac{1}{m}$ and the $k_2 = \frac{1}{cq_e^2}$.

Secondly, the nonlinear PSO kinetics were calculated, via an in-built function named $curve_solve$ from the $SciPy$ package, which minimizes the sum of squared residuals between the model and experimental data. The initial guess applied for $curve_solve$ is the results obtained from the linear regression.

Thirdly, the kinetics were obtained from the revised rate equation (3). Due to the difficulty of integration of the rPSO, Bullen expressed the adsorbed adsorbate at the nth data point as

$$q_n = q_{n-1} + ((t_n - t_{n-1})(k'C_{t(n-1)}(1 - \frac{qn-1}{q_e})^2)) \tag{5}$$

The rPSO parameters k' and q_e were obtained by fitting the model to the experimental data via $curve_solve$ to minimize the sum of squared residuals. Both results from the linear and nonlinear

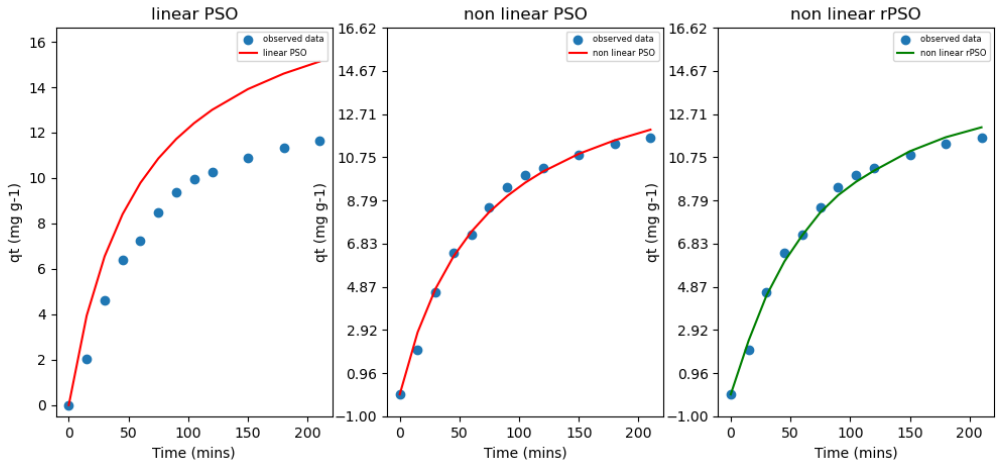

Figure 1: Comparison of linear PSO, non-linear PSO and nonlinear rPSO

PSO were used as the initial guess. They show the same results for the used set of experimental data.

The final results are visualized in figure 1. As shown below, these three approaches show an increase in fitness, as shown by the R^2. However, the equilibrium parameter q_e shows an anomaly, which should be fixed in the next stage.

```
manna: linearised PSO
qe: [19.35490626]
k2: [0.00088104]
R^2: 0.8126970681448343

manna: non linearised PSO
qe: 16.009098109960387
k2: 0.0008896635700572193
R^2: 0.9922481565761747

manna: nonlinear rPSO
qe: -407226944.25609887
kprime: 0.0032538604500831026
R^2: 0.9938910215084947
```

3 Future Plan

1. (Now - 8 July) Define the proper boundary conditions and initial guesses for rPSO model optimization.
2. (9-15 July) Error calculations of the three models.
3. (16-20 July) Run the scripts with other datasets from the literature, then classify and compare with the results.
4. (21 July - 1 August) Build the QT interface.
5. (2-15 August) Writing the final thesis.

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