Modified kinetic models for Cr (VI) adsorption in polymer inclusion membranes

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Abstract. Hexavalent chromium is a highly toxic environmental inorganic pollutant. To eliminate toxic Cr (VI) ions in natural waters, polymer inclusion membranes (PIMs) have been developed for highly selective metal ion transport applications. The investigation of the effectiveness of Cr (VI) recovery in aqueous solutions using PIMs with varying amounts of plasticizer was studied. The pseudo-first order (PFO) kinetic model was modified to describe the amount of Cr (VI) ions that have accumulated onto the PIMs at a specific time and to evaluate the performance of the PIMs. A quantitative analysis of the modified PFO a model based on their non-linear representation and using the coefficient of determination indicates that the adsorptive properties of the PIMs are best described by the modified non-linear pseudo-first-order kinetic model ($R^2 > 0.9748$), suggesting that the sorption process is physisorption. To show the applicability of the modified model to other transport studies, modified PFO was fitted into the experimental data that studies the transport of Zn (II) ions onto PIM ($R^2 > 0.95$).

1. Introduction
Heavy metals occur in the environment naturally, and it has a density greater than that of the water which means its components are much more held together [1]. A common environmental pollutant is chromium, which is widely used in various industrial processes, from leather treatment to manufacture of steel and paint. As an environmental pollutant, it has two oxidation states, Cr (III) and Cr (VI), of which the latter is significantly more toxic [2]. Accordingly, there is a need for the environmental chromium concentrations to be reduced to acceptable levels because chromium concentrations that exceed 0.25 mg/L are considered harmful [3].

Other Due to the high-risk effects on health of this heavy metal ion, other conventional methods in extracting hexavalent chromium ions were also reported from different studies where membrane extraction was utilized, including ion exchange resins, ultrafiltration, and liquid membranes. Different liquid membrane modalities are being utilized through the years, supported liquid membranes (SLMs) have been used widely to separate different pollutants from aqueous solutions [4]. The disadvantage of using SLMs in separating pollutants was the loss of either the carrier or the membranes solvent, or both, on the aqueous phase which resulted in its inability to be exploited industrially [5].

On the other hand, polymer inclusion membrane (PIM) was introduced by Sugiura in 1980 as an alternative for SLMs. It is a thin film cast from an ion carrier, a base polymer and a membrane plasticizer. The extraction of Cr (VI) ions and other metal ions using PIMs was reported in different
studies that involve equilibrium and kinetic data. There are several adsorption models developed to study the process of physisorption and chemisorption, including Lagergen’s Pseudo-First Order Model and Elovich Model [6]. However, these models only describe the adsorption capacity as a function of time, and not the more experimentally observed parameter of accumulation factor with contact time.

In this paper, the Pseudo First Order Model was modified to fit the experimental data that describes the relationship of accumulation factor with time. This paper also interpreted the prime cause of the gradual decrease of Cr (VI) ions that accumulates in the membrane as time increases using the initial conditions: pH=1, 10 ppm of Cr (VI) ions in HCl in the feed phase; 0.1 M NaOH in the strip phase.

The ability of the modified model to describe the relationship of accumulation factor with time will significantly aid not only the study of membrane adsorption but industrial operations as well since the more directly observable parameter was described here. Also, this model can predict the relationship between pH and time which is known to gradually change because of the effect of the HCl- media used in the feed phase. Since the modification of kinetic models that describe the relationship of accumulation factor concerning time was not yet reported, this can be very useful to have a better understanding of the effect of saturation on heavy metal ion transport caused by the pH and stripping phase.

The modified model that showed a good fit on the experimental data of Cr (VI) transport in PIMs was also fitted in the experimental data on Zn (II) transport that uses a different composition of PIMs to show the versatility of the developed model. This paper did not dwell more on the study of the PIMs physicochemical composition but focused on its ability to recover Cr (VI) ions as well as the factors that affect it during the sorption process.

2. Methodology

2.1. Experimental Data

All experimental data needed were collected from previous studies that involve Polymer Inclusion Membranes (PIMs) having different CTA/PBAT blend with Aliquat 336 [7] and PIMs having 2-hydroxy-5-nonylacetophenone oxime (LIX 84I) and di(2-Ethylhexyl) phosphoric acid (D 2 EHPA) as their composition [8].

2.2. Transport Studies

The adsorption capacity of metal ions per mass unit of adsorbent ($Q_t$) at time $t$ is calculated by:

$$Q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

where $C_o$ is the initial concentration of metal ions (mg/L), $C_t$ is the concentration of a metal ion in the liquid phase at time $t$ (mg/L), respectively. $V$ is the volume of the aqueous phase (L) and $m$ is the mass of the adsorbent (g).

The accumulation factor (AF) was used to determine the efficiency of PIMs in the transport of Cr (VI) using the equation (2):

$$AF = \frac{C_{mem}}{C_0} \times 100\% \quad (2)$$

where $C_{mem}$ (mg/L) is the concentration of the metal ion that accumulates in the membrane phase at time $t$ (hr) and is equal to $C_{mem} = C_0 - C_t$.
2.3. Pseudo-first-order (PFO) kinetics model modification

Hexavalent chromium adsorption kinetics can be modelled by the PFO (Largeren) equation based on the capacity to uptake the Cr (VI) ions. PFO model usually assumes that the sorption of metal ions into the sorption sites of the membrane and the initial surface coverage of sorbent is zero [9]:

\[
S_{\text{solid}} + M_{\text{aqueous}}^{\text{aq}} \rightarrow SM_{\text{adsorbed phase}}^{\text{adsorbed}}
\]  

Lagergren initially introduced PFO which is generally described as [10]:

\[
\frac{dQ}{dt} = k_1(Q_e - Q_t)
\]  

after integrating equation (4) with boundary conditions of \( Q_t = 0 \) to \( Q_t = Q_e \) and \( t = 0 \) to \( t = t \) the linearized equation will be:

\[
\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303}t
\]  

Lastly, its analytical equation can be expressed as:

\[
Q_t = Q_e \left(1 - e^{-K_1t}\right)
\]  

Since the PFO model is known to only describe the relationship of adsorption capacities and contact time, the analytical equation of the PFO kinetic model was modified to be expressed in terms of accumulation factor (AF), initial concentration (\( C_0 \)) and equilibrium concentration (\( C_e \)):

\[
Q_t = \frac{C_0 \cdot AF \cdot V}{100 \% \cdot m}
\]  

\[
Q_e = \frac{(C_0 - C_e) \cdot V}{m}
\]  

\[
\frac{C_0 \cdot AF \cdot V}{100 \% \cdot m} = \frac{(C_0 - C_e) \cdot V}{m} \left(1 - e^{-K_1t}\right)
\]  

simplifying the equation will result in the accumulation factor as a function of time:

\[
AF = \frac{(C_0 - C_e) \left(1 - e^{-K_1t}\right)}{C_0} \times 100 \%
\]  

Since the relationship of pH with time can be expressed as [11]:

\[
pH = \log(at^b)
\]  

and the membrane adsorbent concentration as [12]:

\[
C_m = \frac{C_e}{1 + \alpha}
\]  

\[
\log \alpha = pH - pk_a
\]
The final form of the modified PFO used in this study is:

\[ C_e = C_m \left( 1 + 10^{\frac{\log a \cdot e^{-pK_1}}{1 - e^{-K_1}}} \right) \]

2.4. Parameters estimation and model fitting

Python 3.8 Matplotlib package was used to fit the experimental data to the modified PFO model [13]. Initial parameters were first graphically estimated and then further optimized using the nonlinear optimization function curve fit in the SciPy package [14]. The goodness of fit of the modified PFO model was evaluated using sums of squares method.

| Symbol | Description |
|--------|-------------|
| AF     | Accumulation Factor of Cr (VI) in the membrane |
| a      | Numerical constant from equation (11) |
| b      | Numerical constant from equation (11) |
| Ce     | Equilibrium concentration of Cr (VI) in strip phase |
| Cm     | Maximum concentration of Cr (VI) in strip phase |
| Cmem   | Concentration of Cr (VI) in the membrane phase |
| Co     | Initial concentration of Cr (VI) in the feed phase |
| Ct     | Concentration of Cr (VI) in the feed phase |
| K1     | Rate constant of adsorption process using PFO kinetic model |
| Qe     | Adsorption capacity of adsorbent at equilibrium |
| Qt     | Adsorption capacity of the adsorbent |
| α      | Dissociation constant at equilibrium |
| t      | Contact time |

3. Results and Discussion

3.1. Adsorption kinetics models

Adsorption kinetics is described as the uptake or release of solute as a function of time. These models are also used to determine the mechanisms which may influence the process which includes the chemical reaction and the mass transfer that occur [15]. Several adsorption models were tried, including PFO and Elovich models; however, only the PFO showed promising fit to the experimental data obtained from Sellami et al. and Wang et al.

3.1.1. PFO Model for Cr (VI). The modified PFO model fitted to the transport of Cr (VI) is shown in figure 1. The calculated parameters of the modified non-linear model are shown in table 2, as observed the rate constant K1 increased with plasticizer content. This can be due to the plasticizers on the membrane that improves its permeability to enhance the PIM’s capacity for carrier movement. Also, the polarity and viscosity of the membrane plasticizer has a substantial effect on Cr (VI) transport [16]. The results indicated that the modified PFO model has a good fit with the data published by Sellami et al. [7]. A good correlation coefficient (R²) was obtained for the modified PFO model, which showed that the transport of the hexavalent chromium process followed the rate expression of pseudo-first order. The goodness of fit of the modified PFO to the experimental data is further proven by the
values of the maximum concentration ($C_m$) of the Cr (VI) ions in the liquid phase that is predicted from the model, as those have positive values and is less than the initial concentration ($C_0$). The high quantity of carriers and plasticizers also influences transport properties positively [7] as it can be adjusted to achieve a high recovery factor [17].

The good fit of the Sellami et al. data to the modified PFO model indicates that the hexavalent chromium adsorption onto the PIM that uses Aliquat 336 as the carrier is more inclined towards physisorption. Physisorption is mainly associated with forces that are formed because of the physical changes happening during the process such as the pore volume, surface area, and the functional groups along the surface of the PIM [18], these physical changes are because of the saturation that is influenced by the stripping phase and the change of pH concerning the contact time.

![Figure 1](image_url)

**Figure 1.** (a) Kinetic model plot using modified PFO for the Cr (VI) transport using 70CTA/30Aliquat 33, $R^2=0.9813$; (b) Kinetic model plot using modified PFO for the Cr (VI) transport using 52.5CTA/17.5PBAT/30Aliquat 336, $R^2=0.9796$; (c) Kinetic model plot using modified PFO for the Cr (VI) transport using 35CTA/35PBAT/30Aliquat 336, $R^2=0.9768$; (d) Kinetic model plot using modified PFO for the Cr (VI) transport using 17.5CTA/52.5PBAT/30Aliquat 336, $R^2=0.9748$.

**Table 2.** Modified pseudo-first-order kinetics parameters for Cr (VI) ions.

| PIM                      | $R^2$  | $C_m$   | a     | b     | $K_i$  |
|--------------------------|--------|---------|-------|-------|--------|
| 70CTA-30Aliquat 336      | 0.9813 | 5.0424  | 0.0157| 2.2203| 1.433  |
| 52.5CTA-17.5PBAT-30Aliquat 336 | 0.9796 | 5.0651  | 1.2139| 0.5920| 1.995  |
| 35CTA-35PBAT-30Aliquat 336 | 0.9768 | 6.0785  | 0.5620| 0.5553| 13.765 |
| 17.5CTA-52.5PBAT-30Aliquat 336 | 0.9748 | 6.6258  | 0.8560| 0.8351| 31.953 |
Physical changes due to the stripping phase are constituted with the strength of the chosen stripping medium. In this case, NaOH was chosen to remove the extracted Cr (VI) ions. The strength of sodium hydroxide solution has substantially affected the Cr (VI) transport because the driving force for the diffusion through the polymer inclusion membrane has become saturated, due to the concentration of the metal complexes at the interface of the membrane phase and strip phase [19]. On the other hand, in conditions of initial pH of the solution, it is expected to change gradually because of the reverse transport of HCl therefore as shown in Table 2, the constants for pH change vary with the composition of the PIM. As shown, the PIM without plasticizer on its composition will observe a faster change of pH since plasticizers are known to help the membrane be more flexible and be a better medium for carrier movement.

3.1.2. PFO Model for Zn (II). The To support the fitting of the modified PFO model to the study of accumulation factor as a function of time, the recent study that transported Zn (II) ions onto PIM was also fitted to the non-linear model (figure 2). The experiment was conducted using the following experimental data: Feed solution: $C_0 = 32.69$ mg/L of Zn (II) ions, pH=4, and Stripping solution: H2SO4. As shown in Table 3, the non-linear modified PFO model fitted the experimental data published by Wang et al. [8] produced high values of correlation coefficient ($R^2 > 0.95$). The membranes with different compositions where the PIM that fitted well in the model is composed of 45% D 2 EHPA and 55% of PVC [8].

![Figure 2](image-url)
Table 3. Modified pseudo-first-order kinetics parameters for Zn (II) ions.

|   | PIM                  | R²        | C_m      | a        | b        | K₁      |
|---|----------------------|-----------|----------|----------|----------|---------|
| M1, D2EHPA: PVC: NPOE =30:40:30 | 0.96928   | 0.9035   | 3.31x10⁻⁸ | 1.0002   | 0.01064 |
| M2, D2EHPA: PVC =45:55       | 0.96908   | 2.5724   | 0.05     | 1.0000   | 0.17929 |
| M3, D2EHPA: PVC =55:45       | 0.95079   | 0.2554   | 1.00     | 1.0000   | 0.18385 |

The arbitrary constants calculated from fitting the modified model with the experimental data could shed light in the effects of pH and time in the physical adsorption of ions and solutes in the membrane. However, further experimental data using various metal ions and polymer blends with well-characterized molecular and supramolecular structures and properties would be needed to fully describe the adsorption behavior of solutes in polymer membranes.

4. Conclusion

The composition of the membrane, specifically the amount of plasticizer, increases the ability of the metal to be recovered by improving the permeability of the membrane. Cr (VI) transport of hexavalent chromium was also affected by pH. As the maximum adsorption rate is achieved, pH also changed. Which caused a gradual decrease of in Cr (VI) ions accumulated in the membrane. To better evaluate adsorption mechanisms, models showing the relationship between accumulation factor and contact time are developed. Non-linear modified pseudo-first order (PFO) is used in modelling the kinetics of Cr (VI) adsorption in PIM with different CTA/PBAT blends. Correlation coefficient (R²) values for the modified PFO model ranges from ~ 0.91 to 0.98 which indicates that the Cr (VI) adsorption follows pseudo-first order rate expression. The Cr (VI) maximum concentration predicted from the model also has values less than the initial concentration. The effect of plasticizer with Cr (VI) transport was also observed as the rate constant value (K) increases with an increase unproportionally with the PBAT amount for each PIM used. A good correlation coefficient was also obtained from experimental data collected from a Zn (II) transport study with D2EHPA-based PIM using the modified PFO model. The experimental data fit the modified pseudo-first-order (PFO) model is an indication that the Cr (VI) adsorption onto PIMs is inclined toward physisorption.

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