

Untreated Mining Influenced Water Sludge (MIWS) for Lead Adsorption: Modelling Mass Transfer Effects

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Contamination of water sources by heavy metals, such as lead, presents a significant environmental challenge. This study explored the kinetics of adsorption using a novel industrial waste by-product, mining influenced water sludge (MIWS), for the adsorption of lead in aqueous solutions. By varying agitation speeds – 150, 200 and 250 rpm – and average particle diameters – 1, 2 and 3 mm – the impact of external mass transfer effects and internal mass transfer effects was studied. It was observed that varying average adsorbent particle diameters had an impact on the adsorption kinetics, particularly regarding the time required to achieve equilibrium and maximum Pb(II) removal efficiency. At set conditions – same initial Pb(II) concentration, temperature, adsorbent dosage, and adsorbate solution pH – adsorption kinetics were notably faster for 1 mm adsorbate particles compared to 3 mm particles, requiring only half the time to reach equilibrium. The longer contact time required to reach equilibrium indicates the impact of internal mass transfer effects. Crank's mass transfer model was used to quantify the effective diffusivity, providing operational parameters required for continuous process design. This research offers a sustainable remediation option by valorising an untreated waste sludge that can ideally be utilised in continuous flow processes, contributing to environmentally sound water treatment practices by lowering production energy requirements and reducing emissions.

1. Introduction

Rapid industrialisation over the past few decades has resulted in increased amounts of heavy metals being released into the environment (Bača and Vanýsek, 2023). This contamination affects the quality of ambient air, surface and ground water, and soils (Paustenbach and Galbraith, 2006). The remediation of water sources contaminated with heavy metals is of paramount importance due to their adverse effects on human health and ecosystems (Yang et al., 2019). Lead is a particularly pervasive pollutant often found in industrial wastewater. It poses significant environmental and health risks due to the various pathways of exposure from a range of anthropogenic activities (Cilliers et al., 2021). Among the traditional technologies available such as chemical precipitation, ion exchange, and electrochemical treatment, adsorption emerges as a promising, widely adopted method due to its cost efficiency, ease of operation and effectiveness (Mahapatra et al., 2023).

Adsorption includes a series of steps, starting with the transport of the adsorbate from the bulk liquid phase to the boundary layer, followed by movement to the adsorbent surface (external mass transfer), and finally, diffusion through the material's pores to the active sites (internal mass transfer). In the adsorption process, it is crucial to determine whether a system is mass transfer limited or reaction rate limited (Fogler, 2010). This aids in optimising adsorbent performance and designing efficient continuous treatment systems. Mass transfer governs the rate at which the adsorbate is transported from the bulk liquid phase, through the boundary layer to the surface of the adsorbent, and finally, diffusion takes place as the adsorbate adsorbs onto the active sites in the particle (Worch, 2021). Kinetic experiments were conducted using optimised parameters – including initial contaminant concentration, pH, adsorbent dosage, and temperature – from previous batch studies. These parameters were kept constant for each kinetic run, with only the stirrer speed and particle size varied to establish external and internal mass transfer effects, respectively. External mass transfer effects were excluded by conducting experiments at different stirrer speeds of 150, 200 and 250 rpm respectively. This was done to establish the optimal stirrer speed allowing for a reduced boundary layer, enhanced mass transfer and overall

enhanced adsorption. Internal mass transfer effects were investigated by conducting kinetic experiments at adsorbent particle sizes of approximately, 1, 2 and 3 mm to establish the effects influencing the adsorption kinetics and the equilibrium behaviour.

Crank's diffusion model was used to determine the internal mass transfer effects in the adsorbent-adsorbate system (Largitte and Pasquier, 2016). This model quantifies the effective diffusivity allowing for the determination of the possible rate limiting step (Muedi et al., 2022). Model parameters were fit to experimental data to determine how well the model describes the adsorption kinetic process.

For this study, a mining influenced water sludge (MIWS) was used as an adsorbent. The material is a waste by-product from an industrial water treatment process. This is the first study showing the use of this waste material as an adsorbent. Utilisation of the waste sludge promotes sustainable remediation with the benefit of minimised material processing cost (Mattoso et al., 2024). In encouraging sustainable environmental practices, it is imperative to consider multiple factors and their interplay. These include emission reduction and energy saving. The preparation of MIWS involves drying, grinding, and sieving, making the process less energy-intensive compared to traditional adsorbents. Traditional adsorbents often require extensive processing, such as high-temperature activation and the use of chemical agents. These contribute to higher energy consumption and increased emissions. This elevates the production cost and results in a greater environmental impact due to higher emissions and resource use. In contrast, the MIWS achieved high removal efficiencies at relatively low operational temperatures minimising the operational energy requirements for treatment while also minimising the environmental impact associated with production. By utilising an industrial by-product waste as an adsorbent, carbon footprint is reduced. The remediation process itself results in clean water leading to healthier ecosystems and communities. Overall lower energy-consumption for material preparation contributes to reduced energy use for power generation. This is essential especially given that in the national context (that is in South Africa) this energy is largely sourced from fossil fuels (Department of Energy, 2019).

2. Methods and Materials

Kinetic experiments were conducted to determine the adsorption kinetic behaviour of the lead-MIWS adsorbate-adsorbent system.

2.1 Material preparation

The MIWS was initially subjected to drying overnight. It was then milled using a pestle and mortar, producing particles of various sizes. To ensure uniformity, an IRIS FTL-0200 electromagnetic sieve shaker (Filtra vibración, Barcelona, Spain) was used to sieve the particles. Particles with an approximate size of 1 mm, 2 mm and 3 mm were collected for investigation in the kinetic studies. A 1,000 mg/L Pb(II) stock solution was prepared by dissolving 1.6 g of Pb(NO₃)₂ in distilled water in a 1,000 mL volumetric flask. Dilutions were prepared from this solution to ensure consistency.

2.2 Kinetic experiments

Experiments were conducted at stirrer speeds of 150, 200 and 250 rpm to study external mass transfer effects. Kinetic profiles were evaluated at different particle sizes – 1, 2 and 3 mm – while maintaining adsorption parameters including dosage concentration, solution pH, temperature and initial lead concentration. The thermal shaker's agitation speed was set at 200 rpm for all the runs. Samples of lead were withdrawn periodically from the reaction vessel. These samples were centrifuged before analysing the residual lead concentration using an AAAnalyst 400, Atomic Absorption Spectrometer (AAS) (PerkinElmer, Waltham, MA, USA). The amount of adsorbate adsorbed by the MIWS at set time intervals – q_t – was calculated by Eq(1). C_o and C_t are the initial concentration and the concentration at the set sampling times respectively in mg/L, V is the volume in L of the lead contaminated solution treated and m is the mass of adsorbent utilised in g.

$$q_t = \left(\frac{C_o - C_t}{m} \right) V \quad (1)$$

2.3 Determination of possible external and internal mass transfer effects

To mitigate the external mass transfer effects and determine the optimal stirrer speed, kinetic experiments were conducted at increasing stirrer speeds of 150, 200 and 250 rpm with other adsorption parameters kept constant. To determine whether the kinetics of the system are internal mass transfer limited, kinetic experiments were conducted at the optimal stirrer speed and varied average adsorbent particle sizes of 1, 2 and 3 mm. The kinetics of adsorption were modeled using Crank's diffusion model. The model gives an effective diffusivity of the particle giving insight into the kinetics of the adsorption system.

Crank's internal mass transfer model describes the internal mass transfer of an adsorbate within an adsorbent (Largitte and Pasquier, 2016). The model is described by Eq(2), with its analytical form given by Eq(3). A constant effective diffusivity (D_e) is fitted as Q/Q_{max} ratio increases. In Eq(2) to (4) Q is the adsorption capacity over time, Q_{max} is the maximum adsorption capacity achieved, and R is the adsorbent radius, assuming a spherical adsorbent particle. These parameters were substituted into Eq(4), simplifying the sum to infinity in Eq(3) (Van Veenhuizen et al., 2021). D_e provides some insight into the limitations of the rate of diffusion.

$$\frac{\partial Q}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial Q}{\partial r} \right) \quad (2)$$

$$\frac{Q}{Q_{max}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_e n^2 \pi^2 t}{R^2}\right) \quad (3)$$

$$\frac{Q}{Q_{max}} = \begin{cases} 6 \left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} \left[\pi^{-\frac{1}{2}} - \left(\frac{1}{2}\right) \left(\frac{D_e t}{R^2}\right)^{\frac{1}{2}} \right], & \frac{Q}{Q_{max}} < 0.8 \\ 1 - \frac{6}{\pi^2} \exp\left(\frac{-D_e \pi^2 t}{R^2}\right), & \frac{Q}{Q_{max}} \geq 0.8 \end{cases} \quad (4)$$

Eq(4) was fitted to experimental data using Python to obtain the fitted parameter D_e when it is assumed that the MIWS particles are initially clear of adsorbate. A sensitivity analysis was conducted to determine the reliability of the model.

3. Results and Discussion

The results of the kinetic runs at varied stirrer speeds are shown in Figure 1, where q_t is normalised using the maximum adsorption capacity achieved at equilibrium (q_e). This effectively compares the rates of adsorption, illustrating how quickly the system approaches equilibrium. From this figure, it was deduced that the optimal stirrer speed is 200 rpm as the 200 and 250 rpm data sets are nearly coincident (Guiza et al., 2019). At increased stirrer speeds, the boundary layer was reduced diminishing resistance and increasing the rate at which the adsorbate reaches the adsorbent (Fogler, 2010).

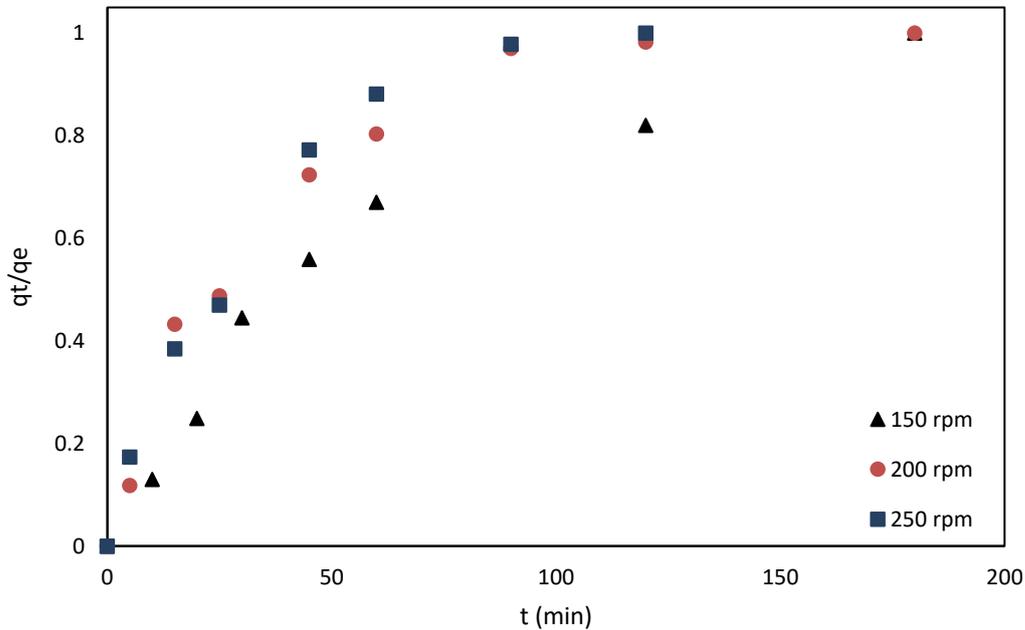


Figure 1: Kinetic behaviour of lead removal at different stirrer speeds for external mass transfer effects mitigation

From the observed data, after 200 rpm an increase in stirrer speed no longer improves the apparent kinetics of the system. This suggests that internal mass transfer may be the overall rate limiting step at this point. To investigate whether this is the case, internal mass transfer effects were studied by varying the average

adsorbent particle diameter between 1, 2 and 3 mm. This was done utilising the optimised 200 rpm. The experiments were conducted in triplicate with data illustrated in Figure 2. For each of the curves, q_t is normalised by q_e .

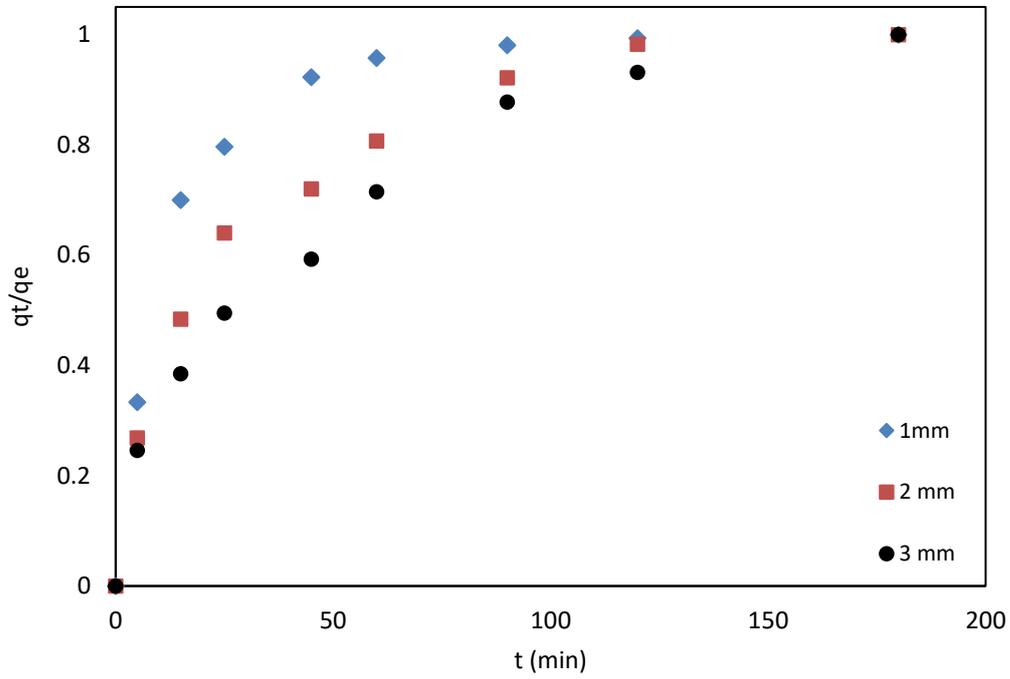


Figure 2: Kinetic profiles at different particle sizes for internal mass transfer effects investigation

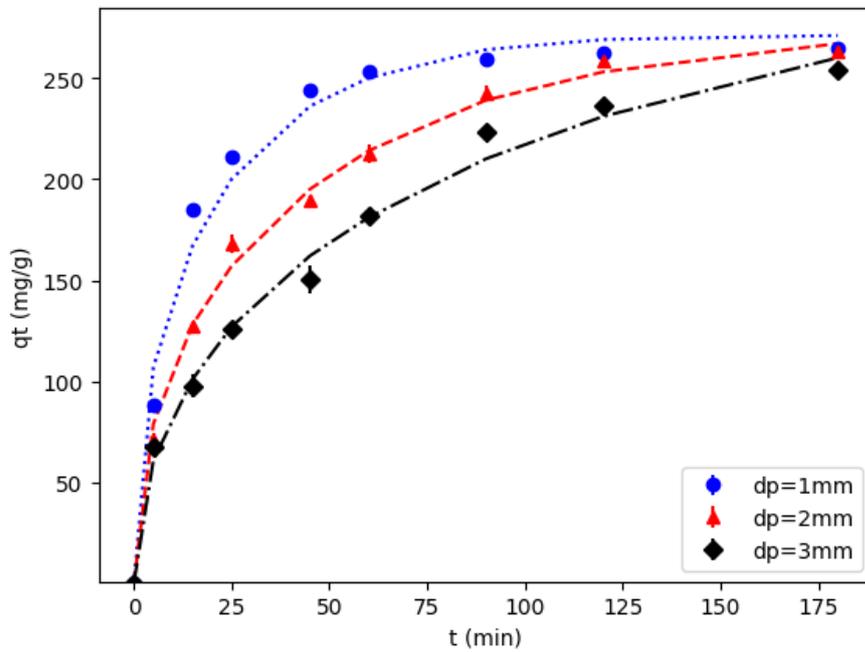


Figure 3: Crank's internal diffusion model fitted to kinetic profiles

From the generated kinetic profiles, it is evident that an increase in average adsorbent particle size affects the rate of adsorption. Possible reasons for a reduced removal efficiency at set contact times given an increased average adsorbent particle diameter include decreased surface area and mass transfer limitations (Ruthven, 1984). Non-porous solid particles have a reduced surface area per unit mass when compared to similar smaller particles (Badawy and Pandey, 2017).

Since adsorption occurs primarily on the surface, a decrease in surface area would mean fewer active sites available for adsorption leading to decreased removal efficiencies. The similar end-point kinetic behaviour suggests that the material is porous; the total active sites and the total surface area available for adsorption are likely similar. Larger adsorbent particles may impede adsorbate-adsorbent interactions due to longer transport pathways (Fogler, 2010). This may impede diffusion into the adsorbent, delaying contact with active sites and reducing overall efficiency. The apparent kinetics observed in Figure 2 show that the rate of adsorption in the system is decreased as the adsorbent particle size used increases. The kinetics of adsorption were modelled using Crank's diffusion model to determine effective diffusivities for each of the particle sizes. Python, leveraging its robust libraries and capabilities, was employed to generate fitted curves for the kinetic profiles obtained at different adsorbent particle sizes. Assuming spherical particles of 1, 2 and 3 mm, constant effective diffusivities were approximated respectively. Figure 3 graphically illustrates the fitted curves.

In Table 1, the fitted parameters obtained are shown. It is observed that in all instances Crank's model provides a suitable fit for the kinetics, indicating significant internal mass transfer effects. The results obtained align with expectations as particle size is directly proportional to resistance.

Table 1: Optimised parameters for Crank's model

	$d_p \approx 1 \text{ mm}$	$d_p \approx 2 \text{ mm}$	$d_p \approx 3 \text{ mm}$
$D_e \text{ (m}^2\text{/min)}$	3.48×10^{-9}	1.73×10^{-9}	7.88×10^{-10}
R^2	0.986	0.996	0.993

A sensitivity analysis was performed on the effective diffusivity (D_e) parameter to determine how robust and reliable the model's fit to the experimental data is. The sensitivity curves are illustrated in Figure 4. From the sensitivity analysis conducted, it was observed that there is minimal sensitivity to changes in D_e overall. For the 1 mm adsorbent particle size, an initial spike followed by a flatter response suggests an initial rapid adsorption process. This suggests that there are limitations to the model's applicability to the kinetics. This is despite the computed R^2 values shown in Table 1 suggesting that the model is a good fit for the obtained data. It is possible that there are other dominating factors responsible for the kinetic behaviour observed.

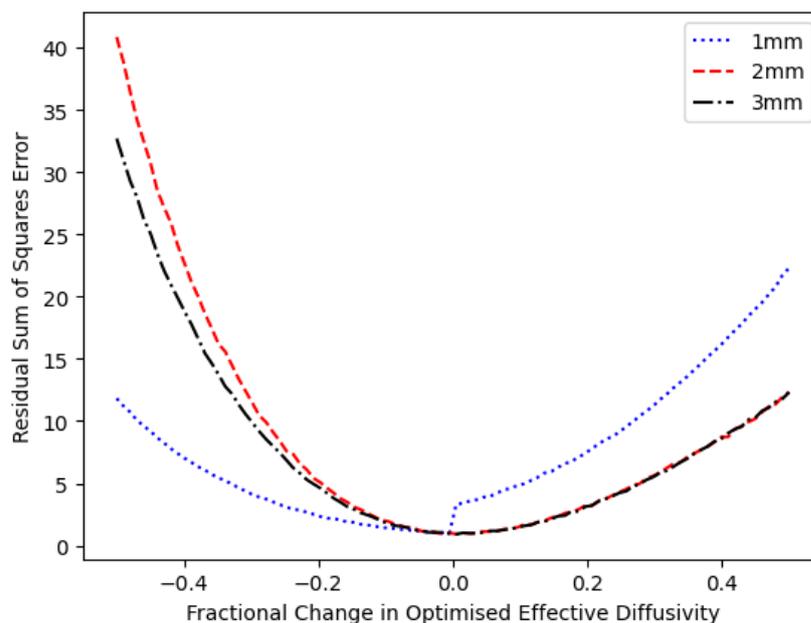


Figure 4: Sensitivity analysis of effective diffusivities

Further studies must be conducted to determine the cause of the apparent low sensitivity. Incorporation of additional relevant parameters such as D_e not as a constant but as a function of time and space, where space refers to the radius of the respective particles shrinking as diffusion occurs, would provide a more complex and possibly more accurate and robust model for the predicted parameter.

4. Conclusions

Kinetic experiments conducted studied the external and internal mass transfer effects of the lead-MIWS adsorption process. The optimal stirrer speed was found to be 200 rpm, beyond this no significant improvement in the apparent kinetics was observed. Varied adsorbent particle sizes were tested to demonstrate the greater resistance to mass transfer presented by an increase in adsorbent particle size. This resulted in decreased adsorption efficiencies with the contact time required to reach equilibrium doubling from 90 minutes for the 1 mm adsorbent particle diameter to 180 minutes for the 3 mm adsorbent particle diameter. Application of Crank's model provided a suitable fit for the kinetic data. However, a sensitivity analysis of D_e (the model's fitted parameter) indicated minimal sensitivity to changes in D_e suggesting some limitations in the model's applicability. Overall, the utilisation of MIWS as a LCA provides an efficient method for lead removal while promoting sustainable environmental practices with the benefit of energy savings and emission reduction by lowering production energy requirements associated with water treatment thus reducing emissions.

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