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Kinetics of adsorption of pollutants removal from mine wastewater by a coal fly ash-based coagulant

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Abstract: This work discusses the results of experimental investigation on the study of coagulation's adsorption aspect for removing toxic ions from mine wastewater using fly ash-based coagulant. The studied mine wastewater was susceptible to the coagulation process. The important part of this research was to analyse the mechanism of the pollutant coagulation process using a fly ash-based coagulant. Several kinetic models were used to test the coagulation data and to examine the mechanism controlling coagulation adsorption. The present results of pollutant removal well-fit pseudo-second-order model. Film diffusion and intraparticle diffusion were involved in the process. The intraparticle diffusion coefficients for the different pollutants were calculated from Weber–Morris and Boyd's models; the results showed that the intraparticle diffusion coefficients for the specific pollutants range from $1.8 \cdot 10^{-11}$ to $0.57 \cdot 10^{-13}$ cm²/sec and $1.05 \cdot 10^{-12}$ to $1.87 \cdot 10^{-12}$ cm²/sec, respectively (except for Ni and Ca for the Weber–Morris model).

Keywords: adsorption kinetics; coagulation; coal fly ash-based complex coagulant; hydroxide precipitate; toxic ions.

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Biographical notes: M. Clotilde Apua obtained her PhD in Chemical Engineering from the University of the Witwatersrand, Johannesburg, South Africa. Her research interests include the treatment and beneficiation of solid waste that may be classified as hazardous, nanotechnology in wastewater treatment, coagulation methods in wastewater treatment, and mineral processing.

1 Introduction

Water pollution is one of the world's most undesirable environmental problems and requires solutions. Coal mining industries produce a lot of acid mine drainage (AMD), which is one of the main water contaminants in several countries. In general, AMD contains low pH (pH < 3), high concentrations of sulphate (1–20 g/L), and dissolves high concentrations of Al, Ni, Mn, Fe, Cu, Cr, Se, Pb, Cd, Hg, Ag, Zn and As. This wastewater is very toxic due to its high ionic content and high acidic pH. Harmful heavy

metals such as Zn, As, Cr, Ni, Ag, Cu, Se, Pb, Hg and Cd, are not biodegradable and can accumulate in living organisms, causing various diseases and disorders (Pereira et al., 2020; Barrera et al., 2017). Therefore, their removal from wastewater becomes environmentally important. A variety of metal ion treatment techniques have been developed, including adsorption, electrochemical oxidation, ion exchange, biological treatment, membrane separation (microfiltration, ultrafiltration, nanofiltration, reverse osmosis), aerobic and anaerobic degradation using various microorganisms, and coagulation (Saleh et al., 2022; Qasem et al., 2021). Amongst these techniques, coagulation process is widely applied to remove dissolved and suspended particles (Montaño-Medina et al., 2023; Aboulhassan et al., 2006). Coagulants based on aluminium and iron, widely used coagulants in industrial processes, are composed of inorganic salts of aluminium and iron (Ebrahimi et al., 2015). However, these conventional coagulants are expensive and corrosive (Koul et al., 2022; Yan et al., 2012). Furthermore, other elements such as magnesium, silicon and calcium ions have been reported as potential coagulants for wastewater treatment. Since coagulants based on aluminium, iron, magnesium, silicon, and calcium have different advantages and disadvantages for waste effluent treatment, a complex coagulant composed of iron, aluminium, magnesium, silicon and calcium constituents is ideal as it has the benefits of all coagulants and prevents or reduces their drawbacks (Kajjumba et al., 2021; Mohamad et al., 2021; Li et al., 2018; Fan et al., 2000). Moreover, a complex coagulant is effective because its multivalence strongly attracts colloids and ensures a high removal rate (Apua and Nkazi, 2022; Apua, 2020).

It has been reported that every year millions of tons of coal fly ash solid waste are generated worldwide, with around half being utilised in different forms, and the other half remaining unused, resulting in various types of pollution. Most coal fly ash contains suitable quantities of aluminium, iron, silicon, magnesium, and calcium oxides for the synthesis of complex coagulants (Apua, 2023; Yadav et al., 2022).

Generally, the mechanism by which impurities are removed during the coagulation process could be better described as an adsorption phenomenon on recently precipitated particles (Kristianto et al., 2022; Ohale et al., 2020; Menkiti et al., 2018; Bouyakoub et al., 2011). Research is currently underway into the use of the adsorption mechanism for coagulation by hydroxide precipitates derived from a complex coagulant based on coal fly ash. Colloidal particles present in wastewater generally have negative electrical charges, while the coal fly ash-based complex coagulant contains large quantities of Fe^{3+} , Al^{3+} , Si^{4+} , Mg^{2+} , and Ca^{2+} ions which are multi-charged. During the coagulation process, Fe^{3+} , Al^{3+} , Si^{4+} , Mg^{2+} , and Ca^{2+} in the coagulant are hydrolysed, producing polymeric and monomeric hydroxy complex ions such as $\text{Si}_2\text{O}(\text{OH})_6$, $[\text{Fe}_{13}(\text{O}_4(\text{OH})_{12})_7]^{7+}$, $[\text{Al}_{13}(\text{O}_4(\text{OH})_{12})_7]^{7+}$, $\text{Mg}_4(\text{OH})_4^{4+}$, $[\text{Fe}(\text{OH})]^{2+}$, and $[\text{Al}(\text{OH})]^{2+}$. These monomeric and polymeric hydroxy complex ions can compress the electric double layer of the particles, electrically neutralise, and adsorb colloidal particles (Apua, 2020; Cheng and Chi, 2002; Rose and Waite, 2003). There is a great interest in finding inexpensive and effective alternatives to existing commercial coagulants.

In our previous work, coal fly ash was used to synthesise a complex coagulant (Apua and Nkazi, 2022) that was utilised in this study to treat mine wastewater for the removal of total dissolved solids (TDS), Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn. The present research aimed to understand better the kinetics of adsorption of Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn removal from mine wastewater by hydroxide precipitates derived from the coal fly ash-based complex coagulant. The adsorption reaction kinetic models such as

pseudo-first-order, pseudo-second-order, Elovich, and second-order equations; and adsorption diffusion kinetic models such as Weber-Morris, Boyd, and Bangham's equations were used to determine the adsorption kinetics.

2 Materials and Methods

2.1 Characterisation of the mine wastewater and coagulant

The concentrations of elements in the mine effluent before and after treatment and the chemical composition of the coal fly ash-based complex coagulant were analysed using a Spectro Arcos inductively coupled plasma-optical emission (ICP/OES) spectrometer. The spectrometer was calibrated with standard solutions at 1, 5, 10, 20, 40, 60 and 80 ppm before each analysis. A test blank was performed before each series of samples. The concentrations of TDS in the untreated and treated mine water were measured using a 912-conductivity metre Metrohm. determination of the pH of untreated and treated wastewater was carried out using a pH metre-model pH-210.

2.2 Mine wastewater

The mine effluent was collected at the point of discharge from the Witbank coal mine in the Mpumalanga Province, South Africa. The wastewater was collected using a polyethylene container and refrigerated to prevent biodegradation. The pH and concentrations of Fe, Mg, Ni, Mn, Al, Si, Ca, Zn, and TDS were determined before treatment. Results are given in Table 1.

Table 1 Chemical analysis of the untreated and treated mine wastewater by the complex coagulant

Parameter	Value	
	Untreated mine wastewater	Treated mine wastewater
pH (value)	3.23 ± 0.04	5.58 ± 0.03
Colour	Yellowish	Absent
TDS (mg/L)	720.20 ± 3.04	308.10 ± 2.12
Al (mg/L)	13.86 ± 1.54	0.19 ± 0.00
Mg (mg/L)	30.18 ± 0.18	19.42 ± 0.17
Fe (mg/L)	1.64 ± 0.06	0.00 ± 0.00
Zn (mg/L)	0.93 ± 0.01	0.13 ± 0.00
Mn (mg/L)	13.52 ± 0.16	7.25 ± 0.03
Si (mg/L)	0.91 ± 0.01	0.52 ± 0.00
Ni (mg/L)	13.86 ± 0.01	0.39 ± 0.00
Ca (mg/L)	31.13 ± 0.22	23.07 ± 0.12

2.3 Coagulant

The procedure for preparing the complex coagulant based on coal fly ash is described in our previous article (Apua and Nkazi, 2022). Briefly, Al, Mg, Fe, Ca, and Si were

extracted from coal fly ash by sulphuric acid leaching to produce the coagulant used in this study. Table 2 shows the chemical composition of the coal fly ash-based complex coagulant.

Table 2 Chemical composition of the coal fly ash-based complex coagulant

<i>Properties of the complex coagulant</i>	
pH	0.72± 0.04
Colour	dark green
Fe (mg/L)	21731.89 ± 2.01
Ca (mg/L)	796.70 ± 2.00
Al (mg/L)	603.18 ± 4.03
Mg (mg/L)	1366.70 ± 3.04
Si (mg/L)	96.00 ± 3.13

2.4 Coagulation experiments

Coagulation tests were carried out using the beaker test technique. Different reaction conditions (coagulant concentration 2 to 50 mg/L, pH 4 to 10, temperature 20 to 50°C, and time 1 to 50 minutes) were used to determine the optimum coagulant dosage, pH, temperature, and coagulation time. The coagulation tests were conducted at a wastewater/coagulant ratio of 1:0.4, which lies within the conditions reported as optimal (Apua, 2020). Initially, 25 mL of mine wastewater was poured into the beaker. The initial pH value of the mine effluent was adjusted to the required value with concentrated NaOH solution. The wastewater was then dosed with the coagulant and stirred using a magnetic stirrer. After stirring at rapid speed for 5 minutes at 300 rpm to homogenise the mixture, the speed was then slowed for 20 minutes at 30 rpm to allow coagulation. Following stirring, the mixture was allowed to settle for 150 minutes and the supernatant sample was filtered through a 0.45 µm micro filter before analysis. The percentages of residual Fe, Mg, Ni, Mn, Al, Si, Ca, Zn, and TDS at time *t*, were evaluated using equation (1).

$$R(\%) = \left(\frac{C_t}{C_0} \right) \times 100 \tag{1}$$

where *R* (%) is the residual efficiency of pollutant, *C*₀ (mg/L) is the initial concentration in the raw wastewater for the pollutant and *C*_{*t*} (mg/L) the concentration in the effluent at time *t* (minute). The experiments were conducted in triplicate and the results represent the mean value ± standard deviation.

2.5 Kinetic study

The process of adsorption generally involves three consecutive steps, which are the outer mass transfer of the adsorbate from the bulk solution to the external surface of the sorbent; the inner diffusion of the adsorbate onto the active sites of the sorbent; and the adsorption process (Ohale et al., 2020). The kinetics of adsorption of the present system was studied using two types of kinetic models, namely the adsorption reaction kinetic models and the diffusion kinetic models. Four reaction kinetic models, namely, pseudo-first-order, pseudo-second-order, Elovich model, and second-order model

equations, were used. Furthermore, three diffusion kinetic models namely Weber-Morris (intra-particle diffusion), Boyd's, and Bangham's model equations were investigated. The experimental data were used to fit these kinetic models to determine the appropriate model for the coagulation process and the diffusion behaviour of the elements implicated in the process. The kinetic studies for different metals and silicon were performed using the optimal coagulation conditions (i.e., complex coagulant dose: 20 mg/L, pH: 7). The treated mine wastewater samples were collected at predefined time intervals ranging from 1 to 50 minutes, and the concentrations of the pollutants were determined in the same way. The change in residual metal and silicon concentration as a function of time is presented in Table 1. The amount of pollutant removed at time t , q_t (mg/mg), was calculated using equation (2) (Hussain et al., 2013).

$$q_t = \frac{(C_0 - C_t) \times V}{D} \quad (2)$$

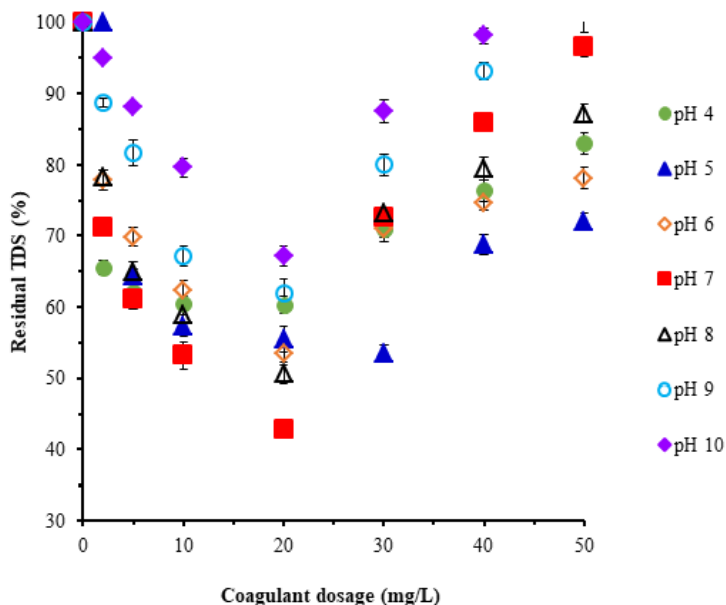
where C_0 (mg/L) is the initial concentration and C_t (mg/L) is the concentration of the impurity at time t in the wastewater, V (mL) represents the volume of the wastewater, and D (mg/L) represents the coagulant dosage (as Fe + Al + Si + Mg + Ca). The amount of pollutant removed at saturation (or equilibrium), q_e (mg/mg), was determined by equation (2) with q_e = maximum value of q_t for each impurity.

3 Results and discussion

3.1 Influence of coagulant dose

The effect of coal fly ash-based coagulant dosage on the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn is presented in Figures 1 and A1–A8. The study was carried out with a coagulant dosage ranging from 2 to 50 mg/L at pH of 4 to 10, mine water/coagulant ratio of 1:0.4, and a coagulation time of 20 minutes at ambient temperature. At the beginning of the process, removal efficiency accelerated as the coagulant dosage increased to a certain coagulant dosage. Further increase in coagulant dosage resulted in a reduction in removal efficiency, as depicted in Figures 1 and A1–A8. A direct relationship was observed between TDS and toxic element concentrations. The removal efficiency increases with increasing coagulant dosage, but the residual impurity rate increases with increasing coagulant dosage above a certain coagulant dosage. The minimum residual (i.e., maximum removal) was observed to be 6% Fe (or 0.10 mg/L), 42.78% TDS (or 308.1 mg/L), 33% Si (less than 0.30 mg/L), 0.66% Mg (or 0.20 mg/L), 1.36% Al (or 0.19 mg/L), 0.57% Mn (or 0.08 mg/L), < 1.10% Ni (or 0.01 mg/L), 6.88% Ca (or 2.14 mg/L) and 0.36–1.13% Zn (or 0.00–0.01 mg/L), at a coagulant dosage of 20 mg/L for TDS, Si, Mg, Al, Mn, and calcium; 2–20 mg/L for Fe; and 10–20 mg/L for Zn and Ni. The same observations were reported by Fu and Wang (2011). These dosages could be considered the optimal dosages for the removal of Fe, TDS, Si, Mg, Al, Mn, Ni, Ca, and Zn respectively. The increase in removal efficiency with increasing coagulant dosage is the result of a progressive increase of available coagulant active sites which enhanced charge neutralisation. Ahead of the optimal coagulant dosage, particles present in the wastewater are too enclosed by the coagulant and, consequently, their surface become saturated. This phenomenon led to the restabilisation of particles in wastewater, and thus decline the coagulation efficiency.

Figure 1 Influence of coagulant dosage and pH on removal of TDS from mine wastewater (see online version for colours)



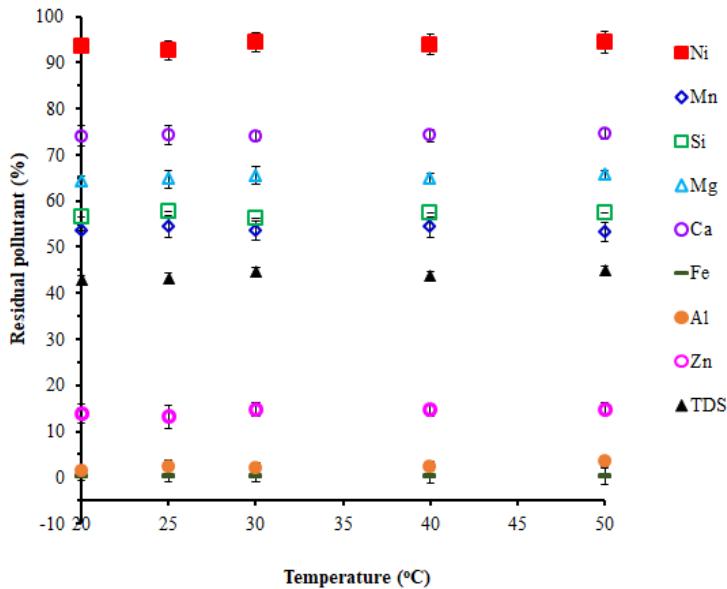
Notes: Initial TDS concentration was 720.2 mg/l, initial pH: 4–10; mine wastewater/coagulant ratio: 1:0.4; ambient temperature; 5 minutes rapid mixing at 300 rpm; 20 minutes slow mixing at 30 rpm; settling time: 150 minutes.

3.2 Influence of mine wastewater pH

Figures 1 and A1–A8 show the impact of initial pH on the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn from the mine wastewater using coal fly ash-based coagulant. From Figures 1 and A1–A8, the overall pattern is that the percentage of residual impurities declined as the coagulation pH increased. As shown in Figure A1 the complex coagulant was not effective in removing Fe from the mine wastewater in the pH range 4 to 6, at a coagulant dosage of more than 20 mg/L. Similar behaviour was noticed for pH values 7 and 8 but at coagulant doses higher than 30 mg/L. It is seen in Figure A7 there was no effectiveness of the coagulant in removing Ni from the mine wastewater at pH 7 and 8 at a coagulant dosage above 20 mg/L and at pH 9 and 10 at a coagulant dosage above 40 mg/L. The lowest residual impurities were recorded at a pH of 7 for TDS (Figure 1), pH 6–10 for Fe (Figure A1), pH 7–10 for Al (Figure A4), pH 9 and 10 for Si and Zn (Figures A2 and A3, respectively), pH 10 for Mn, Mg and Ni (Figures A5, A6 and A7, respectively), and pH 12 for Ca (Figure A8). Rebhum and Lurie (1993) and Chaukura (2021) reported a similar observation. At optimum pH, Si^{4+} , Fe^{3+} , Al^{3+} , Mg^{2+} , and Ca^{2+} ions in the coal fly ash-based complex coagulant are hydrolysed leading to a series of metal and silicon hydroxide precipitates (positively charged ions). The complex coagulant was therefore highly effective because it allowed electrical compression of the double layer and electrostatic neutralisation to destabilise the pollutant particles, followed by adsorption of the impurity particles. Hydrolysis of cations (Si^{4+} , Fe^{3+} , Al^{3+} , Mg^{2+} , and Ca^{2+}) generally occurs above the optimum pH, reducing the formation of hydroxide

precipitates and the ability of the coagulant to adsorb the pollutant particle, which reduces the efficiency of impurity removal (Cruz-Lopes et al., 2021; Gao and Yue, 2005). The 20 mg/L coagulant dosage is considerably more efficient because of significant hydroxide precipitation and a process known as sweep flocculation which produced low concentrations of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn. Accordingly, in the following studies, experiments were carried out with a coagulant dosage of 20 mg/L. As the composition of the mining wastewater used is complex, the optimum pH value found for TDS (i.e., pH 7) was taken into account for further experiments.

Figure 2 Influence of coagulation temperature on the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn from mine wastewater using coal fly ash-based coagulant (see online version for colours)

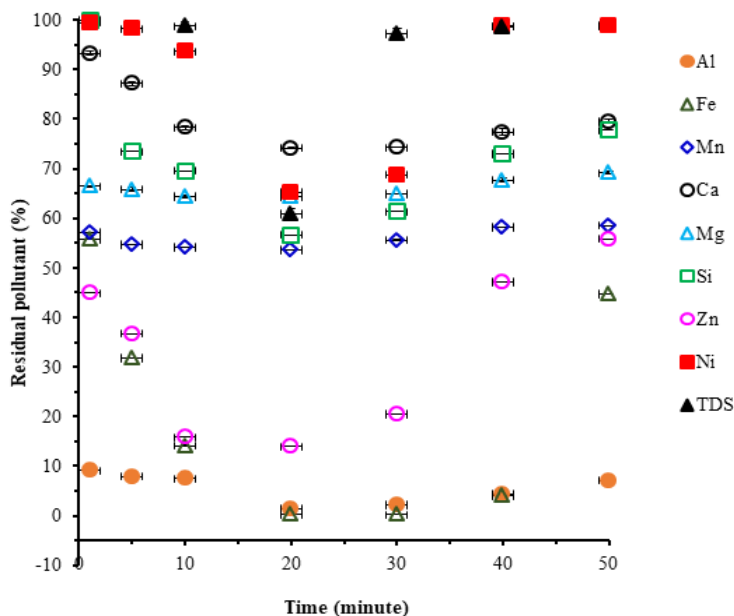


Notes: pH 7, coagulant dosage: 20 mg/l, coagulation time: 20 minutes, temperature: 20–50°C, and settling time: 150 minutes.

3.3 Influence of temperature

The removal of TDS, silicon, and metals was studied at different temperatures in the range of 20–50°C at pH 7 and a coagulant dosage of 20 mg/L (Figure 2). It is a known fact that with increasing temperature, a reduction in the viscosity of the mine effluent occurs, Brownian motion becomes enhanced and the inorganic coagulant hydrolyses quickly, accelerating coagulation. The operating conditions used in this study allowed sufficient time for reaction and settling, so temperature (20–50°C) only slightly impacted the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn. Similar observations have been reported by Sui et al. (2010).

Figure 3 Influence of coagulation time on the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn from mine wastewater using coal fly ash-based complex coagulant (see online version for colours)



Notes: Coagulant dosage: 20 mg/l, pH 7, ambient temperature, coagulant time: 1–50 minutes.

3.4 Influence of coagulation time

Optimal coagulant dosage and pH were used to investigate the effects of time on the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn from mine wastewater using coal fly ash-based coagulant, as shown in Figure 3. Figure 3 presents the influence of coagulation time on the percentage of residual TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn using the complex coagulant. It was observed that the complex coagulant was ineffective in removing TDS for times below and above 20 minutes. A gradual decrease in the percentage of residual Si, Ca, Fe, Zn, and Ni in the treated mine effluent was observed over time, reaching saturation in 20 minutes. But, beyond 20 minutes of coagulation time, the residual percentage increased progressively with increasing coagulation time. Al, Mn, and Mg coagulation behaviour indicated that the percentages of residual Al, Mn, and Mg in the mine wastewater decreased slightly up to 20 minutes and improved a little up to 50 minutes. 20 minutes was found to be the optimum coagulation time. The reduction in the percentage of residual impurities occurring before 20 minutes can be attributed to faster adsorption caused by a high initial driving force. But as the coagulation time increased, the rate of adsorption slowed as a result of the reduction in the driving concentration difference between the bulk solution and the surface, which delayed the movement of the pollutant particles towards the adsorbent surface (hydroxide precipitate). Minimum percentages of residual TDS, Al, Mg, Fe, Mn, Ni, Zn, Si, and Ca were 60.83, 1.36, 64.35, 0.23, 53.61, 65.29, 13.95, 56.57, and 74.13% respectively at 20 minutes. It was determined that the optimum coagulation time was 20 minutes. Based on a coagulation

review, it was observed that no information on the coagulation of the investigated pollutants is available in the literature.

It was generally found that the optimum conditions for the coagulation process were 20 mg/L complex coagulant dosage, pH 7–11, and 20 minutes coagulation time. Nevertheless, considering that the mine wastewater used in this study is a multi-constituent aqueous solution, pH 7 (for TDS) was considered optimal. The properties of the treated mine wastewater after optimisation (pH 7, coagulant dosage: 20 mg/L, room temperature, coagulation time: 20 minutes) are shown in Table 1. The comparison of the untreated and treated mine wastewater shows that there has been a change in the concentrations of residual impurities for TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn. It is therefore clear that these pollutants were removed during the coagulation process. The concentrations of residual impurities in the treated mine wastewater are as follows: TDS (308.1 mg/L), Fe (0.00 mg/L), Mg (19.42 mg/L), Ni (0.39 mg/L), Mn (7.25 mg/L), Al (0.19 mg/L), Si (0.52 mg/L), Ca (23.07 mg/L), and Zn (0.13 mg/L).

Table 3 Amount of pollutants removed at time t (q_t)

Time (minute)	q_t (mg pollutant/mg complex coagulant)							
	Al	Fe	Mn	Mg	Ca	Si	Ni	Zn
1	15.74	0.91	7.26	12.66	2.62	0.00	0.00	0.64
5	15.94	1.39	7.66	12.90	5.00	0.30	0.01	0.73
10	16.03	1.76	7.75	13.44	8.46	0.35	0.03	0.98
20	17.08	2.04	7.84	13.45	10.07	0.49	0.18	1.00
30	16.95	2.04	7.50	13.24	10.02	0.44	0.16	0.92
40	16.55	1.96	7.06	12.17	8.79	0.31	0.01	0.61
50	16.09	1.13	7.00	11.64	7.98	0.25	0.01	0.51

3.5 Kinetic analysis

The study of kinetic behaviour or models is essential for designing and scaling up the coagulation process, as they describe the rate at which pollutants are removed by the coagulant, which is linked to the coagulation time. An understanding of the mechanism and the rate-determining of the process can be gained by analysing the kinetic behaviour. A variety of reaction kinetic models including pseudo-first-order, pseudo-second-order, Elovich model, and second-order model equations were applied to assess the suitability of these reaction kinetic models to the experimental data. Diffusion kinetic models including the Weber-Morris (intra-particle diffusion), Boyd, and Bangham equations were also investigated to study the diffusion in the sorption process. Using equation (2), the quantity of pollutant eliminated at time t , q_t , was determined. The q_t values are given in Table 3 where it can be seen that the quantity of pollutant (q_e , mg/mg) with time until 20 minutes. Subsequently, as time increases, adsorption slows down.

3.5.1 Adsorption reaction models

3.5.1.1 Pseudo-first-order rate equation

The pseudo-first-order kinetic model is based on the assumption that the rate of adsorbate removal as a function of time is proportional to the difference in adsorption capacity,

which is generally appropriate for describing the initial stage of an adsorption process. Generally, the pseudo-first-order kinetic model is adapted to a system in which the initial adsorbate concentration is high and which has only a few active sites on the adsorbate. The pseudo-first-order model can be described as follows (Wang and Guo 2020),

$$\frac{dq_t}{dt} = k_p (q_e - q_t) \quad (3)$$

Integrating equation 3 with initial conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives (Yuh-Shan, 2004; Kristianto et al., 2022)

$$\ln \left(\frac{q_e}{q_e - q_t} \right) = k_p t \quad (4)$$

which can be rearranged to:

$$\ln(q_e - q_t) = \ln q_e - k_p t \quad (5)$$

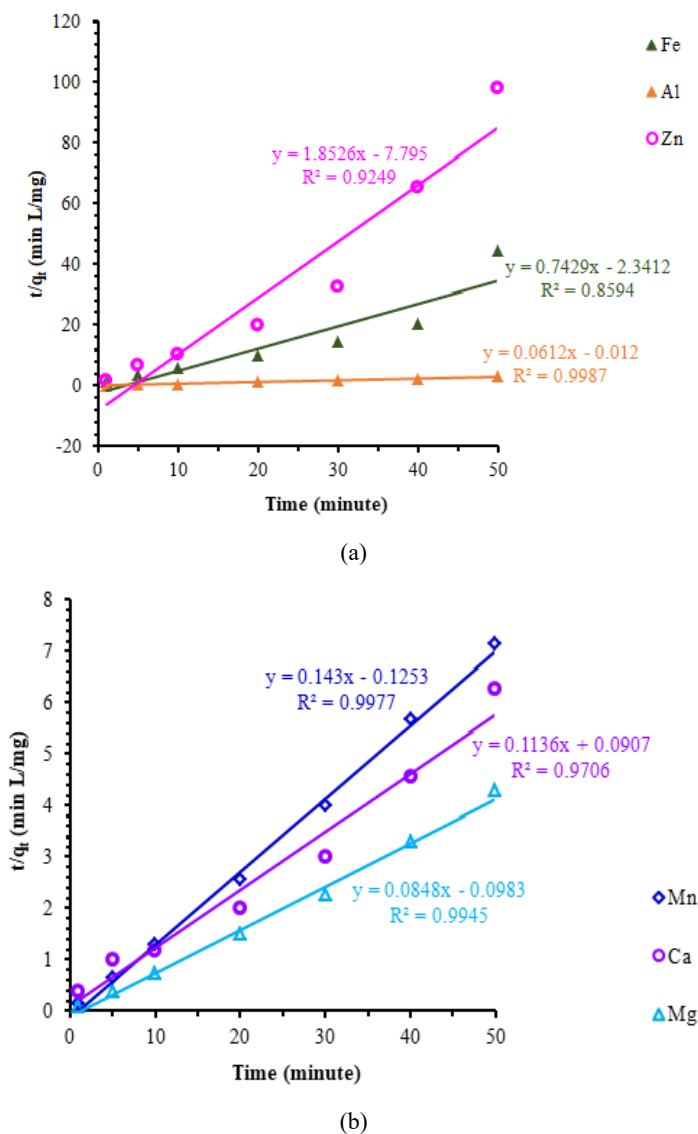
where q_t and q_e (mg/mg) are the adsorption capacities at time t (minute) and saturation (or equilibrium), respectively. k_p (min^{-1}) represents the pseudo-first-order rate constant for the kinetic model.

The rate constant k_p and q_e for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn were determined by plotting $\ln\{q_e - q_t\}$ against t . Figures A9–A12 display the plots of $\ln\{q_e - q_t\}$ against t for Al, Fe, Mn, Mg, Ca, Si, Zn, and Ni, respectively, and Table 4 displays the kinetic parameters of the pseudo-first-order kinetic model for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn.

Table 4 Kinetic parameters of the pseudo-first and pseudo-second-order kinetic models for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn

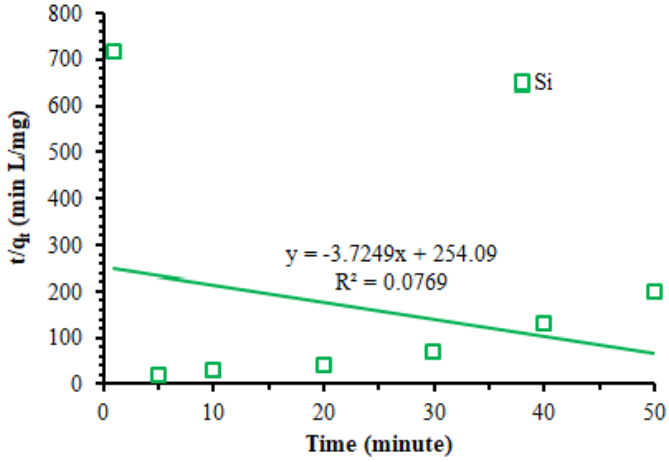
Impurities	q_e , experimental (mg/mg)	Pseudo-first-order		Pseudo-second-order	
		q_e calculated (mg/mg)	k_p (1/min)	q_e calculated (mg/mg)	k_p
Fe	2.050	0.260	−0.0249	1.346	−0.2357
Mg	13.500	0.183	0.0321	11.793	−0.0732
Ni	0.185	0.076	−0.0025	0.006	−20.5670
Mn	7.900	0.192	0.0246	6.993	−0.1632
Al	17.09	0.478	−0.0119	16.340	−0.3121
Si	0.500	0.136	−0.0061	−0.269	0.0546
Ca	10.070	1.116	−0.0299	8.803	0.1423
Zn	0.997	0.038	0.0264	0.540	−0.4403

Figure 4 Pseudo-second-order reaction kinetics for the adsorption onto hydroxide precipitate for (a) Fe, Al and Zn (b) Mn, Ca and Mg (c) Si and (d) Ni (coagulant dosage 20 mg/l, pH: 7, and RT $23 \pm 2^\circ\text{C}$) (see online version for colours)

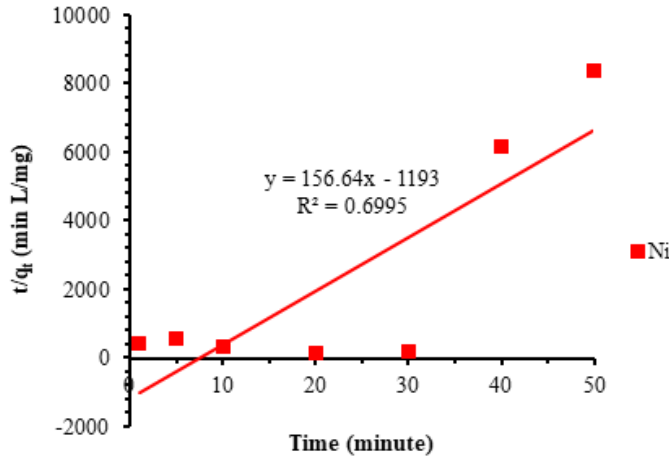


Note: Coagulant dosage 20 mg/l, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

Figure 4 Pseudo-second-order reaction kinetics for the adsorption onto hydroxide precipitate for (a) Fe, Al and Zn (b) Mn, Ca and Mg (c) Si and (d) Ni (continued)(see online version for colours)



(c)



(d)

Note: Coagulant dosage 20 mg/l, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

The pseudo-first-order constants, k_p , and saturation capacity, q_e , were determined from the slopes and intercepts of the curves (Figures A9–A12). As shown in Table 4, the values of the rate constant (k_p) are negative for Fe (−0.0249), Al (−0.0119), Ca (−0.0299), Si (−0.0061), and Ni (−0.0025). The values of k_p , however, are positive for Mg (0.0321), Mn (0.0246), and Zn (0.0264). Table 4 also shows that the values of the maximum adsorption capacity, q_e , calculated by the pseudo-first-order equation are not consistent with the experimental q_e for all the adsorption processes studied. This may imply that the adsorption of Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn onto hydroxide precipitate (derived from the coagulant) is not a pseudo-first-order reaction.

3.5.1.2 Pseudo-second-order rate equation

The pseudo-second-order kinetic model is convenient for describing the adsorption process for adsorbates with low concentrations and when the adsorbent has many active sites on its surface (Wang and Guo 2020). It is assumed that the adsorption process is second-order with chemical sorption as the rate-determining step. The high level of active sites and their interaction with the adsorbate through covalent forces and electron exchange are responsible for chemical sorption (Qiu et al. 2009). The pseudo-second-order equation can be defined as follows (Ho, 2006).

$$\frac{dq_t}{dt} = k_p (q_e - q_t)^2 \quad (6)$$

where k_p is the pseudo-second-order rate constant.

Integrating equation (6) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives the linear form given in equation (7).

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_p} \quad (7)$$

The constants $\frac{1}{q_e}$ and $\frac{1}{q_e^2 k_p}$ were determined experimentally by plotting $\frac{t}{q_t}$ against t .

The plots of $\frac{t}{q_t}$ against t for each pollutant are shown in Figure 4, from which the maximum adsorption capacity, q_e , and the rate constant of the pseudo-second-order kinetic model, k_p , can be calculated. The kinetic parameters of the pseudo-second-order kinetic are presented in Table 4.

Similar to the pseudo-first-order, negative values of the rate constant were noticed for Fe (−0.2357), Mg (−0.0732), Ni (−20.567), Mn (−0.1632), Al (−0.3121), and Zn (−0.4403), but positive values were found for Si (0.05461) and Ca (0.14228). However, the theoretical q_e values from the pseudo-second-order were more in agreement with the experimental q_e values than those calculated from the pseudo-first-order model. These findings imply that the adsorption of Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn on the hydroxide precipitate (adsorbent) follows the pseudo-second-order kinetic model, which also suggests that chemical adsorption is the rate-controlling step (Ho and McKay, 2000).

3.5.1.3 Elovich's equation

Elovich's kinetic model assumes an exponential decrease in the rate of adsorption of the adsorbate as the quantity of adsorbate adsorbed increases (Wang and Guo, 2020). This model is generally useful to describe the kinetics of adsorbate chemisorption on heterogeneous adsorbents. Elovich's equation can be presented as follows (Low, 1960):

$$\frac{dq_t}{dt} = \beta e^{-\alpha q_t} \quad (8)$$

where q_t (mg/mg) represents the amount of pollutant adsorbed at time t , β (mg/mg) is the desorption constant, and α (mg/mg min) the initial adsorption rate. The linear form of equation (8) is presented as:

$$q_t = \left(\frac{2.3}{\alpha} \right) \log(t + t_0) - \left(\frac{2.3}{\alpha} \right) \log t_0 \quad (9)$$

$$\text{With } t_0 = \frac{1}{\alpha\beta} \quad (10)$$

A straight line with an appropriate value of t_0 should be produced by plotting q_t versus $\log(t + t_0)$. Assuming $\beta\alpha \gg 1$, equation (9) was integrated using the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ to provide (Ho, 2006):

$$q_t = \alpha \ln t + \alpha \ln(\beta\alpha) \quad (11)$$

Figure A13 shows the plots of q_t versus $\ln t$ for different pollutants. The calculated parameters (α and β) of the Elovich model for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn are given in Table 5.

Table 5 Kinetic parameters of the Elovich and second-order kinetic models for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn

<i>Elovich</i>			<i>Second-order</i>		
<i>Impurities</i>	α (mg/mg min)	β (mg/mg)	k_2 (L/mg min)	C_0 (mg/L) calculated	C_0 (mg/L) experimental
Fe	0.197	1358.574	1.2963	0.02	1.64
Mg	-0.134	-2.440E-42	1.00E-04	21.65	30.18
Ni	0.018	101.112	0.0045	0.381	0.42
Mn	-0.055	-6.010E-59	0.0003	8.44	13.52
Al	0.238	2.270E+29	0.0258	0.80	13.85
Si	0.077	50.592	0.0061	0.73	0.91
Ca	1.733	3.503	0.0001	27.62	31.13
Zn	0.002	1.323E+211	-0.0032	0.26	0.93

In Table 5, it was observed that the value of the chemisorption rate, α , for Ca (1.733 mg/mg min) is greater than those for Al (0.238 mg/mg min), Fe (0.197 mg/mg min), Si (0.077 mg/mg min), Ni (0.018 mg/mg min), Zn (0.002 mg/mg min), Mn (-0.055 mg/mg min), and Mg (-0.134 mg/mg min).

The plotted graphs for all the elements studied showed non-linear behaviour. This confirmed that the experimental data do not fit the Elovich model, although the assumption made ($\beta\alpha \gg 1$) for all the elements studied is true. Consequently, the assumption of exponential coverage of adsorption sites, which implies multilayer adsorption, does not agree with the experimental data for all the pollutants studied.

3.5.1.4 Second-order rate equation

The second-order rate equations typical of solution systems can be described as follows (Ho, 2006):

$$\frac{dC}{dt} = -k_2 C_t^2 \quad (12)$$

By integrating equation (12) with the boundary conditions of $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$ to give the linear form

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_0} \quad (13)$$

where C_0 (mg/L) is the initial concentration of solute, C_t (mg/L) the concentration of solute at time t , k_2 (L/mg min) the rate constant, and t the time (min).

The plots of $1/C_t$ against t for different pollutants are presented in Figure A14. The calculated parameters of the second-order model for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn are provided in Table 5.

The second-order rate constants are determined as $1.2963 > 0.0258 > 0.0061 > 0.0045 > 0.0003 > 0.0001 > 1 \times 10^{-6} > -0.0032 \text{ Lmg}^{-1} \text{ min}^{-1}$ for the adsorption of Fe, Al, Si, Ni, Mn, Ca, Mg and Zn, respectively. Moreover, Table 5 shows that the initial concentration values calculated from the graph do not agree with the experimental initial concentration for all the studied pollutants. This can suggest that the adsorption of Al, Fe, Mn, Mg, Ca, Si, Zn and Ni onto hydroxide precipitate (derived from the coagulant) is not a second-order reaction. Thus, the rate constants from the model equation are not of significant.

3.5.2 Adsorption diffusion models

The discussion of the models includes the kinetics behaviour up to the saturation of the adsorption process, after which the kinetics graph shows a decrease in adsorption capacity.

3.5.2.1 Weber–Morris model or intraparticle diffusion model

It is important to use the Weber–Morris model since internal diffusion determines the adsorption rate in most liquid systems. An illustration of the kinetics is provided by equation (14), in which the intercept is linked to the mass transfer across the boundary layer and the value of the exponent is estimated to be 0.5 (for Fickian diffusion and plate geometry).

$$q = k_{in} t^{0.5} + C \quad (14)$$

Based on the Weber–Morris model equation (15), solute intake changes nearly proportionally with $t^{0.5}$ instead of the contact time t (An, 2020). The rate constant, k_{in} , was calculated from the plot of q_t versus $t^{0.5}$ and is associated with the respective intraparticle diffusion coefficient (D) according to equation (16).

$$q_t = k_{in} t^{0.5} + C \quad (15)$$

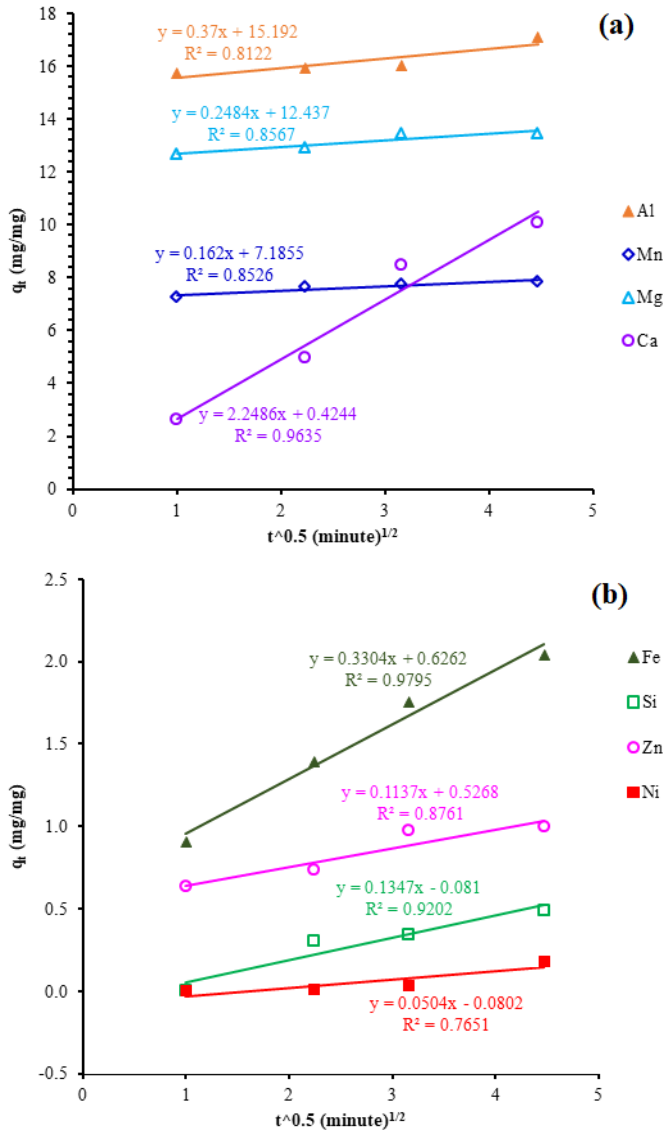
$$k_{in} = 6 \frac{q_0}{r} \sqrt{\frac{D}{\pi}} \quad (16)$$

Table 6 kinetic parameters of the Weber-Morris and Boyd kinetic models for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn

Pollutants	Weber-Morris			Boyd		
	$k_s (\text{mg L}^{-1} \text{min}^{-1/2})$	$D (\text{cm}^2/\text{min})$	$D (\text{cm}^2/\text{sec})$	$\beta (\text{min}^{-1})$	$D_{eff} \times 10^{-11} (\text{cm}^2/\text{min})$	$D_{eff} \times 10^{-12} (\text{cm}^2/\text{sec})$
Fe	0.3304	6.672×10^{-11}	1.112×10^{-12}	0.2496	6.6277	1.10
Mg	0.2484	1.283×10^{-8}	19.720×10^{-11}	0.3056	8.1146	1.35
Ni	0.0504	1.021×10^{-13}	1.702×10^{-15}	0.2571	6.8268	1.14
Mn	0.1620	1.095×10^{-9}	1.820×10^{-11}	0.2828	7.5092	1.25
Al	0.3700	6.001×10^{-9}	10.000×10^{-11}	0.2365	6.2798	1.05
Si	0.1347	3.427×10^{-12}	0.570×10^{-13}	0.3516	9.3361	1.56
Ca	2.2486	1.119×10^{-6}	1.865×10^{-8}	0.423	0.1123	1.87
Zn	0.1137	2.535×10^{-12}	0.420×10^{-13}	0.4036	0.1072	1.79

where k_{in} ($\text{mg L}^{-1}\text{min}^{-1/2}$) represents the intraparticle diffusion rate constant and r is the radius of the adsorbent particle (hydroxide precipitate = 5.11667×10^{-5} cm). The different mass-transfer mechanisms appear as different slopes in the linear plot of q_t versus $t^{0.5}$, derived by piecewise linear regression. These mechanisms are related to different consecutive stages of mass transfer with a decline rate: external mass transfer and intraparticle diffusion in the macroporous, mesoporous, and microporous structure of the adsorbent (Aroua et al., 2008).

Figure 5 Weber-Morris diffusion kinetics for the adsorption onto hydroxide precipitate for (a) Al, Mn, Mg and Ca and (b) Fe, Si, Zn and Ni (see online version for colours)



Note: Coagulant dosage 20 mg/l, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

For each pollutant studied, the Weber-Morris model equation was used on experimental data for the initial concentration and the plots are shown in Figure 5. Weber-Morris rate constant values were obtained from the slopes of the linear plots of q_t against $t^{0.5}$ for different impurities. The resulting rate constants k_{in} and the intraparticle diffusion coefficients D determined by equation (16) are displayed in Table 6.

The intraparticle diffusion coefficients calculated for Fe, Mg, Al, Mn, Si, and Zn are in the range of $1.8 \cdot 10^{-11}$ to $0.57 \cdot 10^{-13}$ cm²/sec, which is appropriate for intraparticle or pore diffusion as proposed by Karthikeyan et al. (2010). Nevertheless, the intraparticle diffusion coefficients obtained for Ni and Ca are not within the range of the study by Karthikeyan et al. (2010) and it can therefore be concluded that they are not consistent with the intraparticle diffusion model. The calculated diffusion coefficient for Ca is within the film diffusion as rate-determining step (Karthikeyan et al., 2010). In addition, the intercept values that give an indication about the boundary layer thickness (i.e., the higher the intercept, the bigger the boundary layer effect) (Kavitha and Namasivayam, 2008; Kannan and Sundaram, 2001) reveal that the boundary layer effect is bigger for Al (15.192) than for Mg (12.437), Mn (7.1855), Fe (0.6262), Zn (0.5268), Ca (0.4244), Ni (−0.0802) and Si (−0.081).

3.5.2.2 Boyd's model

One of the most widely used models for studying the kinetic mechanism of adsorption is currently Boyd's particle diffusion model (Boyd et al. 1947; Malash and El-Khaiary 2010). It is applied to kinetic data to determine the rate-limiting step, particle diffusion or film diffusion. This model is also used to calculate the effective intraparticle diffusion coefficient (D_{eff}). Boyd's film-diffusion model was first proposed for intraparticle diffusion in a spherical particle. In its application to external mass transfer, it assumes a linear relationship through the origin between $F = \frac{q}{q_e}$ (the fractional approach to saturation or equilibrium) and t (time) (Boyd et al., 1947):

$$\ln(1 - F) = kt \quad (17)$$

where, k represents the external mass transfer coefficient. The overall solution of the model used for solid phase control is as follows:

$$F = \frac{q}{q_t} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \beta t} \quad (18)$$

$$\text{For } n = 1, F = 1 - \frac{6}{\pi^2} e^{-\beta t} \quad (19)$$

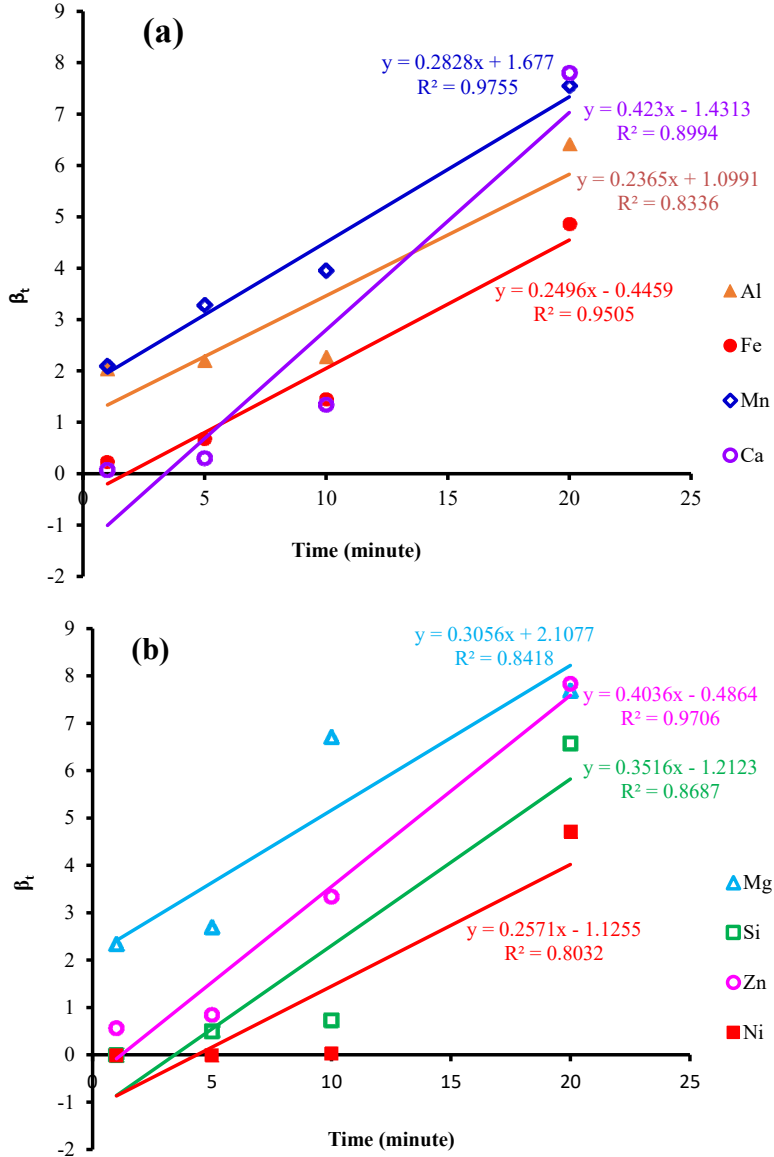
where the rate coefficient β (min^{−1}) is associated with the effective diffusion coefficient (D_{eff}) and the adsorbent (hydroxide precipitate) particle radius ($r = 5.11667 \times 10^{-5}$ cm) in the form $\beta = \pi^2 \frac{D_{eff}}{r^2}$. The relationship between the fractional approach to saturation (or equilibrium) F and the rate coefficient β , using the Fourier transform, is as follows:

$$\beta_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F(t)}{3}} \right)^2 \text{ for } F(t) \leq 0.85 \quad (20)$$

and

$$\beta_t = -0.498 - \ln(1 - F(t)) \text{ for } F(t) > 0.85 \quad (21)$$

Figure 6 Boyd's diffusion kinetics for the adsorption onto hydroxide precipitate for (a) Al, Fe, Mn and Ca and (b) Mg, Si, Zn and Ni ((see online version for colours))



Note: Coagulant dosage 20 mg/L, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

From the linear plot of β_t (derived by Equations (20) or (21) against time (Boyd plot), $f(F)$, the rate parameter β (by the slope of β_t against t) is evaluated. If there is an intercept (i.e., the value of the intercept $\neq 0$), this suggests the effect of a second mass transfer mechanism (outer mass transfer). Using each kinetic data, $F(t)$ was determined as $\frac{q_t}{q_e}$

(equation (18)) and β_t was calculated from equation (20) if $F(t) \leq 0.85$ or equation (21) if $F(t) > 0.85$. To obtain the kinetic parameter β and the respective effective diffusion coefficient (D_{eff}), a linear representation of β_t vs. t was applied. Table 6 and Figure 6 show the results of the Boyd model for the pollutants studied (Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn).

Table 6 shows that the D_{eff} values of Al, Fe, Ca, and Ni (6.2798×10^{-11} , 6.6277×10^{-11} , 1.1232×10^{-11} , and 1.0717×10^{-11} cm²/min, respectively) are nearly the same as those of the Morris and Weber model (6.0009×10^{-11} , 6.6719×10^{-11} , 1.1187×10^{-11} , and 2.5352×10^{-11} cm²/min, respectively). However, the D_{eff} values for Mn, Mg, Si, and Ni (7.5092×10^{-11} , 8.1146×10^{-11} , 9.3361×10^{-11} , and 6.8268×10^{-11} cm²/min, respectively) are greater than the ones of Morris and Weber model (1.0949×10^{-11} , 1.2831×10^{-11} , 3.4274×10^{-11} , and 1.0210×10^{-11} cm²/min, respectively). This comparison was made although many of the pollutants studied based on an adsorption survey show that there is very little or no information in the literature based on Fe, Mg, Ni, Mn, Al, Si, Ca, Zn and removal by coagulation adsorption. Moreover, all the impurities studied (Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn) showed an intercept, suggesting that diffusion is not the only transfer mechanism observed. There is therefore a second mass transfer mechanism (external mass transfer). The diffusion coefficients calculated range from 1.05×10^{-12} to 1.87×10^{-12} cm²/sec, making them physically suitable for intraparticle or pore diffusion according to the study by Karthikeyan et al. (2010); consequently, based on the diffusion coefficient, the film diffusion model is unsuitable for these processes.

3.5.2.3 Bangham's model (pore diffusion model)

The linearised form of Bangham's equation is described in equation (22) (Wahab, 2007).

$$\log \left[\log \left(\frac{C_0}{C_0 - q_t m} \right) \right] = \log \left(\frac{K_0 m}{2.303 V} \right) + \alpha \log t \quad (22)$$

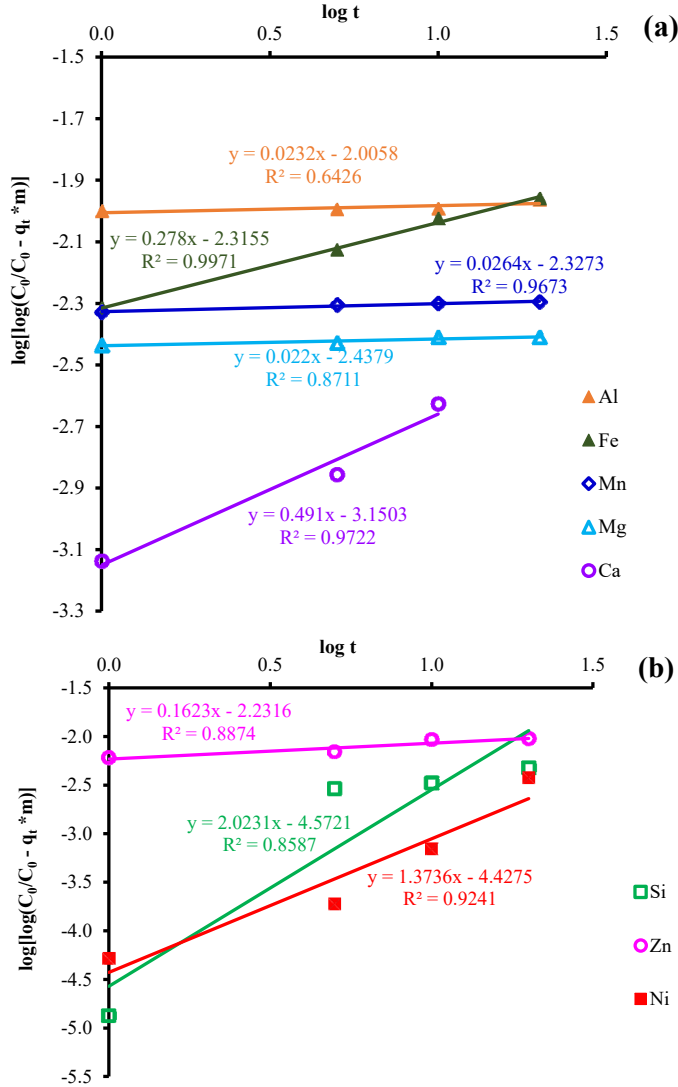
where C_0 (mg/L) is the initial concentration of adsorbate in solution, V (mL) is the volume of wastewater used, m (g/L) is the amount of coagulant, q_t is the amount of pollutant in solution at time t and α (< 1) and K_0 are constants that can be obtained from the slope and intercept, respectively. Pore diffusion is the rate-controlling step if the experimental data fits well with equation (22). The coagulation data for Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn were then utilised to determine whether or not pore diffusion is the only rate-controlling step in the actual adsorption system utilising the Bangham equation

(equation (22)). Plots of $\log \left[\log \left(\frac{C_0}{C_0 - q_t m} \right) \right]$ against $\log t$ for different pollutants are

shown in Figure 7. Table 7 summarises the calculated parameters of the Bangham model for Fe, Mg, Ni, Mn, Al, Si, Ca and Zn. For all the processes, the constant α is less than 1

except for Si and Ni, which was determined as the slope of the straight line. These findings demonstrate that pore diffusion is the rate-determining factor for these processes.

Figure 7 Bangham's diffusion kinetics for the adsorption onto hydroxide precipitate for (a) Al, Fe, Mn, Mg and (b) Ni, Si and Zn Ca (see online version for colours)



Note: Coagulant dosage 20 mg/L, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

Table 7 Kinetic parameters of the Bangham's kinetic model for Fe, Mg, Ni, Mn, Al, Si, Ca and Zn

<i>Impurities</i>	α	K_0
Fe	0.2780	13.9221
Mg	0.0220	10.5028
Ni	1.3736	0.1076
Mn	0.0264	13.5489
Al	0.0232	28.4056
Si	2.0231	0.0771
Ca	0.4910	2.0366
Zn	0.1623	16.8890

3.5.3 Coefficient of determination

From comparing all chemisorption models, as reported in Table 8, it can be seen that the correlation coefficients are higher for the second-order kinetic studies. However, Figure 4(c) shows that the pseudo-second-order model was not well fitted to Si ($R^2 = 0.0769$). But, after a coagulation time of 1 minute, a good fit of this model to the silicon experimental data was obtained, with an R^2 value of 0.9164 (Figure 8). Hence, all the experimental data showed better conformity with the pseudo-second-order chemisorption kinetic model for hydroxide precipitates in terms of higher correlation coefficient values. It can be concluded that the pseudo-second-order kinetic model well describes the experimental data, indicating the chemical sorption nature of the coagulation process. Zewail and Yousef (2015), and Alyüz and Veli (2009) found that the removal of Ni and Zn ions were well fitted by second-order model.

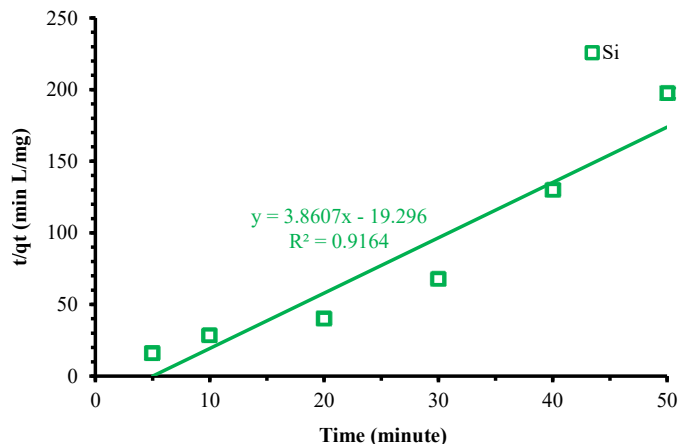
Table 8 Linear kinetic coefficients of determination (R^2) for reaction and diffusion kinetic models.

<i>Pollutants</i>	<i>Reaction kinetic models</i>				<i>Diffusion kinetic models</i>		
	<i>Pseudo-first-order</i>	<i>Pseudo-second-order</i>	<i>Elovich</i>	<i>Second-order</i>	<i>Weber-Morris</i>	<i>Boyd</i>	<i>Bangham</i>
Fe	0.0501	0.8594	0.3468	0.0395	0.9795	0.9505	0.9971
Mg	0.1714	0.9945	0.0739	0.0861	0.8567	0.8418	0.8711
Ni	0.0008	0.6995	0.1	0.0253	0.7651	0.8032	0.9241
Mn	0.2127	0.9977	0.0481	0.0878	0.8526	0.9755	0.9673
Al	0.0133	0.9987	0.3963	0.0796	0.8122	0.8336	0.6426
Si	0.0068	0.0769	0.4655	0.1535	0.9202	0.8687	0.8587
Ca	0.0365	0.9706	0.7553	0.4549	0.9635	0.8994	0.9722
Zn	0.0321	0.9249	0.0001	0.0006	0.8761	0.9706	0.8874

For the diffusion models (Table 8), the correlation coefficient ranges from 0.64 to 0.997 implying that multiple adsorption stages took place and that intraparticle or porous diffusion is not the only one involved in the diffusion mechanism. The linearity of the pattern also indicates that adsorbate pore diffusion is not the only rate controlling step.

Multilinear profiles were found for the plot of intraparticle diffusion model over the whole-time range investigated, and this plot is not passing by the origin, suggesting that boundary layer diffusion is also involved in the adsorption mechanism.

Figure 8 Pseudo-second-order for the adsorption of silicon after 1 min coagulation time (see online version for colours)



4 Conclusions

The performance of a coal fly ash-based coagulant in the removal of TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn in mine effluents was studied. Various experimental parameters including coagulant dosage, pH, temperature and coagulation time were studied for the coagulation process. The coagulant has proved effective in removing these pollutants from mine wastewater. The efficiency of the coal fly ash coagulant in coagulating the wastewater depends mainly on the dosage of the coagulant, the pH value, and the time. With a coagulation time of 20 minutes, the coagulant proved effective in effluent treatment. The best coagulant effect for TDS removal was achieved at pH 7 at 20 mg/l coagulant dosage. For the removal of Si and Zn, the coagulant favours pH 9 and 10 at 20 mg/L coagulant dosage. The removal of Al has an optimum coagulant dosage of 20 mg/L at pH values in the range of 7 to 10. For Fe removal, the coagulant favours coagulant dosage ranging from 2–20 mg/L at pH values of 6–10. An optimal coagulation dosage of 20 mg/L at pH 10 was obtained for the removal of Mn and Mg. The best results for Ca and Ni removal were found with a coagulant dosage of 20 mg/L at pH 12 and 10–20 mg/L at pH 10, respectively. Nevertheless, given that the mine wastewater utilised in this study is a multi-component aqueous solution, it was determined the following optimum process conditions: coagulation time: 20 minutes, coagulant dosage: 20 mg/L, and pH: 7 (relative to TDS). In these conditions, the residual rate was 60.83, 0.23, 64.35, 65.29, 53.61, 1.36, 56.57, 74.13, and 13.95% TDS, Fe, Mg, Ni, Mn, Al, Si, Ca, and Zn, respectively.

A kinetic model study to describe the current data was carried out using adsorption reaction kinetic models such as pseudo-first-order, pseudo-second-order, Elovich, and second-order equations; and adsorption diffusion kinetic models such as Weber-Morris, Boyd, and Bangham's equations. Among the different adsorption reaction models studied, the pseudo-second-order model best describes the experimental data. It is therefore proposed that chemisorption is the rate-controlling step for the sorption of impurities onto hydroxide precipitates. The adsorption diffusion models indicated that both intraparticle diffusion and film diffusion contribute to the coagulation processes. This is based on the intraparticle diffusion coefficients, for specific impurities, calculated from the Weber-Morris and Boyd's models which are in the range of $1.8 \cdot 10^{-11}$ to $0.57 \cdot 10^{-13}$ cm²/sec and $1.05 \cdot 10^{-12}$ to $1.87 \cdot 10^{-12}$ cm²/sec, respectively, (except for Ca and Ni for the Weber-Morris model). Such ranges are suitable for the case of intraparticle diffusion control. The existence of an intercept in Boyd's model, for all the pollutants investigated, suggests the existence of an external diffusion mechanism. The Bangham model showed that the pore diffusion is the rate-determining factor for these processes (except for Ni and Si). Based on the correlation coefficient, the adsorption kinetics of all studied impurities in mine wastewater with hydroxide precipitates was well described by the Weber-Morris, Boyd, and Bangham models. This indicates that the diffusion mechanism occurred in multiple adsorption stages, namely, film diffusion and intraparticle or pore diffusion.

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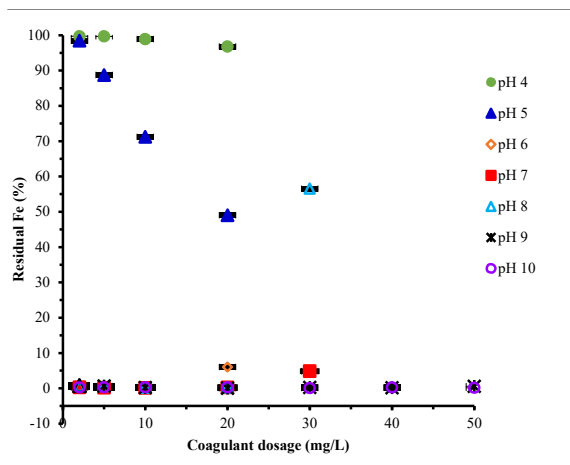
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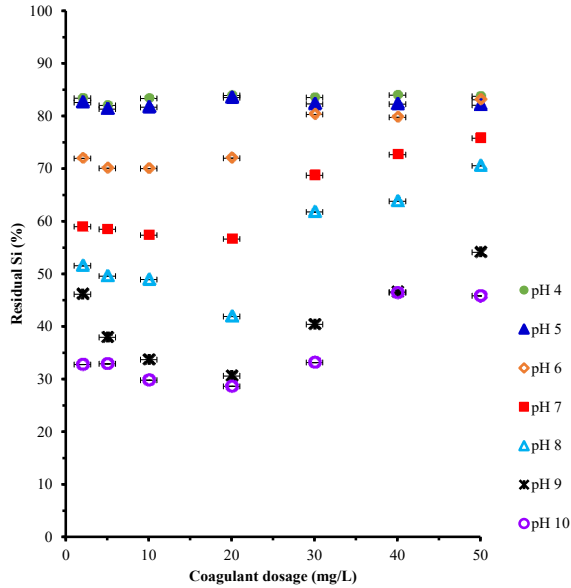
Appendix

Figure A1 Effect of coagulant dosage (mg/L) and pH on removal of Fe from mine wastewater (see online version for colours)



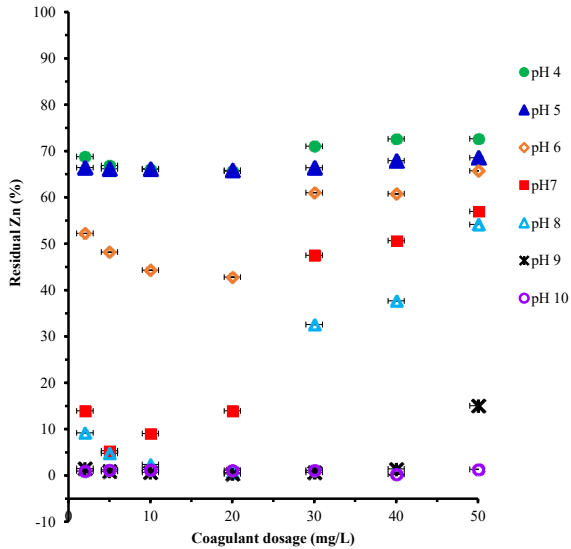
Notes: Initial Fe concentration: 1.64 mg/L, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A2 Effect of coagulant dosage (mg/L) and pH on removal of Si from mine wastewater (see online version for colours)



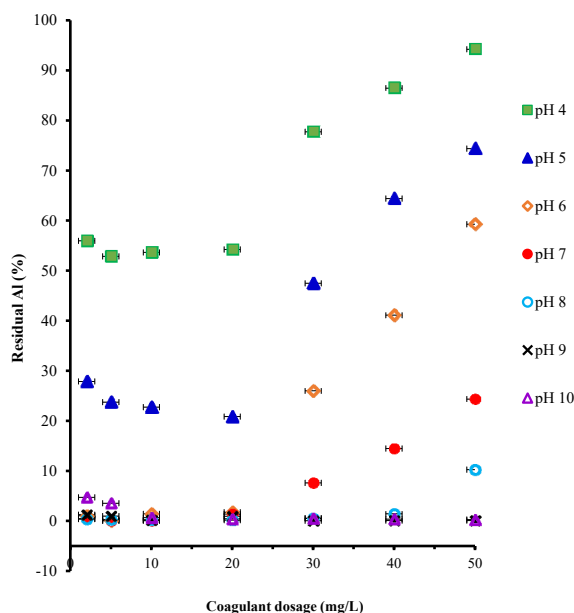
Notes: Initial Si concentration: 0.91 mg/L, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A3 Effect of coagulant dosage (mg/L) and pH on removal of Zn from mine wastewater (see online version for colours)



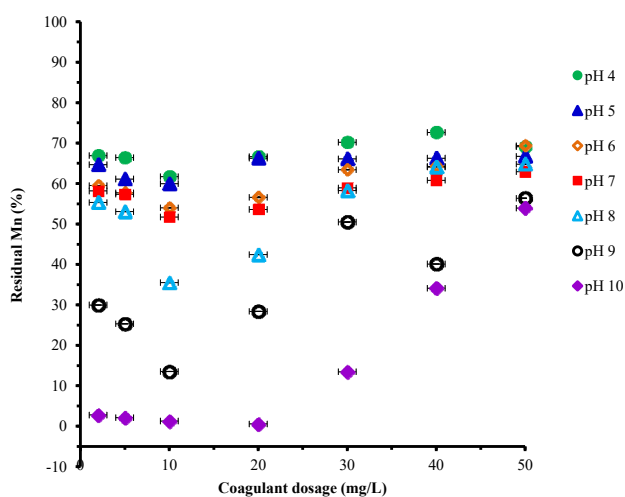
Notes: Initial Zn concentration: 0.93 mg/L, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A4 Effect of coagulant dosage (mg/L) and pH on removal of Al from mine wastewater (see online version for colours)



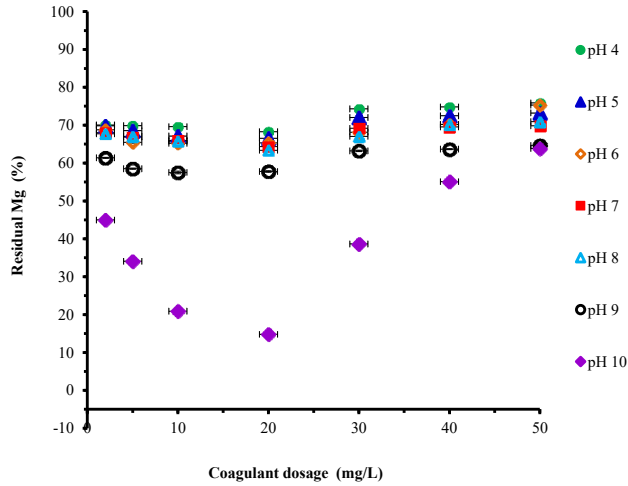
Notes: Initial Al concentration: 13.86 mg/L, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A5 Effect of coagulant dosage (mg/L) and pH on removal of Mn from mine wastewater (see online version for colours)



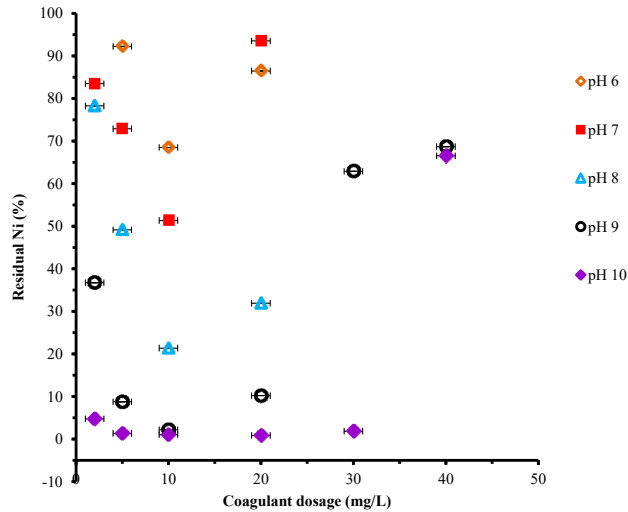
Notes: Initial Mn concentration: 13.52 mg/L, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A6 Effect of coagulant dosage (mg/L) and pH on removal of Mg from mine wastewater (see online version for colours)



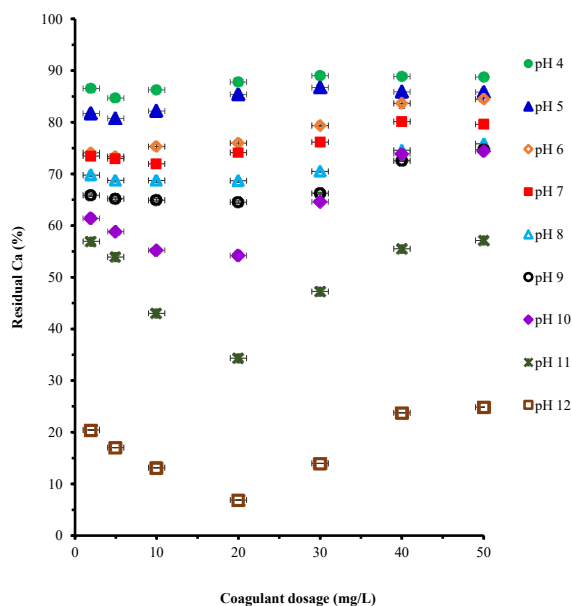
Notes: Initial Mg concentration: 30.18 mg/L, initial pH: 4–10; mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A7 Effect of coagulant dosage (mg/L) and pH on removal of Ni from mine wastewater (see online version for colours)



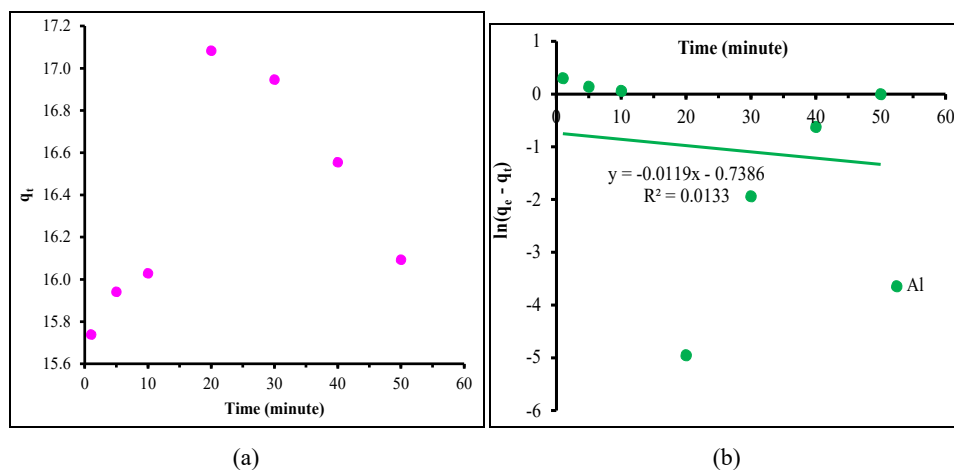
Notes: Initial Ni concentration: 13.86, initial pH: 4–10, mine wastewater/coagulant ratio: 1:0.4, ambient temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A8 Effect of coagulant dosage (mg/L) and pH on removal of Ca from mine wastewater (see online version for colours)



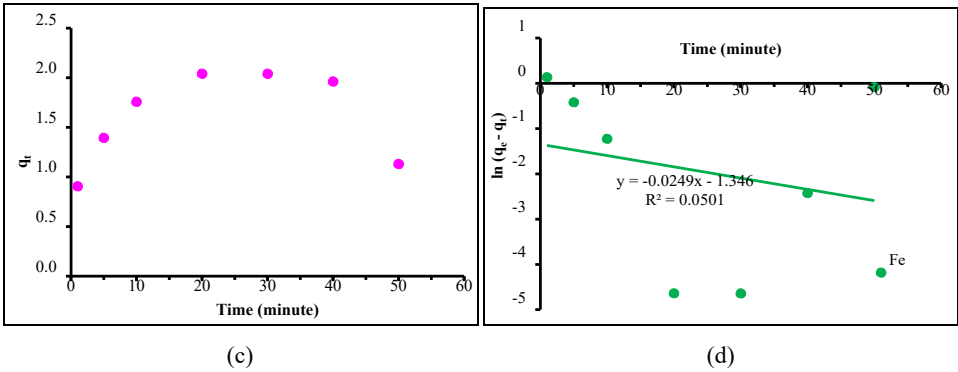
Notes: Initial Ca concentration: 31.13 mg/L, initial pH: 4–12, mine wastewater/coagulant ratio: 1:0.4, room temperature, 5 minutes rapid mixing at 300 rpm, 20 minutes slow mixing at 30 rpm.

Figure A9 (a) Adsorption rate curves of Al (b) pseudo-first-order reaction kinetics for the adsorption of Al onto hydroxide precipitate (c) adsorption rate curves of Fe and (d) pseudo-first-order reaction kinetics for the adsorption of Fe onto hydroxide precipitate (see online version for colours)



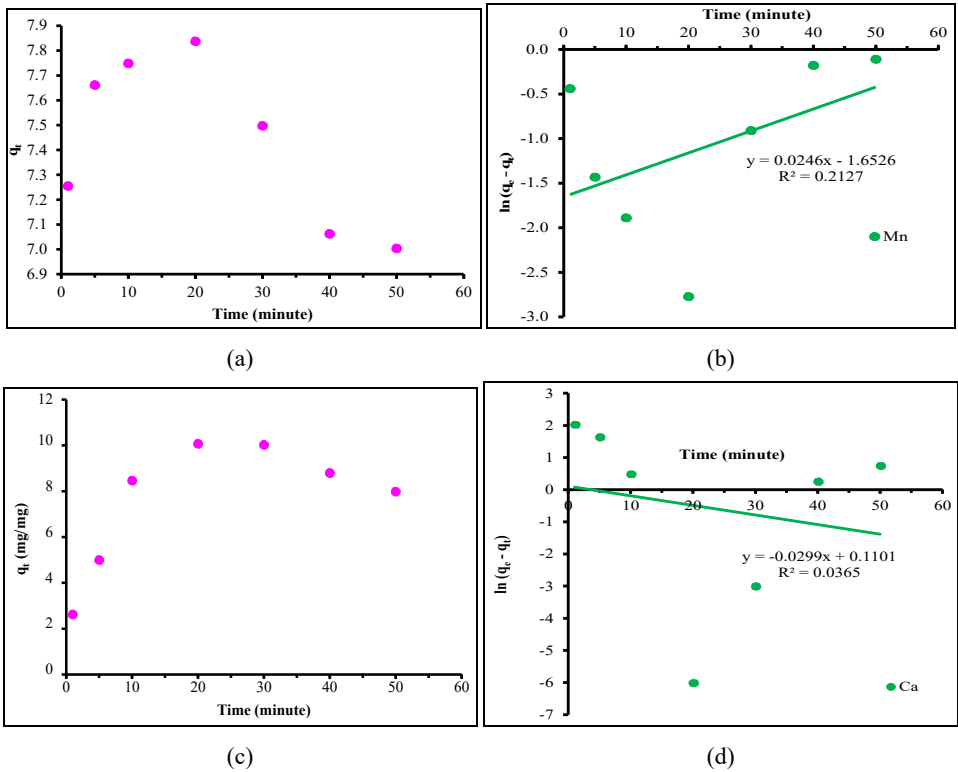
Note: pH: 7, coagulant dosage 20 mg/L, and RT $23 \pm 2^\circ\text{C}$.

Figure A9 (a) Adsorption rate curves of Al (b) pseudo-first-order reaction kinetics for the adsorption of Al onto hydroxide precipitate (c) adsorption rate curves of Fe and (d) pseudo-first-order reaction kinetics for the adsorption of Fe onto hydroxide precipitate (continued) (see online version for colours)



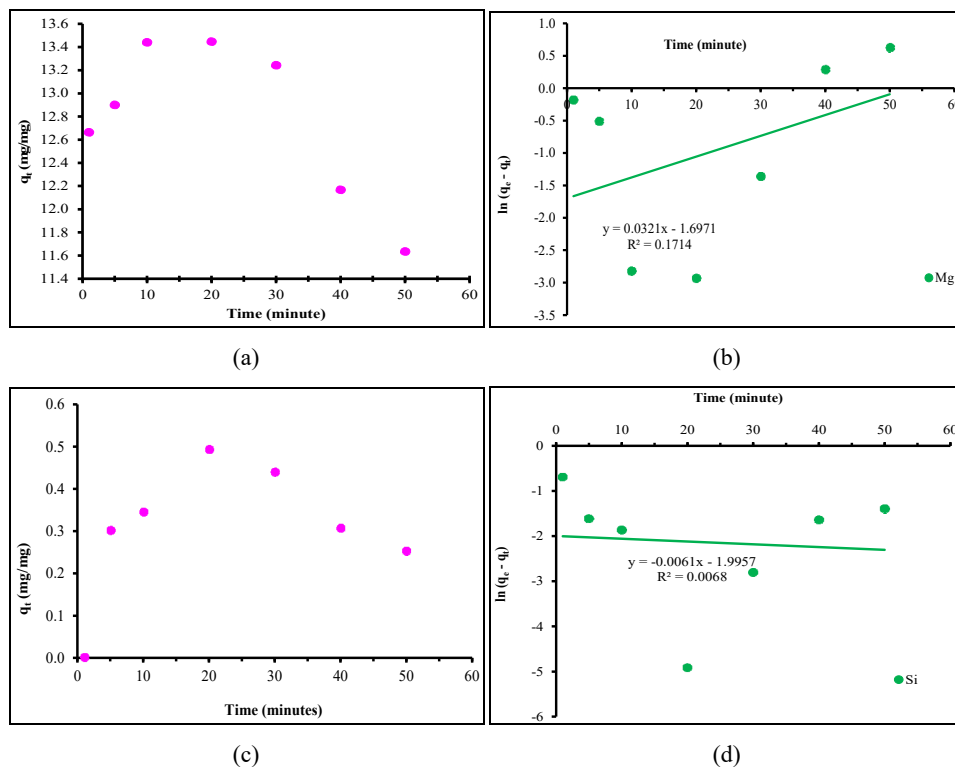
Note: pH: 7, coagulant dosage 20 mg/L, and RT $23 \pm 2^\circ\text{C}$.

Figure A10 (a) Adsorption rate curves of Mn (b) pseudo-first-order reaction kinetics for the adsorption of Mn onto hydroxide precipitate (c) Adsorption rate curves of Ca and (d) pseudo first order reaction kinetics for the adsorption of Ca onto hydroxide precipitate (see online version for colours)



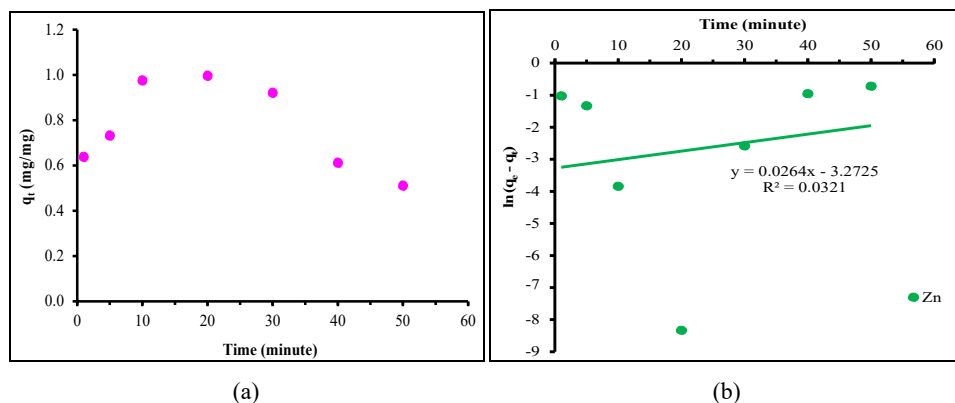
Note: pH: 7, coagulant dosage 20 mg/L, and RT $23 \pm 2^\circ\text{C}$.

Figure A11 (a) Adsorption rate curves of Mg and (b) Pseudo-first-order reaction kinetics for the adsorption of mg onto hydroxide precipitate (c) adsorption rate curves of Si and (d) pseudo-first-order reaction kinetics for the adsorption of Si onto hydroxide precipitate (see online version for colours)



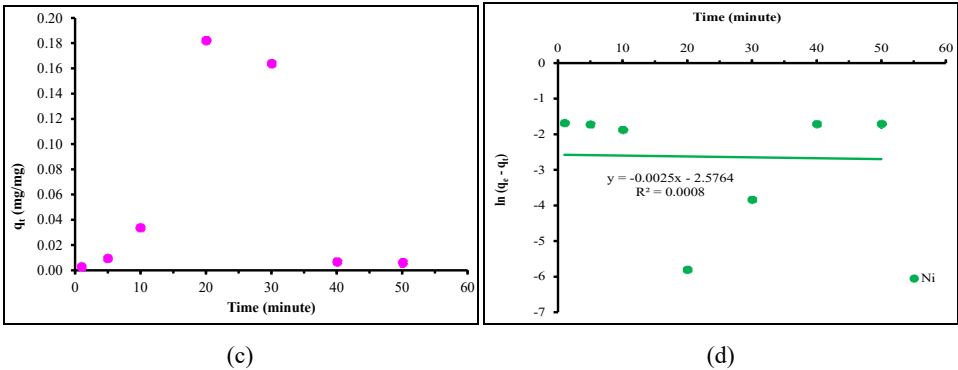
Note: pH: 7, coagulant dosage 20 mg/l, and RT $23 \pm 2^\circ\text{C}$.

Figure A12 (a) Adsorption rate curves of Zn and (b) Pseudo-first-order reaction kinetics for the adsorption of Zn onto hydroxide precipitate (c) adsorption rate curves of Ni and (d) pseudo-first-order reaction kinetics for the adsorption of Ni onto hydroxide precipitate (see online version for colours)



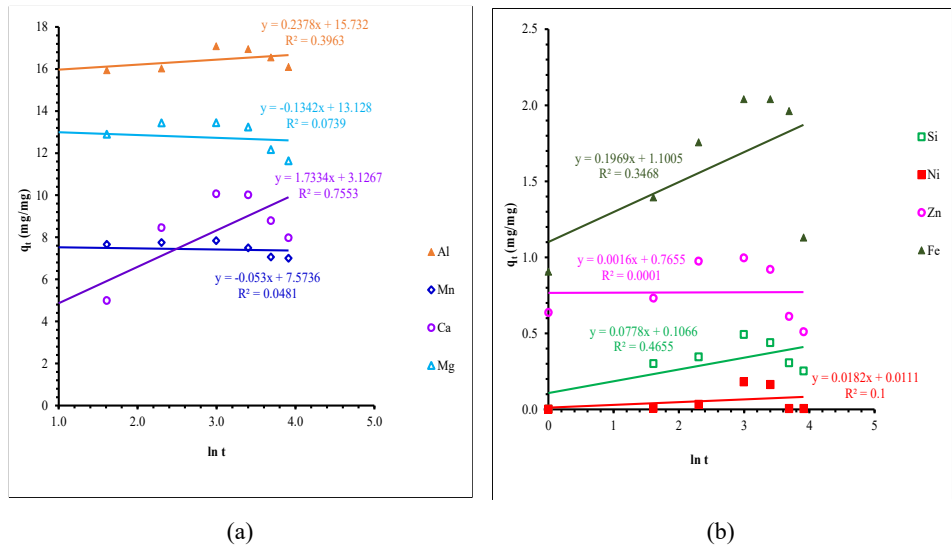
Note: Coagulant dosage 20 mg/L, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

Figure A12 (a) Adsorption rate curves of Zn and (b) Pseudo-first-order reaction kinetics for the adsorption of Zn onto hydroxide precipitate (c) adsorption rate curves of Ni and (d) pseudo-first-order-reaction kinetics for the adsorption of Ni onto hydroxide precipitate (continued) (see online version for colours)



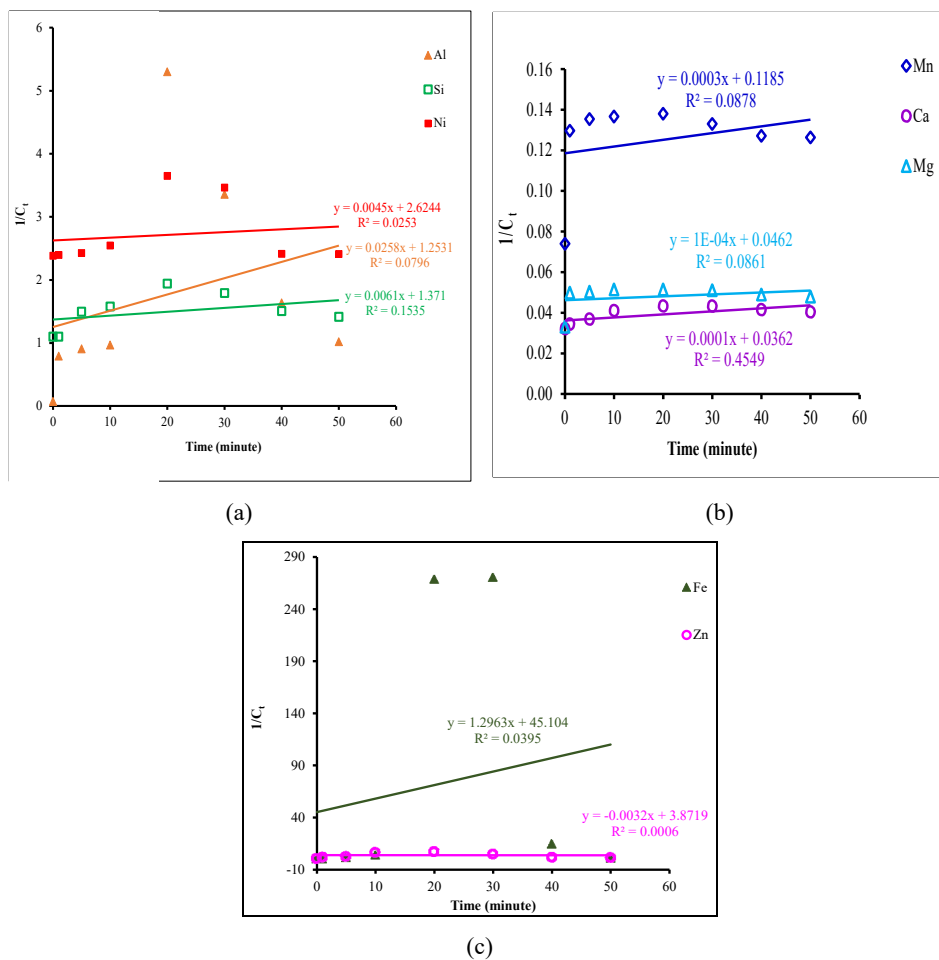
Note: Coagulant dosage 20 mg/L, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

Figure A13 Elovich reaction kinetics for the adsorption onto hydroxide precipitate for (a) Al, Mn, Ca and Mg and (b) Si, Ni, Zn and Fe (see online version for colours)



Note: Coagulant dosage 20 mg/L, pH: 7, and RT $23 \pm 2^\circ\text{C}$.

Figure A14 Second-order reaction kinetics for the adsorption onto hydroxide precipitate for (a) Al, Si and Ni (b) Mn, Ca and mg and (c) Fe and Zn (see online version for colours)



Note: Coagulant dosage 20 mg/l, pH: 7, and RT $23 \pm 2^\circ\text{C}$.