

## REMOVAL OF FLUORIDE FROM WASTEWATER BY CALCINED GYPSUM: ADSORPTION AND KINETICS STUDY

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### Abstract

Adsorption studies were performed to assess the removal of fluoride ions using calcined gypsum. Calcined gypsum introduces free calcium ions to form a precipitate of  $\text{CaF}_2$ . Fluoride ions were removed by 68% at room temperatures. Langmuir isotherm was found to best fit the adsorption behaviour. Thermodynamic parameters such as  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  indicated that the removal of fluoride ions by calcined gypsum was exothermic and non-spontaneous at temperatures higher than 50 °C. The pseudo-second-order model was found to best fit the kinetic adsorption data.

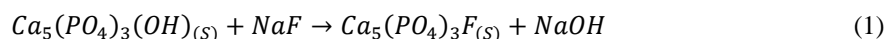
Keywords: Adsorption, Calcined gypsum, Fluoride, Kinetics study, Pseudo-second order.

## 1. Introduction

World Health Organization (WHO) sets a 1.5 mg/L as the higher limit of fluoride content in drinking water [1]. The high concentration of fluoride leads to dental and skeletal fluorosis such as mottling of teeth, softening of bones and ossification of tendons and ligaments [2]. In 2013, it was reported that more than 200 million people in more than 30 countries are affected by fluorosis [3]. Most of the fluoride reached human bodies comes from drinking water. Drinking water resources are mostly contaminated with fluoride by geochemical reactions or anthropogenic activities for example; the disposal of industrial wastewater [4]. Many factors affect the amount of fluoride in groundwater such as the geological, chemical, and physical characteristics of the aquifer, the availability and solubility of fluoride minerals, rate of flowing water, temperature, pH, and concentration of other chemicals [5].

Diverse types of techniques are used for defluoridation like; precipitation-coagulation [6], membrane separation process [7], electrolytic defluoridation [8], electrodialysis [9], ion exchange [10] and adsorption, which is the most commonly used method due to its low cost [11, 12]. Different types of adsorbent materials were used for the removal of fluoride from water. Both natural and synthetic adsorbent materials have been used like; activated carbons, activated alumina, bauxite, hematite, polymeric resins [13], activated rice husk, brick powder, pumice stone, red soil, charcoal, brick, fly ash, serpentine, granular ceramics, chitosan, modified ferric oxide/hydroxide, hydroxyapatite (HAP), zirconium and cerium modified materials, titanium-derived adsorbent, modified cellulose, clays, zeolite, modified zeolite, magnesium-modified sorbent [4], carboxymethylated starch-based hydrogels loaded with  $Fe^{2+}$  [14] and calcium metal-containing compounds [15]. Calcium metal-containing compounds like;  $Ca(OH)_2$ ,  $CaCl_2$ , and  $CaSO_4$  have shown a potential efficiency in the area of water defluoridation [16, 17]. Such compounds precipitate fluoride as calcium fluoride, in addition, to serving as an adsorbent surface for the fluoride ion [18]. Fluoride ion is precipitated as calcium fluoride after reaction with lime, limestone, calcium chloride, calcium phosphate, calcium nitrate and calcium sulfate [19].

Adler et al. [20] conducted the first attempt for the removing of fluoride from water using calcium-containing compound. They used tricalcium phosphate as adsorption material. Goodwin et al. reduced the concentration of fluoride ion from 5.0 mg/l to 0.42 mg/l using tri-calcium phosphate; they suggested that the removal process took place by adsorption and formation of fluorapatite (FAP) [21]. Spinelli et al. [22] proved that fluoride ion can be removed by precipitation as fluoroapatite as shown in following Eq. (1):



Other researchers utilised calcite to remove fluoride ion from industrial wastewater containing HF [23, 24]. Gogoi and Dutta [25] revealed that the addition of phosphoric acid to limestone enhanced the removal of fluoride by increasing the removal capacity to 4.38 mg/g of limestone. In another study by Nath et al. [15], acetic and citric acid were added to the fluoride water before passing through limestone column, in which, fluoride removed as  $CaF_2$ . In addition, it was revealed that addition of HCl with calcite to wastewater is beneficial [26]. Reardon [27] used carbon dioxide to generate calcium ion as a first step, then fluoride precipitated as

CaF<sub>2</sub> as a second step. Wongrueng et al. [28] proposed the adsorption of fluoride from an aqueous solution onto dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). They found that dolomite sorbent required 12 hours of contact time to reach equilibrium with a fluoride adsorption capacity of 0.000581 mM/g, and the kinetic adsorption fitted well with a pseudo-second-order kinetic reaction with a rate constant of 21.07 g/mm·min. Fufa et al. [29] removed fluoride from groundwater using gypsiferous limestone (GLS) and this removal affected by contact time, dose, pH, initial fluoride concentration and thermal activation.

The work presented in this paper aimed to study the removal of fluoride ions by calcined gypsum by adsorption. And to evaluate the thermodynamic parameters, adsorption isotherm, and kinetic model that best describe the adsorption behaviour.

## 2. Methods

### 2.1. Experimental setup for fluoride removal and isotherms:

Wastewater was taken from Tafila Wastewater Treatment. A certain weight of sodium fluoride salt was dissolved in 3 L of the wastewater to increase fluoride ion concentration to 147 ppm and then used to prepare the desired fluoride concentration for the removal experiments. Samples of 100 mL were taken for each precipitation trial. The calcined gypsum samples from a local supplier (Rawabi for Mining Co, Calcination temperature 170-200 °C), were mixed with this partial-synthetic fluoride-containing water, and the mixture was stirred by magnetic stirrer at the desired temperature (20, 30 50 and 70 °C) and time (10, 20, and 30 min). The samples were then filtered using 125-Blueband paper and were taken to the analysis of F<sup>-</sup> by ion chromatography (Dionex-100 with an AG4A-SC guard column, AS4SC separating column, an SSR1 anion self-regenerating suppressor and a conductivity meter). The water samples were collected in polyethylene bottles. Electrical conductivity and pH were measured using ORION model 162 conductivity meter and CG 712 (SCHOTT GERAETE) pH meter, respectively.

### 2.2. Models

#### 2.2.1. Adsorption isotherms

Langmuir isotherm assumes that a single layer of sorbate forms on the sorbent at equilibrium. Moreover, Langmuir isotherm assumes that no more adsorption is possible after the formation of the aforementioned mono-layer on the surface of the sorbent, for the attraction between molecules decreases as they get further from the adsorption surface [30]. The isotherm can be expressed as the following equation:

$$Q_e = \frac{V_m \times C_e}{(1/k) + C_e} \quad (2)$$

where  $Q_e$  is the adsorbed mass of fluoride (mg/g),  $C_e$  is the equilibrium fluoride concentration (mg/L),  $V_m$  is the monolayer capacity (mg/g), and  $k$  is the equilibrium constant (L/mg).

Freundlich isotherm is employed to describe the adsorption behaviour on heterogeneous surfaces [31]. The isotherm can be expressed as the following equation:

$$Q_e = K_f \times C_e^{1/n} \quad (3)$$

where  $K_f$  is the Freundlich constant (mg/g) and  $1/n$  is the adsorption intensity.

Mass balance on the added fluoride will be used in order to evaluate the solid phase concentration, as shown in the following equation:

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \quad (4)$$

where  $C_0$  is the initial fluoride concentration (mg/L),  $V$  is the sample volume (L), and  $m$  is the mass of sorbent (mg).

### 2.2.2. Adsorption thermodynamics

The different thermodynamic parameters of the adsorption process will be evaluated through the effect of temperature on the thermodynamic equilibrium constant ( $K$ ), which is defined as follows:

$$K = \frac{a_s}{a_e} = \frac{(v_s \times Q_e)}{(v_e \times C_e)} \quad (5)$$

where,  $a_s$  is the activity of the adsorbed ion,  $a_e$  is the activity of the in-solution ion at equilibrium,  $v_s$  is the activity coefficient the adsorbed ion, and  $v_e$  is the activity coefficient of the in-solution ion at equilibrium. The activity coefficients can be assumed to equal 1, as the in-solution ions concentration approaches zero. Equation (5) can be simplified to:

$$\lim(Q_e \rightarrow 0) \Rightarrow K = \frac{a_s}{a_e} = \frac{Q_e}{C_e} \quad (6)$$

The change in standard free energy of adsorption ( $\Delta G^0$ ) is calculated by:

$$\Delta G^0 = -R \times T \times \ln(K) \quad (7)$$

where  $R$  is the universal gas constant ( $8.314 \times 10^{-3} \text{ kJ/K}$ ) and  $T$  is the temperature ( $K$ ).

Entropy ( $\Delta S^0$ ) and Enthalpy ( $\Delta H^0$ ) are evaluated through the Van't Hoff equation:

$$\ln(K) = \Delta S^0/R - \Delta H^0/RT \quad (8)$$

### 2.2.3. Adsorption kinetics

Adsorption kinetics describes the uptake rate of fluoride, which can describe the residence time of ions at the solid-liquid interface. The kinetics of adsorption depends mainly on the sorbent surface area and the nature-concentration of the active sites responsible for the interaction with the targeted ions [32].

Two kinetic models were used to analyse the adsorption of fluoride ions; the pseudo-first-order and pseudo-second-order. Pseudo-first order kinetics can be represented as follows [33]:

$$\frac{dQ_t}{dt} = K_1 \times (Q_e - Q_t) \xrightarrow{\text{Integration}} \ln(Q_e - Q_t) = K_1 \times t + C_1 \quad (9)$$

where  $K_1$  is the first order adsorption rate constant (1/min),  $Q_t$  the adsorbed amount at time  $t$  (mg/g), and  $C_1$  is the integration constant.

Pseudo-second order kinetics can be represented as follows [34]:

$$\frac{dQ_t}{dt} = K_2 \times (Q_e - Q_t)^2 \xrightarrow{\text{Integration}} \frac{1}{(Q_e - Q_t)} = K_2 \times t + C_2 \quad (10)$$

where  $K_2$  is the second order adsorption rate constant (g/mg/min) and  $C_2$  is the integration constant. Values of the rate constants can be evaluated as the slope in the linear plots of Eqs. (9) and (10).

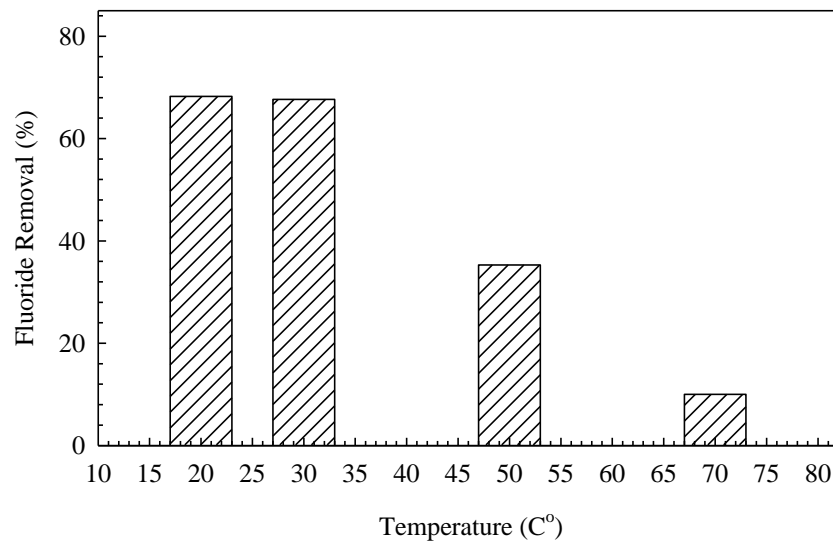
### 3. Results and Discussions

#### 3.1. Water samples

Water samples used in the study had a pH of 7.5 to 8.5, while the conductivity was found be (9.1 mS/cm). It must be added that EC decreased with time and increased with the addition of calcined gypsum and rising temperatures.

#### 3.2. Fluoride removal capacity

Figure 1 shows the fluoride removal percentage by calcined gypsum at different operating temperatures. Calcined gypsum was able to remove up to 68.2% of added fluoride at 20 °C. Calcined gypsum introduces free calcium ions to form a precipitate of  $\text{CaF}_2$ . This removal percentage was lower than previously reported values [20]. Removal percentage remained the same when the temperature was raised to 30 °C. However, the percentages drop significantly when the temperature was further raised; dropping to 35% and 10% at 50 and 70 °C, respectively. The observed decrease in removal efficiency at elevated temperatures is further discussed in Section 3.5.



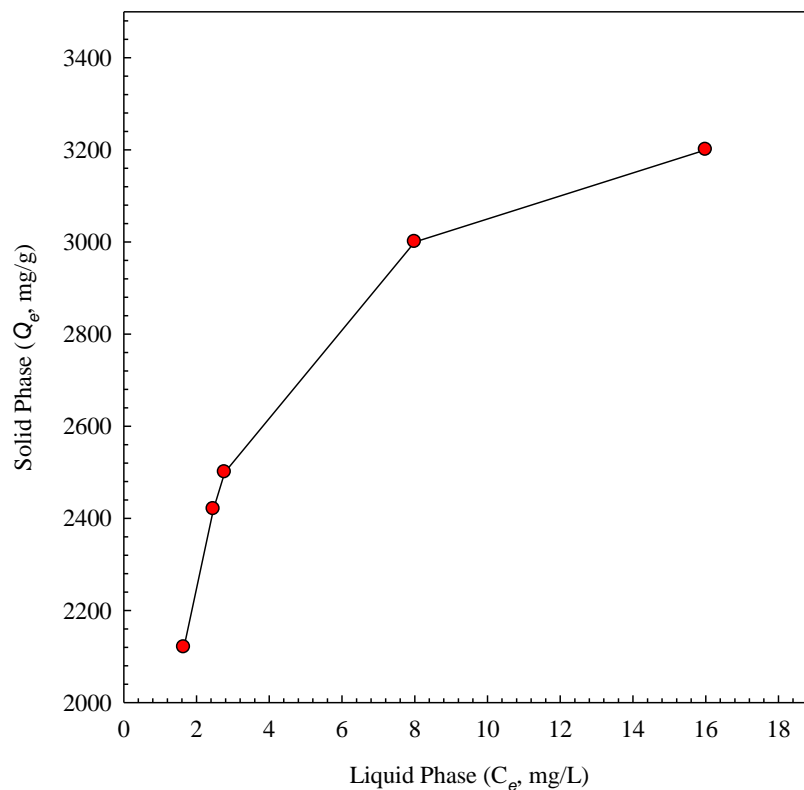
**Fig. 1. Fluoride removal percentage at various temperatures.**

Comparing these results with previous work in literature for adsorbents containing calcium compounds, gave an indicator for prospective use of calcined gypsum as a fluoride adsorbent. Nasr et al. [35] used calcite in combination with acetic acid for fluoride removal from its solution. They found that, at low fluoride concentration, the removal efficiency increased from 17.4% without acid to 30.4%

with 0.1 M acetic acid. At high fluoride concentration, the removal efficiency was equal to 9.5% without acid and 94.3% with the addition of 0.1 M acetic acid. Fan et al. [36] investigated the adsorption capacity of low-cost materials. The tested materials adsorption capacities follow the order: Hydroxyapatite > Fluorspar > Quartz activated using ferric ions > Calcite > Quartz. The removal efficiency of hydroxyapatite raised from about 10% without shaking to 94% with shaking after 2 hours.

### 3.3. Phase distribution

Figure 2 shows the phase distribution of fluoride at equilibrium. As it can be seen in the figure calcined gypsum illustrated high affinity for adsorption towards fluoride. This can be seen by the fact that the majority of fluoride ions in the system resided at the solid phase. This fact explained calcined gypsum ability to remove fluoride from the system.



**Fig. 2. Phase distribution of fluoride at equilibrium.**

Many factors influence the adsorption capacity such as initial adsorbate concentration, pH value, the adsorbent particle size and doze, and the nature of the solute [37]. To find the optimum conditions, all these factors must be studied, but this is beyond our investigation.

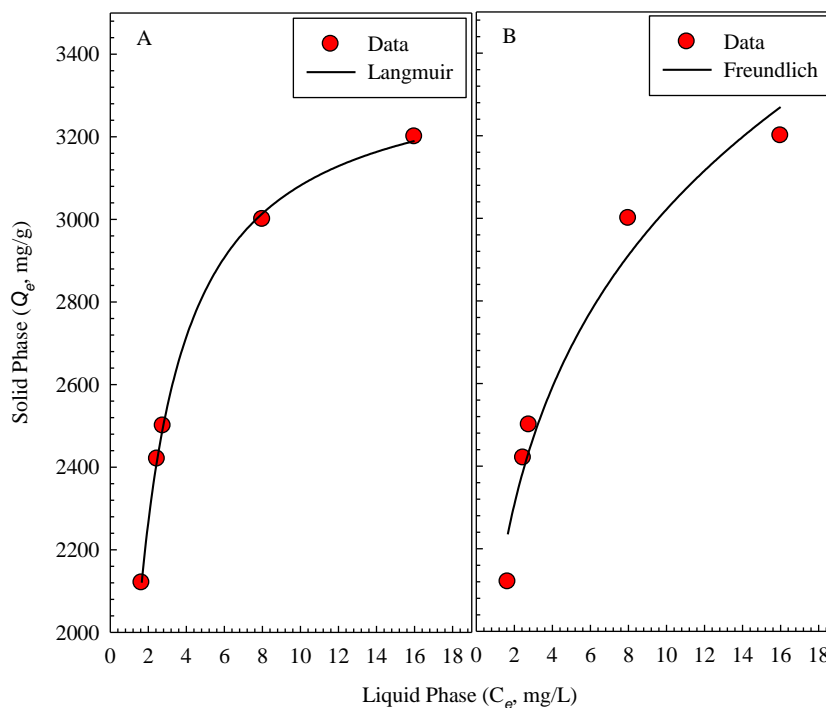
### 3.4. Adsorption isotherms

Phase distribution data were fitted to the Langmuir and Freundlich isotherms. Results are shown in Figs. 3(a) and (b). Table 1 shows the parameter values for each model.

**Table 1. Langmuir and Freundlich isotherms model parameters.**

	Parameters	$R^2$
Langmuir isotherm (Eq. (2))	$V_m = 3387.15 \pm 10.97^a$ (mg/g) $k = 1.0 \pm 0.015$ (L/mg)	0.999
Freundlich isotherm (Eq. (3))	$K_f = 2053.46 \pm 76.62$ (mg/g) $N = 5.96 \pm 0.69$	0.968

a: Best estimate  $\pm$  Standard Error



**Fig. 3. Phase distribution data fitted to both isotherms: (a) Langmuir, (b) Freundlich.**

As shown, the adsorption behavior of fluoride on calcined gypsum fitted both isotherms. However, the Langmuir isotherm had the better fit compared to the Freundlich isotherm, evident by their  $R^2$  value of 0.999 and 0.968 for the Langmuir isotherm and Freundlich isotherm, respectively. As seen in the figure, the Langmuir isotherm better fitted the adsorption behavior of fluoride, with a value of  $V_m$  of

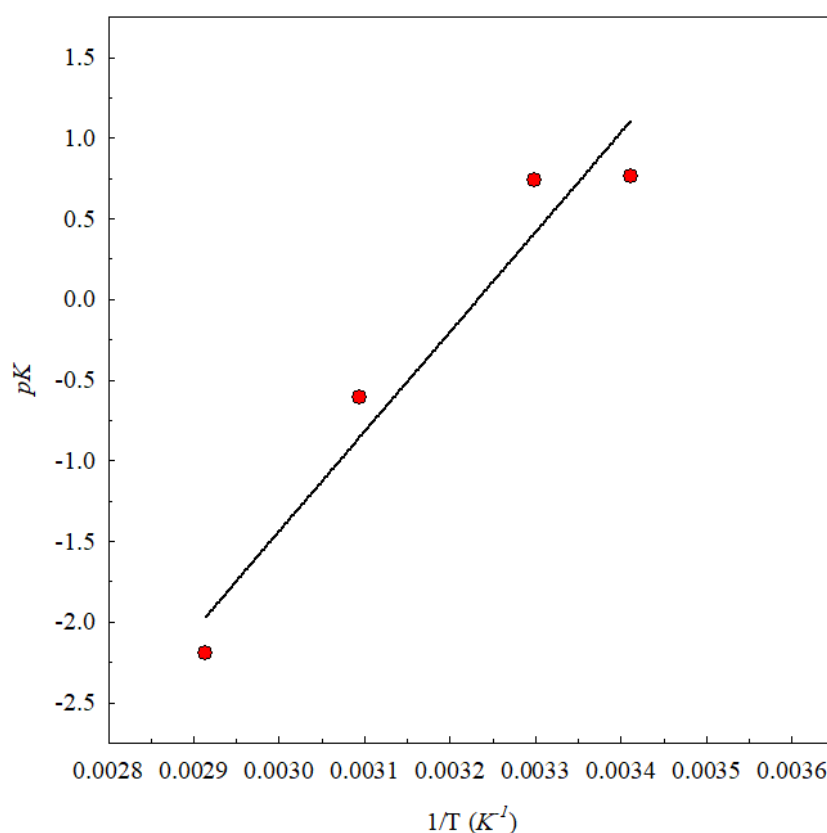
3400 (mg/g) and  $k$  of 1 (L/mg). This indicates that, theoretically, the extent of fluoride removal calcined gypsum is limited by the amount of the latter.

### 3.5. Adsorption thermodynamics

Table 2 shows the different thermodynamic parameters for the adsorption process, and Fig. 4 shows the Van't Hoves plot for the system.

**Table 2. Thermodynamic properties for adsorption of fluoride on calcined gypsum.**

Temperature (°C)	$K$ (mol/L)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (kJ/mol/K)
20	2.148	-1.895		
30	2.091	-1.828		
50	0.545	1.503	-51.418	-0.166
70	0.111	5.447		



**Fig. 4. Van't Hoff plot for adsorption of fluoride on calcined gypsum. Straight line represents Eq. (8) in form:  $y = 6183.3x - 19.98$  with an  $R^2$  value of 0.942.**

As seen in Table 2, the values of  $\Delta G^0$  changed from negative to positive as the temperature was increased, indicating that the process is becoming less



spontaneous as temperature increases. The setting time of the calcined gypsum decreases with increasing temperature.

The longer the setting time, the more the calcium is introduced in the solution, and hence, the more efficient the defluoridation process. The fact that  $\Delta H^0$  was negative explains that the process is exothermic. Therefore, high temperatures will have a negative effect on the process.

This explains the lowered removal percentage calculated at higher temperatures. Moreover, due to a negative  $\Delta S^0$ , the process of adsorption will increase disorder and randomness

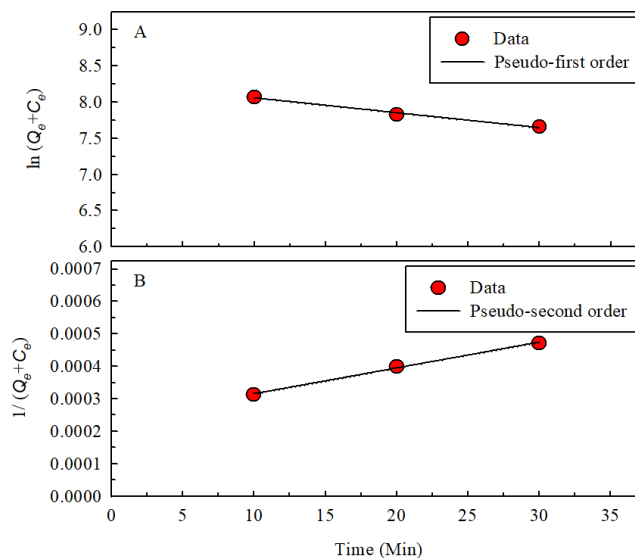
### 3.6. Adsorption kinetics

Table 3 shows the kinetic parameters for the pseudo-first and pseudo-second-order models fitted to the dynamic adsorption data. Figures 5(a) and (b) show the linearized kinetic models with the adsorption data.

**Table 3. Rate constants for the kinetic models.**

	Rate constant	$R^2$
Pseudo-first order ( $K_1$ , g/mg)	$-2.06 \times 10^{-2} \pm 2.40 \times 10^{-3a}$	0.9870
Pseudo-second order ( $K_2$ , g/mg/min)	$7.96 \times 10^{-6} \pm 4.56 \times 10^{-7}$	0.9967

a: Best estimate  $\pm$  Standard error



**Fig. 5. Kinetic fluoride adsorption data fitted kinetic models: (a) Pseudo-first order, (b) Pseudo-second order.**

The degree of goodness for the linear plots for both kinetic models is evident in the value of their determination coefficient. This parameter could be used as a measure of the adequacy of the two kinetic models. Based upon that, the pseudo-

second-order model more likely represents the kinetic behaviour of the adsorption of fluoride on calcined gypsum. This observation (second order more representative than first order) may suggest that the driving force behind the adsorption process will result in higher adsorption rates at higher values of the driving force ( $Q_e - Q_t$ ).

The pseudo-first-order and pseudo-second-order kinetics are used in the literature to describe the kinetic data of the system. In most cases, the second order is best fits with the experimental data [38]. Even many systems previously reported as first order kinetics when tested, the highest correlation coefficients were obtained for the pseudo-second-order kinetic model [39]. Overall, the sorption process obeys pseudo-first-order kinetics at the high initial concentration of solute, while it obeys the pseudo-second-order kinetics model at a lower initial concentration of solute [40]. Our results fit with pseudo-second-order model.

#### 4. Conclusions

The removal percentage of fluoride ions by adsorption to calcined gypsum was studied. The following points were concluded:

- Calcined gypsum is capable of removing fluoride ions from water samples with removal percentage up to 68%, at relatively ambient temperatures. The removal percentage drops significantly with increasing temperatures.
- The adsorption of fluoride ions on calcined gypsum is best described by Langmuir isotherm.
- Adsorption of fluoride ions was found be exothermic, with decreasing spontaneity at increasing temperatures due  $\Delta G^0$  changing values from negative to positive as temperature increases.
- The pseudo-second-order model best fitted the kinetic adsorption data. Suggesting that lower values of the driving force will result in a lower adsorption rate; fast adsorption followed by slower adsorption.

It is recommended that further studies should be performed to investigate the real-life applications for this process.

#### Nomenclatures

$a_e$	Activity of the ion in-solution at equilibrium
$a_s$	Activity of the adsorbed ion
$C_0$	Initial fluoride concentration (mg/L)
$C_1$	Integration constant
$C_2$	Integration constant
$C_e$	Equilibrium fluoride concentration (mg/L)
$K_1$	First order adsorption rate constant (1/min)
$K_2$	Second order adsorption rate constant (g/mg/min)
$K_f$	Freundlich constant (mg/g)
$k$	Equilibrium constant (L/mg)
$m$	Mass of sorbent (mg)
$1/n$	Adsorption intensity
$Q_e$	Adsorbed mass of fluoride (mg/g)
$Q_t$	Adsorbed amount at time $t$ (mg/g)

$R$	Universal gas constant ( $8.314 \times 10^{-3} \text{kJ/K}$ )
$T$	Temperature (K)
$t$	Time (s)
$V$	Sample volume (L)
$V_m$	Monolayer capacity (mg/g)
$v_e$	Activity coefficient of the in-solution ion at equilibrium
$v_s$	Adsorbed ion activity coefficient
<b>Greek Symbols</b>	
$\Delta H^0$	Enthalpy (kJ)
$\Delta S^0$	Entropy (kJ/K)

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