



## Removal of fluoride ions from aqueous solution by waste mud

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### ABSTRACT

The present study was carried out to assess the ability of original waste mud (o-WM) and different types of activated waste mud which are acid-activated (a-WM) and precipitated waste mud (p-WM), in order to remove excess of fluoride from aqueous solution by using batch technique. The p-WM exhibited greater performance than the others. Adsorption studies were conducted as a function of pH, contact time, initial fluoride concentration, adsorbent concentration, temperature, etc. Studies were also performed to understand the effect of some co-existing ions present in aqueous solutions. Adsorption process was found to be almost independent of pH for all types of waste mud. Among the kinetic models tested for p-WM, pseudo-second-order model fitted the kinetic data well with a perfect correlation coefficient value of 1.00. It was found that the adequate time for the adsorption equilibrium of fluoride was only 1 h. Thermodynamic parameters including the Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) revealed that adsorption of fluoride ions on the p-WM was feasible, spontaneous and endothermic in the temperature range of 0–40 °C. Experimental data showed a good fit with the Langmuir and Freundlich adsorption isotherm models. Results of this study demonstrated the effectiveness and feasibility of WM for removal of fluoride ions from aqueous solution.

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### 1. Introduction

Fluoride is a natural mineral that is found in many foods and in all waters and wastewaters. Low concentration of fluoride in drinking water is recognized as an essential micronutrient for both humans and animals to impede dental carries and facilitate the mineralization of hard tissues. Fluoride is beneficial especially to young children below 8 years of age when present within allowable limits for calcination of dental enamel and bone formation [1]. On the contrary, when the fluoride concentration is high, it can act as a health hazards. The negatively charged fluoride ion is highly attracted by positively charged ions, like calcium ions, of bones and teeth, which results in dental, skeletal and non skeletal fluorosis [2,3]. Also it leads irregular formation of collagen, which serves as a major structural component of skin, ligaments, tendons, muscles, cartilage, bones and teeth. Most evidence indicates that fluoride can interfere with DNA synthesis [4]. The high concentrations of fluoride can also interfere with carbohydrates, lipids, proteins, vitamins and mineral metabolism. Fluoride disperses to the environment through water, food, drugs, cosmetics and several engineering process such as semiconductor manufacturing, coal power plants, glass and ceramic production, uranium refinement, electroplating, rub-

ber, fertilizer manufacturing and natural sources [5,6]. According to the World Health Organization (WHO) the maximum allowable concentration of fluoride is  $1.5 \text{ mgL}^{-1}$  [7]. For these reasons, the removal of the excess fluoride from waters and wastewaters is important in terms of protection of public health and environment.

Defluoridation of drinking water is the only practicable way to overcome the problem of excessive fluoride in drinking water. Several treatment technologies, based on the principle of ion exchange [8], precipitation-coagulation [9], membrane processes such as reverse osmosis [10], Donnan dialysis [11], electrodialyses [12], nano-filtration [13] have been developed for the removal of fluoride from waters and wastewaters. Among the traditional methods; ion exchange method is a reliable way to remove fluoride from water supplies but the efficiency of the method is reduced in presence of other ions like sulfate, carbonate, phosphate and alkalinity. Also this technique is expensive due to high cost of the resins. In precipitation-coagulation method, alum is the most commonly used coagulant. By using this process, only a smaller portion of fluoride can remove in the form of precipitates and converts a greater portion of ionic fluoride into soluble aluminium fluoride complex ion. The soluble aluminium fluoride complex is itself toxic so this technique is not desirable for defluoridation of water. Although the membrane process is highly effective for fluoride removal, by using this technique all the ions present in waters can remove, though some minerals are essential for living organisms and also this technique is very expensive [14,15].

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Among the different wastewater treatment techniques, adsorption is one of the most popular separation and purification method due to its high selectivity, easy handling, lower operating cost, high efficiency in reducing quantity of chemical and biological sludge and regeneration of adsorbents [16]. Adsorption is a process where a solid is used for removing a soluble substance from water. The adsorption process consists of several mechanisms including chemisorption by ion exchange, complexation, coordination, chelating, physical adsorption and microprecipitation [17]. The efficiency of the adsorption technique mainly depends on the nature of the adsorbents, so new, easy available, and high loading capacity adsorbents having a strong affinity for under study ion are needed. Several adsorbents were tried for the removal of fluoride from waters and wastewaters namely activated alumina [18], activated carbon [1], calcite [19], clay [20], and hydrated cement [21], etc.

In this study we have used a waste mud as an adsorbent, which was obtained from a Cu–Zn mine industry, for removal of fluoride from aqueous solutions. The waste mud is one of the most promising adsorbent due to its zero price and easy availability. The waste mud emerges as an undesired by-product during the industrial applications. These wastes represent unused resources and in some cases serious disposal problems present so the utilization of waste mud for removal of impurities, is an important application.

The aim of the present study was to evaluate the feasibility of using waste mud for removal of fluoride ions from aqueous solutions. Three different forms of the waste mud were tested for their fluoride removal performance: (i) original waste mud (o-WM), (ii) acid-treated waste mud (a-WM), and (iii) precipitated waste mud (p-WM).

The residual fluoride concentration in the aqueous phase was analyzed by using potentiometric method with a fluoride ion-selective electrode. Ion-selective electrodes (ISE) are the chemical sensors with the longest and probably the most frequent routine application. Potentiometric detection based on ion-selective electrodes, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. Besides, they are ideally suitable for on-site analysis and, nowadays, they are found to be applicable in the analysis of some biologically relevant ions, process control, and environmental analysis [22,23].

The present study includes an observation of the effects of several experimental parameters such as contact time, initial pH of the solution, initial fluoride concentration, waste mud concentration etc. The Langmuir and Freundlich isotherm models were used to describe equilibrium data. The adsorption mechanisms of fluoride on the waste mud were also evaluated in terms of thermodynamics and kinetics.

## 2. Materials and methods

### 2.1. Preparation of different types of activated waste mud

The waste mud was obtained from Cu–Zn mine-industry in Çayeli, Rize/Turkey (Inmet Mine Corp. Canada). The chemical composition of waste mud is 11.7% SiO<sub>2</sub>, 8.9% Al<sub>2</sub>O<sub>3</sub>, 48.4% Fe<sub>2</sub>O<sub>3</sub>, 0.7% ZnO, 0.7% CuO and 29.6% other constituents [24]. The composition of waste mud was determined by a flame atomic absorption spectrometer (Unicam AA-929) for Al, Fe, Zn and Cu, and silica content was determined gravimetrically. The activation of waste mud by different techniques is considered as an effective way for increasing the specific surface area of waste mud. Therefore the waste mud activated with different methods was used in this study in order to evaluate their fluoride removal performance.

The o-WM was prepared by washing several times with distilled/deionized water and dried at 110 °C for 2 days. The a-WM was

prepared by refluxing 10 g of water-washed and dried waste mud with 200 mL of 20% HCl solution for 2 h. After activation, the content was filtered through 0.45 μm nitrocellulose membrane (Sartorius Stedim Biotech. GmbH). The filtrate was kept for preparing the precipitated waste mud. The obtained solid was washed several times with deionized water and dried 110 °C for 2 days. For preparing the p-WM, the reflux solution which was obtained from acid activation was cooled to room temperature, and then the 25% ammonia solution was added drop by drop until complete precipitation. Then the precipitate was filtered and washed thoroughly several times with deionized water until free from ammonia. The obtained solid was dried at 110 °C for 2 days [25].

### 2.2. Adsorption experiments

All chemicals and reagents used were of analytical reagent grade. All glassware and sample bottles were soaked in diluted HNO<sub>3</sub> solution for 24 h and washed three times with deionized water. The NaF (Merck) was used for preparation of standard fluoride stock solution (5000 mg L<sup>-1</sup>). The required concentration of fluoride solution was prepared by appropriate dilutions of the stock solutions. Distilled/deionized water was used for all dilutions. The pH of the solutions was adjusted to the desired value with 0.1 M HCl and NaOH solutions. The adsorption experiments were carried out by batch technique. For this, 10 mL of fluoride solutions in the concentration range of 5–950 mg L<sup>-1</sup> were transferred into a polyethylene centrifuge tube. Then 10–200 mg of adsorbent (1–20 g L<sup>-1</sup>) were added to the solution, and the mixture was agitated on a mechanical shaker (Edmund Bühler GmbH) at 400 rpm for 4.0 h. After reaching the equilibrium, the adsorbent was removed by vacuum filtration through 0.45 μm nitrocellulose membrane. The fluoride concentration in the supernatant was analyzed electrochemically with a fluoride ion-selective electrode (Mettler Toledo DX219, dynamic range: 10<sup>-1</sup>–10<sup>-6</sup> M) by use of total ionic strength adjustment buffer (TISAB) solution (58 g of sodium chloride, 57 mL of glacial acetic acid and approximately 150 mL of 6 M NaOH in a volume of 1000 mL) to maintain pH 5.0 and to eliminate the interference effect of complexing ions. The fluoride samples and the fluoride standard solutions were diluted 1:1 with a total ionic strength adjustment buffer solution [26]. All experiments were conducted in triplicate and the averages of the results were used for data analysis.

### 2.3. Adsorption kinetics

The kinetics of adsorption is an important parameter from the point of view that it offers significant insights into the adsorption mechanisms and reaction pathways. Several kinetic models have been developed to predict the adsorption kinetics and rate controlling step. In order to evaluate the kinetics of fluoride adsorption on the p-WM, pseudo-first-order, pseudo-second-order and intraparticle diffusion models were checked.

The pseudo-first-order Lagergren model is expressed as [27];

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \quad (1)$$

where  $Q_e$  (mg g<sup>-1</sup>) and  $Q_t$  (mg g<sup>-1</sup>) are the amounts of the fluoride adsorbed on the adsorbate at equilibrium and at any time  $t$ , respectively; and  $k_1$  (min<sup>-1</sup>) is the rate constant of the first order adsorption.

After integration and applying boundary conditions  $Q_t = 0$  at  $t = 0$  and  $Q_t = Q_t$  at  $t = t$  the integrated form of Eq. (1) becomes;

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

The value of  $k_1$  and  $Q_e$  can be obtained from the slope and intercept of the linear plot of  $\ln(Q_e - Q_t)$  versus  $t$ , respectively.

The second-order-kinetic model can be written as following form [28];

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (3)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the second-order equation;  $Q_e$  ( $\text{mg g}^{-1}$ ) is the maximum adsorption capacity;  $Q_t$  ( $\text{mg g}^{-1}$ ) is the amount of adsorption at time  $t$  (min).

After definite integration by applying the conditions  $Q_t = 0$  at  $t = 0$  and  $Q_t = Q_t$  at  $t = t$  the Eq. (3) becomes the following;

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

The value of  $Q_e$  and  $k_2$  can be obtained from the slope and intercept of the linear plot of  $t/Q_t$  versus  $t$ , respectively.

The intraparticle diffusion equation is expressed as [29];

$$Q_t = k_{id} t^{1/2} + c \quad (5)$$

where  $Q_t$  ( $\text{mg g}^{-1}$ ) is the amount of adsorption at time  $t$  (min) and  $k_{id}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the rate constant of intraparticle diffusion. The value of  $k_{id}$  and  $c$  can be determined the slope and intercept of the plot of  $Q_t$  versus  $t^{1/2}$ , respectively.

#### 2.4. Adsorption isotherms

Adsorption isotherms are one of the most significant tools to predict the adsorption capacity of the adsorbent and the mechanism of the adsorption. In order to evaluate the relationship between the amount of adsorbed fluoride and the fluoride concentration remaining in solution, two well known isotherm models are selected in this study; Langmuir and Freundlich isotherms.

The Langmuir isotherm model assumes that the surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent and adsorbed molecules do not interact. It also predicts all the adsorption occurs through the same mechanism. The Langmuir isotherm model commonly expressed as [30];

$$Q_e = \frac{bQ_{\max}C_e}{1 + bQ_{\max}} \quad (6)$$

where  $Q_e$  ( $\text{mg g}^{-1}$ ) is the amount of the fluoride adsorbed per unit mass of adsorbent,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium fluoride concentration in the solution,  $Q_{\max}$  ( $\text{mg g}^{-1}$ ) is the Langmuir constant related the maximum monolayer adsorption capacity and  $b$  ( $\text{L mg}^{-1}$ ) is the constant related the free energy or net enthalpy of adsorption. The Langmuir model in linear form;

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{bQ_{\max}} \quad (7)$$

The plot of  $C_e/Q_e$  versus  $C_e$  gives a straight line and the values of  $Q_{\max}$  and  $b$  can be calculated from the slope and intercept of the plot, respectively.

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter [31],

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant and  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of fluoride. There are four probabilities for the  $R_L$  value: (i) for favorable adsorption  $0 < R_L < 1$ , (ii) for unfavorable adsorption  $R_L > 1$ , (iii) for linear adsorption  $R_L = 1$  and (iv) for irreversible adsorption  $R_L = 0$ .

The Freundlich isotherm model is based on the adsorption on heterogeneous surfaces and is presented by the following equation [32];

$$Q_e = K_f C_e^{1/n} \quad (9)$$

where  $K_f$  ( $\text{mg g}^{-1}$ ) and  $n$  are Freundlich constants related to adsorption capacity and intensity, respectively. The Freundlich model in linear form;

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

The Freundlich constants  $K_f$  and  $1/n$  are determined from the intercept and slope of linear plot of  $\ln Q_e$  versus  $\ln C_e$ , respectively.

#### 2.5. Adsorption thermodynamics

In order to decide the feasibility and spontaneity of the adsorption process the thermodynamic parameters including Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) were evaluated. These parameters can be calculated using the following equations [33];

$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

This equation can be written as;

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K), and  $K_d$  is the distribution coefficient. The  $K_d$  value was calculated using following equation;

$$K_d = Q_e/C_e \quad (14)$$

where  $Q_e$  and  $C_e$  are the equilibrium concentration of fluoride ions on adsorbent and in the solution, respectively.

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of the plot of  $\ln K_d$  versus  $1/T$ , respectively.

### 3. Results and discussion

#### 3.1. Effect of pH

The pH of aqueous solution usually plays an important role in deciding the amount of fluoride adsorbed on WM. The influence of aqueous phase pH on the uptake of fluoride ions was investigated by using three types of WM; o-WM, a-WM and p-WM. Adsorption experiments were carried out at various aqueous phase pH (2.0–8.0) by keeping all other experimental conditions constant

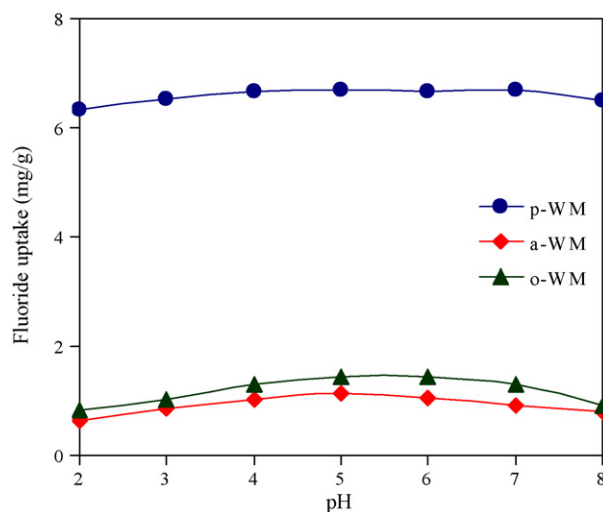
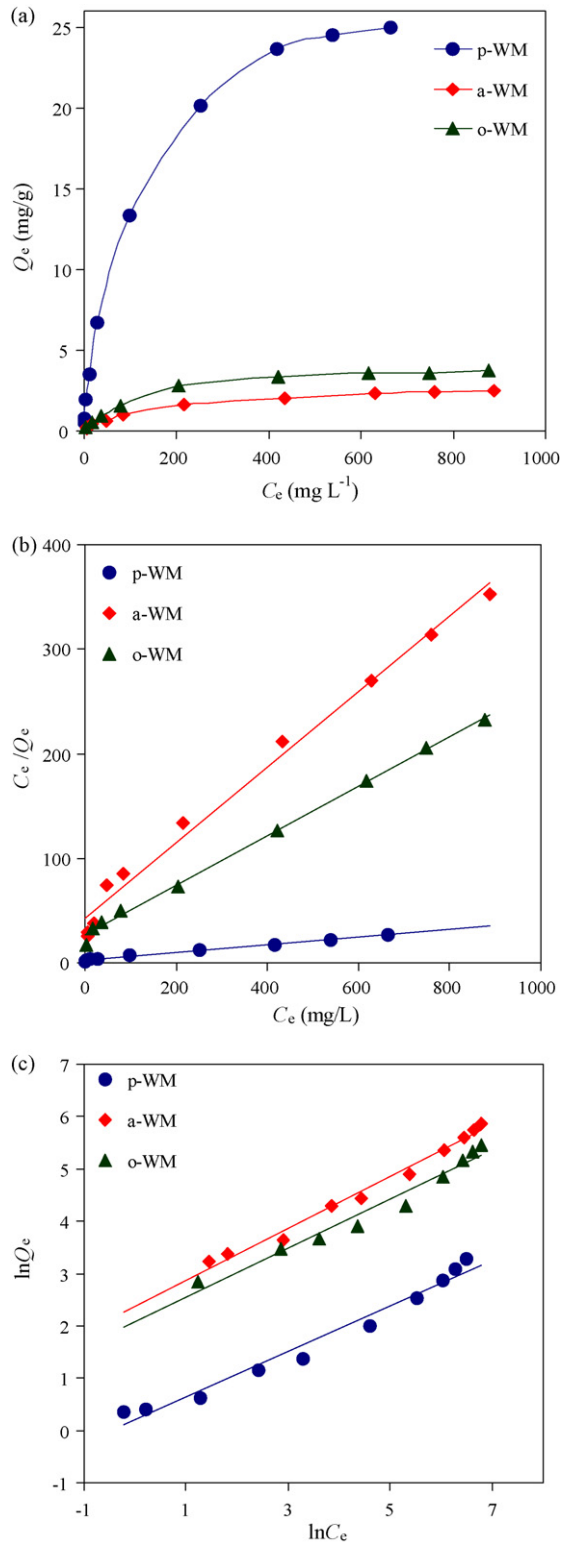


Fig. 1. Effect of initial pH on fluoride uptake by three types of waste mud (initial  $F^-$  concentration:  $80 \text{ mg L}^{-1}$ , waste mud concentration:  $10 \text{ g L}^{-1}$ , contact time: 1 h, temperature:  $20 \pm 1^\circ \text{C}$ ).

(shaking time; 1 h, adsorbent concentration;  $10 \text{ g L}^{-1}$ ; initial fluoride concentration;  $80 \text{ mg L}^{-1}$ ). The fluoride uptake capacity is not affected in the pH range of 2.0–8.0 for all the types of WM so it can be concluded that the present adsorption process is not pH-dependent [34,35]. Furthermore the maximum fluoride uptake was obtained



**Fig. 2.** Removal performance of three type of WM (a)  $C_e$  versus  $Q_e$  graph (b) Langmuir isotherm model, (c) Freundlich isotherm model (initial pH: 5.0, initial fluoride conc.:  $5.4\text{--}914 \text{ mg L}^{-1}$ , contact time: 1 h, WM conc.:  $10 \text{ g L}^{-1}$ , temperature:  $20 \pm 1^\circ \text{C}$ ).

**Table 1**

Freundlich and Langmuir isotherm constants and correlation coefficients for the adsorption of fluoride on three types of WM.

Type of WM	Langmuir constants			Freundlich constants		
	$Q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
p-WM	27.2	0.01544	0.993	1.22	2.290	0.974
a-WM	2.8	0.00866	0.989	10.79	2.02	0.986
o-WM	4.2	0.00913	0.997	7.95	2.13	0.964

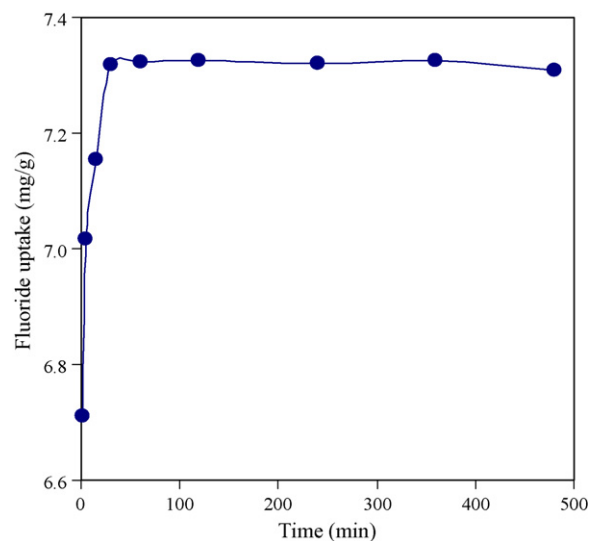
with p-WM (Fig. 1). Hence all subsequent studies were conducted with p-WM at pH 5.0.

### 3.2. The fluoride removal performance of different types of waste mud

In order to decide the best type of waste mud for fluoride uptake, the linearized Langmuir and Freundlich isotherms were obtained for three types of waste mud, o-WM, a-WM, and p-WM. The adsorption process was conducted with initial fluoride ions concentrations between  $5.0$  and  $950 \text{ mg L}^{-1}$  and different types of waste mud concentration of  $10 \text{ g L}^{-1}$  at pH 5.0 and equilibrium time of 1 h. The Langmuir and Freundlich isotherms were plotted as a function of different types of waste mud (Fig. 2(a), (b) and (c)), and the values of isotherm constants and correlation coefficients were calculated for both isotherm models (Table 1) by using the data obtained from these figures. The highest value of  $Q_{\max}$  obtained from Langmuir model for p-WM is  $27.2 \text{ mg g}^{-1}$  with a high correlation coefficient of 0.99. It appears to be the highest in comparison with the uptake obtained by using other type of waste mud.

### 3.3. The effect of contact time and kinetics of adsorption

In order to obtain an appropriate contact time between the p-WM and fluoride ions, the adsorption experiments were carried out by conducting  $97.2 \text{ mg L}^{-1}$  of fluoride solutions at initial pH 5.0 with  $10 \text{ g L}^{-1}$  of p-WM suspensions. The mixtures were agitated at 400 rpm. The samples were taken different periods of time and analyzed for their fluoride concentration. The results showed that a contact time of 60 min was adequate to reach equilibrium and there was no significant increase in the rate of removal with further increase in contact time (Fig. 3). This may be due to the



**Fig. 3.** Effect of contact time on fluoride uptake (initial pH: 5.0, initial fluoride conc.:  $97.2 \text{ mg L}^{-1}$ , p-WM conc.:  $10 \text{ g L}^{-1}$ , temperature:  $20 \pm 1^\circ \text{C}$ ).



**Table 2**  
Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models at  $20 \pm 1^\circ\text{C}$ .

Exp. $Q_e$ ( $\text{mg g}^{-1}$ )	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$k_1$ ( $\text{min}^{-1}$ )	$Q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$Q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_{id}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	$C$ ( $\text{mg g}^{-1}$ )	$R^2$
7.33	$-7.90 \times 10^{-3}$	0.14	0.294	2.72	7.32	1.00	0.0186	7.019	0.436

larger surface area of the p-WM is available at the beginning for the adsorption of fluoride.

The kinetics of fluoride adsorption on the p-WM was determined by using three different kinetic models, which are pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The pseudo-first-order rate constant ( $k_1$ ) and theoretical equilibrium adsorption capacities ( $Q_e$ ) calculated from linear plot of  $\ln(Q_e - Q_t)$  versus  $t$ , are given in Table 2. The value of correlation coefficient is extremely low (0.294) and also  $Q_{e,cal}$  determined from the model is not in a good agreement with the experimental values of  $Q_{e,exp}$ . Therefore it could be said that the adsorption of fluoride on the p-WM does not follow the pseudo-first-order kinetic model.

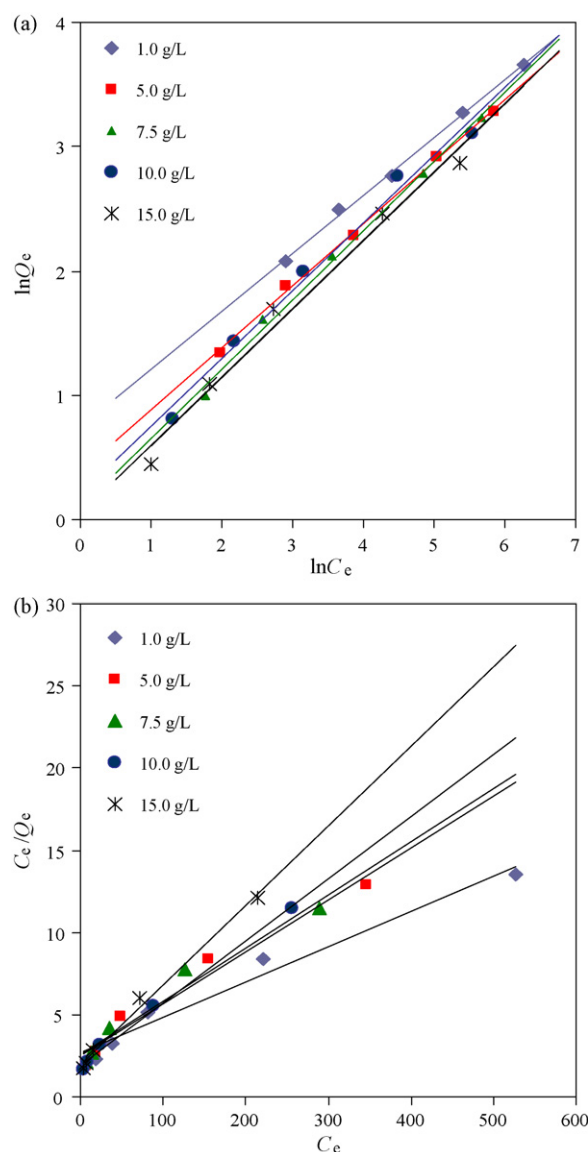
The graph of  $t/Q_t$  versus  $t$  for the linear pseudo-second-order model was plotted, and the second order rate constant  $k_2$  and maximum adsorption capacity  $Q_e$  were calculated from the intercept and slope of this graph, respectively (Table 2). The correlation coefficient value is magnificent (1.00), and the equilibrium adsorption capacity  $Q_{e,cal}$  ( $7.32 \text{ mg g}^{-1}$ ) determined by using the second order model is nearly as same as with the experimentally determined equilibrium adsorption capacity  $Q_{e,exp}$  ( $7.33 \text{ mg g}^{-1}$ ).

The intraparticle rate constant ( $k_{id}$ ) and  $c$  parameters obtained from the plots of  $Q_t$  versus  $t^{1/2}$  for the intraparticle diffusion model are given in Table 2. The value of  $c$  obtained from intraparticle diffusion model is not zero and the correlation coefficient is not satisfactory (0.436), indicating that the intraparticle diffusion may not be the controlling factor in determining the kinetics of the process.

As a result, it can be said that the pseudo-second-order kinetic model suggested a good correlation for the adsorption of fluoride on the p-WM in contrast to the pseudo-first-order model and intraparticle diffusion model, so pseudo-second-order model is suitable for modeling the adsorption of fluoride on the p-WM.

#### 3.4. The effect of p-WM and fluoride concentration on fluoride uptake

The effect of p-WM and initial fluoride concentration on the removal of fluoride from aqueous solutions was studied with initial fluoride concentration between  $26.2\text{--}565 \text{ mg L}^{-1}$  and p-WM concentrations in the range of  $1\text{--}20 \text{ g L}^{-1}$  for 1.0 h contact time at pH 5.0. In order to evaluate the adsorption capacity of p-WM, the equilibrium data for the adsorption of fluoride were analyzed in the light of adsorption isotherms. Fig. 4(a) and (b) depicts the Freundlich and Langmuir isotherm models, respectively. It is evident from the results, as the concentration of p-WM increased; the equilibrium fluoride uptake increased however the percent amount of the adsorbed fluoride ions decreases with increase in the fluoride concentration which indicated that the adsorption depends upon the availability of binding sites for fluoride ions. The values of isotherm parameters and correlation coefficients obtained from the slope and intercept of the plots of each isotherm models are given in Table 3. Both of the adsorption isotherms were defined as suitable models for the adsorption of fluoride ions on the p-WM because the correlation coefficients were satisfactory (in the range 0.964–0.998), indicating that the homogenous and heterogeneous distribution of active sites on the surface of p-WM. The  $R_L$  value ranges from 0.67 to 0.08 for the initial fluoride concentration in the range of  $26.2\text{--}565 \text{ mg L}^{-1}$  at a constant p-WM concentration ( $10 \text{ g L}^{-1}$ ). This parameter indicated that the p-WM is a suitable adsorbent for the adsorption of fluoride ions from aqueous



**Fig. 4.** Effect of p-WM concentration on fluoride uptake (a) Freundlich isotherm model, (b) Langmuir isotherm model (initial pH: 5.0, initial fluoride conc.:  $26.2\text{--}565 \text{ mg L}^{-1}$ , contact time: 1 h, p-WM conc.:  $10 \text{ g L}^{-1}$ , temperature:  $20 \pm 1^\circ\text{C}$ ).

**Table 3**  
Freundlich and Langmuir isotherm constants and correlation coefficients for the adsorption of fluoride on p-WM at various p-WM concentrations at pH 5.0.

p-WM conc. ( $\text{g L}^{-1}$ )	Langmuir constants			Freundlich constants		
	$Q_{max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
1.0	46.7	0.00784	0.972	2.09	2.14	0.998
5.0	31.7	0.01230	0.967	1.46	2.00	0.998
7.5	31.0	0.01234	0.964	1.10	1.79	0.995
10.0	26.5	0.01971	0.993	1.22	1.83	0.987
15.0	20.7	0.02460	0.992	1.04	1.81	0.983

**Table 4**

Thermodynamic parameters of the fluoride adsorption on the p-WM at different temperatures.

$T$ (°C)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K) <sup>a</sup>	$\Delta H^\circ$ (kJ/mol) <sup>a</sup>
0	-2.06	48.22	11.18
10	-2.35		
20	-2.97		
30	-3.42		
40	-3.95		

<sup>a</sup> Measured between 273 and 313 K.

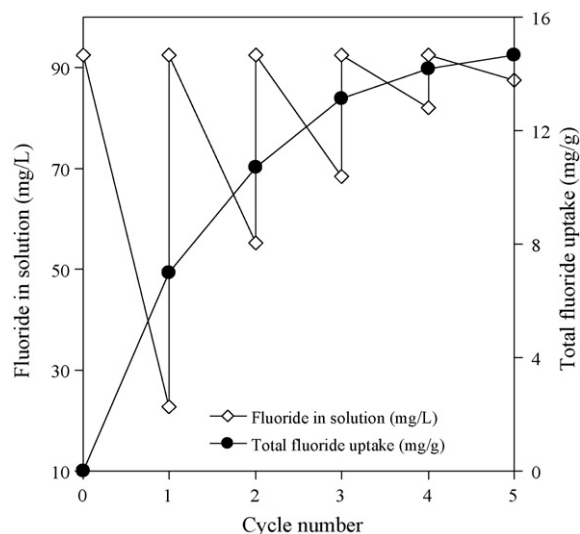
solutions. Also the values of  $1/n$  lying between 0.47 and 0.55 (1.04–2.09 for  $n$  values) suggested that the adsorption process was favorable under studied conditions.

### 3.5. The effect of temperature and thermodynamic parameters of adsorption

In order to evaluate the effect of temperature on the uptake of fluoride ions, the adsorption experiments were conducted in the temperature range of 0–40 °C with p-WM concentration of 10 g L<sup>-1</sup> and initial fluoride concentration of 200 mg L<sup>-1</sup> at initial pH 5.0. In order to control the temperature of the solutions, a cryostat (Nüve BD 402, temperature range: -10 to +40 °C) was used for all thermodynamic studies. The results indicated that the percentage removal of fluoride increased from 71.3% to 82.0% when the temperature was increased from 0 to 40 °C. The increase in adsorption capacity of p-WM with temperature may be attributed to increase in the number of available active surface sites for adsorption on the p-WM. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the adsorption of fluoride ions on the p-WM at different temperature are given in Table 4. The negative values of  $\Delta G^\circ$  indicated that the adsorption process was spontaneous at all temperatures studied. The entropy change ( $\Delta S^\circ$ ) and enthalpy change ( $\Delta H^\circ$ ) for the adsorption process were calculated to be 48.22 J mol<sup>-1</sup> K<sup>-1</sup> and 11.18 kJ mol<sup>-1</sup>, respectively. The positive value of  $\Delta H^\circ$  suggested the endothermic nature of adsorption. The endothermic nature may be also predicted from the increase in value of fluoride uptake of the p-WM with the rise in temperature. The magnitude of  $\Delta H^\circ$  gives an idea about the type of sorption. Adsorption can be either physical or chemical in nature. Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and, like most chemical reactions, frequently involves an energy of activation. The enthalpy for physical adsorption is usually no more than 1 kcal mol<sup>-1</sup> (4.2 kJ mol<sup>-1</sup>) and for chemical adsorption is more than 5 kcal mol<sup>-1</sup> (21 kJ mol<sup>-1</sup>) [36] so it seems that adsorption of fluoride ions on the p-WM is almost a chemical process. The positive value of  $\Delta S^\circ$  suggested an increase in randomness at the solid/solution interface during the adsorption process and a good affinity of fluoride with p-WM.

### 3.6. Reuse of the p-WM without regeneration

In order to evaluate the reusability of the p-WM without regeneration, the adsorption experiments were conducted by using an initial fluoride concentration of 92.5 mg L<sup>-1</sup> at pH 5.0 with 10 g L<sup>-1</sup> of p-WM for 1 hour of contact time. The p-WM loaded with fluoride ions was filtered, air dried and transferred to another 92.5 mg L<sup>-1</sup> of fluoride solution. This process was repeated for five times. After first cycle the adsorbed amount of fluoride was 7.0 mg g<sup>-1</sup> and after each adsorption process, the adsorption capacity of p-WM was decreased as shown in Fig. 5. After cycle 4 and 5, the newly adsorbed amount of fluoride were 1.1 and 0.5 mg g<sup>-1</sup>, respectively indicating that the amount of fluoride removal significantly decreased

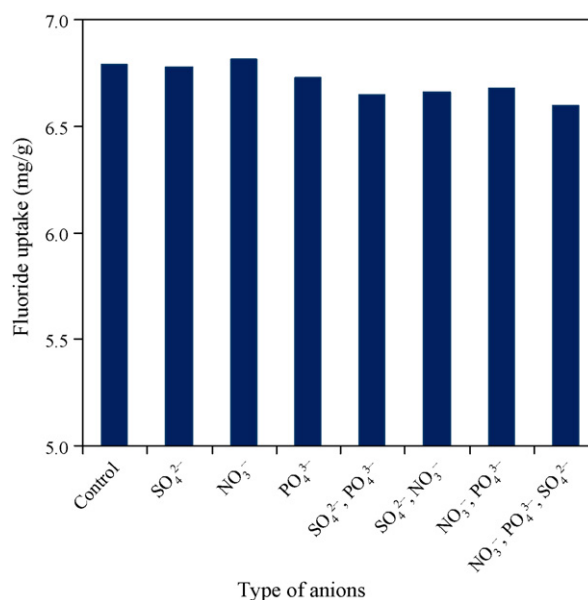


**Fig. 5.** Reuse of the p-WM without regeneration (initial pH: 5.0, initial fluoride conc.: 92.5 mg L<sup>-1</sup>, contact time: 1 h, p-WM conc.: 10 g L<sup>-1</sup>, temperature: 20 ± 1 °C).

compared to the first three cycles. Similar behavior was reported by previous researchers [37]. From the results, the p-WM can be used at least five times without regeneration.

### 3.7. The effect of some common ions over the adsorption yields of fluoride

The fluoride-contaminated drinking and wastewater contain several other co-existing ions such as nitrate, sulfate and phosphate, which can compete with fluoride ions during the adsorption process for the active sites on the p-WM. Hence the effect of these competitive ions on the uptake of fluoride ions should be studied. The anion (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) solutions were prepared by dissolving appropriate amount of their sodium salts. Adsorption experiments were carried out by adding 100 mg L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and mixture of these ions, individually, in 80 mg L<sup>-1</sup> of fluoride solution containing 10 g L<sup>-1</sup> of p-WM. Fig. 6 shows the effect of various co-existing ions on fluoride adsorption by p-WM. From the



**Fig. 6.** Effect of some common anions on the fluoride uptake (initial pH: 5.0, p-WM conc.: 10 g L<sup>-1</sup>, initial anions conc.: 100 mg L<sup>-1</sup>, initial fluoride conc.: 80 mg L<sup>-1</sup>).

results, nitrate, sulfate and phosphate had no significant interfere effect on the adsorption of fluoride.

#### 4. Conclusion

The results exhibit that the p-WM, which was obtained from Cu–Zn mine (Çayeli, Rize/Turkey) is a promising material to remove excess fluoride from waters and wastewaters. The utilization of p-WM is a significant application because it has been produced from an industrial waste material so these wastes represent unused resources and also present serious disposal problems.

The adsorption process was independent of pH for all types of waste mud. Maximum fluoride uptake was obtained with p-WM. The kinetic study indicated that adsorption of fluoride was very rapid, and the equilibrium was reached within 60 min at room temperature. Adsorption kinetics followed pseudo-second-order model with an excellent correlation coefficient value of 1.00. The equilibrium data are best fitted to the Langmuir and Freundlich isotherm models with  $R^2$  value of higher than 0.9, indicating that the homogenous and heterogeneous distribution of active sites on the surface of p-WM. The negative value of  $\Delta G^\circ$  and positive value  $\Delta S^\circ$  showed that the adsorption of fluoride ions on the p-WM was feasible and spontaneous. And also the positive value of entropy change suggested an increase in randomness. The positive value of  $\Delta H^\circ$  confirmed the endothermic nature of adsorption. Some common ions which exist in drinking and wastewater had no significant interfere effect on adsorption of fluoride. The p-WM can be used at least five times for further adsorption process without regeneration. The results obtained from the present study demonstrated that the p-WM can be used as a no cost, highly effective and easy available adsorbent for removal of fluoride from aqueous solutions.

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