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ADSORPTION OF CARBONATE AND BICARBONATE ON FEOOH

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ABSTRACT

Carbonate and bicarbonate contribute to water alkalinity, and represent two of the major pollutants in both groundwater and industrial effluent. This study investigates the efficiency of FeOOH in removing them from water, and studies the effects of different parameters on carbonate and bicarbonate removal efficiency. Results showed that carbonate and bicarbonate were removed efficiently from both types of water, with about 100 % removal of carbonate where FeOOH helped to convert CO_3^{2-} *to* HCO_3^-*. The adsorption of bicarbonate with its initial concentration being 300 mg/L reached about 80 % at a dosage of 16 g/L FeOOH under conditions of initial water pH of 7.0 ± 0.2 and a temperature of 31 °C ± 1 °C. Results showed a direct relationship between the removal percentage and FeOOH dosage. At a lower total alkalinity initial concentration (e.g., below 250 mg/L), removal efficiency reached 100 % at about 30 °C and 10 g/L FeOOH.The pseudo-second-order model demonstrated the best fit of kinetic data for* HCO_3^-*. Adsorption isotherms at various temperatures were developed, and the data fit the Langmuir model. The thermodynamic characteristics of the sorption process were also evaluated experimentally, and the derived negative* ΔG^0 *and positive* ΔH^0 *values indicated that sorption was spontaneous and endothermic. The range of* ΔG *indicated that the adsorption process was a combination of physisorption and chemisorption.*

Keywords: Carbonate and Bicarbonate Removal, Fly Ash, Isothermal Adsorption, Trona.

I. INTRODUCTION

Groundwater, industrial water and wastewater all contain significant levels of contaminants such as heavy metals, trace elements, and salts such as carbonate and bicarbonate, which are sometimes added to water as trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$). In the United States, trona is a major source of the soda ash used as a raw material for desulfurization in power plants, as well as in the glass, chemical, and other major industries [1-3].

A search of the literature shows that very little attention has been paid to the adsorption of carbonate and bicarbonate anions by adsorbents. In 1993, L. Zang *et al.* concluded that the adsorption of carbonate and bicarbonate anions on colloidal silver particles is determined by the concentration of the anion and the thermodynamic stability of the surface complex formed between silver adatoms and adsorbed anions [4]. In a 2006 study, O. Ozdemir *et al.* examined the adsorption of carbonate and bicarbonate salts at the air–brine interface. They concluded that the surface tension of carbonate salts increased significantly with an increased concentration of sodium carbonate, but that the surface tension of sodium bicarbonate solutions did not increase significantly [3]. E. M. Patrito and P. P. Olivera investigated the adsorption of carbon trioxide, carbonate, and bicarbonate on single crystal silver surfaces, focusing on the binding energies and adsorption on different surface levels of silver as well as conducting a comparative investigation of the adsorption of the neutral species carbon trioxide, carbonate, and bicarbonate [5, 6].

The adsorption mechanism of carbonate and bicarbonate on FeOOH was studied by H. Wijnja and C.P. Schulthess in 2000. Using attenuated total reflectance- Fourier transformed infrared (ATR-FTIR) spectroscopy, diffuse reflectance infrared Fourier transformed (DRIFT) spectroscopy, and proton co-adsorption by pH-stat measurements, their study indicated that the bicarbonate adsorption reaction and resulting surface species were consistent with the pH-state data. This, in turn, indicated a co-adsorption between protons from the FeOOH and the adsorption of bicarbonate. Also, the study indicated that the overall effect of CO_3^{2-} adsorption on the FeOOH surface resulted from a complexation reaction and the interaction between certain surface groups and their neighboring surface groups, respectively [7]. Schulthess and McCarthy studied competitive adsorption of carbonate anions on aluminum oxide (δ-$A1_20_3$) and obtained a sequence of the studied anions for the aluminum oxide as $OH^- > CO_3^{2-} >$ acetate $> C1^-$.Further, they stated that these ions adsorb competitively on the same A1 sites, but that the adsorption mechanisms are not necessarily the same [8].

II. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were analytical reagent grade. Sodium carbonate (Rhone-Poulenc) and bicarbonate salts (VWR) were used in all experiments. All solutions were prepared using deionized (DI) water, and initial water pH was adjusted with 1M NaOH, and 1M HNO_3. The adsorbent, FeOOH, was provided by USFilter. Hach digital titrator kit model 16900 was used to determine the concentrations of carbonate and bicarbonate. The titrationkit consist of a digital titrator, a sulfuric acid titration cartridge with two different concentrations (1.60 and 0.16 N), and phenolphthalein and bromocresol green-methyl red indicators.

2.2 Adsorbent Characterization

Three FeOOH samples were characterized by a scanning electron microscope (SEM, JEOL 5800LV, JEOL USA) for surface images. One sample was virgin(i.e., raw FeOOH) and the other two samples were spent, one with bicarbonate at 300 mg/L initial bicarbonate concentration and 10.0 g/L FeOOH dosage, and room temperature of 26.0°C ± 1, and the other with carbonate at 1000 mg/L initial carbonate concentration and 5.0 g/L FeOOH dosage, and room temperature of 26.0°C ± 1. BET was done for FeOOH in the previous study [18], where results showed that the BET specific surface area was 361.4 m^2/g.

2.3 Batch Adsorption Experiments

All adsorption experiments were carried out in batch mode under designed tests conditions; the kinetic experiment studied only bicarbonate. Defined amounts of sodium bicarbonate or sodium carbonate salt were added to 1000 ml of pH 7.0 DI water in order to make initial concentrations of 50, 150, and 300 mg/L. 10 g FeOOH was then added to obtain a 10 g/L suspension for each sample. The suspension was mixed at 250 rpm using a Phipps & Bird jar tester. 25 – 50 ml (depending on concentration) aliquot parts were withdrawn from the suspension during the sorption process at intervals of 0.17, 0.5, 0.75, 1.0, 1.25, 4.5, and 24 hours. The samples were then filtered through Ashless Whatman 8 µm pore size filter paper and titrated for concentrations of bicarbonate. The bicarbonate removal percent was calculated as follows:

$$\text{Removalefficiency}(\%)=\frac{C_i-C_j}{C_i}\times 100\% \qquad \text{(E1)}$$

where C_i is the initial bicarbonate concentrations in mg/L as $CaCO_3$, and C_f is the final bicarbonate concentrations in mg/L as $CaCO_3$.

2.1.1 Adsorption kinetics

A pseudo-second-order kinetic model was applied to fit the collected kinetic data. The kinetic rate equation is expressed as [9, 10]:

$$dq_t / dt = k_2 (q_{eq} - q_t)^2 \qquad \text{(E2)}$$

where k_2 [g-FeOOH/(mg-HCO_3^-.h)] represents the pseudo-second-order rate constant, $q_{eq}$and $q_t$are the adsorption capacity at equilibrium and at time$t$, respectively (mg·g^{-1}). By integrating E2 with the boundary condition of $q_{t=0}$ = 0, the following linear equations can be obtained:

$$\frac{1}{q_{eq}-q_t}=\frac{1}{q_{eq}}+k_2 t \qquad \text{(E3)}$$

or

$$\frac{t}{q_t}=\frac{1}{q_{eq}}t+\frac{1}{V_0} \qquad \text{(E4)}$$

$$V_0 = k_2 q_{eq}^2 \qquad \text{(E5)}$$

where V_0[mg- HCO_3^-/(g-FeOOH.h)] is the initial sorption rate. The q_{eq} in E4 can be derived using the slope of t/q_t vs. t, while k_2 in E3 and E5 can be determined using the intercept of t/q_t vs. t and q_{eq}.

2.4 Adsorption Isotherms

Adsorption isotherms of bicarbonate by FeOOH were obtained at initial water pH 7.0. Initial bicarbonate concentrations used were 50, 100, 200, 300, and 500 mg/L (100 ml solution volumes were used for these tests). The adsorbent dosage was 7.5 g/L and temperatures were maintained at 13, 22, 30, 40, and 45 ºC. The isotherm experiments were conducted using a Labnet International, Inc. I5311-DS shaking incubator.

The adsorption isotherms were characterized using the Langmuir and Freundlich models. The Langmuir model is generally used to characterize the sorption equilibrium between an adsorbent and adsorbate in solution, and it is assumed that adsorptions take place at specific homogeneous sites on the adsorbent.It has proved to be a very good model for many monolayer adsorption processes. The linear expression for the Langmuir model is given as E6 [11, 12]:

$$\frac{C_e}{q_e}=\frac{1}{bq_{\max}}+\frac{C_e}{q_{\max}} \qquad \text{(E6)}$$

where q_e is the amount of HCO_3^- adsorbed onto the FeOOH (mg/g), C_e is the equilibrium HCO_3^- concentration in solution phase (mg/L), q_{max} is the maximum amount of HCO_3^- adsorbed onto FeOOH per unit of weight based on the monolayer adsorption assumption (mg/g), and b is the equilibrium adsorption constant related to the affinity of binding sites of FeOOH (L/mg).

This essential feature of the HCO_3^- Langmuir sorption isotherm is further evaluated in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which describes the type of isotherm [17, 19, 20] as shown below:

$$R_L = \frac{1}{1+bC_i} \tag{E7}$$

where C_i is the initial adsorbate (HCO_3^-) concentration (mg/L). R_L is used to predict the effectiveness of FeOOH for the adsorption of HCO_3^-, signifying that, when R_L is less than 1.0, FeOOH is a favorable sorbent for HCO_3^-; otherwise, FeOOH is unfavorable. A value of R_L between 0 and 1 indicates the linear and irreversible characteristics of HCO_3^- adsorption [17, 19, 20].

The Freundlich isotherm describes adsorption in which the adsorbent has heterogeneous surface adsorption sites with various adsorption energies. The linear form of the Freundlich model is expressed as [11]:

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \tag{E8}$$

where K_f(L/g) is the Freundlich adsorption isotherm constant associated with the sorption capacity of FeOOH, and $1/n$ indicates sorption intensity.

2.2 The effect of other parameters

Other adsorption tests for checking the effects of sorbent dosage, initial concentration, and pH were performedin order to investigate the efficiency of FeOOH for removing carbonate and bicarbonate. The effect of pH was considered only for the removal of bicarbonate.

Five different sorbent dosages (3.0, 5.0, 7.5, 10.0, and 16 g/L) were tested at pH 7.0 to investigate FeOOH capacity and efficiency; adsorption tests were conducted using a Labnet International, Inc. I 5311-DS shaking incubator. In order to evaluate the effect of pH on HCO_3^- removal at 10 g/L FeOOH, experiments were run at initial pH values of 5, 7, and 9with initial bicarbonate concentration of 200 mg/L using a jar tester at 230 rpm. Solutions of 50, 100, 200, 300, and 500 mg/L were used for testing the effects of initial concentrations with 7.5g/L FeOOH and pH 7.0.

III. RESULTS AND DISCUSSION

3.1. Sodium Bicarbonate

3.1.1. Adsorbent Characterization

The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. Pore-size distribution and total pore volume of the FeOOH were measured in a previous work [18],

The morphology and surface element distribution of the FeOOH adsorbent were studied using SEM, with the results shown in Fig. 1. The images obtained (Fig. 1a, Fig. 1b, and Fig. 1c) are for both virgin and spent FeOOH adsorbents, i.e., for virgin FeOOH, spent FeOOH for bicarbonate, and spent FeOOH for carbonate, respectively.Figures 1a, 1b, and 1cshow that particle size of the FeOOH did not change significantly after sorption, i.e., the spent adsorbent measured several hundred micrometers, indicating the appropriateness of using FeOOH as a filtration column medium.

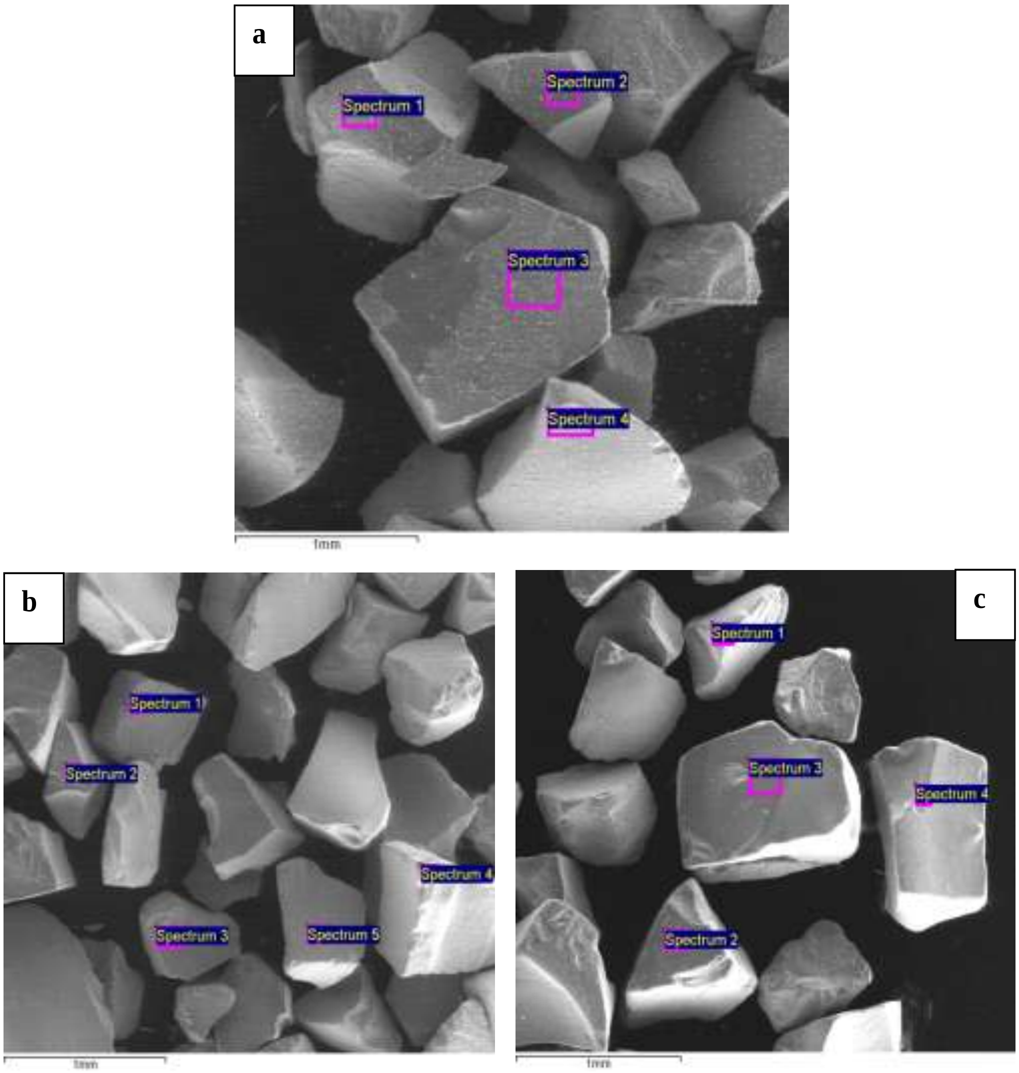

Figure 1: SEM images of (a) virgin FeOOH, (b) spent FeOOH for bicarbonate, at 300 mg/L initial bicarbonate concentration and 10.0 g/L FeOOH dosage, and room temperature of 26.0°C ± 1and (c) spent FeOOH for carbonate at 1000 mg/L initial carbonate concentration and 5.0 g/L FeOOH dosage, and room temperature of 26.0°C ± 1with the magnification of 1:80

3.1.2. Adsorption Kinetics

The kinetics of HCO_3^- adsorption on FeOOH was studied and the results are shown in Fig. 2. The results indicate that about 95% of total bicarbonate was adsorbed rapidly in first hour when the initial bicarbonate was 50 mg/L and 150 mg/L, and about 41% of total bicarbonate was adsorbed in the first hour at 300 mg/L. In the two lower concentrations (50 mg/L, and 150 mg/L), more than 98% was adsorbed at four hours, while at the higher initial bicarbonate of 300 mg/L, about 50% was adsorbed at 14hours, indicating 14 hours as a reasonable equilibrium period. Removal efficiency at equilibrium was greater than 98% for the two lower initial concentrations (50 mg/L, and 150 mg/L) and more than 50% for the 300 mg/L initial concentration test.

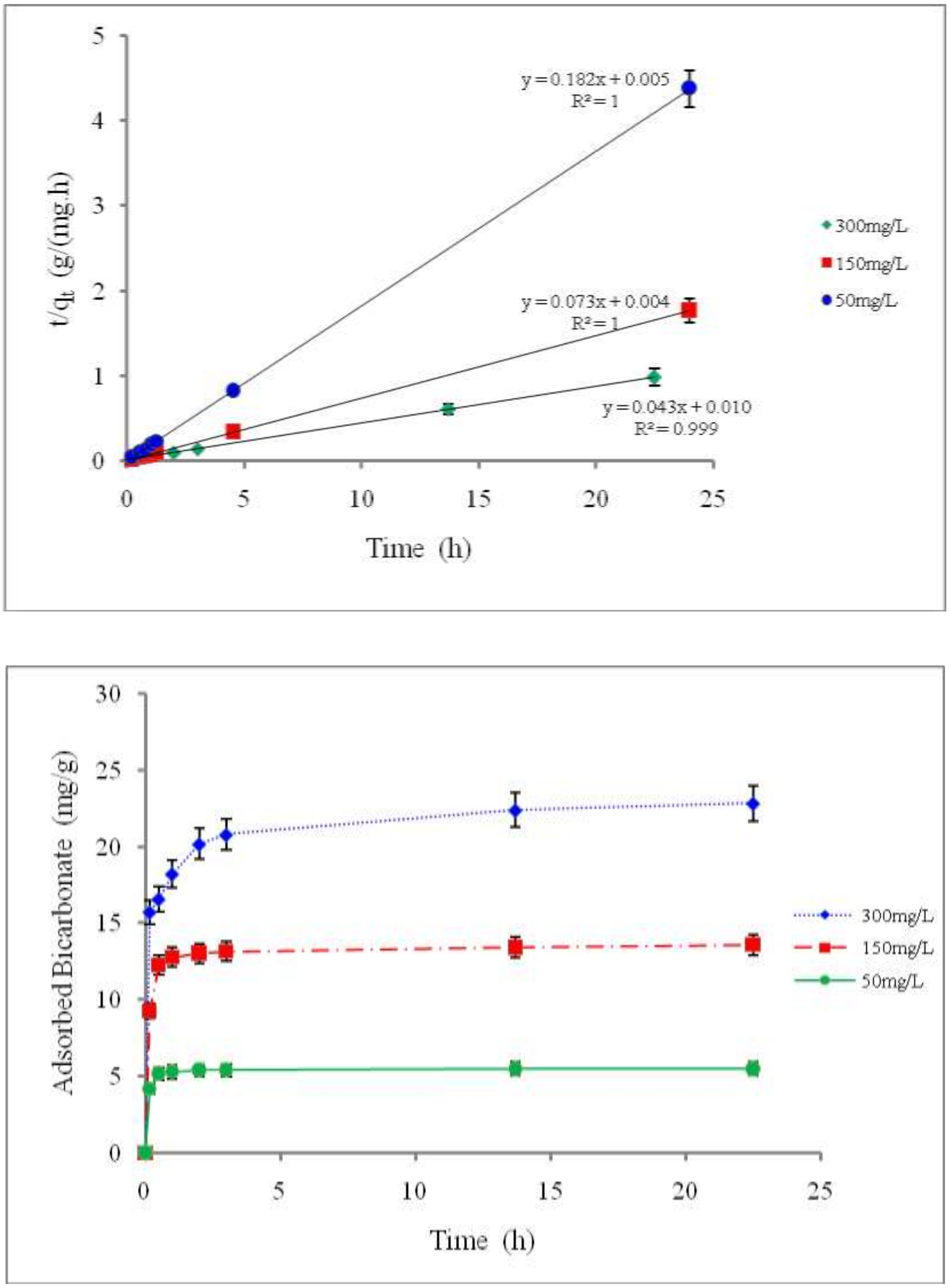

Figure 2. Adsorption kinetics of HCO_3^- on FeOOH adsorbent in 10 g/L suspensions at pH 7.0 ± 0.1 , and 26°C ± 1 with three initial HCO_3^- concentrations (50 mg/L, 150 mg/L, and 300 mg/L): (a) experimental data and (b) pseudo-second-order model fittings.

In addition, Table 1 indicates that, because the derived regression coefficients are all above 0.999, the pseudo-second-order model is highly compatible with the collected adsorption kinetics data. The pseudo second-order adsorption rate constant (k_2), found to be a function of initial bicarbonate concentration, decreased from 6.384 to 0.187 g/mg.h as the initial bicarbonate concentration increased from 50 to 300 mg/L.

Table 1Pseudo-second-order adsorption rate constant (*k*) and adsorption capacity (q_e) derived from three initial bicarbonate concentrations.(pH 7.0 ±0.2; FeOOH dose of 10 g/L; Temperature of 26.0°C ± 1).

Initial HCO_3^- concentration (mg/L)	V_0 [mg/(g.h)]	*k* [g/(mg.h)]	q_e (mg/g)	R^2
50	192.31	6.384	5.49	1.0
150	243.90	1.314	13.62	1.0
300	99.01	0.187	22.99	0.9999

3.1.3. Langmuir Adsorption Isotherm

Fig.3 illustrates the relationship between the uptake of bicarbonate by the adsorbent and the bicarbonate equilibrium concentration in the solution. It is clear that an increase in temperature resulted in an increase in the amount of bicarbonate adsorbed per unit mass of FeOOH. The Langmuir model parameters shown in Table 2 below, for bicarbonate adsorption on FeOOH at different temperatures, pH 7.0 ± 0.05, and adsorbent dosage of 7.5 g/L, were calculated from Fig.4.

The results show that maximum adsorption capacity of FeOOH for bicarbonate are26.18, 27.93, 28.99, 28.57, and 30.86 mg/g, respectively, at 13, 22, 30, 40, and 45 °C. It is clear from the data in Table 2 that the capacity of the sorbent FeOOH increased with an increase in temperature in the temperature range studied. Moreover, FeOOH was one of the most cost-effective sorbents used for industrial water treatment.

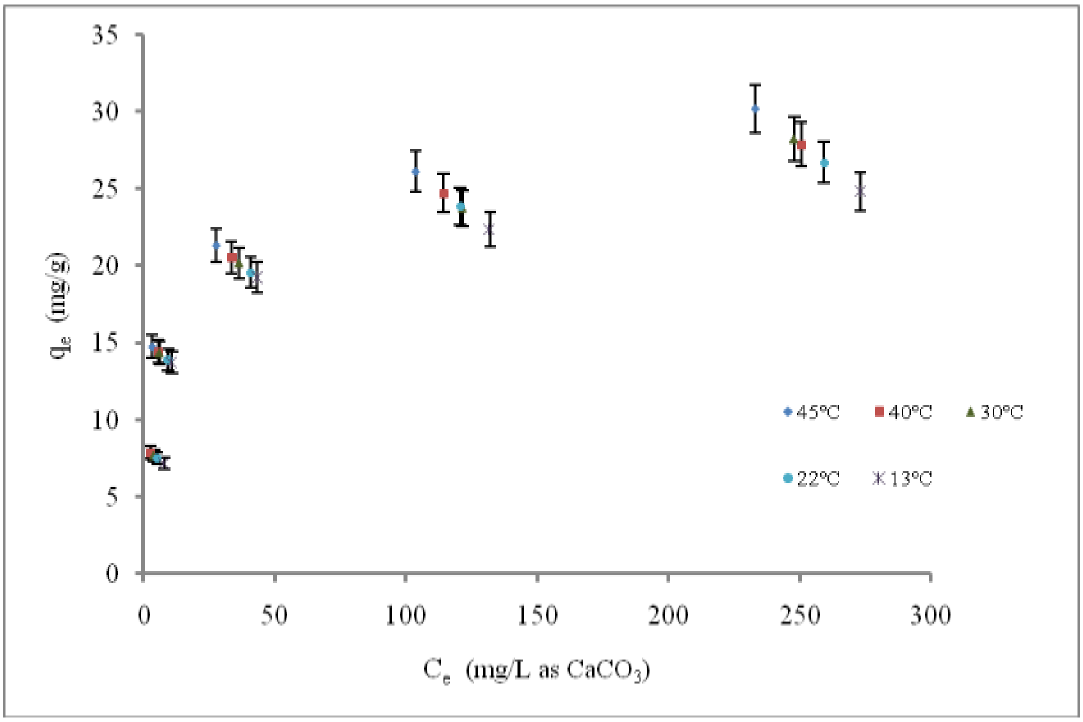

Figure 3. Bicarbonate adsorption isotherm on FeOOH at different temperatures (pH: 7.0 ± 0.05; adsorbent dosage: 7.5 g/L)

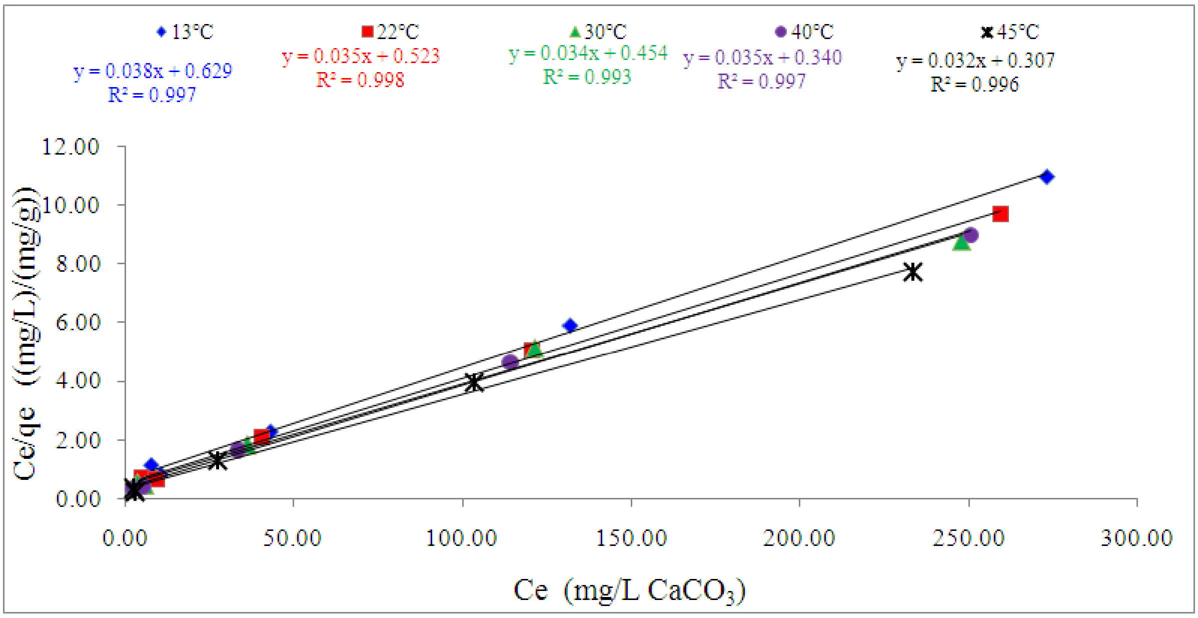

Figure 4. Langmuir model for bicarbonate adsorption isotherm on FeOOH at different temperatures (pH: 7.0 ± 0.05; adsorbent dosage: 7.5 g/L).

Table 3 lists the values of R_L for bicarbonate adsorption at different initial bicarbonate concentrations and temperatures. All of the R_L values are between 0 and 1 and close to zero, which suggests that FeOOH is an effective bicarbonate adsorbent [17]. Further, because R_L values are so close to zero in all cases, the complexation between bicarbonate and FeOOH is practically irreversible [17], a circumstance similar to the adsorption of selenium (in our previous study, [18]), where all R_L values were between 0 and 1 and close to zero.

Table 2 Parameters of the Langmuir model for bicarbonate adsorption on FeOOH at different temperatures (pH: 7.0 ± 0.05; adsorbent dosage: 7.5 g/L).

Temperature (°C)	q_{max} (mg/g)	b (L/mg)	R^2
13	26.18	0.061	0.9985
22	27.93	0.068	0.9983
30	28.99	0.076	0.9933
40	28.57	0.103	0.9974
45	30.86	0.106	0.9961

Table 3 Equilibrium parameters R_L for bicarbonate adsorption on FeOOH.(pH 7.0 ±0.2; FeOOH dose of 7.5 g/L)

HCO_3^- Concentration (mg/L)	R_L				
	13 °C	22 °C	30 °C	40 °C	45 °C
50	0.2479	0.2263	0.2086	0.1630	0.1593
100	0.1415	0.1276	0.1165	0.0888	0.0866
200	0.0761	0.0682	0.0618	0.0464	0.0452
300	0.0521	0.0465	0.0421	0.0314	0.0306
500	0.0319	0.0284	0.0257	0.0191	0.0186

3.1.4. Freundlich Models of Adsorption Isotherm

The Freundlich model was also applied to the bicarbonate adsorption equilibrium data. The Freundlich model showed a regression coefficient of 0.864 – 0.919,which was less than the Langmuir model, where the regression coefficient ranged between 0.9933– 0.9985. The Freundlich parameters derived from equilibrium data are summarized in Table 4.

Table 4 Parameters of the Freundlich model for bicarbonate adsorption on FeOOH at different temperatures (pH: 7.0 ± 0.05; adsorbent dosage: 7.5 g/L).

Temperature (°C)	K_f (L/g)	1/n	R^2
13	6.51	0.36	0.8737
22	7.01	0.34	0.9067
30	7.78	0.31	0.8927
40	8.16	0.29	0.919
45	8.65	0.27	0.864

Fig. 5 shows the Freundlich adsorption isotherm obtained by plotting the logarithmic values of q_e and C_e at the different temperatures studied. All values of *1/n* were between 0 and 1, indicating favorable bicarbonate adsorption on FeOOH[11]. R^2 values showed that the Freundlich adsorption isotherm model was able to adequately describe the relationship between q_e and C_e values at the studied temperatures. However, because Langmuir regression coefficientswere larger than the Freundlich isotherm regression coefficients, the Langmuir adsorption isotherm model better fit the values of q_e and C_e than the Freundlich isotherm.

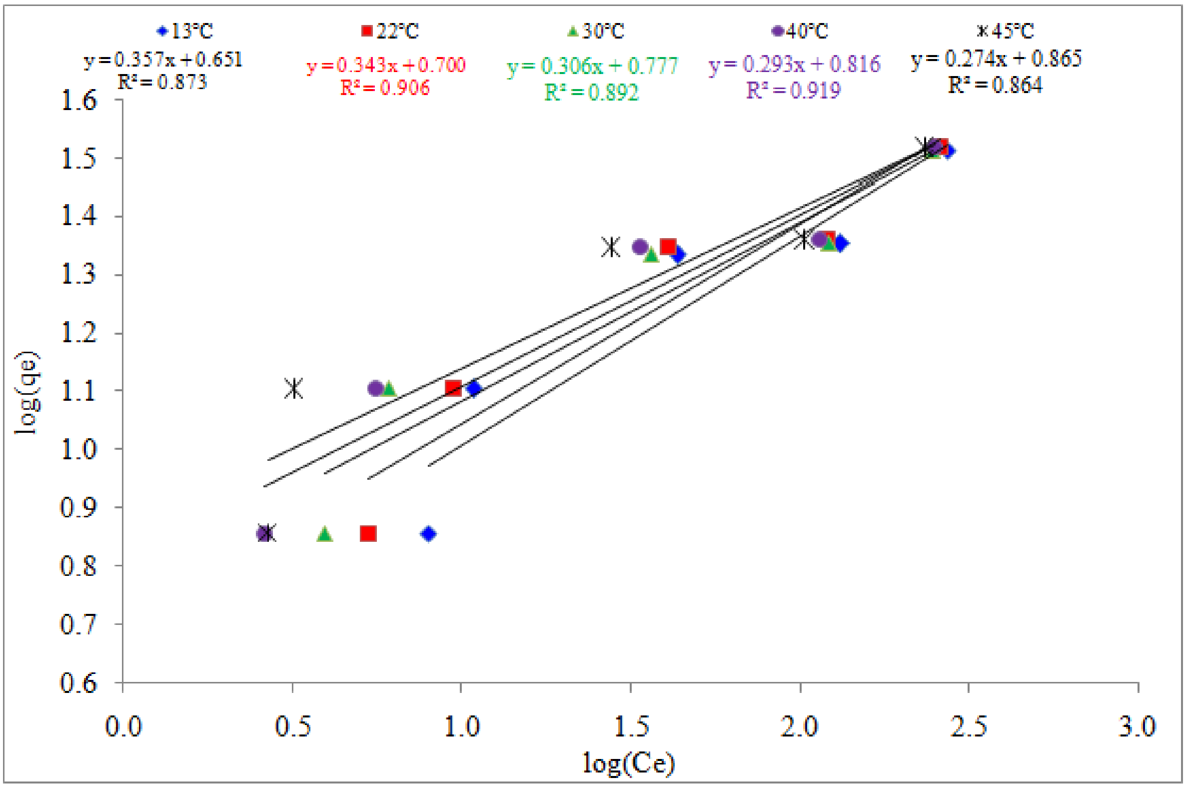

Figure 5.Freundlich model for bicarbonate adsorption isotherm on FeOOH at different temperatures (pH: 7.0 ± 0.05; adsorbent dosage: 7.5 g/L).

3.1.5. Thermodynamic Analysis

Standard Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the adsorption process were calculated based on the variation of the thermodynamic equilibrium constant (*b*) with changes in temperature as given below [21]:

$$\Delta G = -RT\ln(10^{6} \times b) \tag{E9}$$

$$\Delta G = \Delta H - T\Delta S \tag{E10}$$

$$\ln(10^{6} \times b) = \frac{\Delta S}{R} - \frac{\Delta H}{R \times T} \tag{E11}$$

where T is the adsorption temperature in Kelvin (K), and R is the universal gas constant, 8.314 J/mol/ K. ΔG in E9 [13] at a given temperature can be calculated based on the value of the equilibrium adsorption constant derived from E6.

When changes of enthalpy and entropy (ΔH and ΔS) of the adsorption process do not vary with temperature in the studied temperature range (13 – 45 ºC), then ΔH and ΔS can be calculated according to the modified van’t Hoff equation (E11). In other words, the values of ΔH and ΔS can be obtained from the slope and intercept of the $ln(l0^{6} \times b) \sim 1/T$ plot.

The change in Gibbs free energy (ΔG) in the range of −20 and 0 kJ /mol indicates that, generally, the sorption is physisorption, as physisorption together with chemisorption lies in the range of −20 to −80 kJ/ mol, and chemisorption alone lies in the range of −80 to −400 kJ/ mol [14, 15].

Fig. 6 shows the thermodynamic analysis obtained by plotting the $ln(l0^{6} \times b)$ vs. $1/T$ at the different temperatures studied.Table 5 shows the thermodynamic parameters ΔG, ΔH, and ΔS for the adsorption of bicarbonate onto FeOOH. The positive ΔH in Table 5 indicates that the adsorption of bicarbonate on FeOOH is endothermic, a finding consistent with the observation that the adsorption capacity of FeOOH for bicarbonate increases with an increase in temperature. The negative ΔG confirms the spontaneous nature of adsorption, where the Gibbs free energy (ΔG) ranged between -26.293 kJ/mol (at 13 °C) and -30.692 kJ/mol (at 45 °C), indicating that the adsorption was physisorption together with chemisorption in the range from -20 to -80 kJ/mol. The positive value of ΔS suggests an increase of randomness resulting from the interaction between bicarbonate and FeOOH at the solid-solution interface.

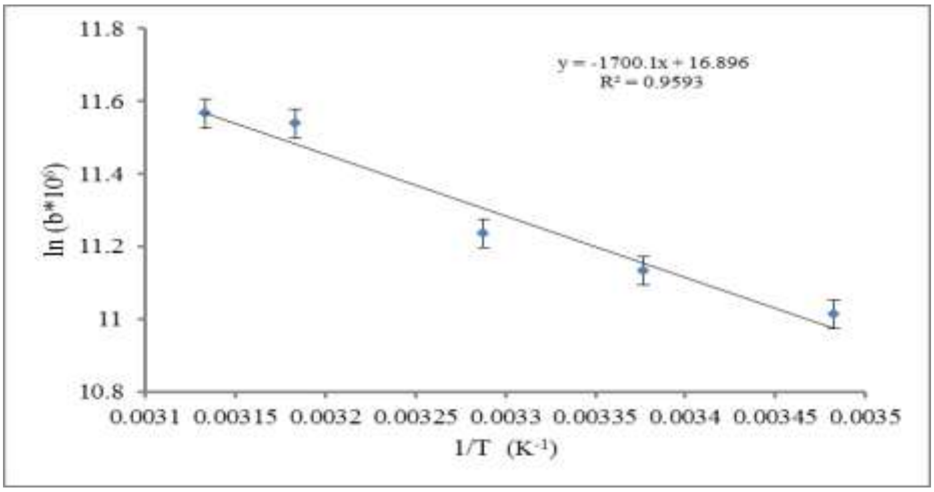

Figure 6: Plot of $ln(b \times 10^{6})$ vs. $1/T$ for estimation of the thermodynamic parameters for adsorption of bicarbonate onto FeOOH, (pH 7.0 ±0.2; FeOOH dose of 7.5 g/L).

Table 5 Thermodynamic parameters for bicarbonate adsorption on FeOOH.(pH 7.0 ±0.2; FeOOH dose of 7.5 g/L; Initial bicarbonate concentrations (50, 100, 200, 300, & 500 mg/L)).

Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol. K)	R^2
13	-26.293	14.135	0.140	0.9593
22	-27.410			
30	-28.414			
40	-30.139			
45	-30.692			

3.1.6. Effect of Feooh Dosage

Data in Table 6, Fig. 7, and Fig. 8 show the direct relationship between FeOOH dosage and removal percentage, wherein the removal of bicarbonate increased from about 23% to 80% when FeOOH was increased from 3 g/L to 16 g/L. However, the removal capacity of FeOOH decreased from 23.1 mg/g at a dosage of 3 g/L FeOOH to 14.8 mg/g at 16 g/L FeOOH, which may be attributed to the increase of the electrostatic interactions of binding sites on FeOOH and decrease in the relative availability of bicarbonate in solutions [15, 16].

Table6 Effect of FeOOH Dosage on removal of bicarbonate prepared from sodium bicarbonate (300 mg/L HCO_3^-; pH 7.0 ± 0.2; T = 31 °C ± 2 °C).

FeOOH Dosage (g/L)	HCO_3^- Removal %	Remaining alkalinity (mg/L as $CaCO_3$)	HCO_3^- Removed (mg/g)
0.0	0.0	302.7	0.0
3.0	22.9	233.3	23.1
5.0	31.9	206.0	19.3
7.5	46.7	161.3	18.8
10.0	60.1	120.7	18.2
16.0	78.2	66.0	14.8

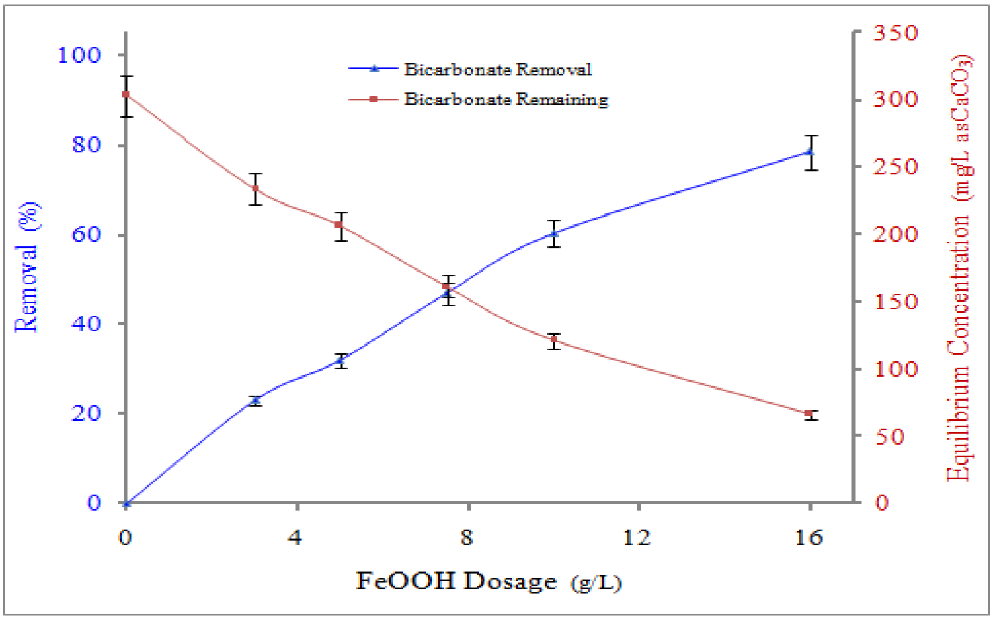

Figure7: Effect of FeOOH Dosage on removal of bicarbonate prepared from sodium bicarbonate, (300 mg/L HCO_3^-; pH of 7.0 ± 0.2; T= 31 °C ± 2 °C).

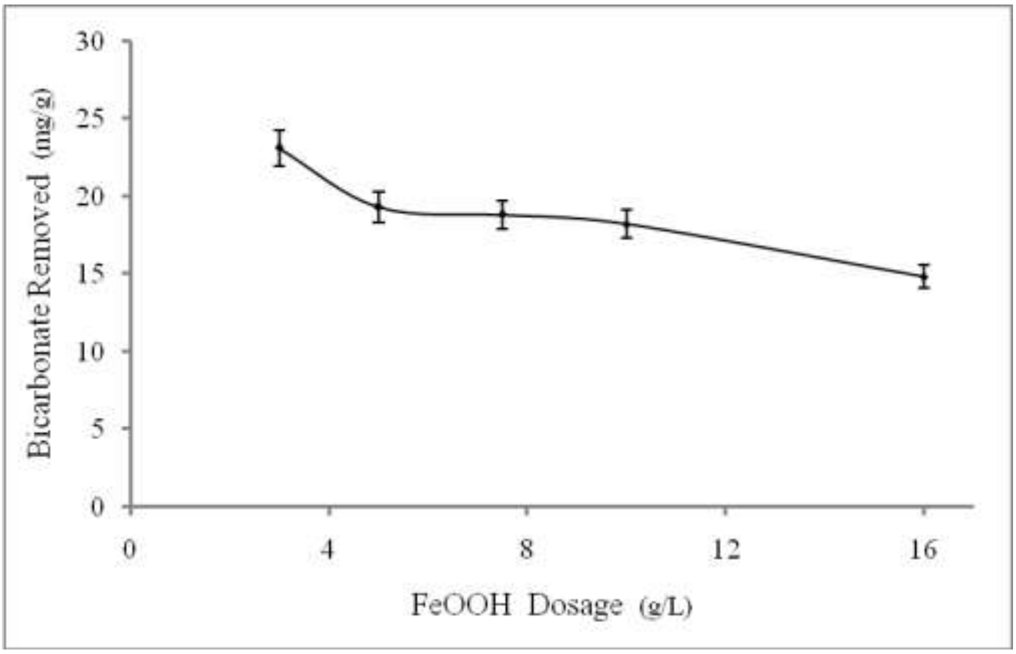

Figure 8. : Bicarbonate removed (mg/g) (capacity of FeOOH) by different FeOOH dosages, at 300mg/L initial $NaHCO_3$ concentration, initial water pH of 7 ± 0.1, and 31.5°C ± 1.

3.1.7. Effect of ph on Removal of Bicarbonate

From Fig. 9, it is abundantly clear that initial water pH has no effect on the removal of bicarbonate, as removal reached more than 99% at all pHs used. One explanation for this may be that the bicarbonate works as a buffer, whereby the three solutions start with different pHs (5.0, 7.0, and 9.0 ± 0.2) but end with nearly the same pH of 8.36 ± 0.2. The operation of this buffer may be represented by the following reaction, which defines it as a solution that resists changes in the concentration of hydrogen ions caused by the addition of an acid or a base:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad \text{(R. 1)}$$

The buffer zone is the pH range, across which there is only a small change in pH upon the addition of acid or other base to a buffer solution.

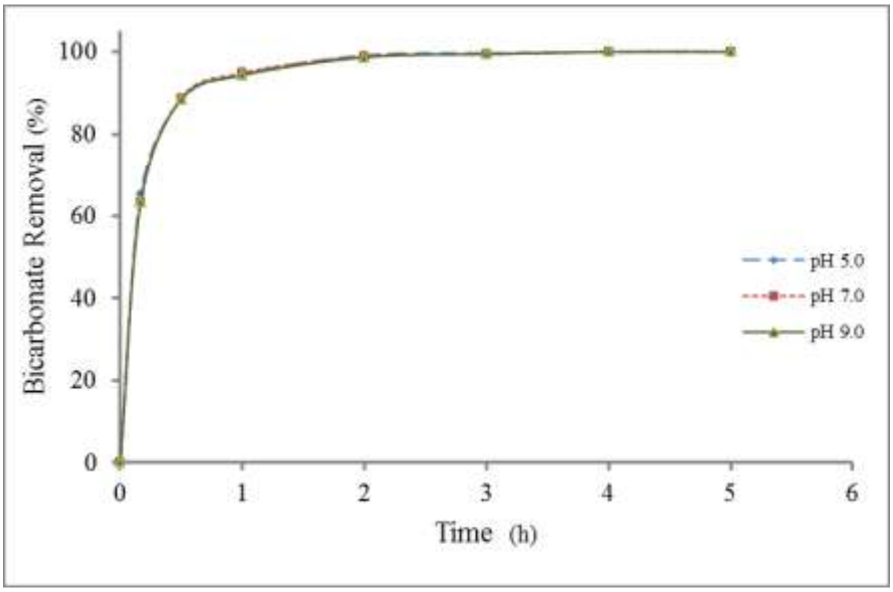

Figure 9. Effect of pH on removal efficiencyof bicarbonate from aqueous solution, at (10 g/L FeOOH; 200 mg/L HCO_3^-; T= 26.0 °C ± 2 °C).

3.2. Sodium Carbonate

Carbonate added to water could immediately convert to bicarbonate upon the addition of FeOOH according to the following reaction

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \qquad \text{(R.2)}$$

3.2.1. Effect of Initial Carbonate Concentration

Figures 10, and 12 shows the effect of initial carbonate concentration on total alkalinity removal percentage and concentration, from the data shown in the Fig. 10, the removal of the total alkalinity decrease by increasing the initial carbonate concentration, where the removal efficiency decreased from more than 95% to about 26% when the initial carbonate concentration was increased from 50 mg/L to 500 mg/L, while the FeOOH capacity increased from 7.8 mg/g at 50 mg/L initial carbonate concentration to more than 17 mg/L at 500 mg/L initial carbonate concentration. Fig. 11 illustrates the converting of the carbonate to bicarbonate, as it’s clear from Fig. 11 at low initial carbonate concentration the sorbent (FeOOH) can adsorb all the alkalinity, but as the initial carbonate concentration the sorbent adsorb portion of the initial carbonate concentration, and another portion converts to bicarbonate until the sorbent get saturated and ineffective to adsorb or convert. Fig. 13shows the total alkalinity adsorption isotherm on FeOOH at 40 °C, 7.5 g/L FeOOH, and five different initial carbonate concentrations (50, 100, 200, 300, and 500 mg/L). One may readily note that the capacity of FeOOH increases with an increase in the initial concentration of carbonate. Fig.14 illustrates the Langmuir adsorption isotherm plot of total alkalinity onto FeOOH at 40 °C, the Langmuir parameters, Calculations show that the maximum adsorption capacity of FeOOH for total alkalinity reached 17.361 mg/g at 40 °C, and the equilibrium adsorption constant “b” 0.0675 L/mg. Also, the regression coefficient is 0.9926, which indicates that the Langmuir adsorption isotherm model characterized FeOOH-based total alkalinity adsorption very well. Fig. 15shows the Freundlich adsorption isotherm results.The calculations show that the Freundlich model also characterized the isotherm adsorption of total alkalinity on FeOOH at 40 °C. The values of $1/n$ was 0.15 (between 0 and 1), which indicate favorable bicarbonate adsorption on FeOOH[11],the Freundlich adsorption isotherm constant associated with the sorption capacity of FeOOH “K_f” is 8.49 L/g and R^2 was 0.9406, showing that the Freundlich adsorption isotherm model was able to adequately describe the relationship between q_e and C_e values at the studied temperature of 40 °C.

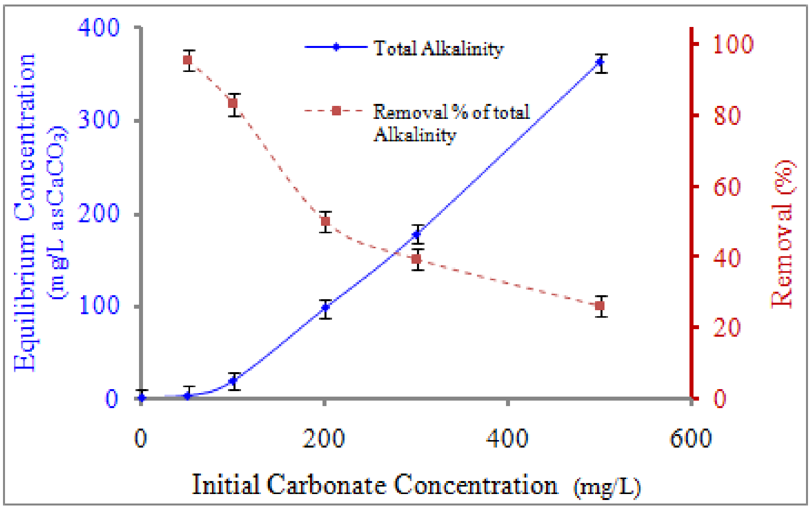

Figure10. Effect of initial carbonate concentration on removal of total alkalinity, at (pH 7.0 ± 0.2; 7.5 g/L FeOOH; T= 24 °C ± 2 °C).

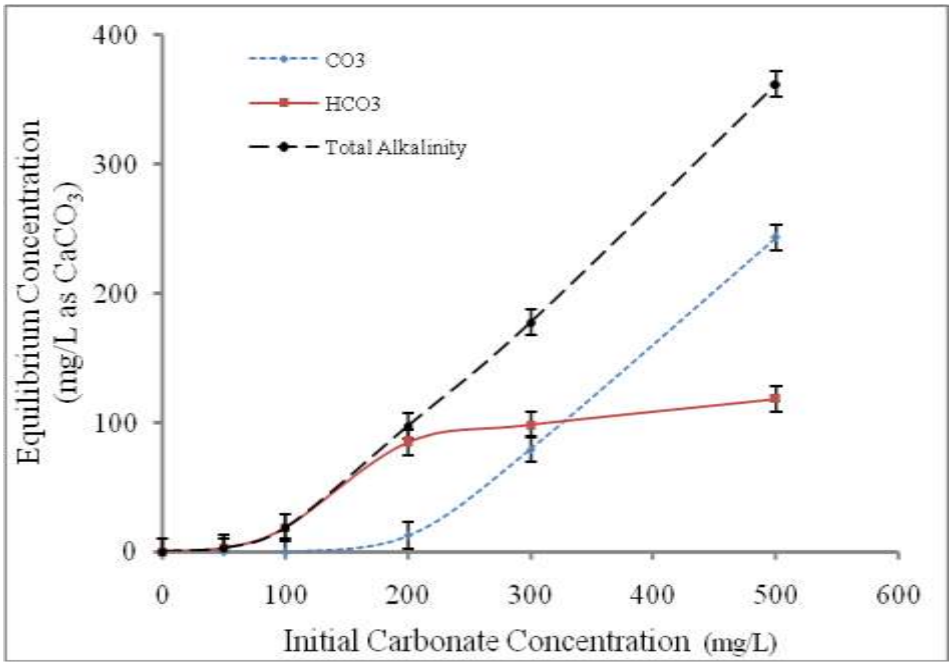

Figure11. Remaining concentration of carbonate, bicarbonate, and total alkalinity with respect to initial carbonate concentration (pH 7.0 ± 0.2; 7.5 g/L FeOOH; T= 24 °C ± 2 °C).

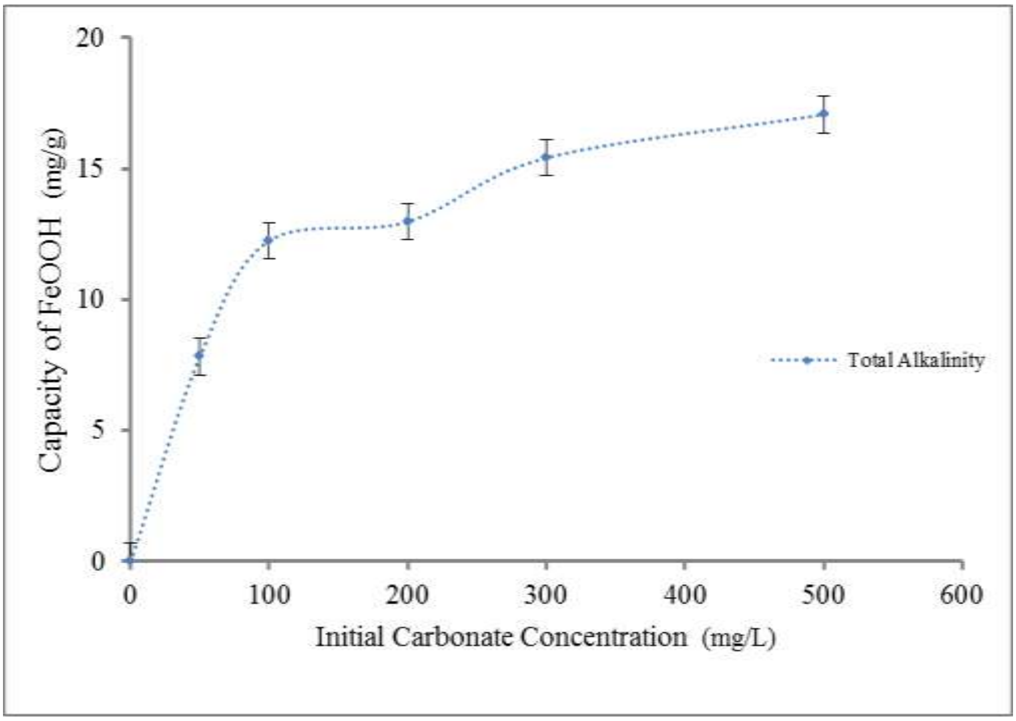

Figure12: FeOOH Capacity on removing alkalinity at different initial carbonate concentrations, (pH 7.0 ± 0.2; 7.5 g/L FeOOH; T= 24 °C ± 2 °C).

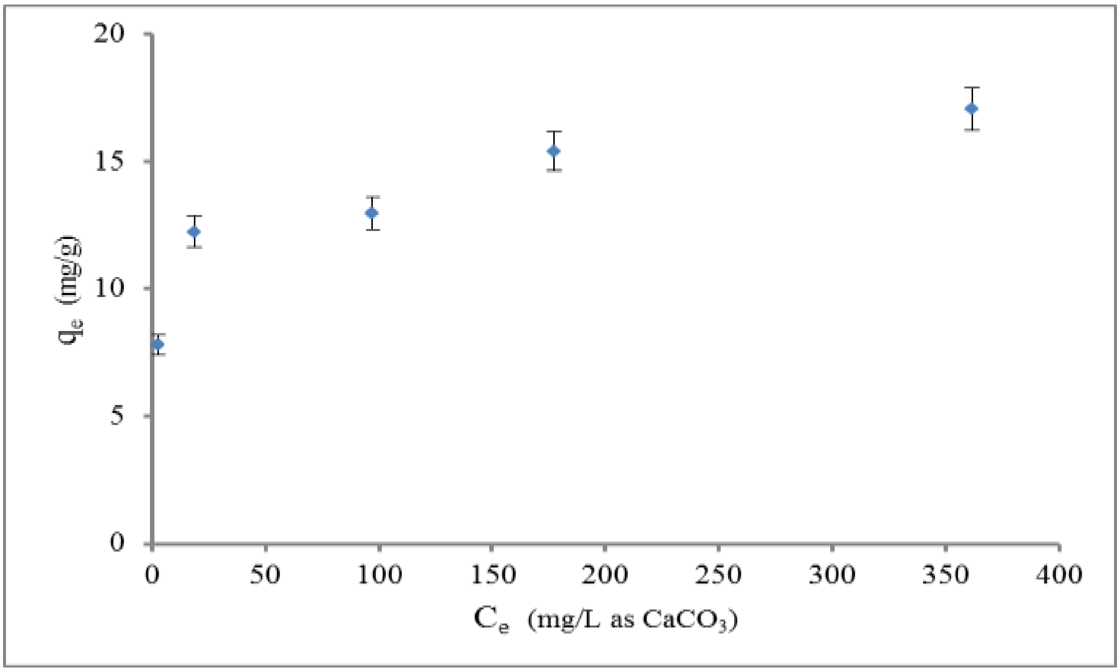

Figure13. Total alkalinity adsorption isotherm on FeOOH (40 °C; 7.5 g/L FeOOH; pH 7.0 ± 0.2).

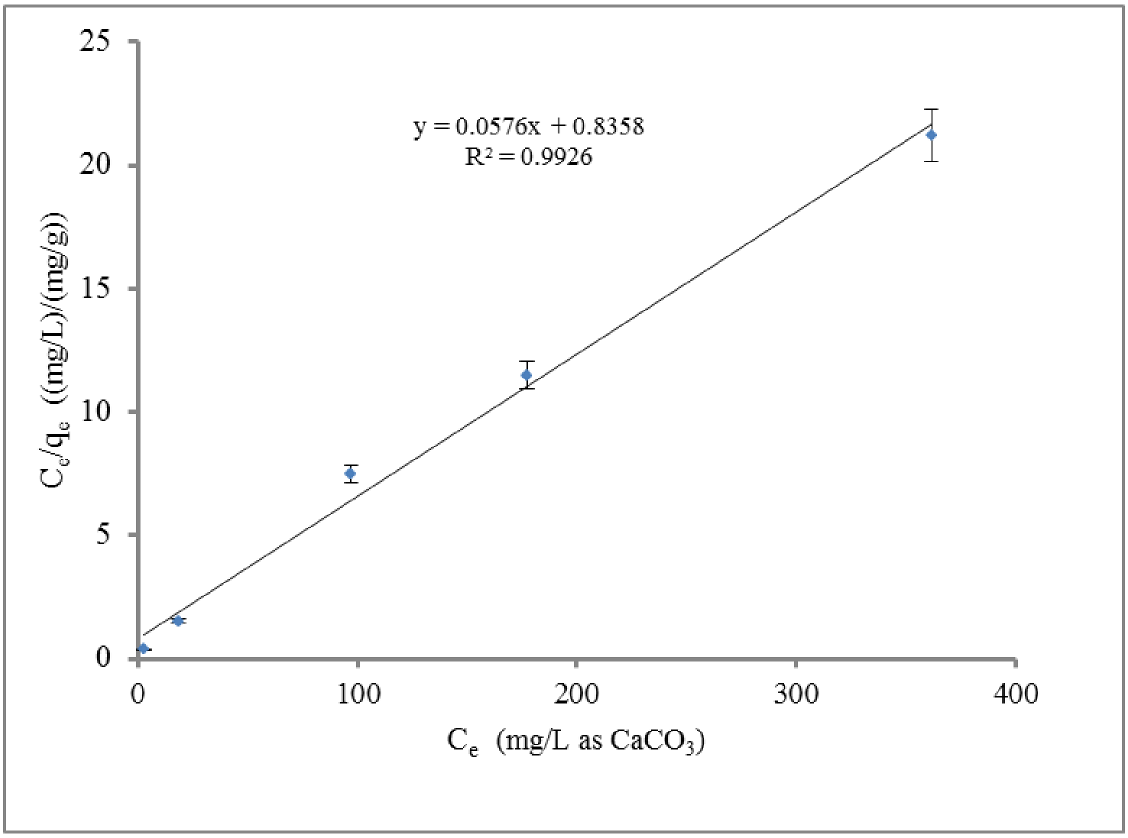

Figure14. Langmuir adsorption isotherm plot of total alkalinity onto FeOOH (40 °C; 7.5 g/L FeOOH; pH 7.0 ± 0.2).

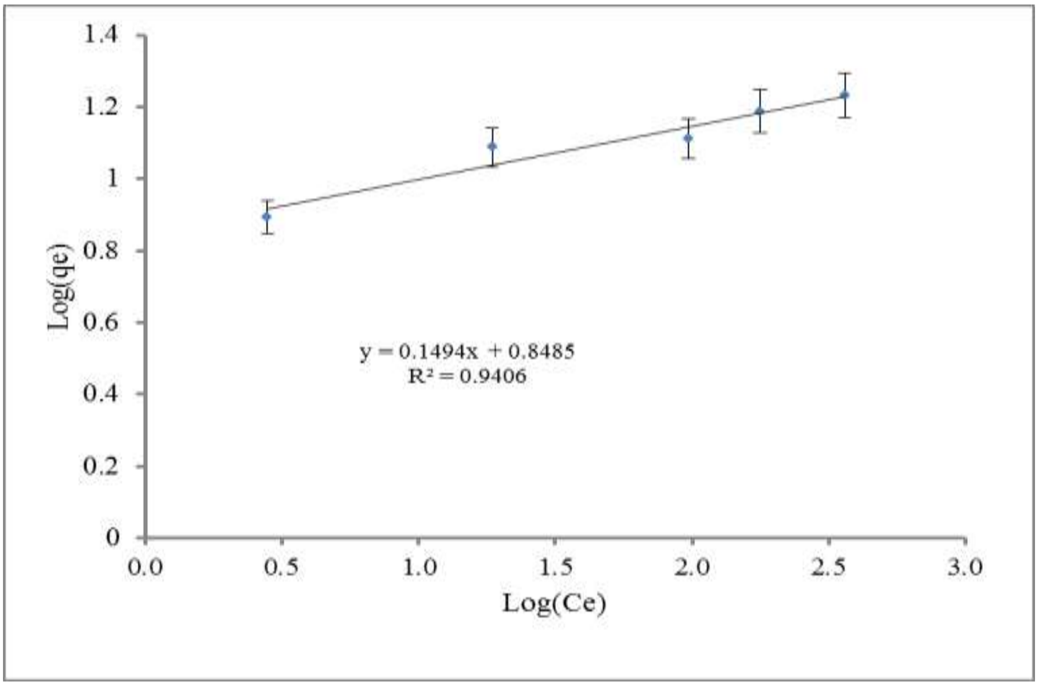

Figure 15. Freundlich adsorption isotherm plot of total alkalinity onto FeOOH (40 °C; 7.5 g/L FeOOH; pH 7.0 ± 0.2).

3.2.2. Effect of Temperature

Fig. 16 represents the effects of change in adsorption temperature on the conversion of carbonate to bicarbonate and the removal of total alkalinity. The results indicate that total alkalinity decreased slightly with increased temperature over the range of temperatures studied. Total alkalinity removal increased from about 42% at 10 °C to about 50% at 40 °C, while the concentration of total alkalinity decreased from 162.4 mg/L (as $CaCO_3$) at 10 °C to 142.8 mg/L (as $CaCO_3$) at 40 °C. For the conversion of carbonate to bicarbonate, remaining carbonate concentrations decreased from about 68.9 mg/L (as $CaCO_3$) at 10 °C to 42.8 mg/L (as $CaCO_3$) at 40 °C.

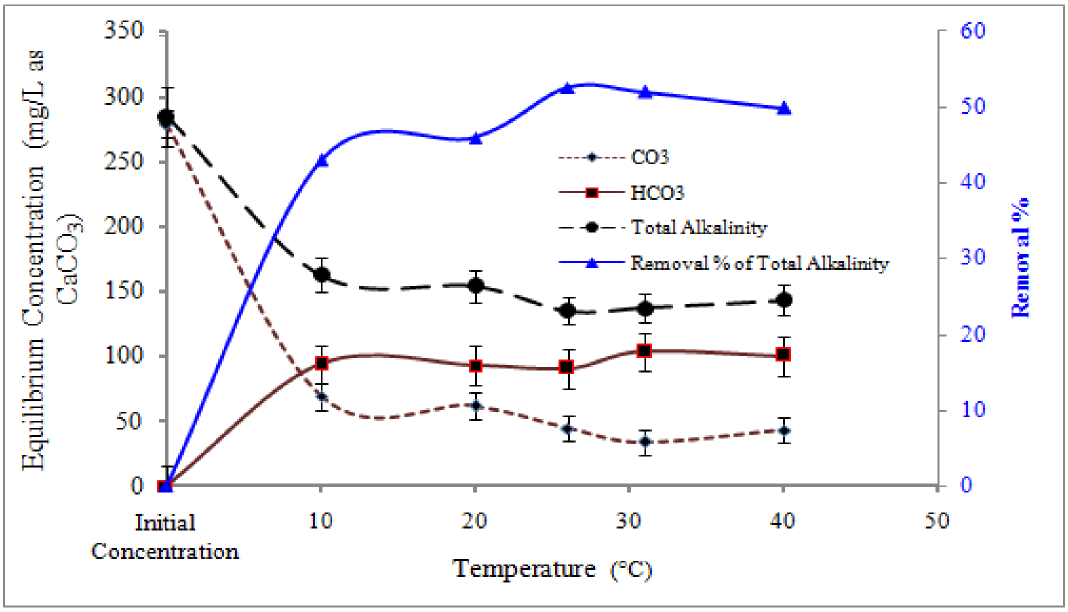

Figure16. Temperature Effect on equilibrium concentration of carbonate, bicarbonate and total alkalinity and removal efficiency of total alkalinity (10 g/L FeOOH; 200 mg/L CO_3^{2-}; pH of 7.0 ± 0.2)

3.2.3. Effect of Sorbent Dosage

Figures 17and 18 illustrate the effect of FeOOH dosage on the conversion of carbonate to bicarbonate and removal of total alkalinity. The results show that both the conversion of carbonate to bicarbonate and removal of total alkalinity increased significantly with an increase in FeOOH dosage. The removal of total alkalinity increased from 16% at 3 g/L FeOOH to about 72% at 16 g/L FeOOH, while the conversion of carbonate to bicarbonate increased from about 24% at 3 g/L FeOOH to 100% at 16 g/L FeOOH.

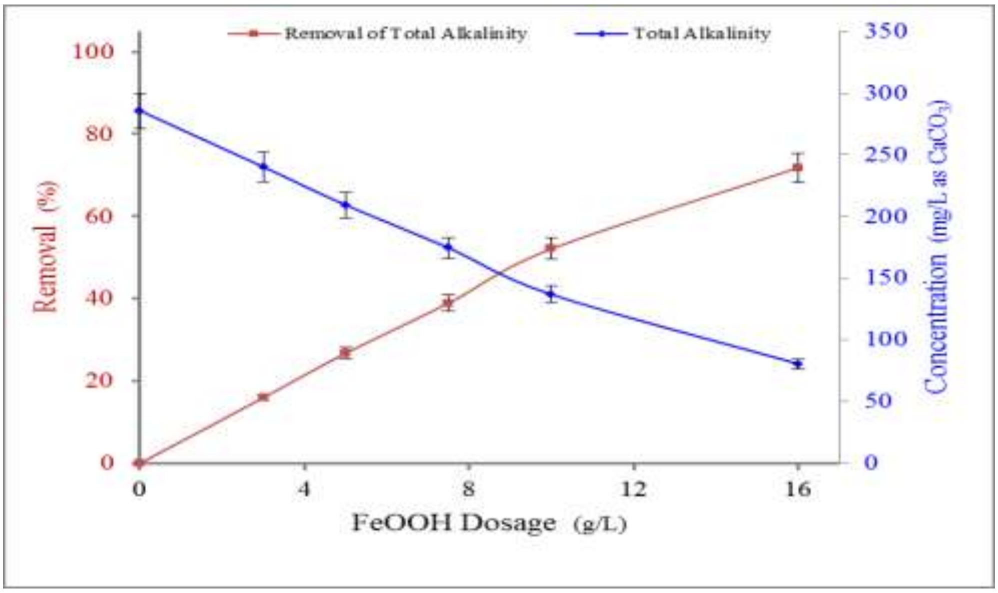

Figure17. Effect of FeOOH dosage on concentration and removal efficiency of total alkalinity (300 mg/L CO_3^{2-}; pH of 7.0 ± 0.2; T= 25 °C ± 2 °C).

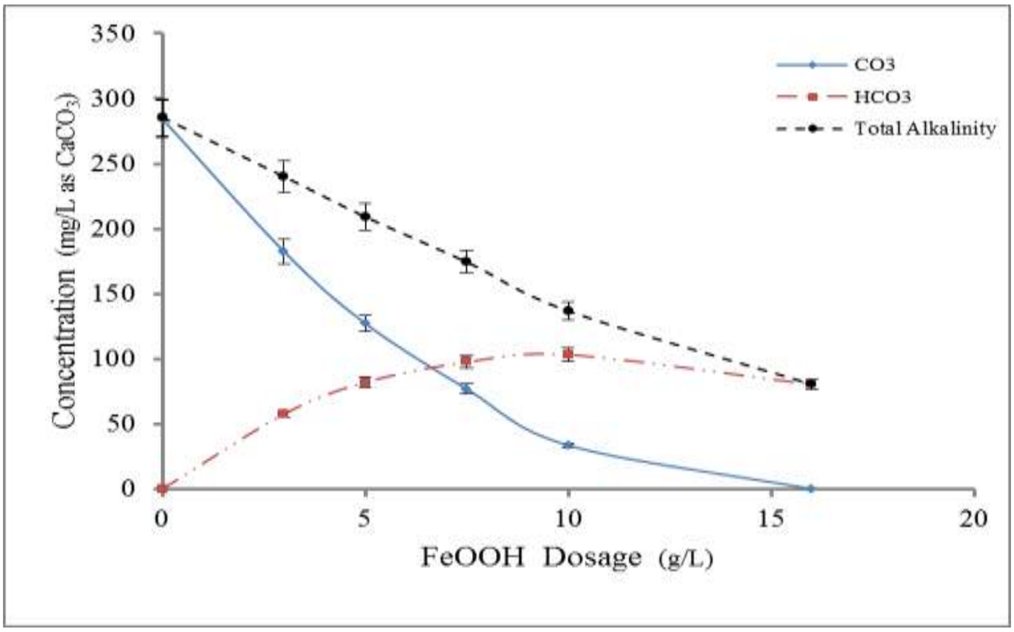

Figure18.Effect of FeOOH dosage on concentration of carbonate, bicarbonate, and total alkalinity (300 mg/L CO_3^{2-}; pH of 7.0 ± 0.2; T= 25 °C ± 2 °C).

3.2.4. Effect of time

The results in Fig.19 indicates that more than 95% of the carbonate was converted to bicarbonate in the first hour, 100% of the carbonate was converted after two hours, and more than 54% of total alkalinity was adsorbed onto FeOOH. After about 16 hours, more than 66% of total alkalinity was adsorbed and the saturated FeOOH could not adsorb any more of the bicarbonate.

Fig. 20 shows the kinetics of total alkalinity on the FeOOH at 150 mg/L carbonate (as $CaCO_3$) and 5 g/L FeOOH. Fig. 21 indicates that, because the derived regression coefficient is above 0.999, the pseudo-second-order model is highly compatible with the collected adsorption kinetics data. The second-order adsorption rate constant is 0.11147 g/mg.h, while the capacity of the FeOOH under these conditions is 22.42 mg/g with initial sorption rate "V_0" of 55.56 mg- HCO_3^-/(g-FeOOH.h).

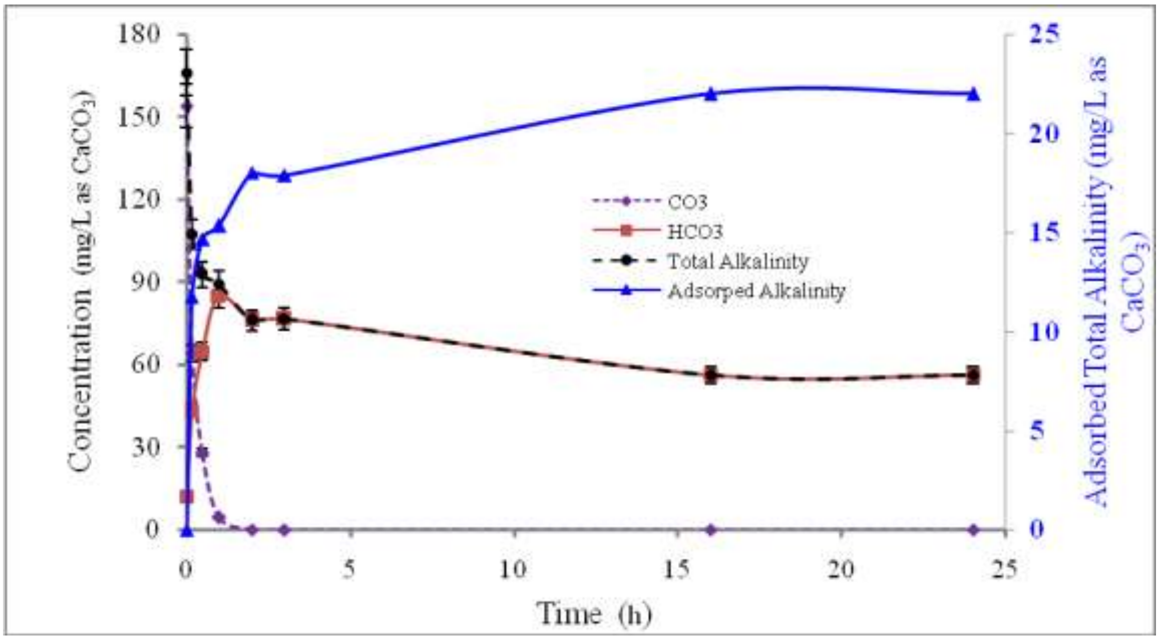

Figure 19: Effect of time on concentration of carbonate, bicarbonate, and total alkalinity (160 mg/L CO_3^{2-}; 5.0 g/L FeOOH; pH of 7.0 ± 0.2; T = 25 °C ± 2 °C).

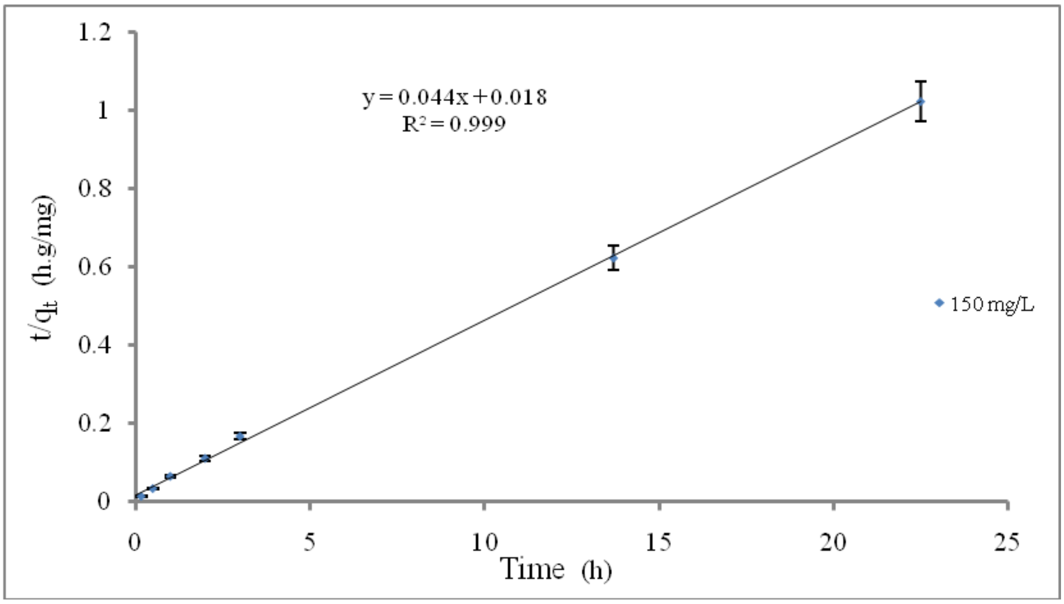

Figure20. Adsorption kinetics of total alkalinity,(pseudo-second-order model fittings), (5.0 g/L FeOOH, pH 7.0 ± 0.1; initial CO_3^{2-} 150 mg/L (as $CaCO_3$)).

IV. CONCLUSION

A commercial adsorbent, FeOOH, was characterized and its potential application performance on carbonate and bicarbonate removal was evaluated. The results showed that FeOOH could efficiently and quickly adsorb carbonate and bicarbonate from an aqueous solution. A pseudo-second-order model can fit the kinetic data obtained under the given test conditions well, and the rate constant is affected by the initial carbonate and bicarbonate concentration. In the test pH range (pH 5, 7, and 9), findings indicated that the use of FeOOH to remove carbonate and bicarbonate from an aqueous solution was not affected with change in pH. The Langmuir and Freundlich isotherm models characterized FeOOH-based carbonate and bicarbonate adsorption very well, but the Langmuir model fit the data better than the Freundlich model. The positive value of ΔH indicated that the adsorption of bicarbonate on FeOOH is endothermic.In summary, the overall performance of FeOOH on carbonate and bicarbonate removal showed the sorbent's promise for lowering carbonate and bicarbonate concentrations to desired or regulated levels in the water and wastewater industries.

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