

Effect of temperature on the removal of cobalt by Friedel's salt

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Abstract

The performance of Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$), a layered double hydroxide (LDHs), as an adsorbent for cobalt (Co^{2+}) removal from its solution was investigated. Friedel's salt was synthesized by reaction of tricalcium aluminate with calcium chloride. The stability of FS at different pHs was studied. Also, the adsorption behaviors of Friedel's salt for cobalt (Co^{2+}) from its solution at different concentrations and pH=4 at room temperature and 50°C was examined. The results showed that, high stability for FS in neutral medium (pH=6) than in basic (pH=8) and acidic medium (pH=4). In addition, the results indicated that the adsorbent FS had an outstanding ability for Co(II) adsorption. The maximum adsorption capacity of the FS for Co (II) removal can reach to 1903.44 mg/g. Furthermore, the increase in the temperature (50° C) effect positively on the rate of adsorption.

Keywords: LDHs, Friedel's salt, adsorption/ion exchange, cobalt, Temperature.

1.Introduction

Cobalt is one of concern of water contamination due to its harmful effects on human health. Harmful health effects that are a result of the uptake of high concentrations of cobalt are vomiting and nausea, vision problems, heart problems and thyroid damage (*Liu et al., 2014*). In recent years, various methods for heavy metal removal from wastewater have been extensively studied such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods (*Fenglian and Qi, 2011*). However, most of them do not lead to a satisfactory depollution considering the operational costs (*Marchetti et al., 2000*). Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated.

Adsorption on solid-solution interface is an important means for controlling the extent of pollution due to heavy metal ions (*Bulut et al., 2007& Raji et al., 1997*). Hence, investigation of new adsorbents with high effectiveness and cost in order to meet large numbers of demands from industrial and civil community is attracting increase attentions. To this end, layer double hydroxide (LDHs), especially, Friedel's salt (FS: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) may be one of the potential candidates due to its ion exchange characteristic.

Friedel's salt is formed in cements such as Portland cement, which contains large amounts of tri- calcium aluminate and belongs to the layer double hydroxide (LDHs) family (*Suryavanshi et al, 1996*). FS is the common name of the chlorinated lamellar double hydroxide (LDH), and called calcium chloroaluminate. Friedel's salt general formula is $\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$ and doubling all the stoichiometry, it can also be written as follows: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$.

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LDHs are a class of synthetic lamellar compounds with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{X+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations respectively A^{n-} is an anion or an organic anion [*Carriazo et al., (2007) & Wan et al., (2012)*]. LDHs with special crystal chemistry characteristics are promising adsorption materials in the treatment of waste water containing metals (*Ma et al., 2009; Wang et al., 2012 and Kwon et al., 1988*).

Stanimirova et al., (2007) involved the potential of hydrocalumite for cation removal. Some studies have shown that the order of cation selectivity is $Ca^{2+} < Mg^{2+} < Mn^{2+} < Cd^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Zn^{2+}$ at low pH via MgAl-LDHs. These provide the possibility of Zn^{2+} removal by hydrocalumite to form new LDHs phase.

Alaa et al., (2007) reported that the solubility of cobalt (II) is greatly decreased as the pH is increased from 2 to 6 causing an increase in adsorption affinity towards the clay surface. Adsorption of cobalt (II) at higher than 6 is inapplicable because of precipitation of cobalt ions at pH= 7.

Hayrettin et al., (2008) proved that the contribution of metal ion precipitation to the adsorption of Co^{2+} ions from aqueous solutions onto sepiolite has been analyzed as a function of pH. Abstraction and precipitation isotherms are constructed to isolate the precipitation of cobalt from the real adsorption. The contribution of all cobalt species against pH is calculated from the available solubility products or acid constants. It is found that at pH 8.2, cobalt hydroxide precipitate.

Feng et al., (2010) and Sheela et al., (2012) proved that there are a number of mechanisms by which heavy metals were adsorbed onto mineral materials from water, including ion-exchange, surfaced adsorption, dissolution-precipitation and (*Wang et al., 2012; Zhang and Hou 2007*) stated that no matter the surface or inner of the FS, ion-exchange played an important role during adsorption process.

Zhang et al., (2013) synthesized Friedel's salt to remove Cd^{2+} from water, the mechanisms of Cd^{2+} adsorption included surface complexation, surface precipitation and inter ion-exchange.

Hence, the objective of this study is to examine the performance of Friedel's salt as an adsorbent for cobalt removal from aqueous solution. The effects of various parameters such as concentration of cobalt solution, temperature and time were tested.

2. Materials and Methods

2.i. Materials:

The materials used in this work are obtained from "Merck" and "BDH" companies. These materials were calcium carbonate ($CaCO_3$), alumina (Al_2O_3), calcium chloride dihydrate ($CaCl_2\cdot 2H_2O$), cobalt chloride dihydrate ($CoCl_2\cdot 2H_2O$), sodium hydroxide (NaOH) and hydrochloric acid (HCl, assay 30→ 32 %). Most of the chemicals used are either analar grade materials or of the highest possible purity.

2.ii. Preparation of tricalcium aluminate C_3A ($3CaO\cdot Al_2O_3$):

Tricalcium aluminate was prepared by well mixing calcite and alumina in the molar ratio of 3: 1 and firing the mixture at 1350°C for 3 hours and three times. The formed C_3A was analyzed using X-ray diffraction technique as well as chemical analysis to be sure that there is no free lime present and the only phase formed is C_3A . The X-ray diffractogram is shown in Figure (1).

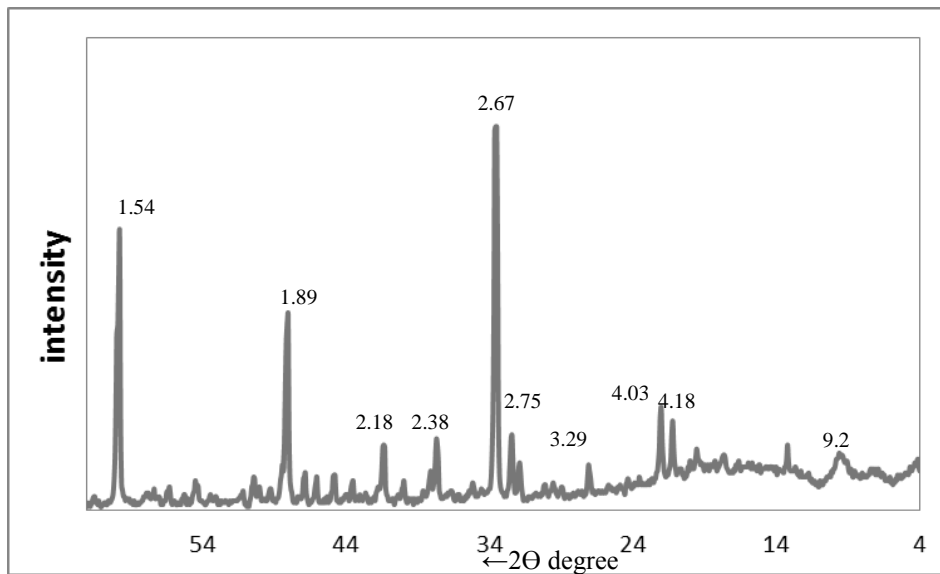


Figure (1): XRD pattern of the prepared C₃A.

2.iii. Preparation of Friedel's salt:

Friedel's salt is prepared by precipitation method, powdered tricalcium aluminate C₃A is slowly added to a solution of 0.10 M calcium chloride dissolved in distilled water and stirring for 24 hrs. The precipitate is collected via filtration then dried in an oven at 50° C for 24 hrs. The prepared Friedel's salt is identified by XRD as it shown in Figure (2).

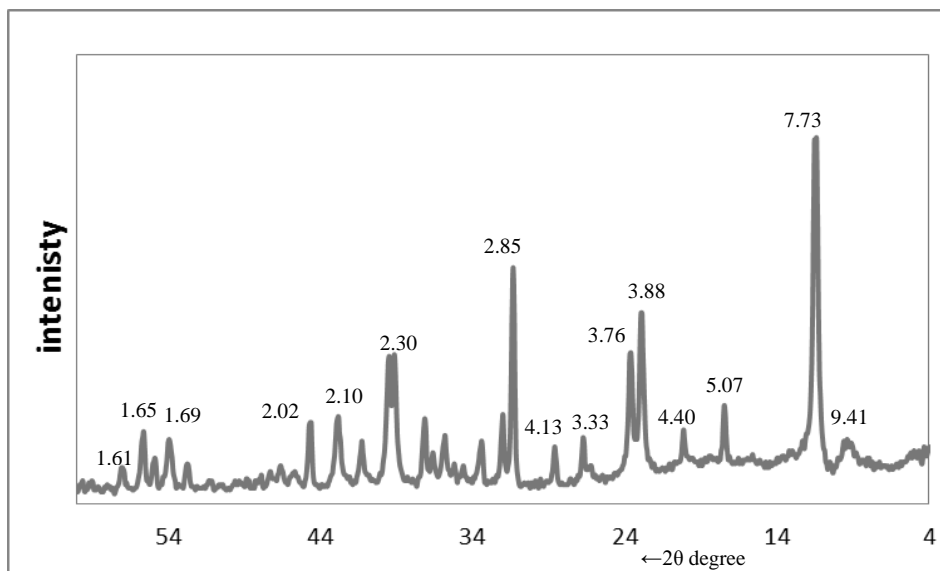


Figure (2): XRD pattern of the prepared Friedel's salt.

2.v. Procedure

To examine the stability of Friedel's salt, 0.10 gm of the prepared FS is added to 50 ml of distilled water after adjusting its pH to 4, 6 and 8 with dilute HCl or NaOH solutions for

different time intervals (0.5h, 3hrs, 6hrs, 1d, 3days and 14days). After each time, the precipitate is collected via filtration and dried at 50° C in an oven.

To examine the adsorption kinetics of Co(II) over Friedel's salt, 0.1 gm. of FS is added to 50 ml of Co(II) solution with initial concentration of 0.50, 3.00, or 8.00 mM with the initial pH equals 4.00 and stirring for different time intervals (0.5h, 3hrs, 6hrs,3days and 14days).

To examine the effect of temperature on the adsorption kinetics, the above experiment is carried out in thermostatic water bath adjusted at 50°C.

3. Results and Discussion

3.i. The solubility and stability of Friedel's salt at different pH values.

The effect of different pH values (4, 6 and 8) on the stability and solubility of Friedel's salt is examined and the results are cited in Table (1) and represented graphically in Figure (3) which represented the concentration of calcium ion in solution. The results showed that the maximum stability of FS is at pH=6 while it decreases at pH = (4 or 8). This decrease in stability of FS is as a result of increase the concentration of the dissolved Ca^{2+} . Hence, the maximum stability of FS is at pH=6. Generally, the concentration of the dissolved calcium Ca^{2+} in solution at different pH values increase by increasing time. The XRD show decrease in the characteristic peak of FS by the time and disappear completely for long ages, anew phase appear at $d=3.01$ for $CaCO_3$ noticed as a result of carbonation. Whereas, at pH= (4 & 6) after (14d) another new phase is noticed at $d= 4.85$ for $Ca(OH)_2$ due to reaction of dissolved Ca^{2+} ions in solution with hydroxyl group, as it illustrated in Figures (4, 5 and 6).

Table (1): The concentration of the dissolved Ca^{2+} ion in the solution at different pH's.

pH	Ca^{2+} (mg/l)					
	0.5 h	3 hrs	6 hrs	1 days	3 days	14 days
4	78.7	81.8	86.7	98.85	104.75	124.8
6	55.9	65.6	66.9	88.25	95.9	108.4
8	173.9	190	191.2	201.4	201.95	208.4

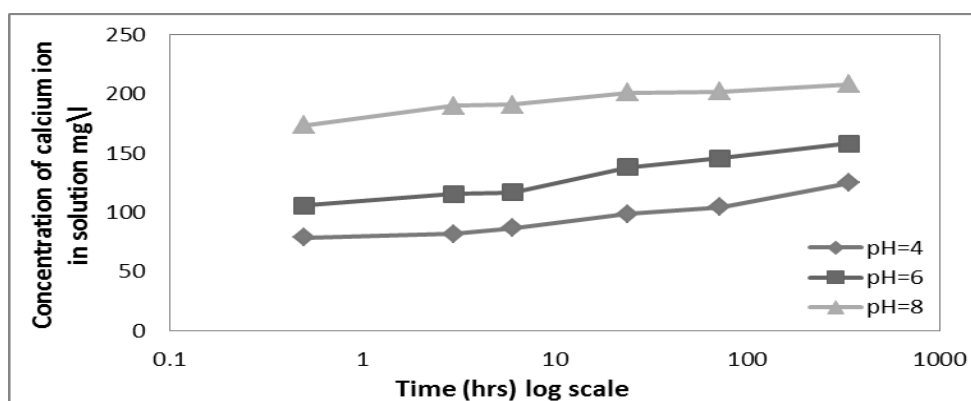


Figure (3): Solubility of Friedel's salt at different pH values

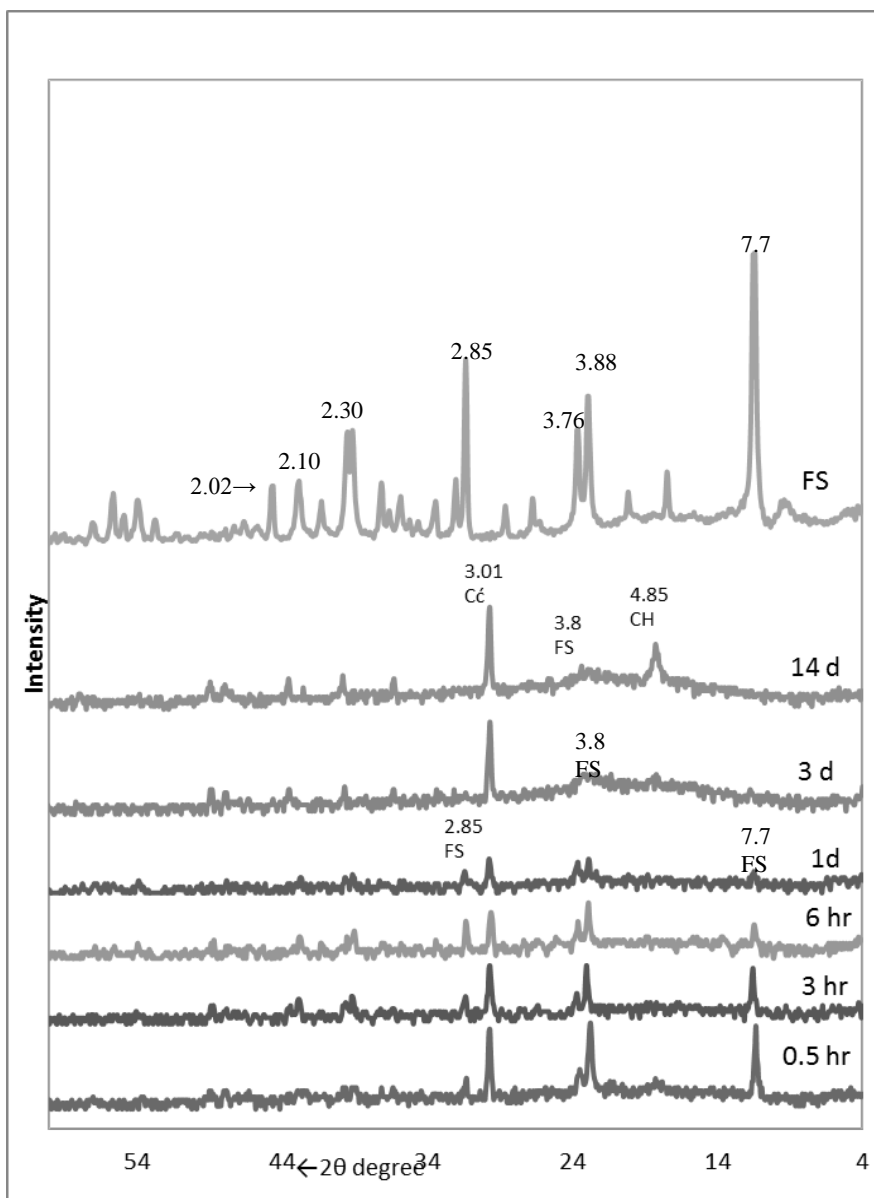


Figure (4): XRD pattern of FS at pH= 4.

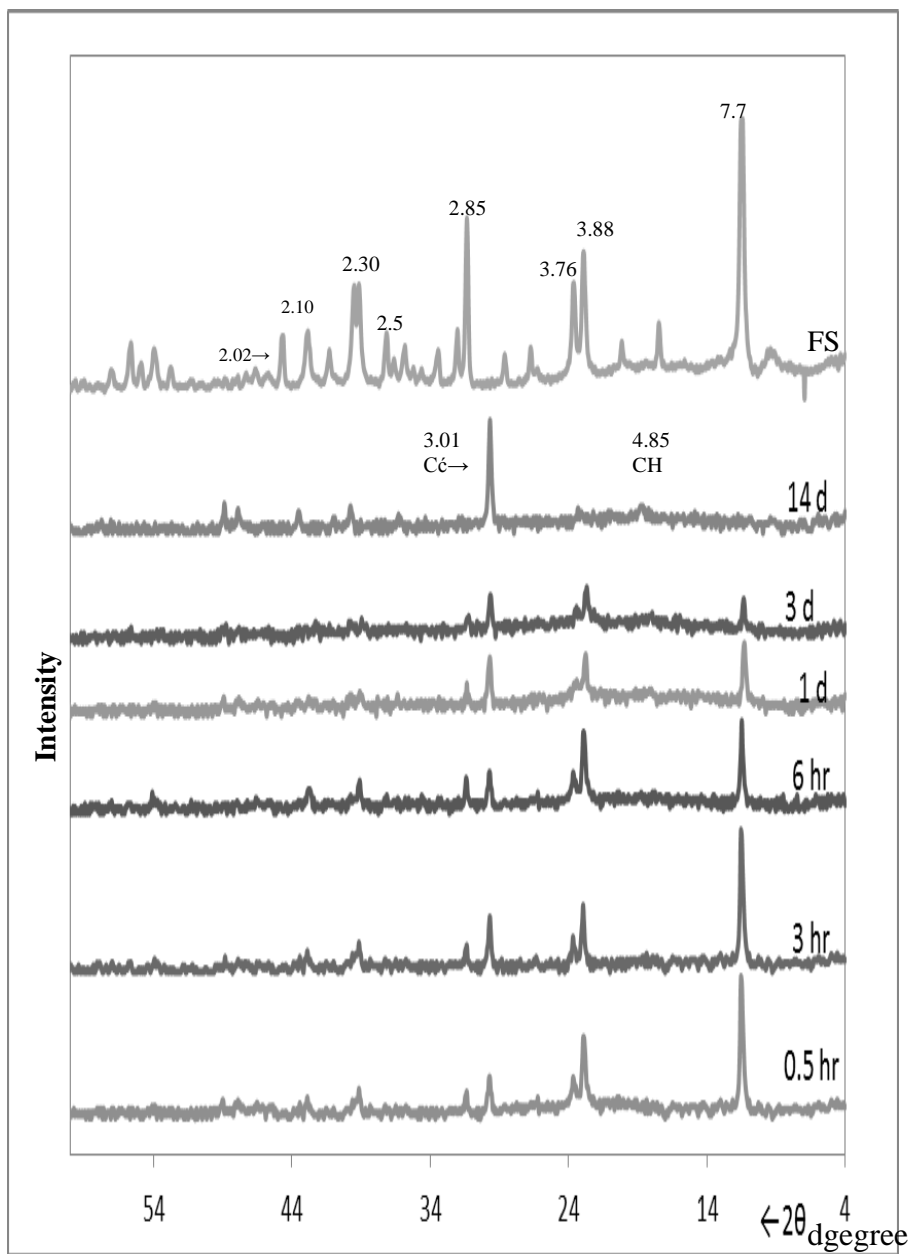


Figure (5): XRD pattern of FS at pH=6.

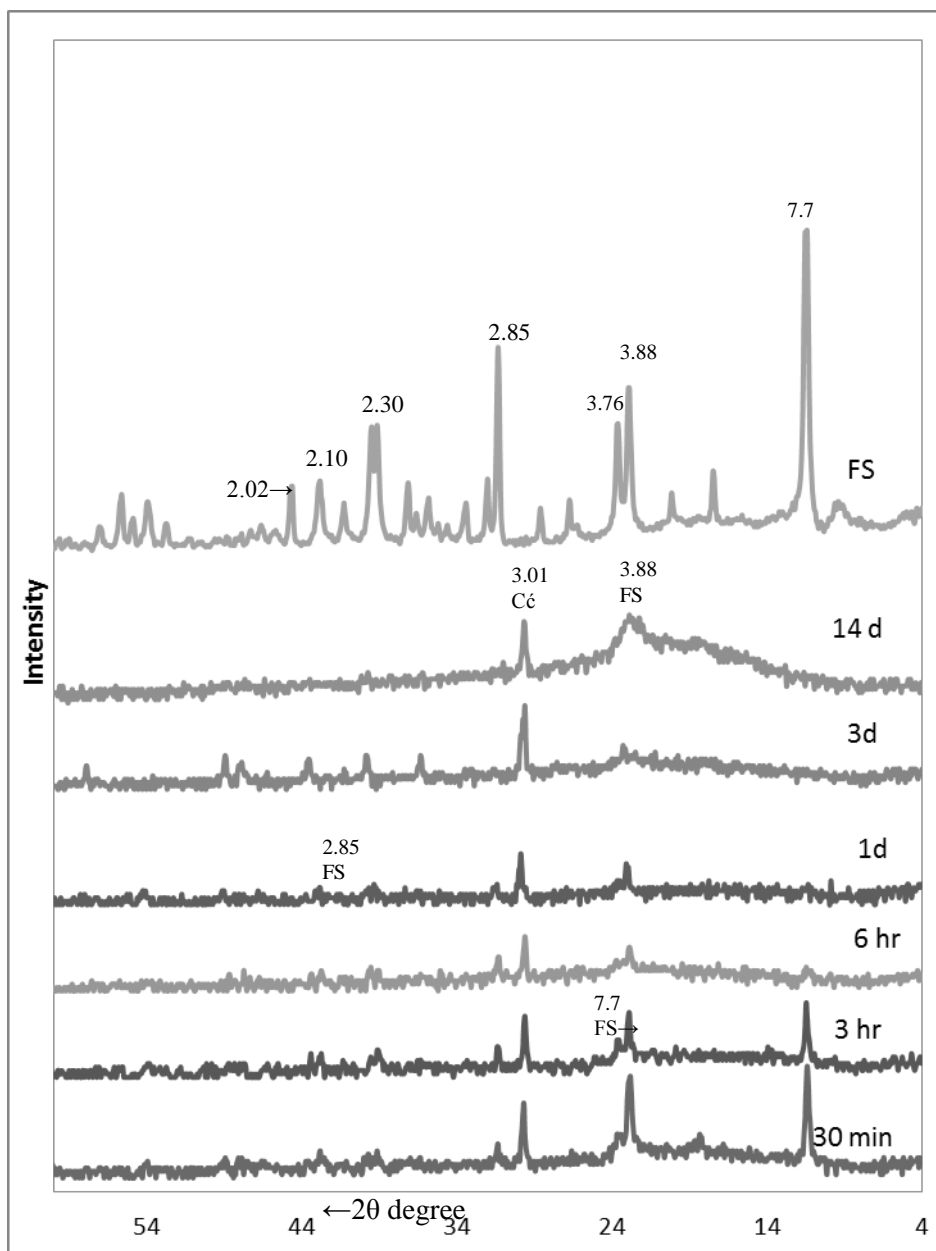


Figure (6): XRD pattern of FS at pH= 8.

3. ii. Adsorption of Co (II) at room temperature

At low concentration of cobalt solution (0.5mM) at pH=4, it is found that the characteristic peaks of FS decrease from 0.5 hour up to 3 days and disappear completely after 14 day. While for high concentration (3 and 8mM) the characteristic peaks of FS disappear completely at different time intervals from 0.5 hour up to 14 days as shown in Figures (8, 9 and 10). While, the concentration of cobalt ions in solution decrease with increasing time as shown in Table (2) and represented graphically in Figure (7).

Table (2): The concentration of residual cobalt ion in solution after adsorption at pH=4

Conc. mM	Co ²⁺ (mg/l)				
	0.5 h	3 hrs	6 hrs	3 days	14 days
0.5	0.13	0.05	0.03	0.01	0
3	0	0	0	0	0
8	50	27.81	19	0.08	0.03

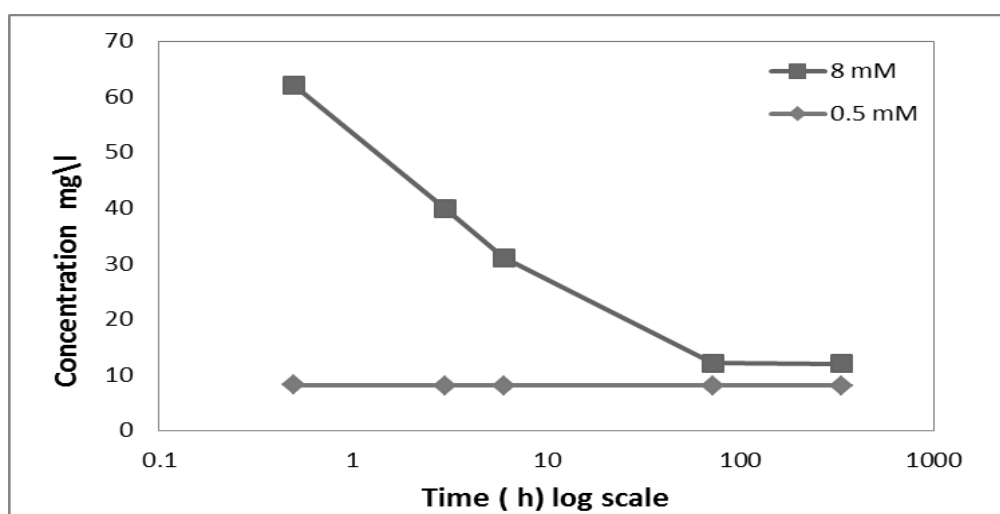


Figure (7): Concentration of cobalt ions in solution after adsorption (0.5 and 8 mM) of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ at pH= 4 for different time intervals.

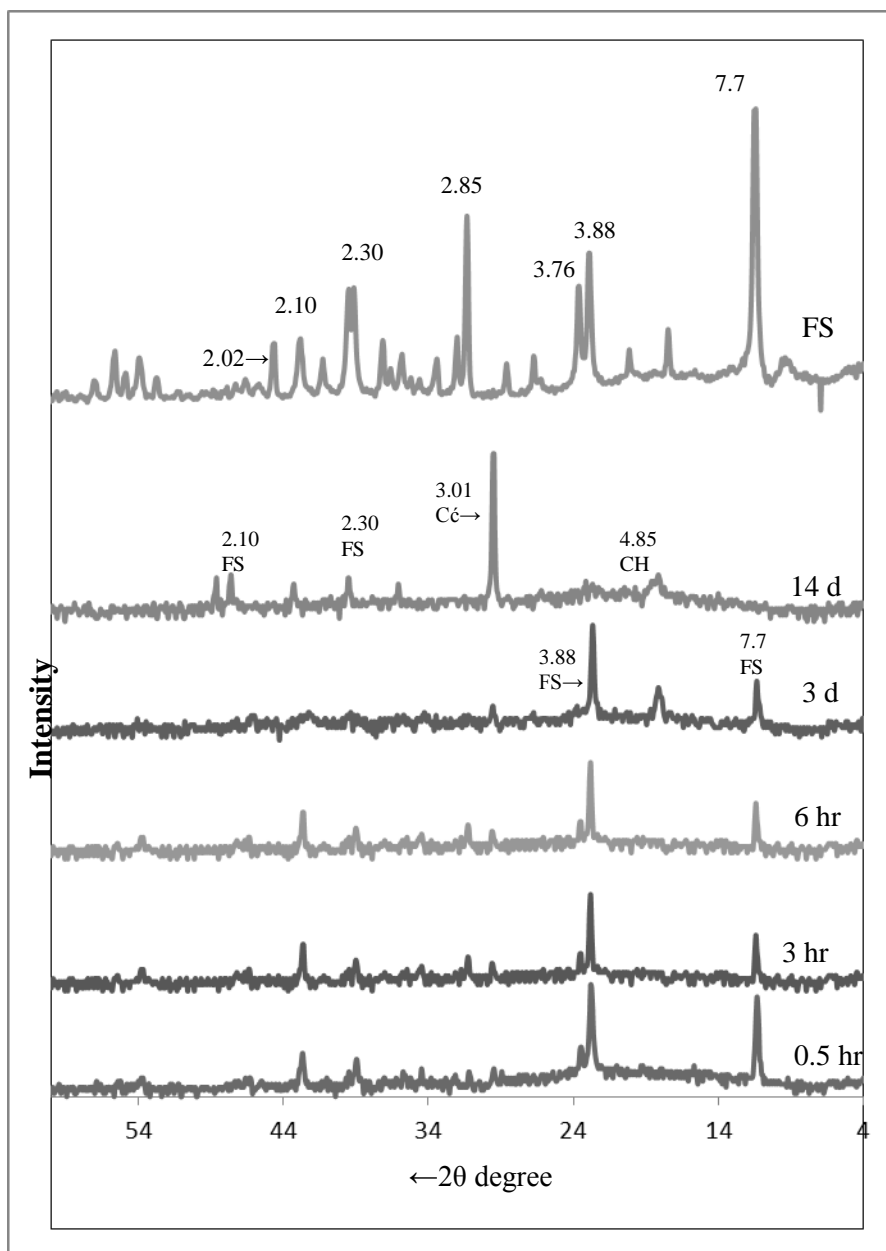


Figure (8): XRD patterns of the mix FS with 0.5 mM $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ at pH= 4

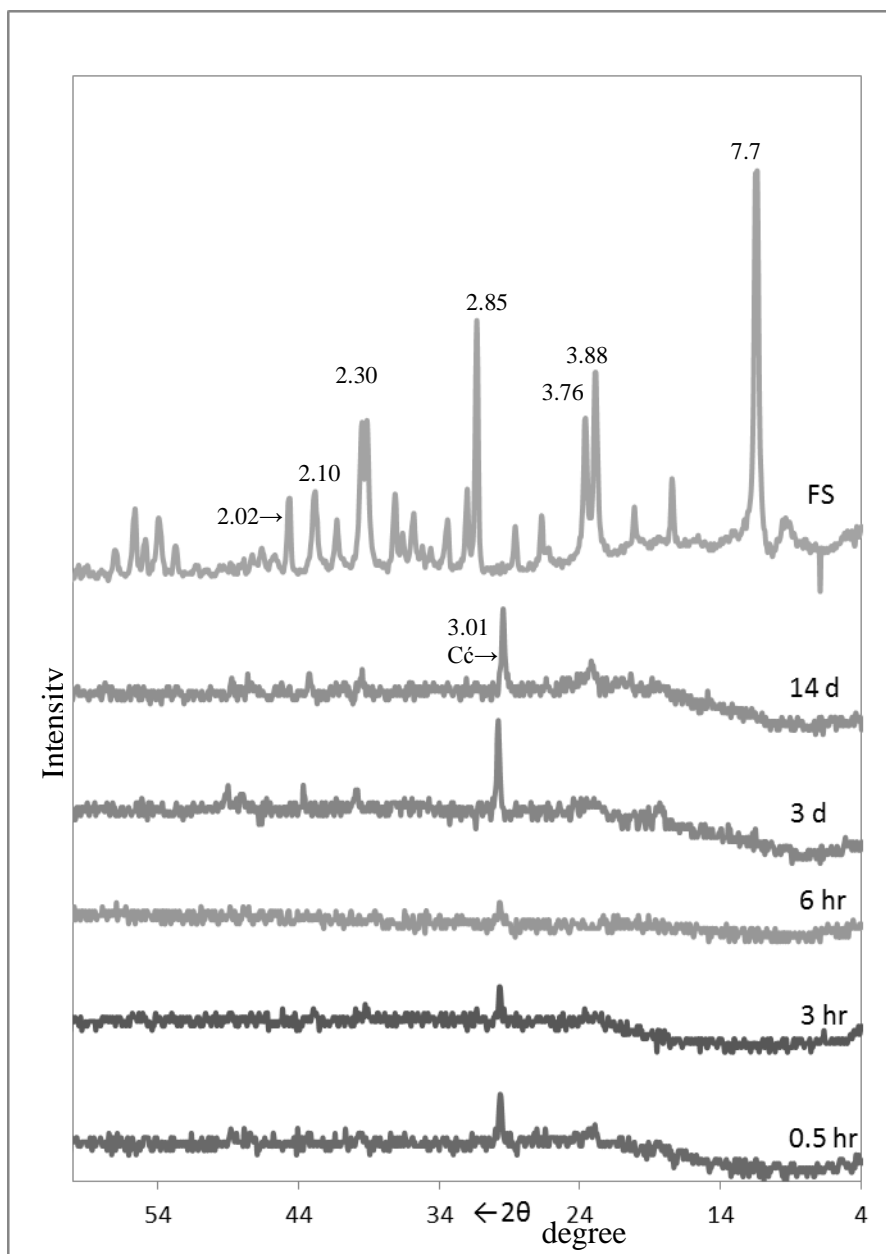


Figure (9): XRD patterns of the mix FS with 3 mM $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ at pH=4.

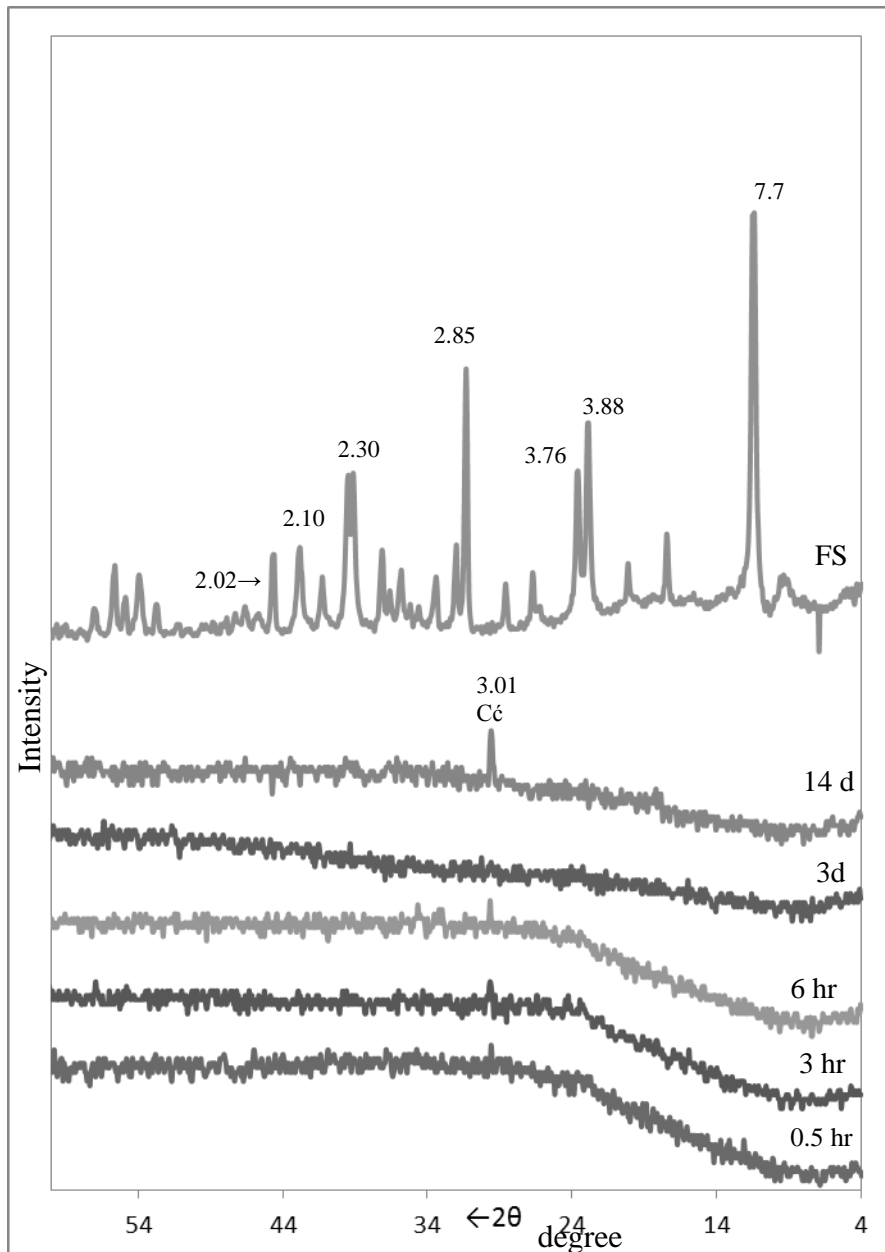


Figure (10): XRD patterns of the mix FS with 8 mM $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ at pH= 4.

3.iii. Effect of temperature on adsorption of 0.5 Mm of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ at pH=4

On comparing the results represented in Figures (8 and 11), we can notice that at room temperature (Figure, 8), increasing time cause a decrease in the intensity of FS characteristic peaks, while at 50°C (Figure, 11) all the characteristic peaks of FS disappeared completely from the first 0.5 hour.

The results of atomic absorption is cited in Table (3) and represented graphically in Figure (12). It is observed that the concentration of cobalt metal ions in solution after adsorption at 50°C fewer than adsorption at room temperature. Hence, it is clear that the temperature effect positively on the rate of adsorption of cobalt on the surface of FS.

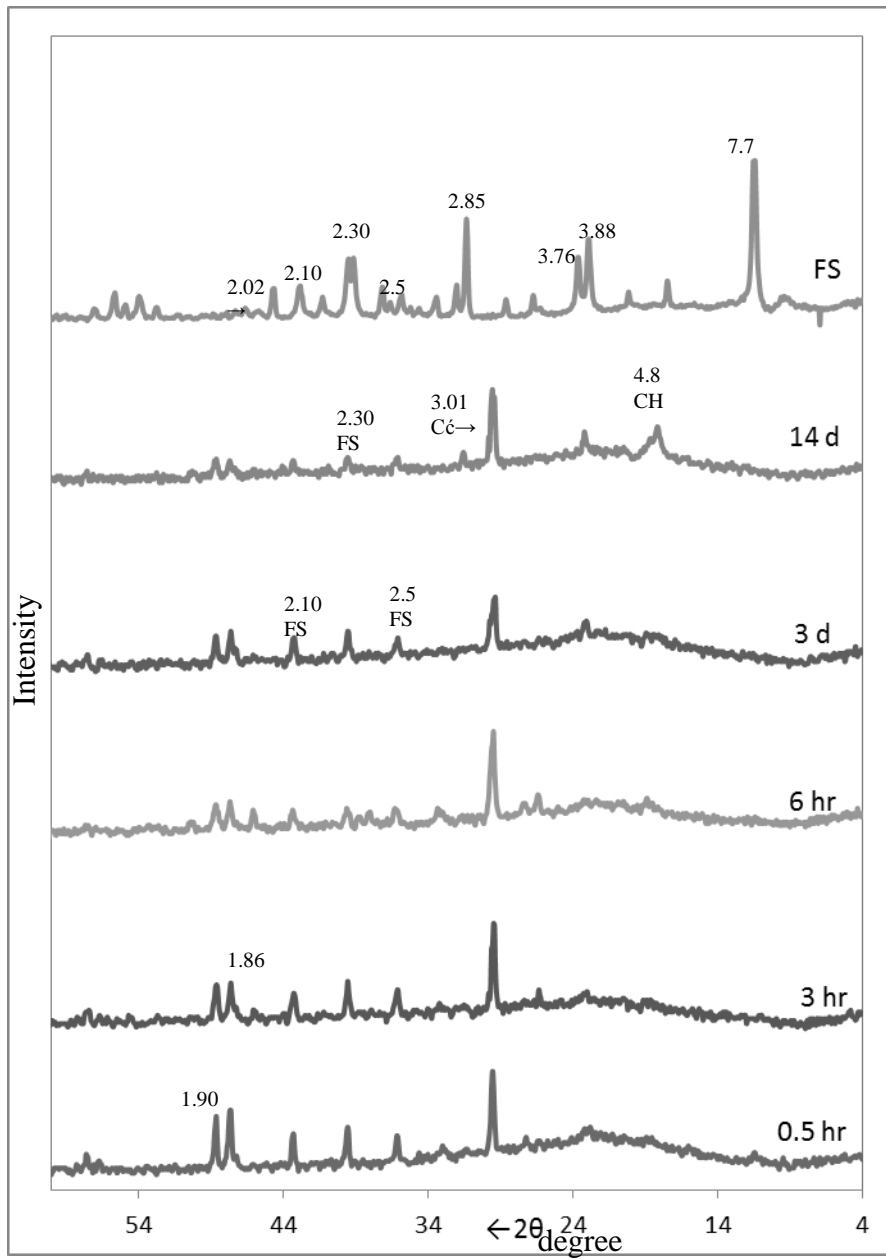


Figure (11): XRD patterns of Co- treated FS at pH= 4 and 50°C.

Table (3): The concentration of cobalt in solution (0.5 Mm CoCl₂.6H₂O) after adsorption at pH=4 at 50°C

pH		Co ²⁺ (mg/l)				
		0.5 h	3 hrs	6 hrs	3 days	14 days
4	Co ²⁺ (soln.)	0.25	0.13	0.06	0	0

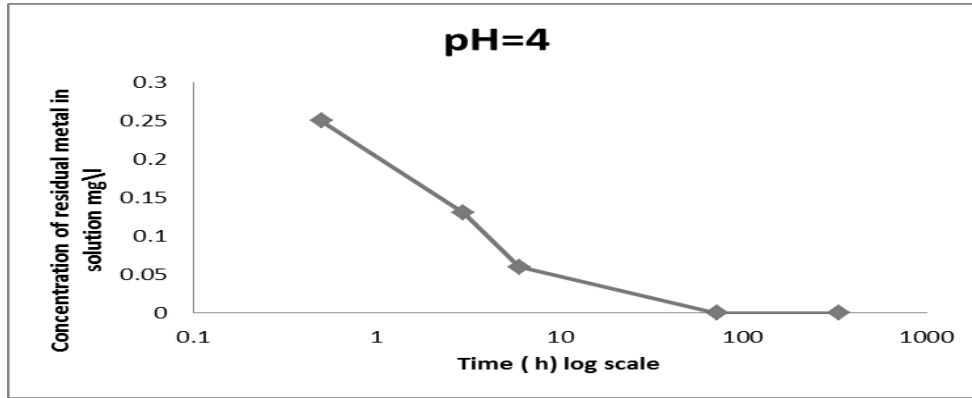
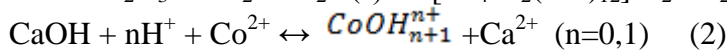
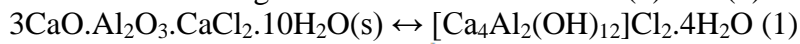


Figure (12): The concentration of cobalt metal in solution after adsorption 0.5Mm of CoCl₂.2H₂O at pH=4 at 50°C for different time intervals.

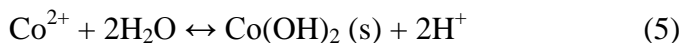
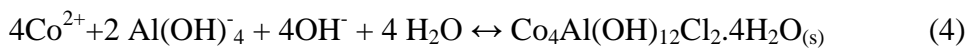
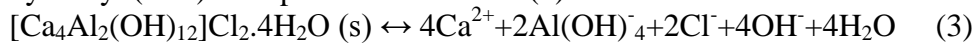
3. iv. Mechanism of cobalt adsorption

Finally, the results indicate that cobalt adsorption did not obviously change the layered crystal structure of FS. The most removal of metal cations (Co²⁺) may be attributed to ion-exchange and surface precipitation as illustrated in the mechanism below.

The mechanisms of Co²⁺ adsorption included surface complexation, surface precipitation and inter ion exchange. Firstly, the surface hydroxyl groups of the FS and cation Co (II) ions would take part in ion-exchange/surface reaction, and surface complexes formed through electrostatic binding reaction. Surface reactions (1) and (2) as followed



Secondly, the surface of the FS partly dissolved as reaction (3). Then, Co (II) can combine with released anions (Al(OH)₄⁻, OH⁻ and Cl⁻) to form surface precipitates as reaction (4). It was consistent with the mechanism proposed by (Liu *et al.*, 2011) for Zn⁺² adsorption on hydrocalumite. Additionally, there could be some Co(OH)₂ precipitates due to dissolved hydroxyl (OH) as expressed in reaction (5):



Thirdly, the Co (II) could replace original interlayer ion Ca⁺² in to the interlayer spacing as reaction (6). The ion-exchange reaction of FS may be schematically depicted by following reaction:



In the present study, the behavior of Co(II) adsorption by FS was significantly affected by surface reactions. The effects of single variables study indicated that the initial Co (II) concentration was main influence factor through the adsorption process. The influence of high Co(II) concentration on Co^{2+} ions diffusion was important. For high initial Co(II) concentration, due to ‘loading effect’, all the surface sorption sites were occupied by Co(II).

Additionally, the XRD results indicated that the particles of Co-treated FS and $\text{Co}(\text{OH})_2$ precipitation were not detected. These results revealed that Co (II) removal by the FS mainly through surface reactions in this experiment.

4. Conclusion

The main points that could be derived from this study are summarized in the following:-

- Friedel's salt is more stable at (pH=6) than (pH=4) and (pH=8), Hence, the stability and solubility of Friedel's salt affected by pH.
- FS is considered as a good adsorbent for cobalt ion (Co^{2+}), FS adsorbed high concentration of cobalt very quickly with a very high efficiency (99.9 %).
- Increase the temperature lead to increase in the rate of adsorption of cobalt ion Co^{2+} by Friedel's salt.
- Temperature is a good catalytic factor for increasing the rate of adsorption of metal ion (Co^{2+}) by Friedel salt.

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الملخص باللغة العربية

تأثير درجة الحرارة على إزالة الكوبلت بواسطة ملح فريدل

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ملح فريدل ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) تم اكتشافه بواسطة العالم فريدل عام 1897 ويعتبر ناتج ومكون أساسي من نواتج تأدريت الأسمنت، يعتبر ملح فريدل من المعادن متبادله الأيونات حيث انه ينتمي لعائلته الهيدروكسيدات مزدوجة الطبقات (LDHs) وهي عبارة عن مركبات تركيبها من الداخل عبارة عن رقائق أو طبقات لذلك ملح فريدل يستخدم لإزالة الكثير من المعادن الثقيلة عن طريق خاصية التبادل الأيوني ومن هذه المعادن الكاديوم، الخارصين والزنك. **الهدف من هذه الرسالة:-**

هو استخدام ملح فريدل لإزالة كاتيون الكوبلت الثنائي Co^{2+} من محاليله تحت ظروف مختلفة من درجة الحرارة وتركيز المحاليل الأولية.

خطوات التحضير:-

- 1 - تم تحضير ثلاثي ألومنيات الكالسيوم (C_3A) في صورة نقيه باستخدام مواد نقيه من أكسيد الألومنيوم و كربونات الكالسيوم.
- 2 - تم تحضير ملح فريدل باستخدام طريقة الترسيب عن طريق تفاعل ثلاثي الومنيات الكالسيوم مع كلوريد الكالسيوم.
- 3 - كما تم تحضير تركيزات مختلفة من كلوريد الكوبلت (0.5، 3 و 8 مللي مول\ لتر) وضبط الأس الهيدروجيني لمحاليل الكوبلت عند (4) وإضافه 0.1 جم من ملح فريدل وتركهم للتقليب عند الأزمنه المختلفه.

وأوضحت الاختبارات التي أجريت على النواتج ما يلي:

- 1 - ملح فريدل أكثر ثباتا في الوسط المتعادل عنه في الوسط الحامضي أو الوسط القاعدي.
- 2 - ملح فريدل له القدرة على امتصاص تركيز عالي من الكوبلت تصل الى 8 مللي مول او ما يعادل 1903.4 مجم\جم.
- 3 - زيادة درجة الحرارة له تأثير إيجابي علي علميه التبادل الأيوني.