Removal of copper ions by Friedel´s salt

Essam A. Kishar[1], Tarek M El-sokary[2], Doaa A. Ahmed1 and Mai Sh. Mohamed[1]*

1.Chemistry Department, Faculty of Girls, Ain Shams University, Cairo, Egypt.

2. Housing and Building National Research center, Cairo, Egypt.

Abstract:

Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) or ($Ca_4Al_2(OH)12Cl_2(H_2O)_4$), a layered double hydroxide (LDHs), is a calcium aluminate hydrate and used as an adsorbent for copper (Cu^{2+}) ions from aqueous solution .In our study,we carefully examined the adsorption behaviors of Friedel's salt toward different concentrations of copper solutionat pH = 4. Both experimental and modeled data indicate that Friedel's salt can adsorb all copper ions from solution at pH=4 for total [Cu/mg] in solution= 724.8 mg/l (3mM/l) with high efficiency >99.9 % of adsorbent FS.The FS, at different pHs,shows a higherstability at pH=6 thanat pH=4 andpH=8. Finallythis study suggests that Friedel's salt is a potential cost − effective adsorbent for Cu [II] removal.

Keywords: LDHs, Friedel's salt, adsorption/exchange, copper.

1.Introduction:

Copper is considered to be an essential trace element for plants and animals; it is a component of many metalloenzymes and respiratory pigments (***Demayo and Taylor, 1981***)

It is also the oxygen coupling site in haemocyanin, the respiratory blood pigment in many molluscs and certain other invertebrates (***Birge and Black, 1979***) and is important for maintaining optimum plant metabolism, and its deficiency results in reduced synthesis of the copper-containing electron carriers' plastocyanin and cytochrome oxidase. The reduction of these electron carriers reduces photosynthesis and respiration ***(Barón et al., 1995)***. However, copper becomes toxic to aquatic biota when biological requirements are exceeded, so the removal of copper is urgently needed. In the recent years, various methods have been developed to remove Cu (II) and Cu(II) is a pH dependent includingion exchangewich has the advantage of allowing the recovery of metallic ions, but it is expensive. 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 C. et al.(1997) reported that the use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs.

---

*Corresponding author**:**email.maishahin21@yahoo.com

Friedel′s salt is a (LDHs) , where LDHs, as ***Orthman et al. (2003) and Braterman P.S. et al.(2004)***reported, are a family of anionic clay minerals consisting of cationic brucite layers and exchangeable interlayer anions.Its chemical formula can be written as$[M_{1-x}^{+2} M_x^{+3}(OH)^{x-}] (A^{n-})_{x/n}.MH_2O$, where M^{+2} represent any divalent metal cation ,M^{+3} any trivalent metal cation and A^{n-} an anion (inorganic or organic) [***Alvarez-Ayuso et al. (2005); Carriazo D. et al.(2007) ; Kameda et al.(2008) and Wan et al. (2012).***

MaJ. et al. (2009) reported that Friedel′s salt is widely used in removing harmful anions and cations such as arsenate, chromium, silicate, phosphate and cadmium by its ion exchange characteristics.***Qian et al. (2006)***found that Friedel′s salt can strongly fix heavy metals from sludge wastes.

Zhang et al. (2007)found that it can rapidly adsorb large amounts of selenate from water. In addition ***Dai et al. (2009)*** examined the adsorption behaviors of Friedel′s salt for chromium (VI) from aqueous solution at different concentrations and pHs. However, there are only a few studies on the interaction between Friedel′s salt and heavy metal cations in solution, especially for the removal of cadmium ***[Juanjuan et al., 2013].***

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

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

The objective of this study is to examine the performance of Friedel's salt as an adsorbent toward copperion from aqueous solution. The effects of various parameters such as concentration of heavy metals, pH and time are tested.

2. Materials and Methods

The materials used in this work are obtained from "Merck" and "B.D.H." companies. These materials are calcium carbonate ($CaCO_3$), alumina (Al_2O_3), calcium chloride dihydrate ($CaCl_2.2H_2O$),copper nitrate hydrate ($Cu(NO_3)_2.10H_2O$), sodium hydroxide and hydrochloric acid (HCl, assay 30→ 32 %).

2.i.a. Preparation of tricalcium aluminate C$_3$A (3CaO.Al$_2$O$_3$):
Tricalcium aluminate is prepared by mixing together calcium carbonate $CaCO_3$ and aluminum oxide Al_2O_3 in the molar ratio 3:1 respectively, then burning at 1400° C for sufficient time.The synthesized C$_3$A is identified by its X-ray diffraction (XRD) patterns as shown in **figure(1).**
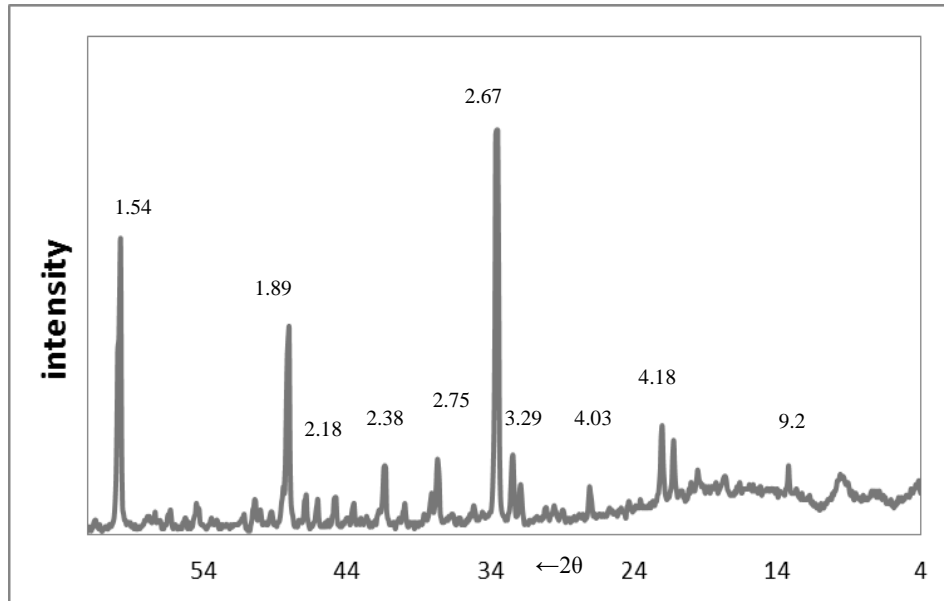
Figure (1): X-Ray diffraction pattern of the prepared C_3A.

2.i.b. Preparation of Friedel's salt:

Friedel's salt is prepared bythe precipitation method.Powdered tricalcium aluminate (C_3A) is slowly added to a solution of calcium chloride dissolved in distillated water under vigorous stirring for 24hrs at least. The precipitate is collected via filtration then dried in an oven at 50° C for 24 hours. The synthesized Friedel's salt is identified by X-ray diffraction (XRD) as shown in **figure(2).**
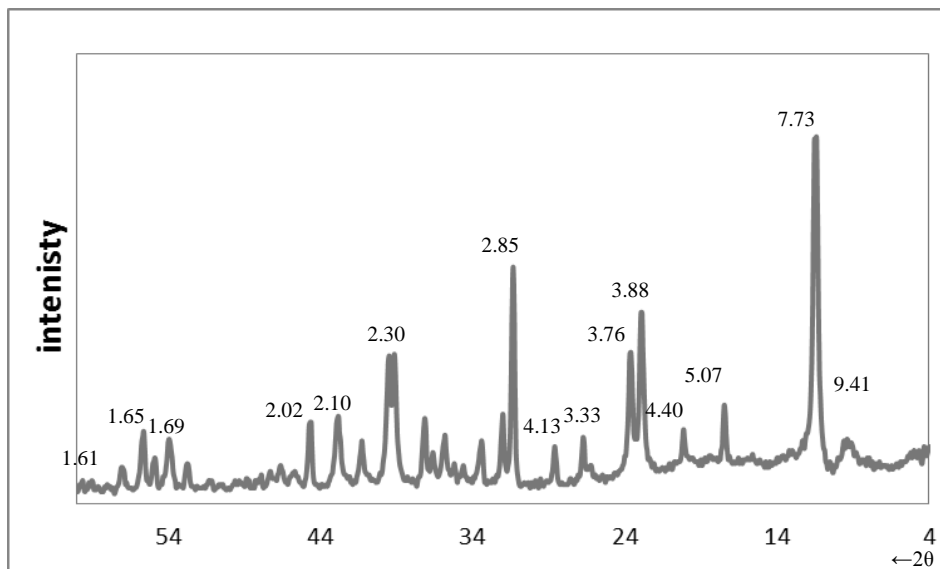

Figure (2): X- Ray diffraction pattern of the prepared Friedel's salt.

2. ii. Procedure.

2. ii.a. Stability of adsorbent FS .

To examine the stability of Friedel's salt, 0.10 gm of the prepared FS is stirred in 50 ml of distilled water after adjusting its pH to (4, 6 or 8) with dilute HCl or NaOH solutions for different time intervals (0.5h, 3h, 6h, 1d, 3d and 14d). The precipitate is collected via filtration and dried at 50°C in an oven, and then analyzed by XRD,while, the filtrate is used for the determination ofCa^{2+} concentration using the atomic absorption techniques.

2. ii.b.Adsorption of Cu (II).

To examine the adsorption kinetics of Cu^{+2}, series of Cu (II) solutions of different concentrations are prepared by dissolving cupper nitrate hydrate (0.5, 3 and 8 mM) and adjusting the initial pH at 4.0 with dilute HCl .In a conical flask, 0.1 gm of FS is stirred with 50ml of the prepared metal solutions for different time intervals (0.5hr, 3 hr, 6hr, 3d and 14 days). After each time interval ,themixture is filtered and the precipitate is collected and dried at 50 °C and examined by XRD.The concentration of the metal ion and calcium ions is determined in the filtrate by atomic adsorption spectroscopy.

3.Results and Discussion

3. i. Structural features of Friedel's salt:

The XRD pattern of the synthesized compound**figure (2)** is in excellent agreement with that recorded on PDF 78–1219 in the database of the International Center for Diffraction Data, which suggests that the synthesized compound is typical of the Friedel phase, with a nominal chemical formula of Ca$_4$Al$_2$(OH)$_{12}$Cl$_2$(H$_2$O)$_4$.

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

The effect of different pHs (4, 6 and 8) on the stability and solubility of Friedel's salt is examined and the result are represented graphically in **figure (3)**. The maximum stability of FS is at pH=6 while it it decrease at higher pH=8 or lower pH=4,since it decompose after 3 hours in pH=4and after 6 hours at pH=8as show from **figure (3)**.Generally, the concentration of the dissolved calcium Ca^{2+} in solution at different pHs increase by increasing time. The XRD patternsillustrated in **figures (4, 5 and 6)**confirmed the result of concentration of dissolved calcium ion in solution.
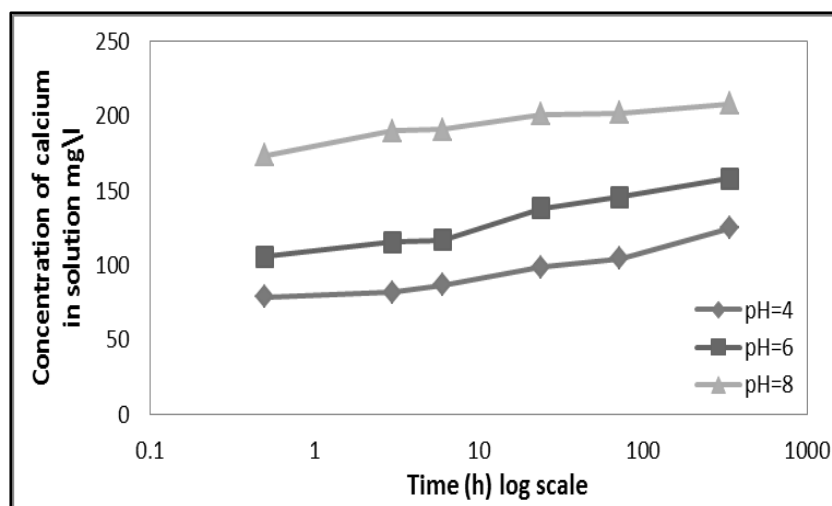
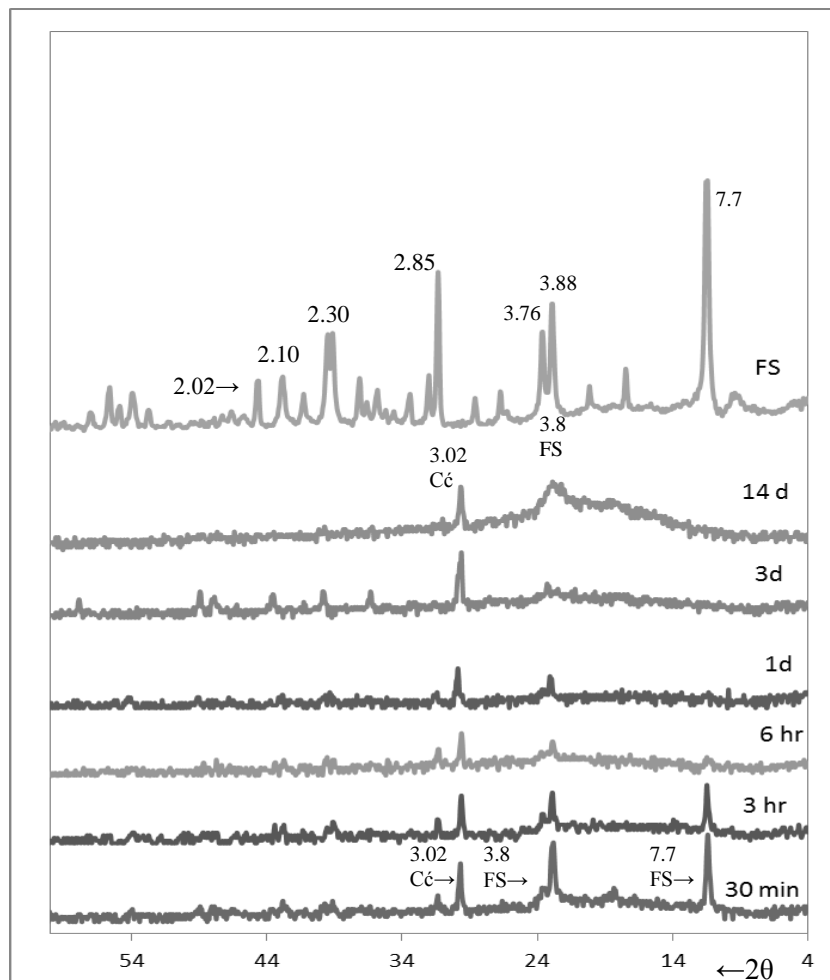**Figure (3):**Solubility of Friedel's salt at different pH values.

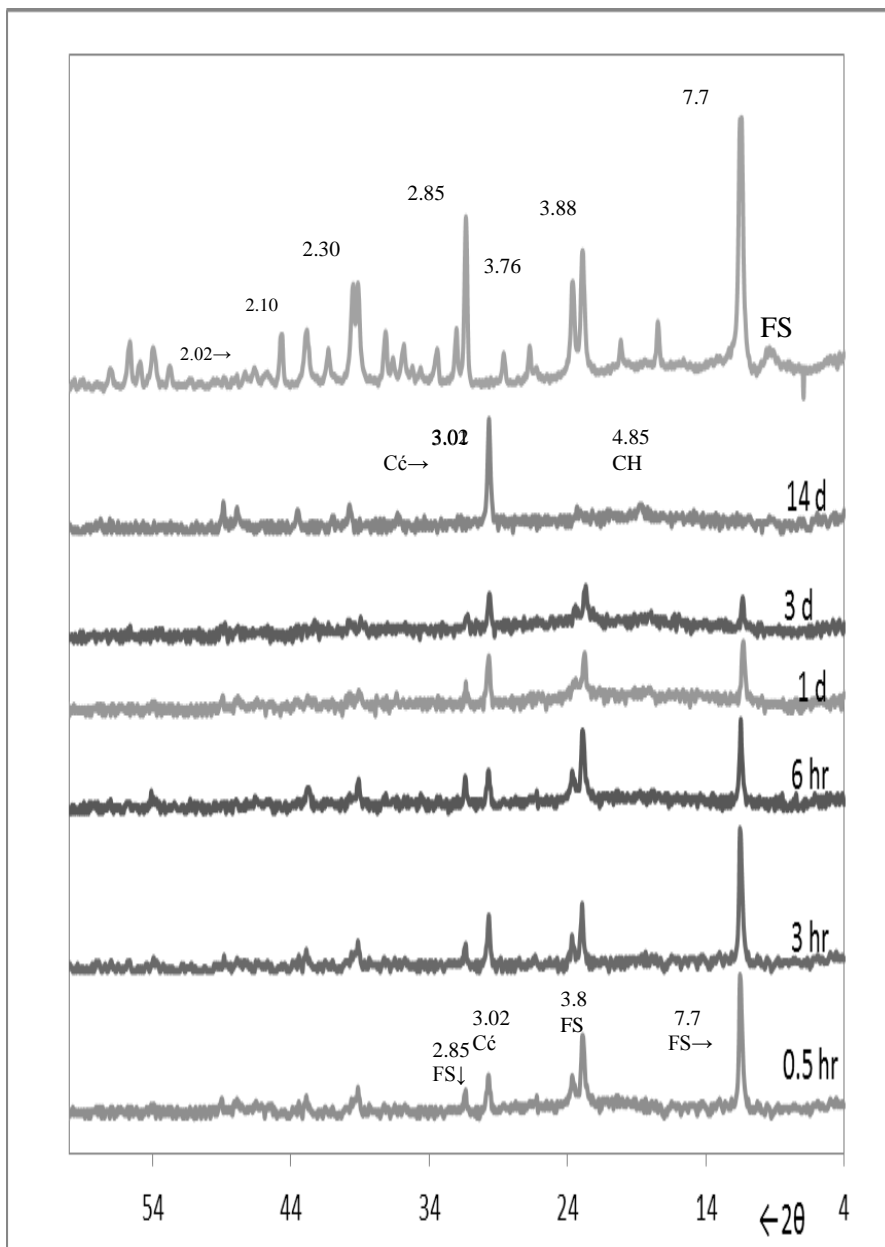**Figure (4):** X-ray diffraction patterns of FS at pH= 4.

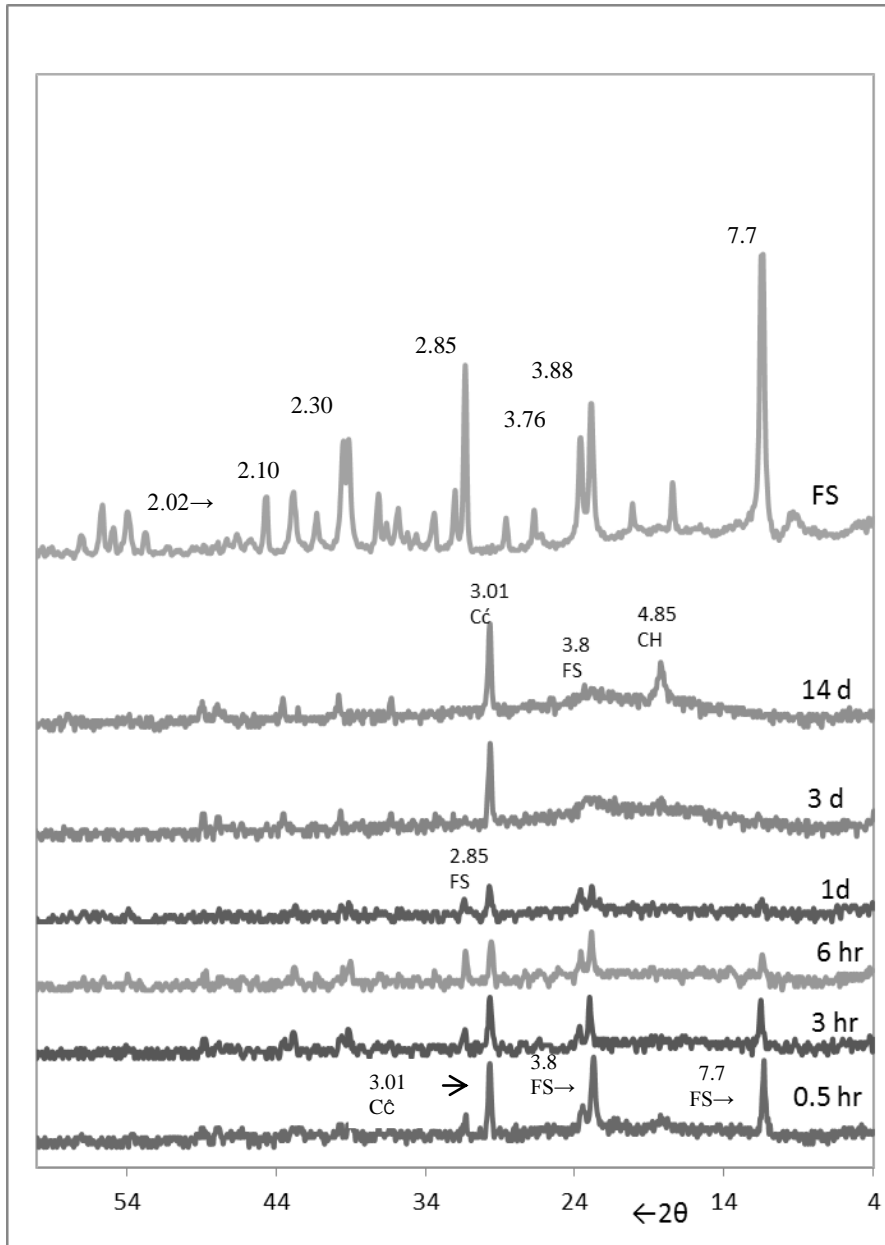**Figure (5):** X-ray diffraction patterns of FS at pH=6.

Figure (6): X-ray diffraction patterns of FS at pH= 8.

3. iii. Adsorptionof copper (II) on FS at pH=4

The adsorption kinetics of Cu^{+2}having different concentrations (0.5, 3 and 8mM/l) at pH =4 and atdifferent time intervals (0.5, 3, 6 hours and 1, 3 and 14days of hydration) by prepared Friedel's salt are studied.

3.iii.a. Atomicadsorption analysis:

The results of this analysis are cited in **table (1)** and show, diagrammaticallyin**figure (7).**The results indicates that in case of 0.5 mM/l copper ion, the amount of copper adsorbed onto FS surface increase with time till 14 days, while all copper ions are adsorbed at FS surface after 0.5 hours till 14 days in case of Cu^{+2}concentration 3mM/l as shown in **table (1)**.

On the other hand , we can observe a complete adsorption of copper ions onto FS surface after one day till 14 days in case of 8mM/l copper ions concentration.

Table (1): The concentration of residual copper (II) ions in solutionafter adsorption at pH=4.

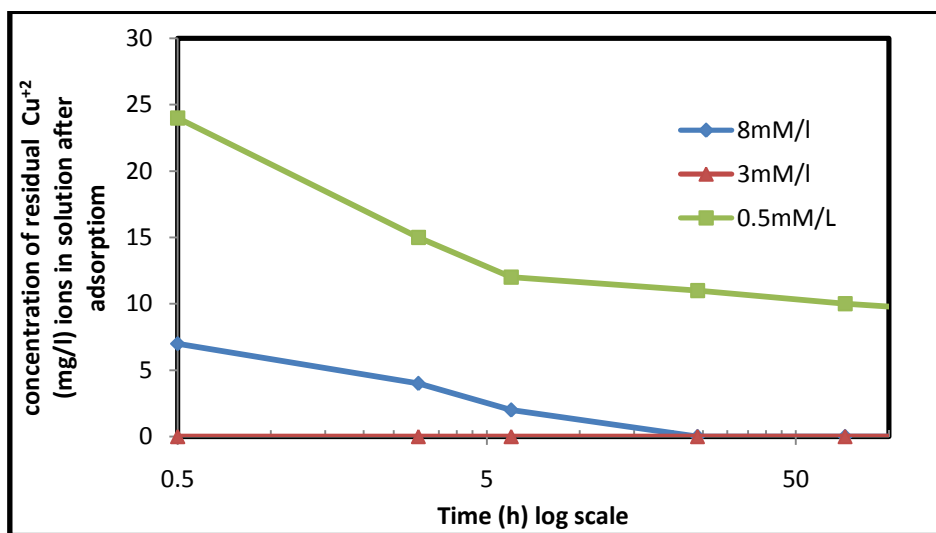| Conc. (mM/l)	Cu^{2+} (mg/l)					
	0.5 h	3 h	6 h	1d	3 d	14 d
0.5	24.00	15.00	12.00	11.0	10.00	9.00
3	0.00	0.00	0.00	0.00	0.00	0.00
8	7.00	4.00	2.00	0.00	0.00	0.00

Figure (7): Relation between residual Cu^{+2}ionsconcentration in solution and time (h) in a semi log scale at pH=4 for different solution.

3. iii.b. Phases composition results.

Thephase's composition of the hydration products after adsorption of copper by FS is examined by using X-ray diffraction techniques.**Figure(8)** illustrates, the X- ray diffractograms for the solid phase of 0.5mM/l of copper ions onto FS at pH=4.The intensity of the peak representing the FS phase disappears completely after 3 hours till 14 days .It is obvious that, calcium carbonate peak appears after 0.5hr and still appears till 14 days, which may be attributed to carbonation.

Figure (9) shows that all the characteristic peaks of F.S. appear sharp after 0.5hr then decrease gradually till 14 days. Also, the characteristic peak for $CaCO_3$at (d=3.02) is clearly noticed till14 days, while the characteristic peak of $Ca(OH)_2$ at (d= 4.8) starts to appear after one day and till 3 days with an increase in its intensity .

The XRD pattern of Cu-treated FS (**Figure 10**)show that the appearance of calcium hydroxide peak at d= 4.8 resulted from the reaction between dissolved calcium in water with hydroxyl group and calcium carbonate peak appearingat d= 3.02 may be due to carbonation.
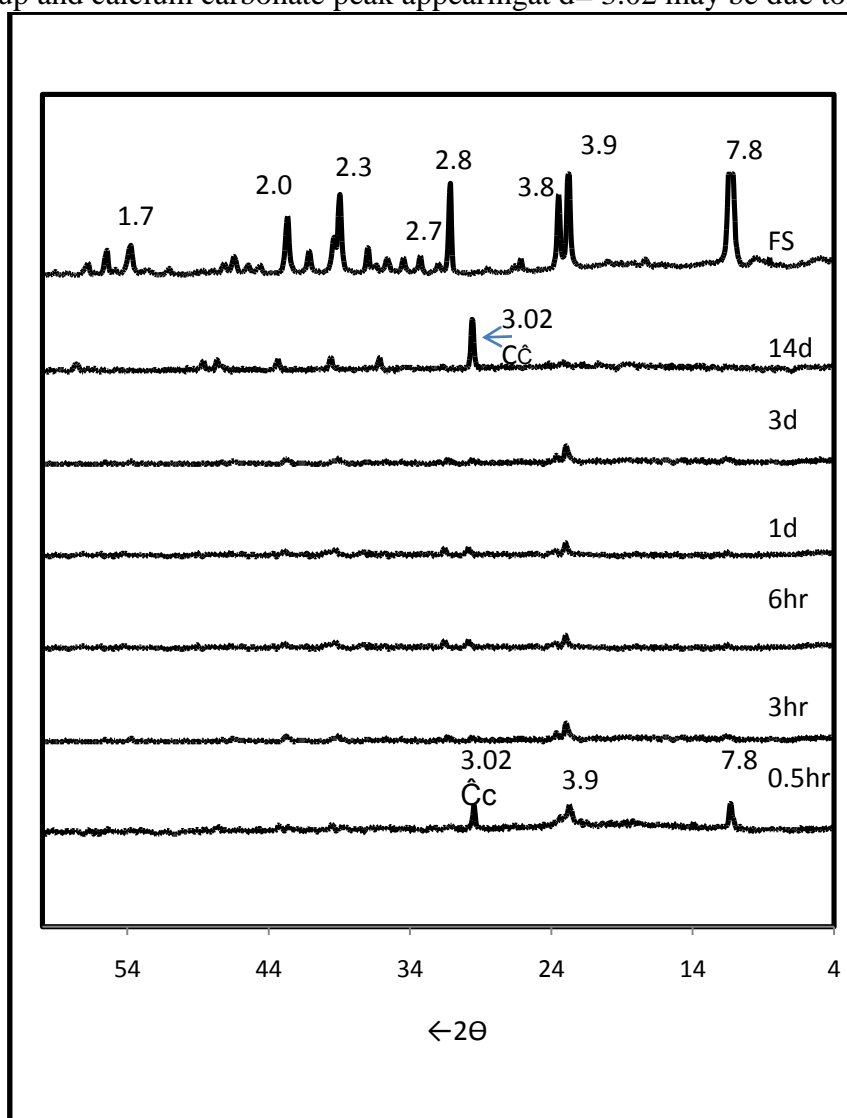

Figure (8): X- ray diffraction of prepared FS after adsorption of 0.5 mM/l of Cu^{+2} at pH=4 at different time intervals.
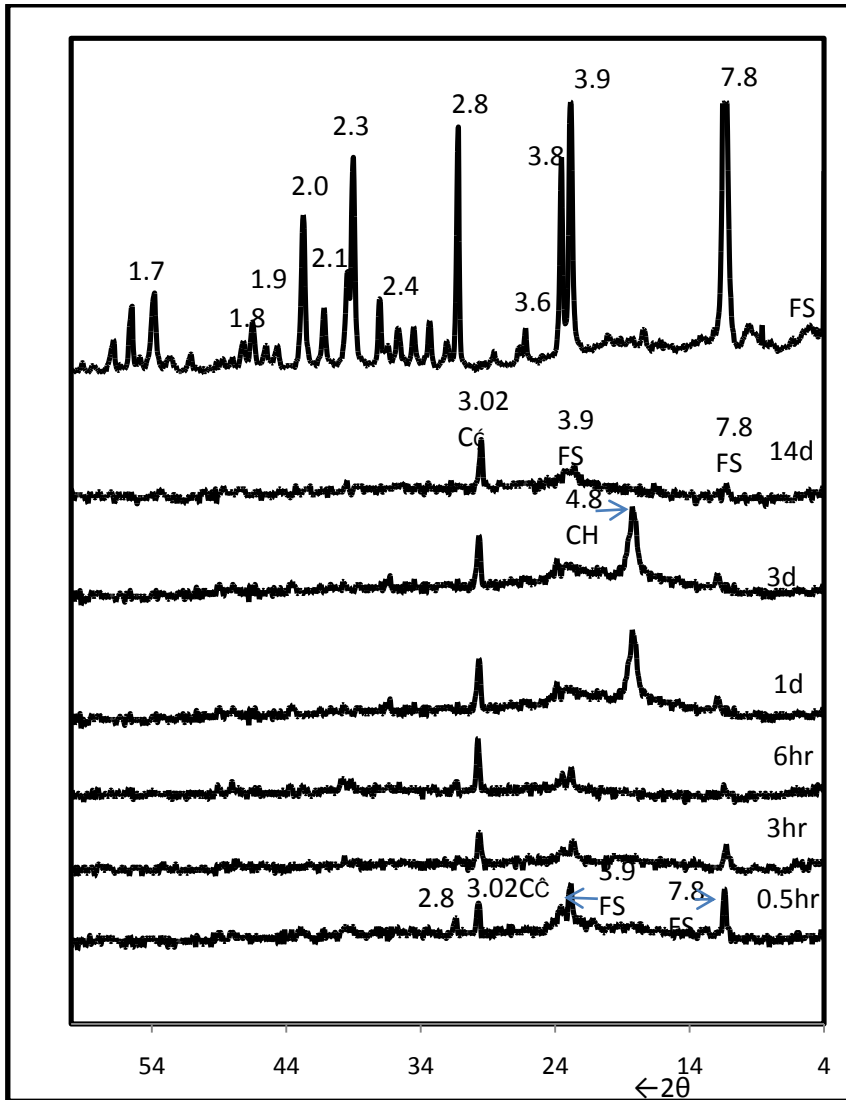
Figure (9):X- ray diffraction of prepared FS after adsorption of 3 mM/l of Cu^{+2} at pH=4 at different time intervals.
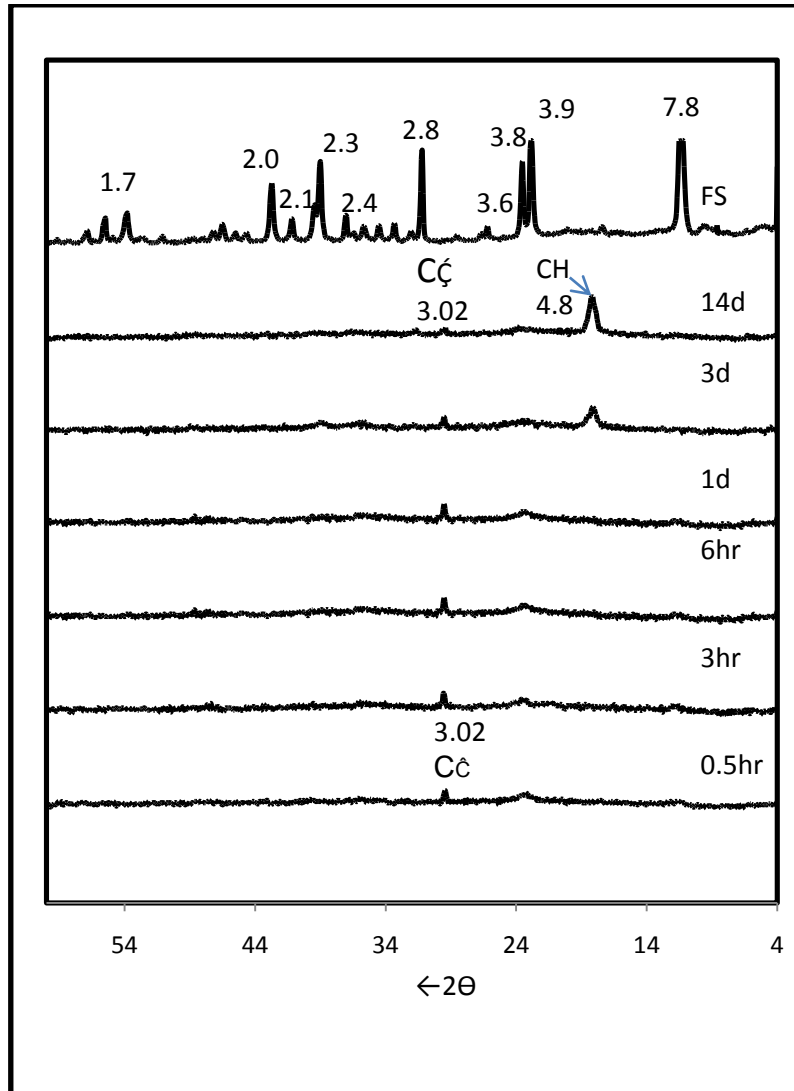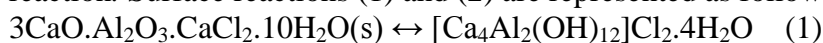
Figure (10): X- ray diffraction of prepared FSafter adsorption of 8 mM/l of Cu^{+2} at pH=4 at different time intervals.

Finally, the results indicate that copper adsorption does not obviously change the layered crystal structure of FS. Most removal of metal cations (Cu^{2+}) may be attributed to ion-exchange and surface precipitation as illustrated in the mechanism below.
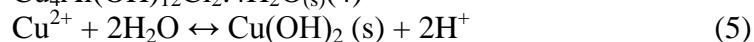
The mechanisms of Cu^{2+} adsorption include surface complexation, surface precipitation and inter ion exchange.

The surface hydroxyl groups of the FS and cation Cu (II) ions would took part in ion-exchange/surface reaction, and surface complexes formed through electrostatic binding reaction. Surface reactions (1) and (2) are represented as followes

$3CaO.Al_2O_3.CaCl_2.10H_2O(s) \leftrightarrow [Ca_4Al_2(OH)_{12}]Cl_2.4H_2O$ (1)

$\equiv CaOH + nH^+ + Cu^{2+} \leftrightarrow \equiv CuOH^{n+}_{n+1} + Ca^{2+}(n=0,1)$ (2)

The surface of FS partly dissolved following reaction (3). Then, Cu (II) can combine with released anions ($Al(OH)^-_4, OH^-$ and Cl^-) to form surface precipitates as shown in reaction (4). It is consistent with the mechanism proposed by ***Liu et al. (2011)*** for Zn^{+2} adsorption on

hydrocalumite. Additionally, there could be some $Cu(OH)_2$ precipitates due to dissolved hydroxyl (OH^-) as expressed in reaction (5):

$$[Ca_4Al_2(OH)_{12}]Cl_2.4H_2O \text{ (s)} \leftrightarrow$$
$$4Ca^{2+}+2Al(OH)^-_4+2Cl^-+4OH^-+4H_2O \quad (3)$$

$$4Cu^{2+}+2 Al(OH)^-_4 + 4OH^- + 4 H_2O \leftrightarrow$$
$$Cu_4Al(OH)_{12}Cl_2.4H_2O_{(s)}(4)$$

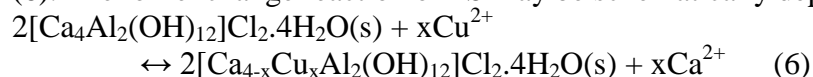$$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2 \text{ (s)} + 2H^+ \quad\quad\quad (5)$$
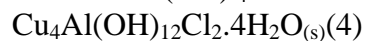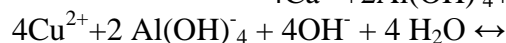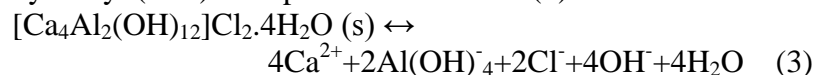
The Cu (II) could replace original interlayer ion Ca^{+2} in to the interlayer spacing as reaction (6). The ion-exchange reaction of FS may be schematically depicted by following reaction:

$$2[Ca_4Al_2(OH)_{12}]Cl_2.4H_2O(s) + xCu^{2+}$$
$$\leftrightarrow 2[Ca_{4-x}Cu_xAl_2(OH)_{12}]Cl_2.4H_2O(s) + xCa^{2+} \quad (6)$$

In the present study, the behavior of Cu (II) adsorption by FS is significantly affected by surface reactions. The effects of single variables study indicate that the initial Cu (II) concentration is the main influencing factor through the adsorption process. The influence of high Cu (II) concentration on Cu^{2+} ions diffusion is important. For high initial Cu (II) concentration, due to 'loading effect', all the surface sorption sites may be occupied by Cu (II). Thus, removal of Cu (II) adsorption may be reduced with increasing initial Cu (II) concentration.

Additionally, the XRD results, indicate that the particles of Cu-treated FS and Cu $(OH)_2$ precipitation cannot be, detected. These results reveal that Cu (II) removal by the FS may be mainly through surface reactions.

4.Conclusion

The main points that could be derived from this study are summarized in the following:-
1- The stability and solubility of Friedel's salt are affected by pH.
2- The stability of FS in solutions is changed according to pHs of the solutions, the higher stability in at pH=6 and lower stability at pH=4and pH=8.
3- There are adsorption properties of FS toward Cu^{+2} in solutions and its properties depend on pHs and concentration of cations.
4- Friedel's salt adsorb all copper ions from the solution at pH = =4, where the total copper concentration in solution is 3mM/l rather than for 0.5 and 8 mM/l copper concentrations.

References

Alvarez-Ayuso E., Nugteren H., "Purification of chromium (VI) finishing wastewaters using calcined and uncalcined Mg–Al–CO3–hydrotalcite", WaterResarch, <u>39</u>, 2535–2542(2005).

Barón, M., Arellano J. and Gorgé J.," Copper and photosystem II:controversial relationship", Journal of Physiological Plant <u>94</u>,174-180 (1995).

Birnin Y. and Glasser F.P. "Friedel's salt, its solid solutions and their role in chloride binding", Cement and Concrete Research, <u>28</u>, 1713–1723(1998).

Braterman P., Xu Z. and Yarberry F., "Hand book of layered materials ", Marcel Dekker, New York, 373-474 (2004).

Dai Y., Qian G., Cao,Y., Chi, Y., Xu Y., Zhou J., Liu Q., Xu Z P.andQiao S., "Effective removal and fixation of Cr(VI) from aqueous solution with Friedel's salt" ,Journal of Hazardous Materials, $\underline{170}$(2-3), 1086-1092(2009).

Demayo, A., and Taylor M.," Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives "Site-Specficguidness", Volume $\underline{1}$Inorganic (1981).

Feng Y A , Gong J L , Zen G M , Niu Q Y , Zhang H Y and NiuC G,"Adsorption of Cd(II) and Zn(II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents".Journal of Chemical Engineering, $\underline{162}$(2): 487– 494(2010).

Juanjuan Z., Zhao He., Hongbin Cao., Heping Li. and Zhibao Li., "Removal of Cd^{2+} from water by Friedel's salt (FS: $3CaO·A1_2O_3·CaCl_2·10H_2O$): Sorption characteristics and mechanisms", Journal of Environmental Sciences, $\underline{25}$(9), 1719–1725(2013).

Kameda T., Takeuchi H. and Yoshioka T, "Uptake of heavy metal ions from aqueous solution using Mg-Al layered double hydroxides intercalated with citrate, malate, and tartrate", journal of Separation and Purification Technology, $\underline{62}$(2): 330–336 (2008).

Liu, Q., Li, Y. J., Zhang, J., Chi, Y., Ruan, X. X., Liu, J.Y., and Qian, G. R., "Effective removal of zinc from aqueous solution by hydrocalumite", Chemical Engineering Journal, $\underline{175}$, 33-38(2011).

Ma J., Li Z., Y G D. and Babacan K., "Desilication of sodium aluminates solution by Friedel's salt (FS: $3CaO·A1_2O_3·CaCl_2·10H_2O$)". Journal of Hydrometallurgy, $\underline{99}$(3-4), 225–230(2009).

Orthman, Zhu H. and Lu G.,"Use of anion clay hydrotalcite to remove coloured organics from aqueous solutions", Journal of Sep. Purif. Technol., $\underline{31}$, 3153–59(2003).

RajiC., Shubha K. andAnirudhan T.," Use of chemically modified sawdust in the removal of Pb(II) ions from aqueous media",Indian Journal of Enviromental Health $\underline{39}$(3), 230-238(1997).

Sheela T., Nayaka Y., Viswanatha R., Basavanna S. and Venkatesha T G, "Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles", Journal of Powder Technology, 217, 163–170(2012).

Wan D., Liu R., Qu J. ,Li S. and Zhang J. "Adsorption of nitrite from aqueous solutions onto calcined (Mg- Al) hydrotalcite of different Mg/Al ratio ", Journal of Chemical Engineering , $\underline{195}$, 241-247 (2012).

Wang, C., Liu J., Zhang Z., Wang, B., and Sun, H., "Adsorption of Cd(II), Ni(II), and Zn(II) by Tourmaline at Acidic Conditions: Kinetics, Thermodynamics, and Mechanisms", Industrial & Engineering Chemistry Research, <u>51</u>, 4397-4406 (2012).

Zhang D., Jia Y., MaJ. and Li Z B. "Removal of arsenic from water by Friedel's salt (FS 3CaO .Al$_2$O$_3$.10H$_2$O)",Journalof Hazardous Materials, 170(2-3) ,1086-1092(2011).

Zhang S. and Hou W., "Sorption removal of Pb (II) from solution by uncalcined and calcinedMgAl-layered double hydroxides", Chineese Journal of Chemistry, <u>25</u>(10), 1455-1460(2007).

الملخص باللغه العربيه

إزاله أيونات النحاس بواسطةملح فريدل

عصام عبد العزيز كيشار[1] طارق محمد السكري [2] دعاء عبد المنعم احمد [1] و[1] مي شاهين محمد

1. قسم الكيمياء ، كليه البنات ، جامعه عين شمس ، القاهره ، مصر
2. مركز بحوث البناء والإسكان ، القاهره ، مصر

تم تحضير وتعريف ملح فريدل (3CaO.Al$_2$O$_3$.CaCL$_2$.10H$_2$O) سنه 1897 علي يد العالم فريدل علي انه ينتمي لعائله الهيدروكسيدات مزدوجه الطبقات (LDHs) و هي مجموعه مكونه من معادن الأيونيه تتكون من حزمه من الطبقات الموجبه وطبقات داخليه متبادله سالبه . ملح فريدل له المقدره علي إزاله الأنيونات والكاتيونات الضاره من المحاليل ، حيث تم إستخدامه لإزاله بعض العناصر الثقيله من مياه الصرف الصحي مثل الكادميوم والخارصرين والرصاص والسيلينات والكروم والفوسفات والسليكات .

والهدف من هذه الدراسه هوإستخدام ملح فريدل لإزاله عنصر النحاس من المحاليل بتركيزات مختلفه و تحت أسهيدروجيري (4) عند أزمنه متفرقه .وقد تم إستخدام ملح فريدل لما له من المقدره علي إمتزاز الأيون علي السطح عن طريق تبادل الايونات وذلك بهدف القضاء علي تلوث المحاليل بهذا العنصروايضا دراسه ميكانيكيه إمتزاز هذا المعدن علي سطح ملح فريدل .

وفيما يلي ملخص لما تم في هذه الدراسه :

١ - تم تحضير ملح فريدل من تفاعل الومينات ثلاثي الكالسيوم مع كلوريدالكالسيوم .

٢ - تم تحضير تركيزات مختلفه من نترات النحاس (0.5 – 3 – 8) ملي مول / لتر .

٣ - ضبط الأس الهيدروجيني لمحاليل النحاس عند 4 وإضافه 0.1 جم من ملح فريدل مع التقليب عند أزمنه مختلفه(0.5، 3 و 6 ساعه، 1،3و 14 يوم) .
وفيما يلي ملخص ماتم إستنتاجه من هذه الدراسه :

١ - الذوبانيه والثبات لملح فريدل يعتمدان علي الأس الهيدروجيني.

٢ ـ يتغير ثبات ملح فريدل بتغيير الأس الهيدروجيني للمحلول ، فأعلي ثبات لملح فريدل يكون عندأس هيدروجيني =6 وأقل ثبات عند أس هيدروجيني = 4.

٣ ـ ملح فريدل له خواص لإمتصاص الكاتيونات مثل كاتيون النحاس وتتغير الخواص بتغير الأس الهيدروجيني وتركيز الكاتيون .

٤ ـ ملح فريدل لديه المقدره علي إمتصاص كل أيونات النحاس من المحلول عند أس هيدروجيني = 4 حيث التركيز الكلي لمحلول النحاس = 3 ملي مول/لتر.