Removal of copper ions by Friedel’s salt

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Abstract:

Friedel’s salt (3CaO.Al₂O₃.CaCl₂.10H₂O) or (Ca₄Al₂(OH)₁₂Cl₂(H₂O)₄), a layered double hydroxide (LDHs), is a calcium aluminate hydrate and used as an adsorbent for copper (Cu²⁺) ions from aqueous solution. In our study, we carefully examined the adsorption behaviors of Friedel’s salt toward different concentrations of copper solution at 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 higher stability at pH=6 than at pH=4 and pH=8. Finally, this 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 including ion exchanger which 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.

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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 $[\text{M}_{1-x}^{2+} \text{M}_x^{3+}(\text{OH})_x^-] (\text{A}^n^-)_{x/n} \cdot \text{MH}_2\text{O}$, where $\text{M}^{2+}$ represent any divalent metal cation, $\text{M}^{3+}$ any trivalent metal cation and $\text{A}^n^-$ 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 plays 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$_2$O$_3$), calcium chloride dihydrate (CaCl$_2$.2H$_2$O), copper nitrate hydrate (Cu(NO$_3$)$_2$.10H$_2$O), 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$_2$O$_3$ 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).
2.i.b. Preparation of Friedel's salt:

Friedel's salt is prepared by the precipitation method. Powdered tricalcium aluminate (C₃A) is slowly added to a solution of calcium chloride dissolved in distillated water under vigorous stirring for 24 hrs 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 (1): X-Ray diffraction pattern of the prepared C₃A.](image1)

![Figure (2): X-Ray diffraction pattern of the prepared Friedel's salt.](image2)

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 of Ca²⁺ concentration using the atomic absorption techniques.

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

To examine the adsorption kinetics of Cu²⁺, series of Cu (II) solutions of different concentrations are prepared by dissolving copper 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 50 ml of the prepared metal solutions for different time intervals (0.5 hr, 3 hr, 6 hr, 3 d and 14 days). After each time interval, the mixture 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 Ca₄Al₂(OH)₁₂Cl₂(H₂O)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 decrease at higher pH=8 or lower pH=4, since it decompose after 3 hours in pH=4 and after 6 hours at pH=8 as show from [figure (3)]. Generally, the concentration of the dissolved calcium Ca²⁺ in solution at different pHs increase by increasing time. The XRD patterns illustrated 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.
3. iii. Adsorption of 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 at different time intervals (0.5, 3, 6 hours and 1, 3 and 14 days of hydration) by prepared Friedel’s salt are studied.

3.iii.a. Atomic adsorption analysis:
The results of this analysis are cited in table (1) and show, diagrammatically in figure (7). The results indicate 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 3 mM/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 8 mM/l copper ions concentration.

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

<table>
<thead>
<tr>
<th>Conc. (mM/l)</th>
<th>Cu$^{2+}$ (mg/l)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.5 h</td>
</tr>
<tr>
<td>0.5</td>
<td>24.00</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>7.00</td>
</tr>
</tbody>
</table>

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

3. iii.b. Phases composition results.

The phase'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 0.5 mM/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 0.5 hr 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 0.5 hr then decrease gradually till 14 days. Also, the characteristic peak for CaCO$_3$ at (d=3.02) is clearly noticed till 14 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 appearing at 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.
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 follows:

$$
\begin{align*}
3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot10\text{H}_2\text{O}(s) & \leftrightarrow [\text{Ca}_4\text{Al}_2(\text{OH})_{12}]\text{Cl}_2\cdot4\text{H}_2\text{O} \quad (1) \\
\equiv \text{CaOH} + n\text{H}^+ + \text{Cu}^{2+} & \leftrightarrow \equiv \text{CuOH}^{n+}_{n=1} + \text{Ca}^{2+}(n=0,1) \quad (2)
\end{align*}
$$

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):

\[
[\text{Ca}_4\text{Al}_2(\text{OH})_12\text{Cl}_2.4\text{H}_2\text{O} (\text{s})] \leftrightarrow 4\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 2\text{Cl}^- + 4\text{OH}^- + 4\text{H}_2\text{O} \quad (3)
\]

\[
4\text{Cu}^{2+} + 2\text{Al(OH)}_4^- + 4\text{OH}^- + 4\text{H}_2\text{O} \leftrightarrow \text{Cu}_4\text{Al(OH)}_2\text{Cl}_2.4\text{H}_2\text{O}_{(s)} \quad (4)
\]

\[
\text{Cu}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_2 (\text{s}) + 2\text{H}^+ \quad (5)
\]

The Cu (II) could replace original interlayer ion Ca$^{2+}$ into the interlayer spacing as reaction (6). The ion-exchange reaction of FS may be schematically depicted by following reaction:

\[
2[\text{Ca}_4\text{Al}_2(\text{OH})_12\text{Cl}_2.4\text{H}_2\text{O}(\text{s})] + x\text{Cu}^{2+} \leftrightarrow 2[\text{Ca}_{4-x}\text{Cu}_x\text{Al}_2(\text{OH})_12\text{Cl}_2.4\text{H}_2\text{O}(\text{s})] + x\text{Ca}^{2+} \quad (6)
\]

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


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الملخص باللغة العربية

إزالة أيونات النحاس بواسطة ملح فريديل

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تم تحضير وتعريف ملح فريديل (3CaO·Al₂O₃·CaCl₂·10H₂O) سنة 1897 علي يد العالم فريديل علي أنه ينتمي لعائلة الهيدروكسيدات مزدوجة الطبقات (LDHs) وهي مجموعة مكونة من معدن الأيونات تتكون من حزمه من الطبقات الموجبة وطبقات داخليه متماثلة سالبة. ملح فريديل له المقدرة على إزالة الأيونات والكاثيونات الضارة من المحاليل ، حيث تم استخدامه لازالة بعض العناصر القلية من مياه الصرف الصحي مثل الكادميوم والخاليين والرصاصات والسيليكات والكروم والفوسفات والسلعات.

والهدف من هذه الدراسة هو استخدام ملح فريديل لإزالة عنصر النحاس من المحاليل. يتم تحضير ملح فريديل من معدن الأيونات عن طريق تفاعل الأيونات وذلك بهدف القضاء على تلوث المحاليل بهذا العنصر. ويتضمن دراسة ميكانيكيه إزالة هذا المعدن علي ملح فريديل.

وفيما يلي ملخص لما تم في هذه الدراسة:

1 - تم تحضير ملح فريديل من تفاعل الومينات ثلاثي الكالسيوم مع كلوريد الكالسيوم.
2 - تم تحضير تركيزات مختلفة من نترات النحاس (0.5 – 3) مللي مول / لتر.
3 - ضبط الآس الهيدروجيني لمحاليل النحاس عند 4 وإضافة 0.1 جم من ملح فريديل مع التقلب عند آزمه مختلفه (0.5, 3 و 6 ساعه، 14 يوم).

وفيما يلي ملخصات استنتاجات من هذه الدراسة:

1 - الذئبيات والثبات لملح فريديل يعتمدان علي الآس الهيدروجيني.
2 - يتغير ثبات ملح فريدل بتغير الأس الهيدروجيني للمحلول، فأعلى ثبات لملح فريدل يكون عند أس هيدروجيني

= 6 و أقل ثبات عند أس هيدروجيني = 4.

3 - ملح فريدل له خواص إمتصاص الكاتيونات مثل كاتيون النحاس و تتغير الخواص بتغير الأس الهيدروجيني

وطريقة الكاتيون.

4 - ملح فريدل لديه المقدار على إمتصاص كل أيونات النحاس من المحلول عند أس هيدروجيني = 4 حيث التركيز

الكلي لملح النحاس = 3 مل مول/لتر.