

E. KARLOVIĆ*, D. MIŠKOVIĆ*

STUDY ON THE POSSIBILITY OF IMPROVEMENT OF CUPRIC HYDROXIDE SEDIMENTATION BY COLLECTION AND COPRECIPITATION

This study is concerned with the effect of pH on sedimentation kinetics of $\text{Cu}(\text{OH})_2$ in the presence/absence of Na-oleate as a collector. Another effect considered is the coprecipitation with $\text{Fe}(\text{OH})_3$ and its influence on kinetics and efficiency of the $\text{Cu}(\text{OH})_2$ sedimentation.

The results indicate that the maximal sedimentation rate of $\text{Cu}(\text{OH})_2$ is achieved at pH 7, which corresponds to the least negative value of zeta potential (-15 mV). The presence of Na-oleate at the level of 10 mg/dm^3 is sufficient to promote a 50% increase in the sedimentation rate of $\text{Cu}(\text{OH})_2$. On the other hand, this increase in the presence of $\text{Fe}(\text{OH})_3$ is in the range of 8–62%, depending on the concentration of $\text{Fe}(\text{OH})_3$. Presence of the $\text{Fe}(\text{OH})_3$ floccules causes a decrease in sedimentation rate of $\text{Cu}(\text{OH})_2$, although it facilitates removal of the finer $\text{Cu}(\text{OH})_2$ particles. The collecting and coprecipitation procedure with Na-oleate and $\text{Fe}(\text{OH})_3$ results in a 98% efficiency of $\text{Cu}(\text{OH})_2$ removal.

1. INTRODUCTION

In common treatment of wastewaters containing ions of heavy metals, precipitation of metal hydroxides is followed by their separation, either by sedimentation or flotation [1]–[6]. Usually, the sedimentation method is used, i.e., the hydroxide particles are separated by the action of gravitation force. The method is efficient provided that the hydroxide floccules are large enough, their densities exceed that of water, etc. [7], [8]. In order to promote particles aggregation, different polymeric flocculants are added [5]. An increase in sedimentation rate can be also achieved via hydrophobization of particles by some surfactants, such as sodium dodecylbenzolsulphonate (DBS) [9].

The objective of this work was to study sedimentation of $\text{Cu}(\text{OH})_2$ alone and in mixtures with $\text{Fe}(\text{OH})_3$ in the presence of Na-oleate, which is easily biodegradable. The advantage of the procedure, in which such an agent for hydrophobization and acceleration of the sedimentation process is employed, is the protection of recipients.

*Institute of Chemistry, Faculty of Sciences, 21000 Novi Sad, V. Vlahovića 2, Yugoslavia.

2. METHODS

Hydroxide suspensions were prepared by precipitation of metal ions from the model solutions with the use of NaOH solutions in concentration of 5 and 1 mol/dm³, respectively. The ratios Cu(II):Fe(III) in the coprecipitation experiments were 50:6, 50:9, and 50:18. The suspensions were diluted either with distilled water, or a dilute solution of the collector. The Cu(II) content in final dilution was 250 mg/dm³, whereas that of Na-oleate was 10 mg/dm³.

From the moment of pH adjustment, the sedimentation of metal hydroxides was monitored by measuring the height of the phase boundary liquid/solid in a sedimentation cylinder [10], [11].

Electrophoretic mobilities of the Cu(OH)₂ particles, remaining in the supernatant after the sedimentation for 30 min, were measured with a ZM-77 (Zeta-meter, Inc. New York) zeta-meter by standard method. The corresponding values of zeta potential (ZP) were determined from the appropriate nomograms [12], [13].

Metal ion contents were determined by the AAS method with the use of a Pye Unicam SP 191 instrument [14]. Concentrations of Na-oleate were determined by the permanganometric method in acidic medium [15].

3. RESULTS

3.1. EFFECT OF pH ON SEDIMENTATION KINETICS OF Cu(OH)₂

The data on sedimentation of Cu(OH)₂ at different pH and in the absence of Na-oleate are presented in fig. 1. To analyse kinetics of the sedimentation process, the following empirical equation was used:

$$h = a \cdot e^{-bt},$$

where h is the height of the liquid/precipitate phase boundary (cm), t denotes the sedimentation time (min), whereas a and b are the corresponding coefficients. The sedimentation curves presented in a semi-log diagram are linear with the slopes corresponding to the sedimentation rates.

It is evident from fig. 1 that the sedimentation kinetics can be satisfactorily described (a high coefficient of determination is obtained) by the above empirical equation. In the studied pH region, the highest value for the sedimentation rate coefficient (b) corresponds to pH 7. The coefficient shows a decrease with an increase in pH, so that, for example, at pH 9 it is lower by 37%.

Figure 2 shows the dependence of the sedimentation rate coefficients of Cu(OH)₂ and the ZP values on pH.

As it can be seen in fig. 2, the Cu(OH)₂ particles have the negative values of zeta

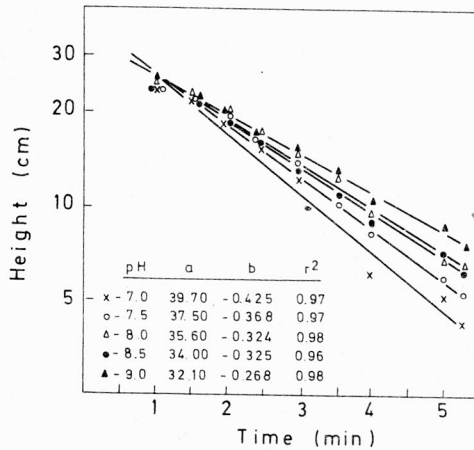


Fig. 1. Effect of pH on sedimentation rate of $\text{Cu}(\text{OH})_2$

potential in the whole region of pH; the least negative value (-15 mV) being observed at pH 7, whereas the most negative (-30 mV) value corresponds to pH 10. In contrast to this, the sedimentation rate coefficient shows a decrease with an increasing pH value. Therefore, it is obvious that the repulsion forces of the charged $\text{Cu}(\text{OH})_2$ particles have their minimum at pH 7, which facilitates the aggregation of particles, i.e., yields a faster sedimentation.

After 30 min of sedimentation, the solution above the precipitate (supernatant) contains a portion of the suspended $\text{Cu}(\text{OH})_2$ ($10\text{--}12$ mg/dm³, expressed as Cu(II)). Thus, an overall efficiency of about 95% was achieved in $\text{Cu}(\text{OH})_2$ removal by both

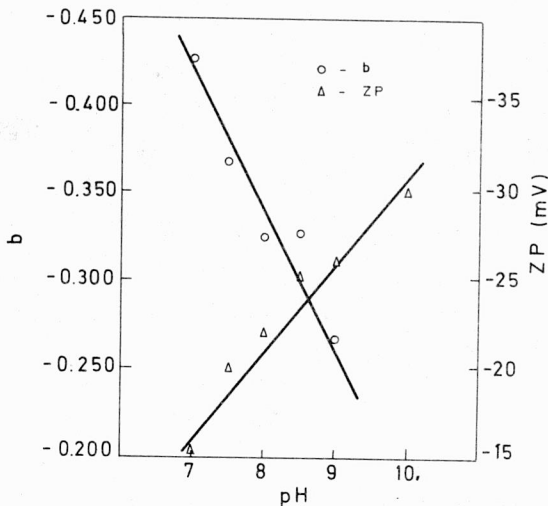


Fig. 2. Dependence of zeta potential of $\text{Cu}(\text{OH})_2$ particles and the sedimentation rate coefficient (b) on pH

precipitation and sedimentation at pH 7. This is a rather high value if the precipitate characteristics (charge, polydispersity, etc.) are taken into account.

3.2. EFFECT OF pH ON SEDIMENTATION KINETICS OF $\text{Cu}(\text{OH})_2$ IN THE PRESENCE OF Na-OLEATE

The data for $\text{Cu}(\text{OH})_2$ precipitation in the presence of Na-oleate (10 mg/dm^3) at different pH are presented in fig. 3. A low concentration of Na-oleate was chosen with regard to the observation that a collector monolayer is sufficient to make metal hydroxide particles hydrophobic [16], [17]. Higher concentrations of Na-oleate may cause a redispersion of the hydroxide precipitate, which was confirmed by some preliminary experiments.

Therefore, for comparison sake, fig. 3 contains an illustration of sedimentation kinetics of $\text{Cu}(\text{OH})_2$ in the absence of Na-oleate. It is evident that the highest sedimentation rate is also obtained at pH 7. A comparison of the two sedimentation rates shows that the presence of Na-oleate promotes acceleration of the process by 50%. Under the optimal experimental conditions, the content of $\text{Cu}(\text{OH})_2$, calculated as Cu (II), in the solution above the precipitate is about 8 mg/dm^3 .

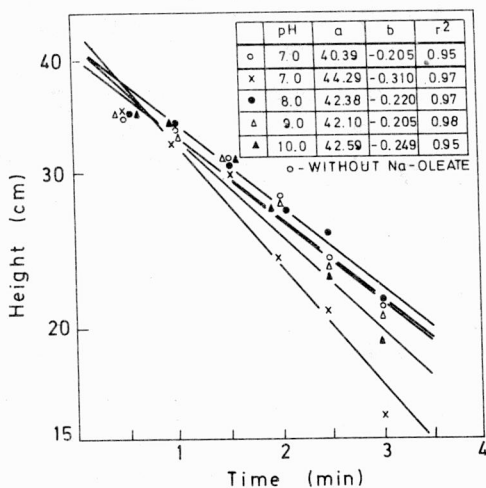


Fig. 3. Kinetics of $\text{Cu}(\text{OH})_2$ sedimentation at different pH in the presence of Na-oleate (10 mg/dm^3)

3.3. EFFECT OF COPRECIPITATION ON SEDIMENTATION KINETICS OF $\text{Cu}(\text{OH})_2$ IN THE PRESENCE AND ABSENCE OF Na-OLEATE

The possibility of coprecipitation of some metal ions with $\text{Fe}(\text{OH})_3$ is a well-known phenomenon [18]. It is also known that flocules of $\text{Fe}(\text{OH})_3$ are used as

the carrier in separation of metal ions by adsorbing colloid flotation [19], [20].

For these reasons the kinetics and efficiency of $\text{Cu}(\text{OH})_2$ sedimentation were studied in the presence of $\text{Fe}(\text{OH})_3$. Due to their voluminosity, $\text{Fe}(\text{OH})_3$ flocs can incorporate smaller $\text{Cu}(\text{OH})_2$ particles, thus improving their sedimentation. The effect was studied both in the presence and absence of Na-oleate.

In figs. 4-6 there are illustrated the results of the studies on different $\text{Cu}(\text{OH})_2 + \text{Fe}(\text{OH})_3$ mixtures carried out at pH 7, and in the presence (10 mg/dm^3) and absence of Na-oleate. Table gives the metal ion contents in the supernatant after sedimentation of the hydroxide mixtures for 30 min.

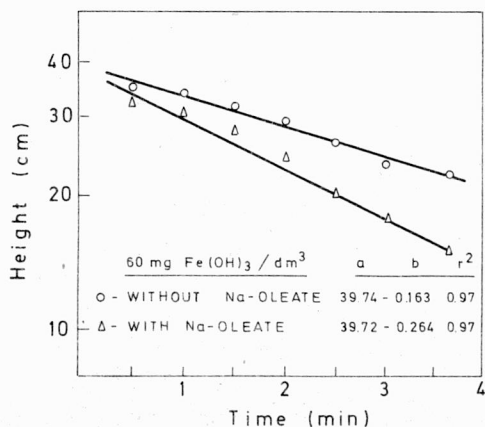


Fig. 5. Sedimentation kinetics of $\text{Cu}(\text{OH})_2$ in the presence of $\text{Fe}(\text{OH})_3$ (60 mg/dm^3) with and without Na-oleate

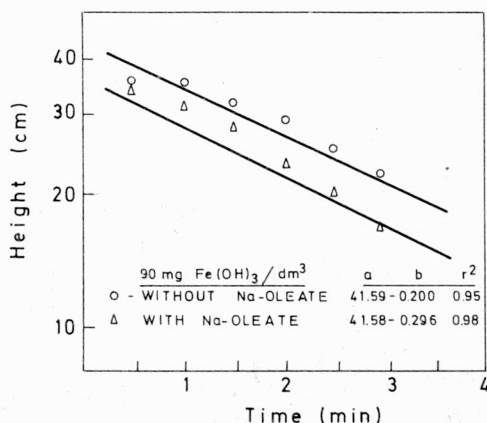


Fig. 4. Sedimentation kinetics of $\text{Cu}(\text{OH})_2$ in the presence of $\text{Fe}(\text{OH})_3$ (90 mg/dm^3) with and without Na-oleate

Table

Contents of copper, iron, and soap in the supernatant after 30 min. of sedimentation of the hydroxides at pH 7

Fe(III) mg/dm^3	Na-01 10 mg/dm^3	Cu(II)* mg/dm^3	Fe(III)* mg/dm^3	Na-01 mg/dm^3
0	without Na-01	12.81	—	—
	with Na-01	7.81	—	1.7
30.0	without Na-01	7.35	0.65	—
	with Na-01	5.81	0.45	2.3
45.0	without Na-01	7.56	2.15	—
	with Na-01	6.57	1.39	2.8
90.0	without Na-01	6.90	1.53	—
	with Na-01	5.83	1.36	5.3

* Total content of metal ions (dissolved + precipitated).

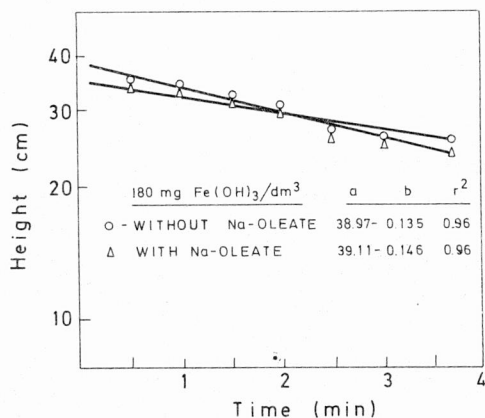


Fig. 6. Sedimentation kinetics of $\text{Cu}(\text{OH})_2$ in the presence of $\text{Fe}(\text{OH})_3$ (180 mg/dm^3) with and without Na-oleate

On the basis of the results shown in figs. 3–6, it can be concluded that sedimentation of $\text{Cu}(\text{OH})_2$ is slower in the presence of $\text{Fe}(\text{OH})_3$ (b within the range -0.135 to 0.200) than in the absence of it ($b = -0.205$). At the same time, the presence of Na-oleate accelerates sedimentation of the hydroxides mixtures by 8–62%, depending on concentration of $\text{Fe}(\text{OH})_3$. As already mentioned, the analogous increase in the absence of $\text{Fe}(\text{OH})_3$ was about 50%. Thus, in the presence of voluminous $\text{Fe}(\text{OH})_3$ (180 mg/dm^3) particles, the positive effect of Na-oleate on $\text{Cu}(\text{OH})_2$ is significantly lower. As it can be seen in the table, the Na-oleate content in the supernatant is somewhat enhanced in the presence of the $\text{Fe}(\text{OH})_3$ floccules, which may be the reason why the corresponding sedimentation rate is lower. In the presence of both the $\text{Fe}(\text{OH})_3$ and Na-oleate the $\text{Cu}(\text{II})$ concentration is about 50% lower than in their absence. The total efficiency of $\text{Cu}(\text{OH})_2$ separation by coprecipitation with $\text{Fe}(\text{OH})_3$ and collection with Na-oleate, under the given experimental conditions, amounts to 98%. From a practical point of view the effluent obtained may be subjected to either filtration or flotation in order to remove completely the metal hydroxides. Probably, dissolved air flotation might be the most suitable technique since the hydroxide particles are already made hydrophobic by the action of Na-oleate [21].

4. CONCLUSIONS

In the pH range within 7–10 and in the absence of $\text{Fe}(\text{OH})_3$ and Na-oleate, the $\text{Cu}(\text{OH})_2$ particles have a negative zeta potential. The rate of $\text{Cu}(\text{OH})_2$ sedimentation is the highest at pH 7, which corresponds to the least negative zeta potential (-15 mV). With an increase in pH, zeta potential of $\text{Cu}(\text{OH})_2$ particles becomes more negative, which is accompanied by a lower sedimentation rate.

As the presence of Na-oleate makes the $\text{Cu}(\text{OH})_2$ particles hydrophobic, the corresponding sedimentation rate is about 50% higher than in the absence of Na-oleate. However, in the case of sedimentation of the $\text{Cu}(\text{OH})_2 + \text{Fe}(\text{OH})_3$ mixtures, this enhancement varies in the range of 8–62%. The overall efficiency of $\text{Cu}(\text{OH})_2$ separation by sedimentation, accompanied by coprecipitation with $\text{Fe}(\text{OH})_3$ and collection with Na-oleate, is about 98%.

REFERENCES

- [1] LEMLICH R. *Adsorptive bubble separation techniques*, Academic Press, New York and London 1972.
- [2] CIANCIA I. *Plating*, 60 (1973), 1037.
- [3] BOSMAN J. *J. Wat. Sci. Tech.*, 15 (1983), 71.
- [4] GRUSIKA E. *New Developments in Separation Methods*, Marcel Dekker Inc., New York, Basel 1976, 117–133.
- [5] HARTINGER L., *Taschenbuch der Abwasserbehandlung für die metallverarbeitende Industrie*, Carre-Hauser Verlag, München-Vien 1976.
- [6] RUBBIN A., *Foam separation of microcontaminants by low-flow-rate methods*, Ph. thesis, Univ. North Carolina, Chapel Hill 1966, USA.
- [7] KOVALCIK R. N., *Chem. Eng.*, 19 (1978), 117.
- [8] TAMBO N., WATANABE Y., *Water Research*, 13 (1979), 409: 429.
- [9] ŽIVANOV Ž., MIŠKOVIĆ D., KARLOVIĆ E. et al., *Review of Research of Science-University of Novi Sad*, 6 (1976), 289.
- [10] ECKENFELDER, W. W., *Industrial water pollution control*, McGraw Hill, New York 1966.
- [11] FOUST A., WENZEL L. et al., *Principles of unit operations*, John Wiley and Sons Inc., New York 1960, 465–472.
- [12] *Standard test methods for zeta potential of colloids in water and wastewater*, ASTM Standards, Vol. 11, 01 D, 4187–82, 139–142.
- [13] RIDDICK T. M., *Control of colloid stability through zeta potential*, Zeta-meter Inc., Creative Press, N. York 1968.
- [14] CSHOVANEZ T., *Ipari vizvizsgálatok*, Műszaki könyvkiadó, Budapest 1977.
- [15] *Standard methods for the examination of water and waste-water*, Fourteenth edition, Amer. Pub. Health Assoc. Inc., 1975.
- [16] PINFOLD T. A., *Separation Science*, 5 (1970), 379.
- [17] KLASSEN V. I., *An Introduction to the Theory of Flotation*, Butterworth and Co, Ltd, London 1963.
- [18] BENJAMIN M. M., HAYES, K. F., LECKIE J. O., *J. W. P. C. F.*, 54 (1982), 1472.
- [19] WILSON D. et al., *Foam flotation of industrial waste waters laboratory and pilot scale*, US Environmental Protection Agency EPA – 600/2–80–138, June 1980.
- [20] CLARKE A., WILSON D., *Foam Flotation. Theory and Applications*, Marcel Dekker, AG-Verlag Publishers, 1983.
- [21] KARLOVIĆ E., MIŠKOVIĆ D., ŽIVANOV Ž., *Kinetics of copper hydroxide separation by flotation using dissolved air in presence of sodium oleate and various salts*, Proceedings from VI Yugoslav Symposium on Surface Active Agents, Vrnjačka Banja, September 1985, 739.

BADANIE MOŻLIWOŚCI POLEPSZENIA SEDYMENTACJI WODOROTLENKU
MIEDZIOWEGO POPRZEZ AGREGACJĘ I WSPÓŁSTRĄCANIE

Zbadano wpływ zarówno odczynu jak i oleinianu sodu (jako czynnika agregującego) na kinetykę sedymentacji $\text{Cu}(\text{OH})_2$. Określono również kinetykę sedymentacji $\text{Cu}(\text{OH})_2$ w procesie współstrącania za pomocą $\text{Fe}(\text{OH})_3$.

Uzyskane wyniki wskazują, że maksymalna szybkość sedymentacji $\text{Cu}(\text{OH})_2$ jest osiągnięta przy pH-7, co odpowiada najmniejszej ujemnej wartości potencjału zeta (-15 mV). Stwierdzono, że dodanie oleinianu sodu o stężeniu 10 mg/dm^3 jest wystarczające, aby zwiększyć szybkość sedymentacji $\text{Cu}(\text{OH})_2$ o 50%. Obecność $\text{Fe}(\text{OH})_3$ zwiększa szybkość sedymentacji w granicach 8–62%. Kłaczki $\text{Fe}(\text{OH})_3$ powodują obniżenie szybkości sedymentacji $\text{Cu}(\text{OH})_2$, ale jednocześnie umożliwiają usunięcie drobnych cząstek $\text{Cu}(\text{OH})_2$. Metoda agregacji i współsącania z zastosowaniem oleinianu sodu i $\text{Fe}(\text{OH})_2$ daje 98% usunięcie $\text{Cu}(\text{OH})_2$.

ИССЛЕДОВАНИЕ ВОЗМОЖНОСТИ УЛУЧШЕНИЯ СЕДИМЕНТАЦИИ ГИДРООКИСИ МЕДИ ПОСРЕДСТВОМ АГРЕГАЦИИ И СОВМЕСТНОГО ОСАЖДЕНИЯ

Исследования касаются влияния реакции и олеата натрия (как агрегирующего агента) на кинетику седиментации $\text{Cu}(\text{OH})_2$. Исследована также кинетика седиментации $\text{Cu}(\text{OH})_2$ в процессе совместного осаждения при помощи $\text{Fe}(\text{OH})_3$.

Полученные результаты показывают, что максимальной быстроты седиментации $\text{Cu}(\text{OH})_2$ достигают при $\text{pH} = 7$, что отвечает наименьшему отрицательному значению потенциала дзета (-15 мВ). Было установлено, что добавление олеата натрия концентрации 10 мг/дм^3 достаточно, чтобы увеличить быстроту седиментации $\text{Cu}(\text{OH})_2$ на 50%. Наличие $\text{Fe}(\text{OH})_3$ увеличивает быстроту седиментации в пределах 8–62%. Хлопья $\text{Fe}(\text{OH})_3$ приводят к понижению быстроты седиментации $\text{Cu}(\text{OH})_2$, но одновременно способствуют удалению мелких частиц $\text{Cu}(\text{OH})_2$. Метод агрегации и совместного осаждения с применением олеата натрия и $\text{Fe}(\text{OH})_3$ дает 98% удаление $\text{Cu}(\text{OH})_2$.