

The Influence of Iron Ion on Chemical Coagulation and Sludge Dewatering for Tannery Wastewater

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ABSTRACT

ABSTRACT In this study, pH adjustment, and chemical coagulation by polyaluminum chloride (PAC) and ferric chloride to remove suspended solid and COD in wet blue tannery wastewater were explored; and the settleability and dewatering characteristics of ferric and aluminiferous sludge were tested. The study can be concluded as follows: (1) without coagulation, the pH adjustment (below 3, or above 11) can remove SS and COD effectively, (2) removal for ferric chloride below 30mg/l rather than PAC below 30mg/l could remove SS and COD more effectively, (3) chemical coagulation with PAC and ferric chloride would be more efficient to remove SS and COD than with PAC alone, (4) sequential coagulation would be conducive to remove COD, (5) coagulation with PAC and ferric chloride would increase the settleability of flocs, and (6) the dewatering of ferric sludge would be better than that of aluminiferous sludge, so the addition of ferric chloride would improve the dewatering of Al sludge. Key Words : Tannery wastewater, Chemical coagulation, Dual coagulation, Sludge dewatering, Ferric Chloride.

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REFERENCES

- 參考文獻 英文部分
- Bajza, Z.; Hitrec, P.; Muzic, M.(2005), " Influence of different concentrations of Al₂(SO₄)₃ and anionic polyelectrolytes on tannery wastewater flocculation " , Desalination, 171(1), 13-20.
 - Bottero, J.Y.; Lartiges, B.(1993), " Separation liquide/solide par coagulation – floculation: les coagulants – floculants, mecanismes d ' agregation, structure et densite des floccs " , Bull. Sci. Geol. 46(1-4), 163-174.
 - Bottero, J.Y.; Manceau, A.; Villieras, F.; Tchoubar, D.(1994), " Structure and mechanisms of formation of iron oxide hydroxide (chloride) polymers " , Langmuir 10, 316-319.
 - Cathalifaud, G.; Mossa, M.T.W.; Mazet, M.(1993), " Preformed ferric hydroxide floccs as adsorbents of humic substances " , Water Sci. Technol. 27, 55-60.
 - Chang, G.R.; Liu, J.C.; Lee, D.J.(2001), " CO-conditioning and dewatering of chemical sludge and waste activated sludge " , Water Research, 35(3), 789-794.
 - Cheng, W. P.(2001), " Treatment of surface water by polyferric sulfate coagulant " , Separat. Sci Technol., 36(10), 2268.
 - Cheng, W. P.; Yu, R. F.; Chen, C. H.; Chi, C. H.(2003), " Enhanced Coagulation on Reservoir Water by Dual Inorganic Coagulants " , Environmental Engineering Science, 20,229-235.
 - Duan, J.(1997), " Influence of Dissolved Silica on Flocculation of Clay Suspensions with Hydrolysing Metal Salts " , PhD Thesis, University of London.
 - Duan, J.; Gregory, J.(2003), " Coagulation by hydrolysing metal salts " , Advances in Colloid and Interface Science, 100-102, 475-502.
 - Duan, J.; Gregory, J.(1998), " The influence of silicic acid on aluminium hydroxide precipitation and flocculation by aluminium salts " , J. Inorg. Biochem. , 69, 193-201.
 - Fargues, C.; Turchiuli, C.(2003), " Structural characterisation of floccs in relation to their settling performances " , Chem. Eng. Res. Des. 81(9), 1171 – 1178.
 - Farley, K.J.; Dzombak, D.A.; Morel, F.M.M.(1985), " A surface precipitation model for the sorption of cations on metal oxides " , J. Colloid Interface Sci. 106, 226-242.
 - Garrote, J. I.; Bao, M.; Castro, P.; Bao, M. J.(1995), " Treatment of tannery effluents by a two step coagulation/flocculation process " , Water Research 29(11), 2605-2608.
 - Gray, K.A.; Yao, C.H.; O ' Melia, C.R.(1995), " Inorganic Metal Polymers: A Comparison of Aluminum and Iron(III) Polymers for Water Treatment. I. Preparation and Characterization of Polymers " , J. Am. Water Works Assoc. 87(4), 136-146.
 - Hanna, G.P.; Rubin, A.J.(1970), " Effect on Sulfate And Other Irons in Coagulation with Aluminum (III) " , J. Am. Water Works Assoc. 62, 315-321.
 - Hayden, P.L.; Rubin, A.J.; in: Rubin, A.J. (Ed.)(1974), " Aqueous-Environmental Chemistry of Metals, Ann Arbor Science Publishers " , Ann Arbor, pp. 180.
 - Hek, H. D.; Stol, R.J.; Bruyn, P.L. D.(1978), " Hydrolysis-precipitation studies of aluminum(III) solutions. 3. The role of the sulfate ion " , J. Colloid Interface Sci. 64, 72-89.
 - Jekel, M.R.(1986), " The stabilization of dispersed mineral particles by adsorption of humic substances " , Water Res. 20, 1543-1544.
 - Johnson, P. N.; Amirtharajah, A.(1983), " Ferric chloride and alum as single and dual coagulants " , J. Am. Water Works Assoc., 75(5), 232-239.
 - Karr, P.R.; Keninath, T.M.(1978), " Influence of Particle Size on Sludge Dewaterability " , Jour. WPCF, 50, 1911.
 - Katsiris, N.(1977), " Bound Water Content of Biological Sludges in Relation to Setting and Filterability " , Doctoral thesis, University of Strathclyde, Glasgow, Scotland.
 - Kawamura, S.(1991), " INTEGRATED DESIGN

OF WATER TREATMENT FACILITIES", John Wiley & Sons, Inc., 605-611. 23. Knocke, W.R.; Hamon, J.R.; Dulin, B.E.(1987), " Effects of Coagulation on Sludge Thickening and Dewatering ", J. Am. Water Works Assoc., 79(6), 89-98. 24. Knocke, W.R.; Wakeland, D.L.(1983), " Fundamental Characteristics of Water Treatment Plant Sludges ", J. Am. Water Works Assoc., 75(10), 516-523. 25. Lapple, C.E.(1968), " Particle-size Analysis and Analyzers ", Chemistry Engineering, 75(11), 149. 26. Letterman, R.D.; Tabatabaie, M.; Ames, R.S.(1979), " Effects of the Bicarbonate Ion Concentration on Flocculation with Aluminum Sulfate ", J. Am. Water Works Assoc. 71(8),467-473. 27. Letterman, R.D.; Vanderbrook, S.G.(1983), " Effect of solution chemistry on coagulation with hydrolyzed Al(III) Significance of sulfate ion and pH ", Water Res. 17, 195-204. 28. Marion, S.P.; Thomas, A.W.(1946), " Effect of diverse anions on the pH of maximum precipitation of " aluminum hydroxide ", J. Coll. Sci. 1, 221-234. 29. Martin, R. B.(1991), " Fe³⁺ and Al³⁺ hydrolysis equilibria. Cooperativity in Al³⁺ hydrolysis reactions ", J. Inorg. Biochem. 44, 141-147. 30. Mason, A.; Vilge-Ritter, A.; Rose, J.; Stone, W.E.E.; Teppen, B.J.; Rybacki, D.; Bottero, J.Y.(2000), " Coagulation-Flocculation of Natural Organic Matter with Al Salts: Speciation and Structure of the Aggregates ", Environ. Sci. Technol. 34, 3242-3246. 31. Matijevic, E.(1973), " Colloid stability and complex chemistry ", J. Colloid Interface Sci. 43, 217-245. 32. Moller, U.K.(1983), " Water Binding. Sludge Characteristics and Behavior " (J.B. Carberry and A.J. Enlande Jr., editors), Martinus Nijhoff Publishers, The Hague, the Netherlands. 33. Montgomery, J.M.(1985), " Water Treatment Principles and Design ", John Wiley and Sons, Inc., New York. 34. Murphy, P.J.; Posner, A.M.; Quirk, J.P.(1976), " Characterization of partially neutralized ferric chloride solutions ", J. Colloid Interface Sci. 56, 284-297. 35. Novak, J.T.(1985), " Historical and Technical Perspective of Sludge Treatment and Disposal ", AWWA Seminar Proc.. 36. Pernitsky, D. J.; D., Ph.; Eng., P.(2003), " Coagulation 101 ", Alberta Water and Wastewater Operator Association. 37. Reynolds, T. D.; Richards, P. A.(1996), " UNIT OPERATIONS AND PROCESSES IN ENVIRONMENTAL ENGINEERING ", PWS Publishing Company, 206-210. 38. Richens, D.T. (1997), " The Chemistry of Aqua Ions: Synthesis, Structure, and Reactivity: A Tour Through the Periodic Table of the Elements ", Wiley, New York. 39. Roalson, S. R.; Kweon, J.; Lawler, D. F.; Speitel JR, G. E.(2003), " Enhanced softening:Effects of lime dose and chemical additions ", J. Am. Water Works Assoc., 95(11), 97-109. 40. Rossini, M.; Garrido, J. G.; Galluzzo, M.(1999), " Optimization of the coagulation – flocculation treatment: influence of rapid mix parameters ", Water Research, 33(8), 1817-1826. 41. Schneider, W.; Schwyn, B., in: Stumm, W. (Ed.)(1987), Aquatic surface chemistry : chemical processes at the particle-water interface, Wiley, New York, 167-196. 42. Smollen, M.(1990), " Evaluation of municipal sludge drying and dewatering with respect to sludge volume reduction ", Water Sci. Technol. 22(12), 153-161. 43. Snoeyink, V. L.; Jenkins, D.(1982), " WATER CHEMISTRY ", 新智出版社, 6, 10, 11, 231-241. 44. Song, Z.; Williams, C.J.; Edyvean, R.G.J.(2000), " Sedimentation of tannery wastewater ", Water Research, 34(7), 2171-2176. 45. Song, Z.; Williams, C.J.; Edyvean, R.G.J.(2004), " Treatment of tannery wastewater by chemical coagulation ", Desalination, 164(3), 249-259. 46. Stumm, W.; Morgan, J.J.(1981), " Aquatic Water Chemistry ", John Wiley and Sons, Inc., New York. 47. Tchoubar, D.; Bottero, J.Y.; Quienne, P.; Arnaud, M.(1991), " Partial hydrolysis of ferric chloride salt. Structural investigation by photon-correlation spectroscopy and small-angle x-ray scattering ", Langmuir 7, 398-402. 48. Thompson, P. L.; Paulson, W. L.(1998), " Dewaterability of alum and ferric coagulation sludges ", J. Am. Water Works Assoc., 90(4), 164-170. 49. Turchiuli, C.; Fargues, C.(2004), " Influence of structural properties of alum and ferric flocs on sludge dewaterability ", Chemical Engineering Journal, 103(1-3), 123-131. 50. Vesilind, P.A.; Martel, C.J.(1990), " Freezing of water and wastewater sludges ", J. Environ. Eng.—ASCE 116, 854-862. 51. Wu, C.C.; Wu, J.J.; Huang, R.Y.(2003), " Floc strength and dewatering efficiency of alum sludge ", Adv. Environ. Res. 7, 617-621. 52. Zhao, Y.Q.(2003), " Correlations between floc physical properties and optimum polymer dosage in alum sludge conditioning and dewatering ", Chem. Eng. J. 92, 227-235. 中文部分 1. 蕭蘊華, 傅崇德(1999)譯, 「環境工程化學」, 滄海書局, pp. 40-42; Clair N. Sawyer, Perry L. McCarty, Gene F. Parkin, " Chemistry for Environmental Engineering ", McGraw-Hill, Inc. 2. 朱世欽(1981), 「相思樹皮的成份分析及有機銅在合成上的應用」, 碩士論文, 淡江大學化學研究所。 3. 張敏超, 莊順興, 黃志彬(1994), 「污泥脫水之化學調理檢測技術」研討會, 財團法人工業技術研究院化學工業研究所。 4. 鄭勝仲(2004), 「製革廢水高級處理性能評估」, 碩士論文, 大葉大學環境工程研究所。 5. 常青, 傅金鎰, 鄺兆龍(1993), 「絮凝原理」, 蘭州大學出版社, pp. 116-147. 6. 戴勁草, 蕭子敬, 葉玲, 黃繼泰(1999), 「多孔粘土材料研究與進展」, 數字化期刊, Vol.18, No.4. 7. 高肇藩(1990), 「給水工程(自來水工程)」, 宏榮堂印刷, pp.248-288. 石橋多聞.上水道學, 技報堂。 8. 林正芳, 林瑤勤, 羅棋穎, 吳忠信譯(2002), 「水及廢水處理理論與實務」, 六合出版社, pp.361-390; Ronald L. Droste(1997)原著, " Theory and practice of water and wastewater treatment "。 9. 黃政賢(1997), 「給水工程」, 高立圖書有限公司, pp.184-201. 10. 楊萬發(1992)譯, 「水及廢水處理化學」, 茂昌圖書有限公司, pp.207-256; Larry D. Benefield, Joseph F. Judkins, JR., Barron L. Weand原著, " Process chemistry for water and wastewater treatment "。