PAINT WASTEWATER TREATMENT USING Fe³⁺ AND Al³⁺ SALTS

Irvin Oupa Lesele Ntwampe

A PhD thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy in Engineering.

Johannesburg 2013

DECLARATION

I solemnly declare that this thesis is my own work. It is being submitted for the Doctoral Degree in Philosophy in the University of the Witwatersrand, Johannesburg. I also declare that it has never been submitted for any degree or examination in another university.

Signature of Irvin Oupa Lesele Ntwampe

------day of -----2013

ABSTRACT

This study involves the investigation of the paint wastewater treatment using inorganic coagulants such as $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ in a jar test during rapid and slow mixing for 250 and 100 rpm respectively, settled the samples, measure the pH and turbidity. The pH, turbidity and area covered by the flocs were used as measurements in this study to determine the quality of treated paint wastewater.

In the first experiment, 200 mL sample of 169.2 g of paint wastewater dissolved in 1L of potable water was poured into six 500 mL glass beakers sample dosed with FeCl₃ only, combined FeCl₃ and Ca(OH)₂ or Mg(OH)₂ as well as FeCl₃-Ca(OH)₂ and FeCl₃-Mg(OH)₂ polymers respectively, run through a jar test with rapid and slow mixing. The supernatant was extracted after 1 hour settling to measure the pH and turbidity. The observations showed that combined FeCl₃ and Mg(OH)₂ as well as FeCl₃-Mg(OH)₂ polymers yielded identical and slightly higher turbidity removal than combined FeCl₃ and Ca(OH)₂ and FeCl₃-Ca(OH)₂ polymers.

Another batch of experiments was carried out using the same metal salts with Ca(OH)₂ and Mg(OH)₂ respectively for pH adjustment. The samples were treated in a jar test using various dosing patterns such as dosages, dosing prior or during mixing, combined dosages interchangeably, retention time. A third batch of experiments was carried out by dosing synthetic polymers of FeCl₂-Ca(OH)₂ and FeCl₂-Mg(OH)₂

respectively using similar dosing patterns. The results obtained in first set of experiments, were Fe³⁺ and Al³⁺ salts were added in paint wastewater showed that the changing pH correlates with turbidity removal. It was also observed that dosing prior or during mixing do not play any significant role in wastewater treatment. Another observation showed that flocculation of the paint wastewater dosed with FeCl₂-Ca(OH)₂ or FeCl₂-Mg(OH)₂ polymers do not show correlation between the pH and turbidity, which indicates that the pH is not an indicator of turbidity removal in a more alkaline solutions such as paint wastewater.

A second study was carried out using the same paint wastewater samples (200 mL) and samples dosed with Fe^{3+} and Al^{3+} salts treated in a jar test and immediately two drops of supernatant were placed on a microscope slide and view it under a microscope connected to a camera, images were captured after 1, 60 and 90 minutes respectively (Exp A). Samples were prepared from the original paint wastewater and the standard solution of Fe^{3+} and Al^{3+} in a small scale using identical metal salt/paint wastewater volume ratios as above. Two drops from the paint wastewater and metal salt solution were place on a microscope slide and images were captured as above using 1, 60 and 90 minutes respectively (Exp B). All the visuals were printed and the visuals obtained in Exp A were compared with their corresponding visuals in Exp B in accordance with time. The results obtained showed that the percentage area covered by the flocs from a microscope slide (Exp B). The results obtained using

this technique also confirm that the reaction between the drops of a sample and the drops of coagulant produces well-developed solid hydrolysis species.

A third study was carried out by pouring 200 mL of the same paint wastewater samples into six 500 mL glass beakers and with Fe³⁺ and Al³⁺ salts as above, run through a jar test during 30, 45 and 60 seconds rapid mixing (250 rpm) only for 2 minutes respectively. The samples settled for 1 hour, and then pH and turbidity were measured. Another experiment was carried out using the similar method as above with samples run through a jar test at 250 rpm during 30, 45 and 60 seconds rapid mixing (250 rpm) for 2 minutes followed by slow mixing (100 rpm) for 10 minutes (combined rapid and slow mixing). The samples settled for 1 hour, and then pH and turbidity were measured. The results obtained from the jar tests (comparison between flocculation during rapid mixing only and combined rapid and slow mixing) showed that the pH in the samples with rapid mixing shows an insignificant change compared to their corresponding samples with combined rapid and slow mixing; turbidity in the samples with 30, 45 and 60 seconds rapid mixing showed that most of the flocs are formed within 30 seconds. There is a correlation between the pH and turbidity when paint wastewater is dosed with Fe³⁺ or Al³⁺ metal ions in their respective metal salts without pH adjustment. The Fe³⁺ and Al³⁺ of the same concentration yield a similar pH and turbidity trend.

PUBLICATIONS AND PRESENTATIONS FROM THIS RESEARCH WORK

1) Influence of flocculation on settlement rate of paint wastewater during treatment using inorganic coagulants. <u>Ntwampe, I.O</u>,; Jewell, L,; Glasser, D,; University of Witwatersrand. (Presented at Water Institute of South Africa Conference, Sun City, South Africa, May 2008).

2) Determination of the effective rate of hydrolysis between coagulation and flocculation process with Fe and Al salts dose. <u>Ntwampe, I.O.</u>; Jewell, L.; Glasser, D.; University of Witwatersrand. Presented as a poster during inter-varsity poster exhibition between the University of Witwatersrand and Tshwane University of Technology, August 2009.

3) Ntwampe, I.O.; Jewell, L.L and Glasser, D.; The effect of mixing on the treatment of paint wastewater with Fe³⁺ and Al³⁺ salts. Journal of Environmental Chemistry and Ecotoxicology (2013) Vol. 5 No. 1, 7-16.

4) Ntwampe, I.O.; Jewell, L.L and Glasser, D.; The effect of water hardness on paint wastewater treatment by coagulation-flocculation. Journal of Environmental Chemistry and Ecotoxicology (2013) Vol. 5 No. 3, 47-56.

5) Ntwampe, I.O.; Jewell, L.L and Glasser, D.; Comparison of a jar tests and microscope slide experiments for flocculation. Journal of Environmental Chemistry and Ecotoxicology (2013) Vol. 5 No. 6, 172-180.

DEDICATION

I dedicate this work to the team of researchers that accepted me to pursue studies towards a PhD at the University of the Witwatersrand, my supervisor and cosupervisors for believing in me and the quality of work I carried out, external examiners, library staff, God who gave me strength and courage to strive towards success and achieve the set goal and my family.

ACKNOWLEDGEMENTS

I humbly express my profound gratitude to the following persons that supported and guided me, while carrying out the experiments and writing up of the thesis:

Professors David Glasser and Linda Jewell for their guidance on my experimental results.

Engineering library staff for invaluable assistance in procurement of material I used for my thesis.

National Research Fund (NRF) for financial support.

The University of Witwatersrand Financial Aid Scheme for financial support.

COMPS for the registration financial assistance.

The Almighty God to bless me with the opportunity, strength, enthusiasm and morality to carry out my work in a satisfactory, dedicatedly and respectable manner.

CONTENTS

PAINT WASTEWATER TREATMENT USING F	Fe ³⁺ AND
Al ³⁺ SALTS	i
DECLARATION	ii
ABSTRACT	iii
DEDICATION	V
ACKNOWLEDGEMENTS	vi
CHAPTER 1: Literature review	1
Introduction	1
Research overview	3
1.1 Background and justification of wastewater treatment	б
1.1.1 Conventional methods in wastewater treatment	15
1.1.2 Other reagents used in wastewater treatment	21
1.1.3 Properties of paint wastewater	21
1.2 Colloids and colloidal suspension	25
1.3 Dispersion of colloidal particles	27
1.4 Theory of coagulation and flocculation	27
1.5 Mixing	42
1.6 Destabilization process	45
1.7 Properties of coagulants	47
1.7.1 Common coagulants in wastewater treatment	47
1.7.2 Combination of coagulant and coagulant-aids dosages	47
1.7.3 Effect of the pH in coagulation-flocculation	50
1.7.4 Factors which affect hydrolysis	53

1.7.5 Hydrolysis and formation of precipitate species	58
1.8 Comparison of aluminium sulphate and ferric chloride	68
1.9 Physical and chemical factors in colloidal suspensions	71
1.9.1 Hydrodynamic interaction between particles	71
1.9.2 Intermolecular forces in a colloid	73
1.10 Challenges in paint wastewater treatment	=75
1.11 Benefits of the study	77
References	78
CHAPTER 2: The effect of metal salts and metal hydroxides on the pH-turbidity in hard paint wastewater treatment	85
2.1 Introduction	86
2.2 Material and methods	92
2.2.1 Paint wastewater sample	92
2.2.2 Coagulants	93
2.3 Procedure in jar tests	94
2.3.1 Experiment A-dosages with Fe and Al salts only	96
2.3.2 Experiment B	98
2.4 Performance evaluation	
2.4.1 pH measurement	99
2.4.2 Turbidity	100
2.5 Results	100
2.6 Discussion	108
2.7 Conclusions	115
References	117

CHAPTER 3: Comparison of jar tests and microscope slide experiments for flocculation	120
3.1 Introduction	121
3.2 Material and methods	124
3.2.1 Preparation of synthetic paint wastewater and coagulant solutions	124
3.2.2 Experiment A: Jar test	124
3.2.3 Experiment B: Microscope slide	125
3.2.4 Sludge drying and characterization	126
3.3 Results and discussion	127
3.4 Conclusions	135
References	136

CHAPTER 5.0 General conclusions17	17	3	
-----------------------------------	----	---	--

LIST OF FIGURES

Figure 1.1: Simplified diagram of water flow in paint manufacturing8
Figure 1.2: Wastewater minimization decision-tree adopted from Perry <i>et al.</i> (1997) and Chereminisinoff <i>et al.</i> (1989)11
Figure 1.3: Suspensions quantified by sedimentation volume (f)38
Figure 1.4: Forces acting on a particle40
Figure 1.5: Movement of colloid during rapid mixing42
Figure 1.6: Ferric hydroxide species distribution curve (Flynn, 1984)60
Figure 1.7: Aluminium hydroxide species distribution curve (Flynn, 1984)66
Figure 1.8: Forces exerted between the colloidal particles74
Figure 2.1: pH vs dosage with increasing Fe ³⁺ and Al ³⁺ salt in separate experiments100
Figure 2.2: pH vs turbidity for samples dosed with $FeCl_3$ and $Al_2(SO_4)_3$ or $AlCl_3$ salts added before and during stirring101
Figure 2.3: pH vs turbidity for samples dosed with either constant (20 mL) FeCl ₃ or increasing $Al_2(SO_4)_3$ or $AlCl_3$ salts or constant $Al_2(SO_4)_3$ or $AlCl_3$ and increasing FeCl ₃ , FeCl ₃ is added in increasing order whereas $Al_2(SO_4)_3$ or $AlCl_3$ salt in decreasing and increasing order103
Figure 2.4: pH vs turbidity for the samples dosed with increasing FeCl ₃ only, FeCl ₃ and Mg(OH) ₂ or Ca(OH) ₂ , FeCl ₃ +Ca(OH) ₂ or Mg(OH) ₂ polymers-104
Figure 2.5: pH, turbidity and dosage for samples with increasing FeCl ₃ , FeCl ₃ and Ca(OH) ₂ or Mg(OH) ₂ during rapid mixing106
Figure 2.6: pH, turbidity and dosage for samples with increasing FeCl ₃ , FeCl ₃ and Ca(OH) ₂ or Mg(OH) ₂ without mixing107
Figure 3.1: Microscopic observation using 0.043 M Fe ³⁺ in FeCl ₃ and Fe ₂ (SO ₄) ₃ dosing128
Figure 3.2: Percentage area covered by flocs vs mass ratio of sludge/solid paint in a solution using 0.043 M Al^{3+} and 0.043 M Fe^{3+} salts129
Figure 3.3a: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M ferric sulphate dosage130
Figure 3.3b: Comparison of the microscopic images of the flocs formed

during a jar test and microscope slide with 0.043 M ferric chloride dosage130
Figure 3.3c: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M aluminium sulphate dosage131
Figure 3.3d: Comparison of the microscopic images of the flocs formed during a jar test and microscope slide with 0.043 M ferric aluminium chloride dosage-131
Figure 4.1a: Measured pH after one hour settling with addition of 10 mL, 20mL and 30 mL respectively of 0.043 M Fe ³⁺ FeCl ₃ 149
Figure 4.1b: Measured pH after one hour settling with addition of 10 mL, 20mL and 30 mL respectively of 0.043 M Fe^{3+} $\text{Fe}_2(\text{SO}_4)_3$ 150
Figure 4.1c: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al ³⁺ AlCl ₃ 150
Figure 4.1d: Measured pH after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} $Al_2(SO_4)_3$ 151
Figure 4.2a: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe ³⁺ FeCl ₃ 151
Figure 4.2b: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Fe ³⁺ $Fe_2(SO_4)_3$ 153
Figure 4.2c: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M Al^{3+} AlCl ₃ 153
Figure 4.2d: Measured turbidity after one hour settling with addition of 10mL, 20mL and 30 mL respectively of 0.043 M $Al^{3+}Al_2(SO_4)_3$ 154
Figure 4.3: Percentage area covered by flocs with $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ dosage in a jar test155
Figure 4.4: pH of the samples using 0.043 M Fe ³⁺ (FeCl ₃) with and without mixing157
Figure 4.5: Turbidity of the samples using 0.043 M Fe ³⁺ (FeCl ₃) with and without mixing157

LIST OF TABLES

Table 1.1: Gisclon et al. (2002) specifications from SABS (2002)8
Table 1.2: Properties of pigment and extender concentrates

Table 1.3: Precipitation of metal hydroxides from dilute solutions vs pH ^a 3	0
Table 1.4: Particle radii for equal perikinetic and orthokinetic flocculation3	5
Table 1.5: Comparison between the properties Fe ³⁺ and Al ³ 5	7
Table 1.6: Comparison between particle size and settling velocity7	1
Table 2.1: Preparation of coagulant solution using distilled water9	94
Table 3.1: pH, turbidity, mass and moles of M^{3+} in the sludge, mass and	
volume of sludge13	4

Appendix A

Figure S1: SEM micrograph of 0.043 M FeCl ₃ -Ca(OH) ₂ and 0.043 M FeCl ₃ -Mg(OH) ₂ polymers17	78
Figure S2: XRD images of the dry sludge using 0.043 M Al ³⁺ (AlCl ₃) and 0.043 M Fe ³⁺ salts1	79
Figure S3: XRD images of the dry sludge using 0.043 M Al ³⁺ (Al ₂ (SO ₄) ₃) and 0.043 M Fe ³⁺ salts1	79
Figure S4: TGA graph of dry paint sludge dosed with 0.043 M Al ³⁺ and 0.043 M Fe ³⁺ salts18	80
Figure S5: SEM images of dry paint sludge dosed with 0.043 M Al ³⁺ and 0.043 M Fe ³⁺ salts magnified 40 times18	80
Figure S6: Flocs formation in a colloidal system due to Brownian motion18	31

Appendix B

Run 1a	182
Run 2a	182
Run 3a	183
Run 4a	183
Run 1b	183
Run 2b	184
Run 3b	184

Run 4b	185
Run 1c	185
Run 2c	185
Run 3c	185
Run 4c	185

Appendix C

Run 1d	186
Run 2d	186
Run 3d	186
Run 4d	186