# Performance assessment of recycled alum sludge in the treatment of textile industry effluent in South Africa

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# Declaration

I declare that this research thesis is my own unaided work. It is being submitted for the Master of Engineering Degree at Cape Peninsula University of Technology, Cape Town. It has not been submitted before for any degree or examination in any other University.

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(Signature)

Signed in Cape Town this ____30th___ day of ________June________ 2019

# Abstract

The textile industry is considered one of the most polluting sectors in terms of the large volume and toxic composition of the effluent that is generated. For example, the effluent contains dyes, which represent an environmental hazard when discharged without proper treatment. This study aimed to assess the use of recycled alum sludge (RAS) as an alternative treatment for the reduction of colour from dye based synthetic textile industry wastewater. To determine treatment efficiency, the colour, chemical oxygen demand (COD), total dissolved solids (TDS), and pH before and after treatment were monitored. The pH at which optimal removal rates were achieved was also determined.

Coagulation/flocculation experiments were conducted on five batches of synthetic wastewater containing disperse dye with an average colour, COD and TDS of 133 ± 13 mg/l (range 115-145 mg/l), 38 ± 4 mg/l (range 32-43 mg/l) and 779 ± 18 mg/l (range 754-804 mg/l), respectively, using a coagulant of alum:RAS mixed in ratios of 1:0, 0:1. 1:1, and 1:2. An average removal efficiency of 89 ± 2% (range: 81-96%) for colour, 29 ± 3% (range: 19-41%) for COD, and 36 ± 4% (range 19-59%) of TDS was recorded during treatment with fresh alum (unmixed). The average removal efficiencies for treatment with RAS (ratio 1:0, i.e. unmixed) were 78 ± 3% (range 67-88%), 22 ± 3% (range 14-34%) and 32 ± 1% (range 29-35%) for colour, COD and TDS, respectively. When fresh alum sludge was mixed with RAS at a ratio of 1:1, average colour and TDS removal efficiencies of 86 ± 3% (range 83-88%), 37 ± 5% (range 30-50%), respectively were achieved, while at ratios of 1:2, the average colour and TDS removal efficiencies were 82 ± 2% (range: 80-84%) and 30 ± 5% (range 22-35%), respectively. Increases in the COD concentrations were observed when fresh alum sludge was mixed with RAS in 1:1 and 1:2 ratios. However, the initial COD concentrations in the synthetic wastewater were low [38 ± 4 mg/l (range 32-43 mg/l)] and increases after treatment were marginal (3 ± 7% and 9 ± 3%, respectively).

A second method was applied for colour removal from the synthetic wastewater, namely adsorption with corn cobs. Results were inconclusive due to high levels of turbidity in the treated effluent caused by leaching of components from the shredded corn cobs.

This study intended to present alternative means or methods for the treatment of textile wastewater containing dye. The findings of this study compared well with previous laboratory studies conducted with synthetic textile wastewater containing dye. The coagulant of fresh alum and RAS mix ratio of 1:1 offered the best alternative to fresh alum in the treatment of synthetic textile wastewater in terms of reduction of disperse dye from the synthetic textile wastewater. The use of RAS could reduce the volume of waste to be discarded as well as the amount of fresh coagulant necessary for the daily operation.

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# Abbreviations and nomenclature

| | |
|---|---|
| ˚C | Degree Celsius |
| µm | Micrometre |
| Al | Aluminium |
| Alum | Aluminium sulphate |
| ASTM | American Society for Testing and Materials |
| COD | Chemical oxygen demand (mg/l) |
| Fe | Iron |
| g | Gram |
| g/l | Gram per litre |
| h | Hour |
| Hz | Hertz |
| kg | Kilogram |
| L | Litre |
| m/m | Metre per metre |
| min | Minute |
| mg | Milligram |
| mg/l | Milligram per litre |
| mg/l Pt/Co | Milligram per litre Platinum-Cobalt |
| ml | Millilitre |
| mm | Millimetre |
| $mm^3$ | Cubic millimetre |
| n | Number or sample |
| nm | Nanometre |
| pH | Negative log of the hydrogen ion concentration logarithmic scale |
| RAS | Recycled alum sludge |
| rpm | Revolution per minute |
| TDS | Total dissolved solids (mg/l) |
| TOC | Total organic carbon |
| TN | Total Nitrogen |
| V | Volt |
| W | Watt |

# 1 Introduction

## 1.1 Background and Motivation

The textile industry refers to a collection of related manufacturing activities such as spinning, weaving, dyeing, printing, and finishing (Tüfekci et al., 2007). The various processes may be disseminated, but in some instances, one facility may be responsible for the entire production pipeline from raw material to finished product (Tüfekci et al., 2007). Final products include clothing, knitwear and other various textile articles (Tüfekci et al., 2007).

There are many types of textiles that are produced using a variety of raw materials and manufacturing processes in order to obtain the final products such as garments, curtains, and carpets (Morshed et al., 2016). Consequently, the amount of water used, and the quality of the wastewater generated by each process is highly variable. The variable water quality is characterised by parameters such as the specific water intake, specific effluent volume, and specific pollutant load (Le Roes-Hill et al., 2017). In general, between 70% and 80% of water used by the textile industry is discharged as wastewater (Tüfekci et al., 2007). This effluent typically contains high concentrations of pollutants such as dissolved solids, recalcitrant organic matter, heavy metals, and dyes, which can be detrimental to the environment if not adequately treated prior to discharge (Chu, 2001; Ong et al., 2014; Le Roes-Hill et al., 2017; Sadri Moghaddam et al., 2010; Holkar et al., 2016; Morshed et al., 2016).

The current trend in South Africa is to ensure that water resources such as rivers, dams and ground water are not polluted by effluent of poor quality. This has led to the development and implementation of many regulations such as the National Water Act (Act 36 of 1998, DWAF). The environmental regulations require that industrial effluent containing harmful pollutants should be treated to comply with specified standards of the governing body of the area prior to discharge; a number of textile industries are non-compliant.

Chemical coagulation has often displayed high treatment efficiencies in the removal of dyestuff contained in dye wastewater (Sadri Moghaddam et al., 2010). However, this treatment method generates high volumes of coagulant sludge that requires specialised handling and disposal to avoid pollution of the environment (Chu, 1999). With the implementation of new stricter regulations, disposal of sludge through methods such as land filling may be prohibited in future. Studies from Zhao et al. (2011) and Nair et al. (2015) have shown that traces of coagulants found in the sludge after flocculation still possess adsorbing power and could therefore be reused in the coagulation-flocculation process. The reuse of recycled alum sludge (RAS) reduces the volume of fresh coagulant required in the operation and generates less waste. This study will assess the potential of RAS in the treatment of the textile industry wastewater containing dye.

## 1.2 Research problem

The manufacturing of textiles is a process that consumes large volumes of water and produces significant amounts of wastewater and sludge. The quality of wastewater produced is typically characterised by high levels of contaminants such as dissolved solids and colorants and contains poorly degradable organic matter. Several treatment methods, such as coagulation-flocculation and adsorption, have been used to remove these pollutants in order to ensure the compliance of effluent prior to discharge. However, to date, success has been very limited for a number of reasons, including the treatment efficiencies in terms of the poor quality of the final effluent, generation of large volumes of sludge, and the difficulties of handling the sludge, and the operational, maintenance and capital costs.

## 1.3 Research Question

The main question addressed in the study is: What is the performance of recycled alum sludge in the treatment of textile wastewater?
Additional questions addressed in this study include:

- What is the quality of effluent treated with recycled alum sludge?
- What are the performances of the recycled alum sludge treatment in comparison with the adsorption with shredded corn cobs?

## 1.4 Objectives of the study

This study sought to assess the potential of recycled alum sludge in the treatment of the textile industry wastewater containing dye. In order to achieve this goal, the following specific objectives were formulated:

- To determine the quality (Colour, COD, TDS) of effluent treated with the coagulation-flocculation process using a coagulant of fresh alum:RAS mixed in ratios of 1:0, 0:1. 1:1 and 1:2.
- To compare the treatment efficiency of the coagulation-flocculation process with the quality of effluent treated using adsorption with shredded corn cobs. The advantages and limitations of recycled alum sludge for the treatment of textile industry wastewater was evaluated against the performance of the adsorption with corn cobs.

## 1.5 Delineation

This study was limited to the assessment of the capability of the recycled alum sludge and shredded corn cobs in the removal of colour, COD, and TDS from synthetic textile industry wastewater. The effects of the change in pH concentration in the treatment efficiency of the recycled alum sludge were also considered and assessed. This study focused on the removal of dye from the wastewater. Therefore, only effluent of the dyeing and finishing process or dye houses was considered as textile wastewater in this study. The outcomes of this study did not apply to the treatment of effluents produced by any other textile wet processing units. However, due to the great complexity and diversity in chemical content in the textile industry wastewater, a synthetic version that highlighted the dye was used for the experiment.

## 1.6 Significance

The study aimed to provide an alternative means of treating textile wastewater containing dye generated by the textile industry. The use of RAS could offer an unconventional pre-treatment technology for the removal of dyestuff from textile industry wastewater.

The outcomes were to offer a method that would improve the quality of textile effluent, while reducing the volume of coagulant required for the treatment and waste generated, and contribute to the reduction of potential environmental and health hazards caused by the discharge of improperly treated textile effluent.

## 1.7 Organisation of thesis

The research design was in alignment with the aims of this study. The work is divided as following:

- Introduction, which provided the outline of the study (chapter 1)

- Literature review (chapter 2): An overview of literature consulted is presented as a chapter in this thesis. The chapter includes a review of the quality of the textile industry wastewater and the available technologies used for its treatment in order to obtain the body of knowledge necessary for the study. Furthermore, sampling and testing methods and quality standards relevant to the South African setting are included.

- Experimental work (chapter 3): This consisted primarily of setting up and operating a scientific mechanical flocculator for coagulation-flocculation using alum sludge and adsorption using shredded corn cobs. In addition, chemical analyses were performed in the laboratory to assess and compare the performance of the different methods. The chapter also includes information about the production of the synthetic wastewater and the analysis of the selected wastewater quality parameters in the laboratory in order to collect the necessary data required for the study.

- Presentation of results (chapter 4): The results obtained from experimental works described in chapter 3 are highlighted in this chapter.

- Discussion of results of the study (chapter 5): Results are evaluated to previous studies in order to assess the viability of the different methods for industrial application.

- Conclusions and recommendations (chapter 6): A synopsis on the treatment performance and typical application of the recycled alum sludge as a coagulant were made following the analysis and comparison of results.

# 2 Literature review and theory

## 2.1 Introduction

Le Roes-Hill et al. (2017) described the textile industry as “a group of related industries that process animal or vegetable fibres through specific operations that range from yarn fabric production to printing and finishing, in order to produce clothing and other textile items”. The textile manufacturing industries can be classified according to the type of fibre processed by the mills, the type of dyestuff used at the factory, the method of dyeing employed, and the type of equipment operated (Tüfekci et al., 2007). Trends in the fashion market and the seasonal variations also influence the water intake, which then affect the quality of the effluent (Tüfekci et al., 2007). The past 50 to 75 years have seen constantly growing efforts to develop manufacturing processes in such a way that they cause minimal damage to the environment (Vineta et al., 2014). At the same time, these efforts are aimed at developing appropriate technologies for wastewater treatment and establishing a functional relationship between regulators and industry (Vineta et al., 2014).

The textile industry is known to be one of the most polluting industries in terms of wastewater quality and quantity (Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al., 2016). Effluents from certain mills such as dyeing mills contain dyestuff which may be harmful to aquatic life and humans, even at low concentrations (less than 1 mg/l) (Sadri Moghaddam et al., 2010; Tüfekci et al., 2007; Holkar et al., 2016). Textile dyeing processes largely use synthetic dyes. Synthetic dye is divided in many different classes, with azo dye representing 65% of the total world production (Vandevivere et al., 1998; Carneiro et al., 2010; Morshed et al., 2016). The azo class includes acid, disperse and reactive dyes (Vandevivere et al., 1998; Carneiro et al., 2010). While most commercial textile dyes are soluble in the presence of water, disperse dyes, which are used for dyeing polyester fabrics, display hydrophobic characteristics and require special application techniques (Carneiro et al., 2010).

Coagulation-flocculation is mostly used for the removal of disperse dye due its efficiency and its operating simplicity (Sadri Moghaddam et al., 2010). However, large volumes of alum sludge are generated, which requires careful handling and specialised disposal to prevent environmental damage (Chu, 1999; Morshed et al., 2016; Jegatheesan et al., 2016). The sludge typically exhibits an average aluminium (Al) concentration of 39% by weight after coagulation (Chu, 1999). This residual sludge is easily accessible in large quantities and can be obtained free of charge (Sadri Moghaddam et al., 2010). Owing to its characteristics, this sludge has a potential for valorisation through recycling.

## 2.2 Textile manufacturing process overview

The processing stage in the textile industry is carried out by various related industries using a wide choice of natural and/or synthetic fibres as stock. Procedures include: blending and spinning of fibres to produce yarn mixes, weaving and knitting to make fabrics, bleaching, dyeing, printing and finishing of materials, and production of soft textile goods from fabrics (Figure 2.1) (Vineta et al., 2014; Holkar et al., 2016).

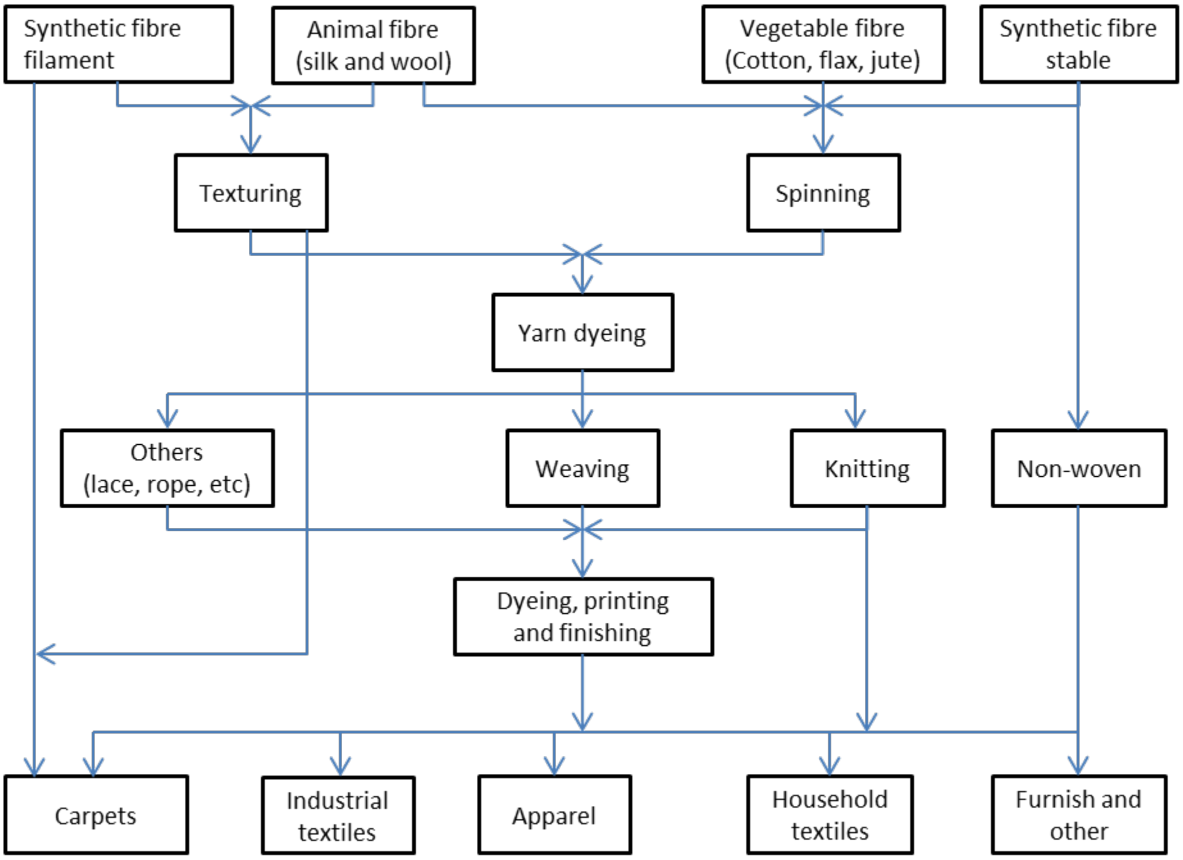


Figure 2.1 Summary of the overall textile manufacturing process [adapted from UNEP (1993)].

The textile industry is widely diversified, making simple descriptions and groupings virtually impossible. However, an attempt at classification can be made with regards to specific purposes. Although factors in each type of classification can be cross-correlated, textiles can be categorised on the following basis: unit operations and types of mills (Tüfekci et al., 2007).

### 2.2.1 Unit operations of textile manufacturing process

The processing of textiles consists of many steps that require the use of water. Although the steps are common to various types of fibres, specific water uses vary according to the type of fibre, equipment, methods, etc. The following bullet points briefly describe major unit operations with regard to their application to various types of fibres (Table 2.1):

- Opening, picking and blending: operations during which packs of raw fibres are opened and collected for the removal of impurities, seeds and short fibres prior to blending them together as per specification (Holkar et al., 2016; Le Roes-Hill et al., 2017).
- Combing and carding: operations where further removal of long fibres takes place. Fibres are aligned along their long axes and cleaned (Tüfekci et al., 2007, Le Roes-Hill et al., 2017 ).
- Spinning: operation during which the fibres are mechanically drawn out into yarn and twisted to produce yarn for dyeing, finishing, knitting, or weaving (Holkar et al., 2016).
- Sizing: operation during which yarns are covered with a thin layer of coat to protect them from abrasion during weaving, reduce yarn hairiness, and strengthen the yarns. Sizing agents may be

natural, synthetic (such as modified starch compounds, polyvinyl alcohol, carboxymethyl cellulose), or a mixture of both natural and synthetic (Holkar et al., 2016, Le Roes-Hill et al., 2017).

- Weaving: operation classified as a dry process. It is conducted under controlled high humidity conditions to increase the flexibility of yarns and minimise yarn breaks on the loom (Le Roes-Hill et al., 2017).
- Singeing: operation during which surface hairiness is removed from woven fabrics (Tüfekci et al., 2007).
- Knitting: dry process during which knitting oils are applied (typically 0.5 to 3.0% m/m) to reduce friction and breaking of yarn. The oils are eventually removed for further processing (Tüfekci et al., 2007, Le Roes-Hill et al., 2017).
- Desizing: operation that consist of the removal of the sizing agent after weaving. Starch sizes are removed using enzymatic degradation and cannot be recovered. Synthetic size, however, can be recovered using membrane techniques. Wool cannot be treated through desizing therefore sizing agents remain on the fibre (Holkar et al., 2016).
- Dyeing: operation during which colour is added to the fabric. It is conducted on the stock, the yarn, or fabric by applying different types of dye stuff (direct, sulphur, pigment, vat, reactive, acid, disperse, cationic etc.) depending on the type of fibre. The methods of applying dye can be either batch or continuous and can be conducted using different types of equipment (jig, jet, beam) with fabric either in rope or open-width form (Holkar et al., 2016, Le Roes-Hill et al., 2017).
- Scouring: operation that consists of the removal of impurities (inherent or added) in raw fibre or fabric. Scouring effluents are generally alkaline and high in sodium. Sodium carbonate and detergents are used for scouring of wool. Cotton is scoured with boiling sodium hydroxide solutions and detergents to remove natural waxes and added oils. Polyester is scoured at 60°C and under mild alkaline conditions in order to prevent excessive saponification of the fibre. Polyester and cotton blend under intermediate alkaline and temperature conditions (Holkar et al., 2016; Le Roes-Hill et al., 2017).
- Mercerising: operation during which cotton fibre, under tension, is treated using a concentrated sodium hydroxide solution at 22 to 26% m/m to boost various characteristics of the fibres i.e. reflectance, dimensional stability, dye-ability, lustre and shear strength. After mercerising, process fibres are rinsed and neutralised by applying a weak organic acid such as acetic or formic acid. Mercerising effluents are highly alkaline (pH> 13.5), with a high temperature due to the exothermic nature of the process and have high residual concentrations of sodium hydroxide (27 to 80 g/l) (Holkar et al., 2016).
- Bleaching: reduction of the natural colour of yarns of fabrics using hydrogen peroxide or hypochlorite solutions as oxidizing agents (Badu et al., 2007; Holkar et al., 2016).
- Finishing: operation that is used to improve the stability and quality of the handle of the fabric such as softening and crease resistance, and to impart special properties to the material (stain resistance and flame proofing) (Holkar et al., 2016; Le Roes-Hill et al., 2017).
- Printing: uses the same types of dyestuff as the dyeing process but the dye is applied in a paste form, which is then bake dried, fixed and washed off. Printing methods range from conventional printing using dispersing dyes to pigment printing with or without hydrocarbon to transfer printing (Holkar et al., 2016; Le Roes-Hill et al., 2017).

Each process generates solid and/or liquid and/or gaseous wastes and by-products (Table 2.1 & Table 2.2). In general, these differ considerably from process to process (Table 2.1, Table 2.2 & Figure 2.3) (Vineta et al., 2014). The quality and quantity of the wastewater depends on the unit processes taking place at each textile facility. Some processes do not generate wastewater. At the opposite end of the scale, some processes such as scouring and dyeing, generate large quantities of hazardous effluent that requires treatment before discharge (see Section 2.3 and 2.4 for details) (Vineta et al., 2014).

Table 2.1 Waste materials generated at various operations of textile processing [adapted from Badu et al. (2007)].

| Process | Air emissions | Wastewater | Residual wastes |
|---|---|---|---|
| Fibre preparation | Little or no air emissions generated | Little or no wastewater generated | Fibre waste; packaging waste; hard waste. |
| Yarn spinning | Little or no air emissions generated | Little or no wastewater generated | Packaging waste; sized yarn; fibre waste; cleaning and processing waste. |
| Slashing/sizing | Volatile organic compounds | BOD1; COD2; metals; cleaning waste, size3 | Fibre lint; yarn waste; packaging waste; unused starch-based sizes. |
| Weaving | Little or no air emissions generated | Little or no wastewater generated | Packaging waste; yarn and fabric scraps; off-spec fabric; used oil. |
| Knitting | Little or no air emissions generated | Little or no wastewater generated | Packaging waste; yarn and fabric scraps; off-spec fabric. |
| Tufting | Little or no air emissions generated | Little or no wastewater generated | Packaging waste; yarn and fabric scraps; off-spec fabric. |
| Desizing | Volatile organic compounds from glycol ethers | BOD from water-soluble sizes; synthetic size; lubricants; biocides; anti-static compounds | Packaging waste; fibre lint; yarn waste; cleaning materials, such as wipes, rags and filters; cleaning and maintenance wastes containing solvents. |
| Scouring | Volatile organic compounds from glycol ethers and scouring solvents | Disinfectants and insecticide residues; Sodium hydroxide; detergents; fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents | Little or no residual waste generated. |
| Bleaching | Little or no air emissions generated | Hydrogen peroxide, sodium silicate or organic stabiliser; high pH | Little or no residual waste generated. |
| Singeing | Small amounts of exhaust gases from the burners. | Little or no wastewater generated. | Little or no residual waste generated. |
| Mercerizing | Little or no air emissions generated | High pH; Sodium hydroxide. | Little or no residual waste generated. |

1 Biological Oxygen Demand; 2 Chemical Oxygen Demand; 3 starch or other polymeric coatings to weaving characteristics of yarn

Table 2.2 Waste materials generated at various operations of textile processing adapted from Badu et al. (2007) (Continued).

| Process | Air emissions | Wastewater | Residual wastes |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Heat setting | Volatilization of spin finish agents applied during synthetic fibre manufacture. | Little or no wastewater generated. | Little or no residual waste generated. |
| Dyeing | Volatile organic compounds | Metals; salt; surfactants; toxics; organic processing assistance; cationic materials; colour; BOD; sulphide; acidity/ alkalinity; spent solvents. | Little or no residual waste generated. |
| Printing | Solvents, acetic acid from dyeing and curing oven emissions; combustion gases; particulate matter. | Suspended solids; urea; solvents; colour; metals; heat; BOD; foam. | Little or no residual waste generated. |
| Finishing | Volatile organic compounds; contaminants in purchased chemicals; formaldehyde vapour; combustion gases; particulate matter. | BOD; COD; suspended solids; toxics; spent solvents. | Fabric scraps and trimmings; packaging waste. |
| Product fabrication | Little or no air emissions generated | Little or no wastewater generated. | Fabric scraps. |

1 Biological Oxygen Demand; 2 Chemical Oxygen Demand; 3 starch or other polymeric coatings to weaving characteristics of yarn

### 2.2.2 Types of textile mills

Textile mills vary widely from one to another, depending on the process or the fibres involved in the manufacture of textile goods. However, the principle types of textile mills are:

- Woven fabric finishing mills: Natural woven fabrics include cottons that were sized at the dry processing stage (Le Roes-Hill et al., 2017). At the woven fabric finishing mills, fabrics are prepared for dyeing and printing through extensive pre-treatment (Holkar et al., 2016). Finishing operations are often affected by the type of fibre and its required characteristics (Holkar et al., 2016). Synthetic woven fabrics usually just require softening as a finishing step, whereas cotton requires a combination of softener and resin (Le Roes-Hill et al., 2017).

- Knit fabric finishing mills: At this stage knitted cotton fabric is prepared for dyeing and finishing. The preparation is done in almost the same fashion as woven cotton, with the difference being the equipment employed and the use of softener only for finishing (Le Roes-Hill et al., 2017). Knitted oil must be removed from the knitted synthetic through a light scouring process before the start of the finishing process (Le Roes-Hill et al., 2017).

- Wool scouring mills: Raw wool requires scouring because of its high content of impurities such as dirt, grease and vegetable matter (Le Roes-Hill et al., 2017). Effluents that are produced from wool scouring mills have very high organic and inorganic pollutant loads (Le Roes-Hill et al., 2017).

- Dry processing mills (Figure 2.2): In South Africa, dry processing mills are often situated on the same site as downstream processing mills (Le Roes-Hill et al., 2017). At dry processing mills, spurn yarn or woven fabrics are produced from raw fibre stock, and sent for either stock yarn dyeing and finishing, or woven fabric finishing (Le Roes-Hill et al., 2017).

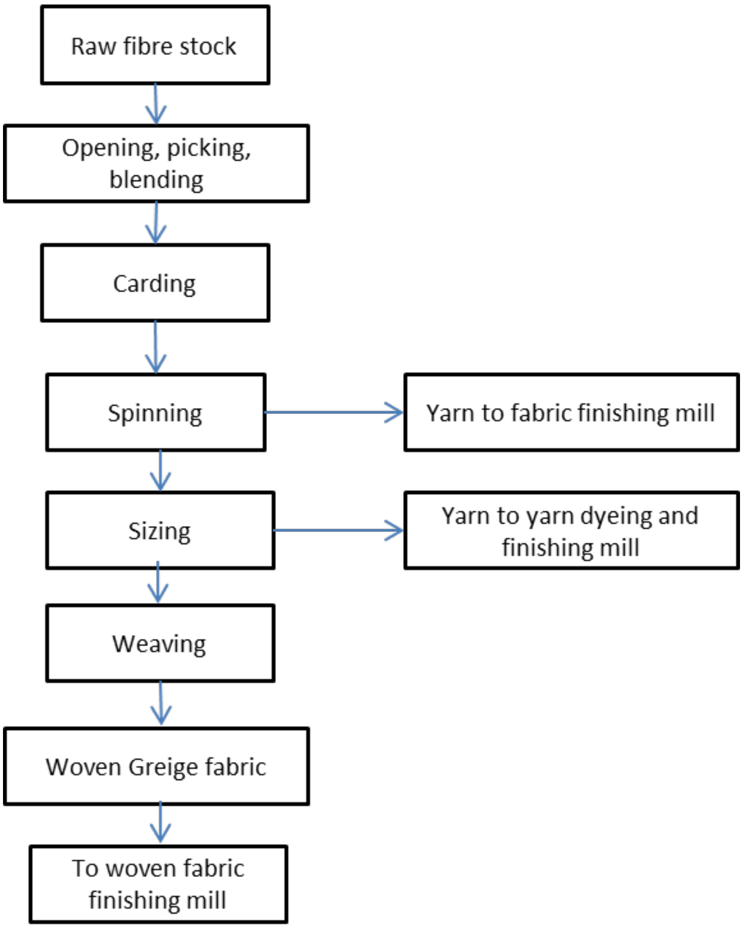


Figure 2.2 Schematic diagram of a typical dry processing mill [adapted from Le Roes-Hill et al. (2017)].

- Wool finishing mills: Most wool finishing mills produce both 100% woollen goods and materials that are wool/synthetic blends (Le Roes-Hill et al., 2017). Wool tops are usually blended and scoured prior to dyeing of the fibres in the form of stock, yarn or fabric (Holkar et al., 2016). Detergents are added to 100% woollen goods for fulling in order to increase the dimensional stability of the material. Worsted and wool- synthetic blends do not require fulling (Holkar et al., 2016).

- Carpet mills: Carpet are either dyed and/or printed after weaving using methods adequate to the type of fibre involved or woven using pre-dyed yarn (Holkar et al., 2016). A foam backing is often applied to the carpet for stabilisation after being washed and dried (Le Roes-Hill et al., 2017).

- Dye houses: Contract dye houses conduct dyeing and finishing operations on various types of fibre and fabric types using batch or continuous processing methods (UNEP, 1993).

- Stock and yarn dyeing and finishing mills (Figure 2.3): At stock and yarn dyeing finishing mills cotton yarns are bleached, mercerised, then dyed and softened; while synthetic yarns are dyed with a light colour before being sent for dyeing and softening (Le Roes-Hill et al., 2017).

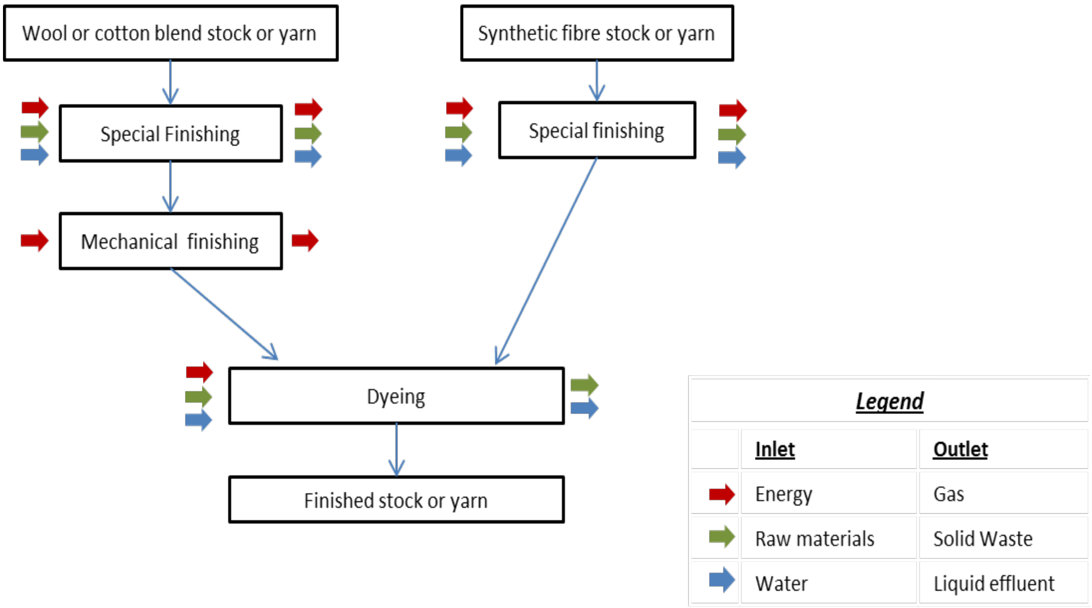


Figure 2.3 Schematic diagram of a typical stock or yarn dyeing and finishing mill [adapted from UNEP (1993)].

## 2.3 Textile wastewater characteristics

Textile industries use large quantities of water and chemicals for finishing and dyeing processes (Chu, 2001; Tüfekci et al., 2007; Vineta et al., 2014; Jegatheesan et al., 2016). Textile industry wastewater is mainly produced in the wet processing stage, especially during the washing, scouring, bleaching, dyeing and finishing steps (Vandevivere et al., 1998; Tüfekci et al., 2007; Morshed et al., 2016). Wastewater generated from the textile industry has a great complexity and diversity in chemical content due to the wide variety of fibres, dyes, process aids and finishing products used during processing stages (Chu, 2001; Tüfekci et al., 2007; Holkar et al., 2016; Jegatheesan et al.,2016). The chemical demand of the processes, especially for dyeing, vary widely because of the difference in chemical compositions of the synthetic fibres (Vineta et al., 2014; Holkar et al., 2016). Wastewater in the textile industry is composed of acids, bases, dissolved solids, toxic components, and colourants; the latter is the most noticeable component, even at low concentrations (Vandevivere et al., 1998; Chu, 2001; Holkar et al., 2016; Morshed et al., 2016). In the case of the production of blend fibres, such as polyester-cotton, the two fibres are either dyed separately, generating two different dyeing wastewaters, or as a blend fibre, producing one dyeing effluent. The manufacture of garments and accessories often requires a number of processing steps that may involve dyeing and finishing, which also affect the quality of the textile wastewater (Morshed et al., 2016).

### 2.3.1 Pollutants of concern

Textile dyehouse effluent has been a major issue in terms of pollution for many years. Colour is the first pollutant to be known in wastewater. In aquatic systems, dyes absorb sunlight which affects the intensity of light absorbed by the hydrophytes and phytoplankton, thus reducing photosynthesis and dissolved oxygen concentration of the aquatic environment (Rangabhashiyam et al, 2013). Further, dye effluents are hard to treat, high in volume, and made of harmful organic and inorganic chemicals that exhibit toxic and carcinogenic effects toward biological systems. The effluents containing dyes are very difficult to treat, since many dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents (da Rosa et al, 2018). Dyeing agents are complicated in structure, making them difficult to remove with conventional treatment methods due to their stability to sunlight, oxidising agents and microbial degradation (Vandevivere et al., 1998; Holkar et al., 2016; Morshed et al., 2016). Dye molecules that are absorbed/adsorbed into/onto the textile fibres are known as chromogens and are aromatic in nature (Vandevivere et al., 1998). Dyes can be classified according to chromogenic groups or their mode of application to textiles (Table 2.3). According to chromogenic groups, there are 12 classes of dyes, with the azo type being the largest, representing between 60 to 70% of dyestuffs employed in the industry. In terms of application to the textile material, dyes can be classified as acid, reactive, metal-complexed, dispersed, vat, mordant, direct, basic and sulphurous (Vandevivere et al., 1998; Holkar et al., 2016).

Reactive dyes are mainly used in research on textile wastewater decolourisation due to the fact that:

- they are used in the dyeing of cotton, which represents 50% of the world fibre production,
- a large portion of the reactive dye used is wasted due to dye hydrolysis in the alkaline dyebath, producing 0.6 to 0.8 g dye $dm^{-3}$ in the dyehouse effluent (Vandevivere et al., 1998).

Table 2.3 Classification of dyes [adapted from Kolorjet chemicals PVT. LTD. (2015), Holkar et al. (2016) & Verma et al. (2012)]

| Type of dye | Characteristics | Descriptions | Material |
|---|---|---|---|
| Disperse dyes | Very low solubility | Require a carrier to swell the fibres to promote the penetration of fine dye particles. Use hot bath like direct dyes, but do not require salt. | Synthetic fibres |
| Reactive dyes | Anionic, water soluble | React with the fibre molecule to form colour. Uses alkali to set off the fixation process.<br>Assistant: salt, soda ash, resist salt, urea, bicarbonate. | Cotton, silk and wool |
| Acid dyes | Anionic, water soluble | Acidified basic dyes. | Wool, nylon and acrylics |
| Premetallized dyes | Anionic, water soluble | Acid dyes with the addition of one or two molecules of chromium. Used by weavers who dye their own yarns. | Wool, nylon. |
| Direct dyes | Anionic, water soluble | Applied directly in hot dyebath without mordant.<br>Assistant: Salt | Cotton and viscose |
| Azo dyes | Anionic, water soluble | Uses similar method as a direct dye. However, extremely fast to washing, bleach and light. | Cotton and viscose |
| Vat dyes | Colloidal, insoluble | Made soluble with alkali then put in a 'vat' with a reducing agent to remove oxygen from the liquid then oxidised in the air to achieve true colour.<br>Assistant: Sodium hydrosulphite. | Cotton and viscose |
| Basic dyes | Cationic, water soluble | Not very fast to light, washing and perspiration. Fastness improved by using after-treatment or steaming. | Acrylic |

Textile mills often struggle to meet the effluent legislative limits, especially in terms of colours, heavy metals (e.g. chromium, copper, sulphide), salts, pH, and dissolved solids. This is partly due to the wide variation in effluent quality and pollutant concentration. If concentrated textile effluent is treated at municipal wastewater treatment facilities, it can have a negative effect on operational performance (Le Roes-Hill et al., 2017; Wang et al., 2011; Jegatheesan et al., 2016).

Since dyes are intentionally designed to resist degradation, most conventional wastewater treatment plants use sorption and aerobic biodegradation, which have a low removal efficiency of reactive and other anionic soluble dyes, leading to coloured effluent being discharged to streams (Vandevivere et al., 1998; Holkar et al., 2016). Rising concerns from the public have resulted in the update and reinforcement of firmer legislation with regards to the protection of the environment with strict controls on the type and the concentration of pollutant discharged (Ong et al., 2014; Sadri Moghaddam et al., 2010).

Although dye is the main pollutant of concern, the level of pollution of the textile industry wastewater is also typically also evaluated by measuring the COD, TDS and pH (Tüfekci et al., 2007; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al.,2016):

- COD: with a maximum limit of 5000 mg/l in the wastewater (Le Roes-Hill et al., 2017), the presence of COD causes depletion of dissolved oxygen (Xu et al., 2009). If not removed, it can have an adverse effect on the aquatic ecological system (Nair et al., 2015).

- TDS: used as an aggregate indicator of the presence of a broad array of chemical contaminants. High hardness in conjunction with high alkalinity or sulphates causes scale. A laxative effect can be caused by high sulphate content (Metcalf & Eddy, 2004). Abnormally high/low dissolved solids disturb osmotic balance of native species. Disposal of effluents containing salts into ground and surface water bodies cause pollution and renders them unfit for domestic, industrial and agricultural use. High salt concentration interferes with proper operation of biological wastewater treatment plants (Metcalf & Eddy, 2004).

- pH: often found to be at a range between 5 and 13, the pH indicates the level of acidity/alkalinity of the wastewater (Chu, 2001; Huang et 2015). It can affect the effectiveness of chemical reactions during the wastewater treatment process (Nair et al., 2015).

## 2.4 Treatment of textile industry wastewater

Over the last two decades, different treatment technologies have been studied to evaluate the sustainable treatment of textile wastewater. The selection of a suitable type of technology depends on the production process and chemical usage of the textile mill, constituents of effluent, discharge standards and location, capital and operating costs, availability of land area, options of reusing/ recycling the treated wastewater and skills and expertise available (Holkar et al., 2016; Jegatheesan et al.,2016). Textile effluent contains high concentrations of inorganic salts (Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al., 2016). It represents over 90% of the COD from a typical plant that dyes and finishes cotton fabrics including from the desizing, scouring, reducing and bleaching stages (Reife & Freeman, 1996; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al.,2016).

### 2.4.1 Treatment methods

There are many available methods for treatment of textile industry wastewater (Table 2.4). These treatment processes can be broadly categorised into three groups that in include:

- *Biological treatment* (Holkar et al., 2016) involves the use of aerobic or anaerobic treatment systems (or a combination of both), which rely on the action of microorganisms to remediate wastewater (Holkar et al., 2016). The biological process removes dissolved matter in a way similar to the self-purification method, but with a higher efficiency than a clariflocculator. According to the different oxygen demand, biological treatment methods can be divided into aerobic and anaerobic treatment (Wang et al., 2011; Holkar et al., 2016):
    - Aerobic digestion in which bacteria present in the sludge use oxygen to metabolise organic matter and convert it into carbon dioxide. This includes treatment systems such as activated sludge, oxidation ditches, trickling filters, and aerated lagoons (Metcalf & Eddy, 2004).
    - Anaerobic digestion can be defined as the degradation of organic matter by microbes under anaerobic conditions. Anaerobic digestion occurs in an environment with substantial organic matter and no molecular oxygen. Microorganisms metabolise organic matter to produce energy and products such as carbon dioxide, methane gas and hydrogen sulphide (Metcalf & Eddy, 2004).

- *Chemical treatment* requires the addition of chemicals to wastewater to promote the removal of pollutants through oxidation or reduction reactions (Holkar et al., 2016). Chemical treatment relies upon the chemical interactions of the contaminants to remove them from water by physical separation (physicochemical treatment) or assist in the destruction or neutralization of harmful effects associated with contaminants (Wang et al., 2011; Holkar et al., 2016). Chemical treatment methods are applied both as stand-alone technologies and/or physicochemical technologies (Ranganathan et al., 2007; Holkar et al., 2016). Currently, Fenton oxidation and ozone oxidation are often used in the treatment of textile industry wastewater

- *Physical treatment* consists of the removal of floating and settleable solids found in the wastewater, usually by mean of gravitational settlement of particles (Wang et al., 2011; Holkar et al., 2016). Chemicals are often also added in the treatment to improve the removal efficiency of suspended materials and, to a certain extent, dissolved particles from the wastewater (Wang et al., 2011; Holkar et al., 2016). A conventional treatment process is comprised of a series of individual unit processes, with the effluent of one process becoming the influent of the next process. The first stage will usually be made up of physical processes (Wang et al., 2011).

The most common physical treatment technology used in the textile industry is coagulation and flocculation. Other physical treatment technologies such as membrane filtration have been recently developed and are also currently used in the treatment of textile wastewater in South Africa (Jegatheesan et al., 2016).

Table 2.4 Advantages and limitations of various textile effluent treatments methods [Robinson et al. (2001); Vandevivere et al. (1998) & Verma et al. (2012)].

| Processes | Advantages | Limitations |
|---|---|---|

| | | |
|---|---|---|
| Fenton oxidation | Full decolourisation; low capital and running costs | High sludge production |
| Electrolysis | Full decolourisation; cost effective | Foaming; short electrode lifespan |
| Membrane filtration | Removes all types of dyes | Concentrated sludge production |
| Activated sludge | Removes bulk COD, N | High residual COD, N, colour, surfactants |
| Coagulation-flocculation | Full decolourisation | High sludge production |
| Ozonation | Full decolourisation | Expensive; aldehydes formed |
| Sorption (carbon, clay, biomass) | Good sorption capacity for acid dyes | Requires long retention time |
| Photocatalysis | Near complete decolourization; removal of toxicants | Only as final polishing step |

### 2.4.1.1 Coagulation and flocculation

Coagulation and flocculation involve the removal of polluting particles by sedimentation or flotation after the addition of a coagulant (Barclay & Buckley, 2004; Holkar et al., 2016). Coagulation (Figure 2.4) refers to the group of reactions and mechanisms that promote the chemical destabilisation of particles and the formation of larger particles through kinetic flocculation.

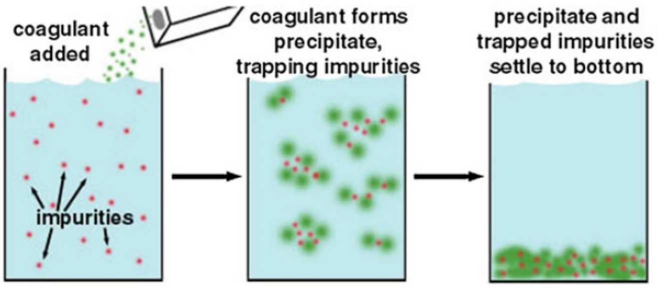


Figure 2.4 Schematic of the coagulation process [adapted from Bahadori et al. (2013)].

A coagulant is a chemical that is added to a fluid to neutralise the charge and promote the destabilisation of particles in the liquid, so flocs can be formed (Engelhardt, 2010).

In theory, since most particles in water are negatively charged, any positive ion can be used as a coagulant. A sodium compound (such as sodium hydroxide), contributes a monovalent ion, $Na^+$. A calcium compound (like calcium hydroxide) contributes a divalent ion, $Ca^{2+}$. Aluminum and iron coagulants contribute trivalent aluminum ions, $Al^{3+}$ and trivalent iron ions, $Fe^{3+}$, respectively. Hence, the greater the charge of the cation, the greater the effectiveness of charge neutralization. Coagulants can be natural or synthetic organic polymers, metals salts such as aluminium sulphate, ferric sulphate, and perhydrolised metal salts like polyaluminium chloride (PACl) and polyiron chloride (PICl) (Metcalf and Eddy, 2004).

Flocculation (Figure 2.5) is the dynamic mixing phase following the dispersion, hydrolysis, and polymerisation of the coagulant in a rapid mix step (Engelhardt, 2010). It is the slow mixing process that encourages collision of particles that are finely divided or chemically destabilised and their gel to form a larger mass known as flocs (Barclay & Buckley, 2004). During this stage, particles are destabilised and develop the cohesion necessary to form larger flocs that can be removed by settling or filtration (Engelhardt, 2010).

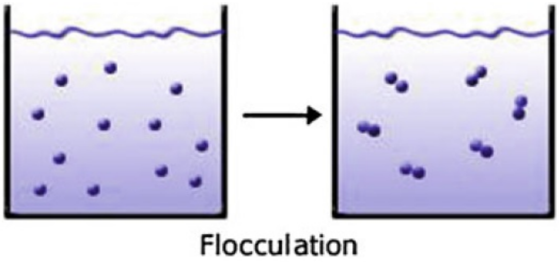


Figure 2.5 Flocculation of colloidal particles in the water [adapted from Bahadori et al. (2013)].

If direct filtration is employed, the flocculated water will proceed directly to filtration without any settling. Flocculation may be carried out by deliberate mixing for a half hour or more and is then followed by settling (Metcalf & Eddy, 2004; Engelhardt, 2010). Flocculation may also occur due to simple random motion of particles in solution – Brownian motion. Brownian motion is usually described as being caused by molecules of the fluid impacting the solid in solution (Metcalf & Eddy, 2004; Engelhardt, 2010). The effect is typically significant only on submicron particles.

Chemical coagulation offers an effective and practical option for the treatment of textile wastewater. However, coagulation produces large amounts of chemical sludge on a daily basis, and coagulants and chemicals for pH adjustments are expensive (Barclay & Buckley, 2004; Vandevivere et al., 1998). Studies from Chu (1999; 2001) have shown that the traces of coagulant (alum) found in the settled sludge after flocculation, still possess adsorbing power and can be reused in the coagulation-flocculation process. These studies highlight the treatment capabilities limitations of coagulation-flocculation.

### 2.4.1.2 Operating conditions of the coagulation-flocculation process

The effectiveness of the coagulation-flocculation process in the removal of pollutants from the wastewater is closely related to a number of factors. The parameters to take into consideration are the type of coagulant, the mixing speed, the mixing period and the settling time (Table 2.5).

*Coagulant dosage*: Determining the dosage of the coagulant is necessary in order to optimise the removal efficiency of polluting particles from the wastewater during the treatment process. It varies according to a number of factors such as the type of coagulant, the type of pollutants, the temperature and the pH of the wastewater (Metcalf & Eddy, 2004).

*Mixing speed*: Rapid mixing promotes the dispersion and hydrolysis of the coagulant the in the wastewater and slow mixing ensures the agglomeration of particles in the water and the formation of flocs (Metcalf & Eddy, 2004). The mixing speed often varies according to the apparatus in use.

*Mixing period*: the timescale for mixing is an important consideration in the design of mixing facilities and operations. According to Metcalf & Eddy (2004), determining the mixing period is extremely important when the reaction between the substance added into the liquid and the liquid is rapid. Mixing time in wastewater typically ranges between 5 and 30 seconds for rapid mixing rapid, and 30 and 60 minutes for flocculation or slow mixing (Metcalf & Eddy, 2004).

*Settling time*: As a general rule, the agglomeration of particles in suspension becomes more complete as time elapses, therefore, a minimum detention time should be determined. According to Metcalf & Eddy (2004), the settling the period ranges between 1.5 and 2.5 hours. However, for wastewater with low suspended solids content, a shorted detention time (0.5 to 1 hour) can be considered.

Table 2.5 Operating conditions of coagulation-flocculation in various studies

| Parameters | | | | | | |
|---|---|---|---|---|---|---|
| Coagulant dosage | | 100 mg/l | - | 900 mg/l | 1000 mg/l | - |
| Rapid mixing | Speed | 80 rpm | 120 rpm | 200 rpm | 200 rpm | 100 rpm |
| | Time | 1 min | 1 min | 1 min | 2.5 min | 2 min |
| Slow mixing | Speed | 30 rpm | 50 rpm | 45 rpm | 40 rpm | 20 rpm |
| | Time | 20 min | 10 min | 30 min | 12 min | 30 min |
| Settling time | | 10 min | 30 min | 60 min | 20 min | 30 min |
| References | | Chu, 2001 | Xu et al., 2009 | Jangkron et al., 2011 | Huang et al., 2015 | Nair et al., 2015 |

### 2.4.1.3 Aluminium sludge for wastewater treatment

Aluminium (Al) based water/wastewater treatment sludge, commonly known as alum sludge, is an inescapable by-product of the processing of drinking water and/or wastewater in treatment works where aluminium salt is used as the coagulant (Yang et al., 2006; Zhao et al., 2011). Aluminium sulphate is arguably the most widely used coagulant in drinking water treatment.

When aluminium sulphate is added to raw water, it dissociates into $Al^{3+}$ and $SO_4^{2-}$. The $Al^{3+}$ ions are immediately surrounded by water molecules and hexaaquoaluminium ($[Al(H_2O)_6]^{3+}$) is rapidly formed (Yang et al., 2006). The hexaaquoaluminium formed then undergoes a series of rapid hydrolytic reactions to form charged polymeric or oligomeric hydroxocomplexes of various structures (Yang et al., 2006). Such hydrolytic products include $[Al(H_2O)_5OH]^{2+}$, $Al(H_2O)_4(OH)_2]^{+}$, $[Al_6(OH)_{15}]^{3+}$, $[Al_8(OH)_{20}]^{4+}$ and $Al(OH)_3(s)$. During coagulation in water treatment processes, these complexes adsorb and modify the surface charge of the colloidal particles and inorganic substances (Yang et al., 2006; Zhao et al., 2011). Thereafter, in the ensuing treatment units including flocculation, sedimentation and filtration, the colloids in the raw water are removed and transferred to the sludge phase together with the hydrolytic aluminium species (Yang et al., 2006).

Alum sludge contains a combination of residual coagulant products and impurities from the water or wastewater such as colour, turbidity, hardness, organics and microorganisms at various concentrations (Zhao et al., 2011; Nair et al., 2015). Alum sludge is mainly composed of amorphous Al of up to 29.7 ± 13.3% dry weight, with larger particle surface areas and a greater reactivity towards anion adsorption than the corresponding crystalline mineral phases (Zhao et al., 2011). The high reactivity of the alum sludge makes it a potentially valuable material in wastewater treatment engineering (Zhao et al., 2011; Nair et al., 2015).

In recent years, the management of alum sludge has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints (Yang et al., 2006). However, as a sustainable approach to mitigate these effects, current trends have indicated a progressive drive towards alum sludge reuse as beneficial material. Such beneficial reuses include the use of alum sludge as an adsorbent for dye removal from wastewaters (Chu, 2001).

Studies showed that dewatered alum sludge has a latent adsorption capacity, and it can be utilized as an alternative sorption medium in wastewater treatment to improve the adsorption and the chemical precipitation process in the removal of various pollutants in the wastewater (Vandevivere et al., 1998; Chu, 2001; Robinson et al., 2001; Qi et al., 2009; Zhao et al., 2011; Nair et al., 2015). It has also been shown that alum sludge can help remove dye in wastewater (Vandevivere et al., 1998; Chu, 2001; Robinson et al., 2001; Yang et al., 2006, Qi et al., 2009; Zhao et al., 2011; Nair et al., 2015). This is attributed to the abundant aluminium ions in the alum sludge, which enhance the processes of adsorption and chemical precipitation that help to remove such pollutants from wastewater (Yang et al., 2006).

Due to its high production during the coagulation process, alum sludge has the advantage of being readily available in large quantities, as it is often regarded as a waste by-product (Zhao et al., 2011; Nair et al., 2015).

#### 2.4.1.4 Flocculator for wastewater treatment

Flocculators or mixers are devices used in coagulation and flocculation processes where solids particles are in a colloidal state and can be relatively dispersed (Metcalf and Eddy, 2004). In order to settle these particles, chemicals are added along with energy to neutralize charges and allow particles to collide then agglomerate forming larger floc particles that permit settling in a clarifier (Metcalf and Eddy, 2004). Typically, the process applies tapered flocculation to the inlet stream, where the first stage has high energy input (velocity gradient), and subsequent stages have a reduced velocity gradient. Flocculator mechanisms can be oriented horizontally or vertically depending upon drive location and/or design preferences (WesTech, 2016).

There are many types of mixers available, depending on the application and the time-scale required for mixing (Metcalf and Eddy, 2004). The principal devices used for rapid mixing in wastewater-treatment applications include static in-line mixers, in-line mixers, high-speed induction mixers, pressurised water jets, and propeller and turbine mixers (Metcalf and Eddy, 2004). Mixing can also be achieved in pumps and with the aid of hydraulic devices such as hydraulic jumps, Parshall flumes, or weirs (Metcalf and Eddy, 2004). Although hydraulic mixing can sometimes be highly efficient, the principal problem is that the energy input varies with the flow rate, therefore incomplete and ineffective mixing can occur at low flow rates (Metcalf and Eddy, 2004).

Laboratory scale mechanical flocculators are used for flocculation (jar) tests on water and effluent samples (WesTech, 2016). They accommodate up to six samples and are specially designed for repeatable conditions between samples and from run to run. The speed of the rotational stainless-steel paddles is monitored by a digital display, which ranges from 25 to 250 rpm (Stuart, 2016).

### 2.4.2 Comparison of the performances of the recycled aluminium sludge with adsorption using shredded corn cobs in the treatment of textile wastewater

The performance of RAS for dye removal was evaluated by Chu (2001). Two commercial chemical dyes were used in the experiment: Dianix Blue FBL-E (which is anionic and hydrophobic dispersed dye with a deep blue colour and a maximum adsorption wavelength of 568 nm) and Ciba-corn Yellow P-6GS (which is an anionic direct dye with hydrophilic characteristics and a yellow colour and a maximum adsorption wavelength of 475 nm). Aluminium sulphate (alum) was used as a coagulant, which reacted with the alkalinity in wastewater to form insoluble aluminium hydroxide sludge. A flocculator was used in the experiment. The standard procedure of 1 min rapid mixing at 80 rpm, followed by 20 min of mixing at 30 rpm, and a 10 min settling period was employed (Chu, 1999; Chu, 2001). Jangkorn et al. (2011) experimented using a flocculator with 6 beakers of 1 L capacity. The mixing was achieved starting with a rapid mixing of 200 rpm for 10 min, followed by a slow mixing of 45 rpm for 30 min, and finally a settling time of 60 min. The hydrophobic and hydrophilic dyes were used at concentrations of 12.5 mg/l and 125 mg/l respectively. The original concentration of fresh alum was established at 10 mg/l (Chu, 2001). A synthetic cationic polyelectrolyte at a concentration of 31.25 mg/l was used to enhance the formation of more rigid sludge with no effect on the pH of the solution (Chu, 2001). The settled wet sludge was dewatered, collected by gravity and reused initially as a coagulant on its own, then was mixed with added fresh alum. The dosage of RAS was determined by quantifying the dry weight of the suspended solids in the slurry at 105$^{o}$C (Chu, 2001). The alum sludge was prepared from previous coagulations operating at the optimum initial pH and fresh alum dosage. After allowing the flocs to settle for 60 min, the supernatant was drained, and the sludge was collected, and the volume of solids measured using the TSS measurement method (Jangkorn et al., 2011).

The removal efficiency was calculated using the following formula (Jangkorn et al., 2011):

$$Efficiency(\%) = \frac{A - B}{A} \times 100 \qquad (2.1)$$

Where,
A is the influent characteristics;
B is the effluent or supernatant characteristics.

Eighty-eight percent of the hydrophobic dye, Dianix Blue, was removed from wastewater with an optimum concentration of alum of 75 mg/l at pH 9.13 (Chu, 2001). In terms of efficiency, every 100 mg of alum usage generated 26 mg of alum sludge (Chu, 2001). However, a major drop in the dye removal rate to 48% was observed as the fresh alum dosage decreased. Restabilisation of dye materials was detected when using high concentrations of fresh alum (Chu, 2001). Negative back diffusion of dye was observed when using RAS from restabilisation, due to the release of the dye that was trapped in the sludge. However, adding fresh alum into the recycling system controlled the back diffusion (Chu, 2001). Overdosed concentrations of RAS (up to 200 mg/l) did not affect the restabilisation of dye. Therefore, precise control of the concentration of RAS was not required, potentially making it a simple add-on process for existing treatment works (Chu, 2001).

Adsorption is the most used method in physicochemical wastewater treatment and can be achieved by mixing the wastewater and the porous material powder or granules, such as activated carbon and clay, or letting the wastewater filter through a bed composed of granular materials (Holkar et al., 2016). Through this method, pollutants in the wastewater are adsorbed and removed on the surface of the porous material or filter (Wang et al., 2011).

The dye adsorption capabilities of corn cobs were evaluated against various dyes in a study conducted by Robinson et al. (2002). The dyes selected were Cibarcon Yellow C-2R, Cibarcon Red C-2G, Cibarcon Blue C-R, Remazol Black B, and Remazol Red RB. A synthetic effluent was obtained by mixing equal amounts of each of dye in distilled water. The corn cobs were dried, and their adsorbing capabilities were tested at particle sizes of 1x4 mm and ≤ 600 µm. It was found that the dye concentration level in the sample affected the treatment efficiency of the corn cobs as it dropped from 81%, 71%, 62% and 42% when treating volumes with initial concentrations of 50, 100, 150, and 200 mg/l, respectively. Equilibrium was reached on all samples after a retention time of 48 h. Particle size also affected the treatment performances of the corn cobs. The efficiency drastically improved when corn cob particles were ≤ 600 µm. Higher surface areas also offered continuous effective binding of dye molecules to the corn cobs at an efficient rate (Robinson et al., 2002). The adsorbed dye was then degraded through solid state fermentation (SSF) with fungi. The authors suggested that the fermented residue (which was enriched with protein) could be used as a soil conditioner (Robinson et al., 2002).

## 2.5 Textile effluent industry standards

Wet processing of textiles involves, in addition to extensive amounts of water and dyes, a number of inorganic and organic chemicals, detergents, soaps and finishing chemicals to aid in the dyeing process to apply the desired properties to dyed textile products (Morshed et al., 2016). Residual chemicals used in these processes often remain in the effluent. In addition, natural impurities such as waxes, proteins and pigment, and other impurities used in processing such as spinning oils, sizing chemicals and oil stains present in cotton textiles, are removed during scouring and bleaching operations (Morshed et al., 2016). This results in an effluent of poor quality, which is high in BOD and COD load (Morshed et al., 2016).

Strict regulations for the emission of textile wastewater have been developed, as this wastewater represents a threat to the environment and population. However, because of the variety of raw materials, products, dyes, technology and equipment, the formulation of standards is complicated. In some countries, national environmental protection departments develop customised standards that take local conditions and environmental protection requirements into account (Wang et al., 2011; Holkar et al., 2016).

There are standard guidelines for the discharge of textile industry effluent in South Africa (Table 2.6). However, the application of one set of wastewater discharge limits for the entire industry is debatable due to the broad variation in the range of chemicals contained in the textile industry effluent (Le Roes-Hill et al., 2017; Holkar et al., 2016; Morshed et al., 2016). Although textile industry effluent guidelines vary according to the local municipality, the South African standard guidelines are all primarily based on the National Water Act (1998: ss13-17) and national wastewater quality standard guidelines (Table 2.6).

Table 2.6 Wastewater limit values applicable to discharge of wastewater into a water resource in South Africa (adapted from DWA, 2010).

| Parameters | Existing standards | Future standards for all discharges |
|---|---|---|
| Chemical oxygen demand | 75 | 65 |
| Colour, odour or taste | No substance capable of producing the variables listed | No substance capable of producing the variables listed |
| Ionised and unionised ammonia (N) | 3.0 | 1.0 |
| Nitrate (N) | 15 | 15 |
| pH | 5.5-9.5 | 5.5-7.5 |
| Phenol index | 0.1 | 0.01 |

| | | |
|---|---|---|
| Residual chlorine (Cl) | 0.25 | 0.014 |
| Suspended solids | 25 | 18 |
| Total aluminium (Al) | - | 0.03 |
| Total cyanide (Cn) | 0.02 | 0.006 |
| Total arsenic (As) | 0.02 | 0.01 |
| Total boron (B) | 1.0 | 0.5 |
| Total cadmium (Cd) | 0.005 | 0.001 |
| Total chromium III (CrIII) | - | 0.11 |
| Total Chromium VI (CrVI) | 0.05 | 0.02 |
| Total copper (Cu) | 0.01 | 0.002 |
| Total iron (Fe) | 0.3 | 0.3 |
| Total lead (Pl) | 0.01 | 0.009 |
| Total mercury (Hg) | 0.005 | 0.001 |
| Total selenium (Se) | 0.02 | 0.008 |
| Total zinc (Zn) | 0.1 | 0.05 |
| Faecal coliforms per 100 ml | 1000 | 1000 |

All parameters expressed in mg/l, except pH

Through reviews of relevant information sources, a table containing the textile industry effluent standard guidelines of the six most representative parameters from various countries have been compiled (Table 2.7).

Table 2.7 Guideline for the six most representative parameters for the textile industry, according to discharge location and country (Adapted from Hessel et al., 2007 and DWA, 2010)

| | | South Africa | China | Germany | Hong Kong | India | Indonesia | Malaysia | Pakistan | Thailand | United Kingdom |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BOD (mg/l) | ⬜ | - | 300 | Yes | 800 | 350 | 150 | - | - | 500 | - |
| | 🟨 | - | 15 | 25 | - | 30 | 50 | - | - | 60 | 20 |
| | 🟩 | - | - | | - | - | - | 50 | 80 | - | - |
| COD (mg/l) | ⬜ | 75 | 500 | Yes | 2000 | No | 300 | - | - | 750 | 1500 |
| | 🟨 | 30 | 60 | 160 | - | 250 | 100 | - | - | 400 | - |
| | 🟩 | - | - | - | - | - | - | 20 | 150 | - | - |
| SS (mg/l) | ⬜ | 1500 | 400 | Yes | 800 | 600 | 400 | - | - | 3000 | - |
| | 🟨 | 25 | 20 | 20 | - | 100 | 200 | - | - | 30 | 30 |
| | 🟩 | - | - | - | - | - | - | 100 | 150 | - | - |
| Chloride or Sulphate (mg/l) | ⬜ | 500 | - | Yes | 800 | 1000 | - | - | - | - | - |
| | 🟨 | 250 | - | 150 | - | - | No | - | - | 600 | - |
| | 🟩 | - | - | - | - | - | - | 600 | 1000 | - | - |
| Detergents (mg/l) | ⬜ | - | 20 | Yes | 25 | - | 10 | - | - | No | Yes* |
| | 🟨 | - | 10 | - | - | - | 5 | - | - | No | - |
| | 🟩 | - | - | - | - | - | - | 10 | 20 | - | - |
| Oils and Greases (mg/l) | ⬜ | 50 | 20 | 20 | 20 | 20 | 10 | - | - | - | 100 |
| | 🟨 | 50 | 20 | 0 | - | 10 | 5 | - | - | - | 50 |
| | 🟩 | - | - | - | - | - | - | 10 | 10 | - | - |

Discharge point

| | | | |
|---|---|---|---|
| ⬜ | Municipal wastewater treatment plant | Yes | Allowed to be found in the stream |
| 🟨 | Environment | No | Not found in the stream |
| 🟩 | Not specified | * | Varies according to municipalities |

## 2.6 Summary

Textile industries are high consumers of water; textile industry effluent is mainly produced in the wet processing stage, and resulting wastewater generated from the textile industry is very complex and poorly degradable. Dye has been a major issue in the treatment of textile mills effluent as colour is the most noticeable component, even at low concentrations. There are many methods used to treat textile effluent; however, factors such as the composition of the effluent and the conditions of the site determine the choice of technology (Chu, 2001; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al., 2016).

Textile industry effluent treatment methods can be categorised as biological treatment, chemical treatment, and physical treatment. Several methods have been used to remove dye from textile industry wastewater, including coagulation and flocculation, and adsorption (Chu, 1999; Chu, 2001; Barclay & Buckley, 2004; Metcalf & Eddy, 2004; Ranganathan et al., 2007; Engelhardt, 2010; Wang et al., 2011; Holkar et al., 2016).

The use of natural substrates such as corn cobs for dye adsorption may be feasible if they are readily available at low cost and in close proximity to the industry. Corn cobs can be shredded and dried to increase the surface area and adsorbency, respectively. The milled residues are mixed with the effluent to promote the reclamation of the water. The adsorbed dye can then be degraded through solid state fermentation (SSF) with fungi. It is possible that the fermented residue (which is enriched with protein) can be used as a soil conditioner (Robinson et al., 2002).

Recycled alum sludge is capable of treating wastewater containing dye with high removal efficiencies and provides a reduction in alum requirements and in sludge production in comparison to conventional alum coagulation. Back-diffusion is a potential problem that could be overcome by the addition of fresh alum to the system. Overdoses of RAS do not promote the restabilisation of dye in the wastewater, potentially making treatment with RAS a simple add-on process to existing treatment works. However, it has been shown that treatment of hydrophilic dyes with RAS results in back-diffusion of dye, hence the poor quality of effluent (Chu, 2001; Jangkron et al., 2011; Nair et al., 2015).

# 3 Research methodology

## 3.1 Introduction

This chapter includes a description of the materials and the methods used for the collection of data and the laboratory equipment and apparatus employed in order to meet the objectives of the study. This chapter also includes a description of the experimental methodology and analytical procedures that were used to analyse the relevant quality parameters of the wastewater.

Experimental work consisted primarily of setting up and operating a scientific mechanical flocculator for coagulation-flocculation using alum sludge, and adsorption using shredded corn cobs. In addition, chemical analyses were performed in the laboratory to assess and compare the performance of the different methods. This chapter also includes information on the collection of samples from industry and the analysis of the selected wastewater quality parameters in the laboratory in order to collect the necessary data required for the study.

## 3.2 Research design

The section describes data required to reach the aim of the study and methods that were used for data acquisition. This section also outlines the analytical methods, data analysis methodology, and the presentation of results in order to obtain meaningful information.

The research design is in alignment with the aims of this study. The work is divided as follows:

- The characteristics of the synthetic wastewater were obtained by analysing sample wastewater produced by diluting textile dye in distilled water to a concentration aligning with the findings in the literature review. Parameters analysed were namely colour, COD, TDS and pH.
- Coagulation-flocculation experiments were conducted on synthetic wastewater according to the existing operating conditions which emphasise on the fresh coagulant-recycled sludge mix ratio as the main design parameter for the removal of dye. The performance of the treatment was assessed by monitoring quality parameters at each unit process and recording the removal efficiency.
- Adsorption with corn cobs experiments were conducted on the synthetic wastewater according to existing operating conditions used in previous case studies which focused on the removal of dye from the wastewater.
- The removal efficiencies of the colour, the COD and TDS from the wastewater at various temperatures and pH by mean of coagulation-flocculation was established and compared to adsorption with shredded corn cobs.

## 3.3 Consumables, materials and equipment.

### 3.3.1 Materials and consumables

- Disperse Blue Dye 1 ($C_{14}H_{12}N_4O_2$) (Sigma-Aldrich, St. Louis, USA) used in the production of synthetic wastewater (Appendix A section A.1).
- Potassium hydroxide (Sigma-Aldrich) was added as a coagulant aid (Appendix A section A.2).

- Aluminium sulphate (alum) (Sigma-Aldrich) (Appendix A section A.3) was used as a coagulant during the laboratory experiment.
- Dried shredded corn cobs were used as an adsorption medium.

### 3.3.2 Equipment

- A Scientific Flocculator SW1 (Stuart) with 6-Pyrex beakers of 1000 ml capacity was used for the treatment of the wastewater using coagulation-flocculation method with aluminium sulphate as a coagulant, according to manufacturer's instructions.
- 50-ml cell tests were used for the treatment of wastewater using adsorption with shredded corn cobs.
- The parameters of concern in this study were colour, COD, TDS, pH and temperature. The parameters of the wastewater were analysed and tested using the following equipment:
    - Photometer (Palintest 7100, Beijing, China) to determine the colour concentration.
    - Merck Spectroquant photometer (Merck, Darmstadt, Germany) to determine the COD concentration in the wastewater with an accuracy of ± 7 mg/l COD.
    - Temperature probe (Eutech, EcoScan Temp 10) was used to determine the temperature of the wastewater.
    - TDS meter (Eutech, Eutech Cond610) was used to determine the total dissolved solid content of the wastewater.
    - pH meter (Eutech, model 700) was used to determine the pH of the sample.

## 3.4 Methodology

Following the objectives assigned to this study, the methodology followed the following steps:

- The characteristics of the synthetic wastewater were obtained by analysing sample wastewater produced by diluting textile dye in distilled water to a concentration aligned with the findings in the literature review. Parameters analysed were namely colour, chemical oxygen demand (COD), total dissolved solids (TDS) and pH. The analytical procedures were conducted as described in Appendix B
- Coagulation-flocculation experiments were conducted on synthetic wastewater according to the existing operating conditions with an emphasis on the fresh coagulant-recycled sludge mix ratio as the main design parameter for the removal of dye. The performance of the treatment was assessed by monitoring quality parameters at each unit process and recording the removal efficiency.
- Adsorption with shredded corn cobs experiments were conducted on the synthetic wastewater according to existing operating conditions used in previous case studies which focused on the removal of dye from the wastewater.
- The advantages and limitations were assessed by comparing the performance (in terms of removal efficiency) of the coagulation-flocculation to the literature and the adsorption highlighted in the study.

### 3.4.1 Data required

Data was selected in alignment with the objectives of this study. The study required the following data (Table 3.1):

- *In terms of quality:* The study focused on the removal of the colour in the wastewater. The COD and TDS solids and pH were also monitored. These quality parameters were selected based on their potential adverse effects on the environment and legislative requirements as described in section 2.3.1.
- *In terms of operating conditions:* The alum dosage, fresh 'alum:RAS' ratios were the key parameters for the coagulation-flocculation experiments; and the shredded corn cobs particle size and the dry corn cobs:wastewater ratio were considered for the adsorption with shredded corn cobs.
- *The monitoring schedul*e was designed in order to offer a better understanding of the required operating time and the sampling occurrence rate.

Table 3.1 List of relevant data and experimental procedures

| Operating Data | Monitoring Schedule | Quality parameters |
|---|---|---|
| Coagulation-flocculation<br>*Fresh alum dosage:<br>100 mg/l<br>*Fresh alum:RAS ratio:<br>1:0 ; 0:1 ; 1:1 ; 1:2 ; 2:1<br>*Mixing speed:<br>Rapid mixing: 80 RPM<br>Slow mixing: 30 RPM | Coagulation-flocculation<br>*Time of stirring:<br>Rapid mixing: 1 min<br>Slow mixing: 20 min<br>*Settling time: 1 hour<br>*Duration of experiment: 1 h 21 min<br>*Sampling:<br>Synthetic water before treatment<br>Treated effluent | Colour (mg/l Pt/Co)<br>(Chu, 2001; Tang and Chen, 2002; Ong et al., 2014)<br>COD (mg/l)<br>(Tüfekci et al., 2007; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al.,2016)<br>TDS (mg/l)<br>(Tüfekci et al., 2007; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al.,2016)<br>pH<br>(Tüfekci et al., 2007; Holkar et al., 2016; Morshed et al., 2016; Jegatheesan et al.,2016) |
| Adsorption with corn cobs<br>*Particle size: 3×3×2 $mm^3$<br>Dry subtract:wastewater ratio:<br>10 g: 100 ml | Adsorption with corn cobs<br>*corn cobs drying period:<br>Overnight<br>*Adsorption time: 48 hours<br>*Sampling:<br>Synthetic water before treatment<br>Treated effluent after 48h | Colour (mg/l Pt/Co)<br>Robinson et al., 2002; Wang et al., 2011; Holkar et al., 2016) |

### 3.4.2 Data collection framework

In line with the aim and objectives of this study, the experimental phase was set as described in Figure 3.1.

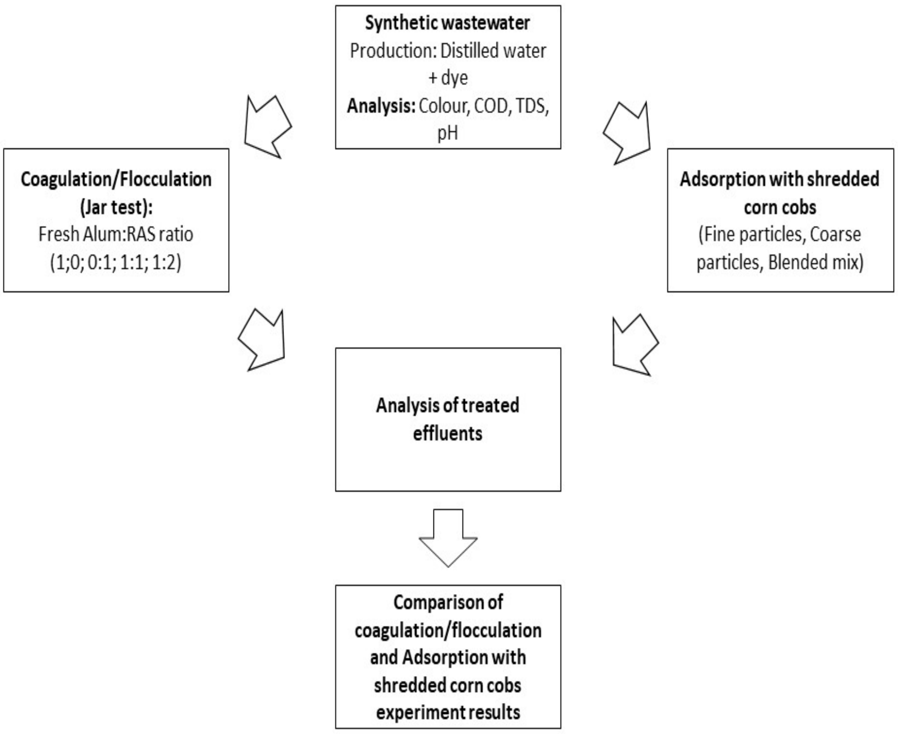


Figure 3.1 Flow diagram of basic experimental steps

### 3.4.3 Experimental procedures

Experimental procedures for this study were conducted according to the guideline described in Appendix C.

#### 3.4.3.1 Preparation of synthetic wastewater

**Optimisation of coagulation-flocculation process**.

Synthetic wastewater was produced by diluting Disperse Blue Dye 1 ($C_{14}H_{12}N_4O_2$) (Sigma-Aldrich) in distilled water. A stock dye solution of 1000 mg/l was prepared in deionised water (Sadri Moghaddam et al., 2010). The stock solution was then diluted to the working concentration of 12.5 mg/l (Chu, 2001). The same synthetic wastewater was used to determine the treatment efficiencies of RAS (Section 3.4.3.2), shredded corn cobs (Section 3.4.3.3).

### 3.4.3.2 Determination of the quality of effluent achieved by the coagulation-flocculation process

***Coagulation-flocculation process***

The Stuart Scientific Flocculator SW1 accommodates up to six beakers of 1 litre in capacity and is specially designed to allow repeatable tests under the same conditions between samples. It is fitted with vertical rotational stainless-steel paddles that mix at speeds ranging from 25 to 250 rpm, monitored by a digital display. Table 3.2 provides further specifications on the flocculator.

Table 3.2 Specifications of the laboratory scale mechanical flocculator [Adapted from Stuart (2016)]

| Specifications | |
|---|---|
| Model | SW6 |
| Description | Flocculator with 6 rotators (without beakers) |
| No. of samples | 6 |
| Speed range | 25 to 250 rpm |
| Timer | 0 to 99 minutes |
| Pre-set programs | 2 |
| Controls keypad | Touch sensitive |
| Digital displays | LED |
| Dimensions (w x d x h) | 750 x 210 x 460mm |
| Net weight | 17kg |
| Power | 230V, 50Hz, 200W |

In order to determine the ideal pH range to achieve optimal treatment efficiency, coagulation-flocculation experiments were conducted on the synthetic wastewater at a pH range between 7 and 13. The pH of the wastewater was increased by adding drops of diluted potassium hydroxide in order to determine the ideal pH range for optimum treatment efficiency.

The synthetic wastewater was treated using a Stuart Scientific Flocculator SW1 with six 1000 ml Pyrex beakers. Before the start of the mixing, aluminium sulphate [$Al_2(SO_4)_3.18H_2O$] was added to the wastewater at a coagulant at a concentration of 100 mg/l (Chu, 2001). The treatment process was conducted in a batch mode

Immediately after mixing, the liquor was mixed at an initial speed of 80 rpm for 1 min. The rotating speed was then reduced to 30 rpm and maintained for a period of 20 min (Chu, 2001). Thereafter the machine was stopped to allow the settling of particles in the wastewater for 60 min (Jangkorn, 2011).

***Collection and analysis of effluent and sludge***

After settling for 60 min, the supernatant was collected and analysed as described in Appendix B. The settled wet sludge was collected and dewatered using the standard method for TDS (ASTM D5907), then dried in an oven (Chu, 2001). The dry alum sludge was then recycled being used as a coagulant in conjunction with fresh alum at ratios (fresh alum:RAS) of 1:1, 1:2 and 0:1. The effluent and the sludge produced were handled in the same manner as during the treatment with fresh alum.

#### 3.4.3.3 Comparison of treatment efficiency of the coagulation-flocculation process using RAS to the quality of effluent treated using adsorption with shredded corn cobs.

***Treatment using shredded corn***

Corn cobs were obtained from a local supermarket. A gravimetric experiment was conducted on the corn cobs to determine the optimum drying time and temperature to reach constant weight. The dry cobs were then shredded using a blender. The shredded corn cobs were sieved and particles of sizes of approximately 1180-2360 µm, 1180-600 µm and <600 µm were collected. The shredded corn cobs were grouped into 3 different types of subtract:

- Coarse particles (Batch 1): made by mixing particles of sizes 1180-2360 µm, 1180-600 µm at 1:1 ratio;
- Fine particles (Batch 2): obtained by mixing particles of sizes ≤ 600 µm at a ratio of 1:1;
- Blend (Batch 3): consists of a mixture of particles in batch 1 and batch 2 at mixing ratio of 1:1.

The adsorption experiments were conducted in a 50-ml cell test containing the dry substrate and synthetic wastewater at a ratio of 10 g: 100 ml (Nigam et al., 2000; Robinson et al., 2002). The mixture was allowed to stand for 48 hours at room temperature, then centrifuged at 10 000 g for 5 minutes. Samples from the supernatant were collected for analysis of parameters.

***Comparative analysis***

The results from the analysis of the effluent from the RAS treatment method were compared to the results of the adsorption with shredded corn cobs effluents.

## 3.5 Analytical procedures

The analysis and collection of data were conducted using the methods and procedures described in Appendix B.

## 3.6 Presentation and analysis of results

The results were presented in the form of graphs and tables. The analysis was conducted by assessing the treatment efficiencies with regard to the selected data and compared to the results of previous studies discussed in the literature review.

# 4 Results

## 4.1 Introduction

This section of the study presents results of the experimental work conducted in line with the aim and objectives of the study. For easy and concurrent readability of this section, average results are presented in tabular and graphical forms. Averages were obtained by determining the mean of each batch. Ranges were used to describe the lowest and highest results obtained in each batch. Details of laboratory report sheets are presented in Appendix D.

## 4.2 Experimental work

This section was designed in alignment with the objectives of this study and the methodology described in Chapter 3. For ease of reading, this section was divided into the following subsections:

- The quality of the effluent achieved by the coagulation-flocculation process which was subdivided into:
    - The optimisation of the coagulation-flocculation process,
    - The quality of the synthetic wastewater in accordance with Section 3.4.1,
    - The quality of the treated effluent using coagulant as fresh alum, recycled alum and a combination of fresh alum and recycle alum sludge at various mixture ratios (1:1 and 1:2).

- The quality of the effluent achieved after treatment by adsorption with shredded corn cobs.

The removal efficiency of each treatment method was calculated using the formula described in the Equation 2.1.

### 4.2.1 Quality of effluent achieved by the coagulation-flocculation process

#### 4.2.1.1 Optimisation of coagulation-flocculation process.

Various pH ranges were studied for removing disperse dye from the synthetic wastewater. The concentration of fresh alum was maintained at the design concentration of 100 mg/l (Section 3.4.3.1.1). The initial pH (7.2) of the synthetic wastewater was used for the experiment, then the pH was gradually increased. The change of pH was achieved by adding drops of diluted potassium hydroxide to the synthetic wastewater. The experiment was conducted using samples with pH ranging from 7.2 to 12.1 (Table 4.1).

Table 4.1 Effect of change in pH in removal colour from wastewater using coagulation-flocculation

| | Synthetic wastewater | | Treated effluent | | Removal efficiency |
|---|---|---|---|---|---|
| | pH | Colour | pH | Colour | Colour |
| Sample 1 | 7.2 | 150 | 4.1 | 145 | 3% |
| Sample 2 | 8.5 | 125 | 4.3 | 120 | 4% |
| Sample 3 | 9.7 | 145 | 4.3 | 120 | 17% |
| Sample 4 | 10.7 | 150 | 4.4 | 80 | 47% |
| Sample 5 | 11.9 | 135 | 8.5 | 15 | 89% |
| Sample 6 | 12.0 | 150 | 10.8 | 100 | 33% |
| Sample 7 | 12.1 | 155 | 11.0 | 115 | 26% |

Colour expressed in mg/l Pt/Co.

The colour removal efficiency peaked at pH 11.9 (Figure 4.1). After treatment, a drop in pH to 8.5 in the treated effluent was observed.

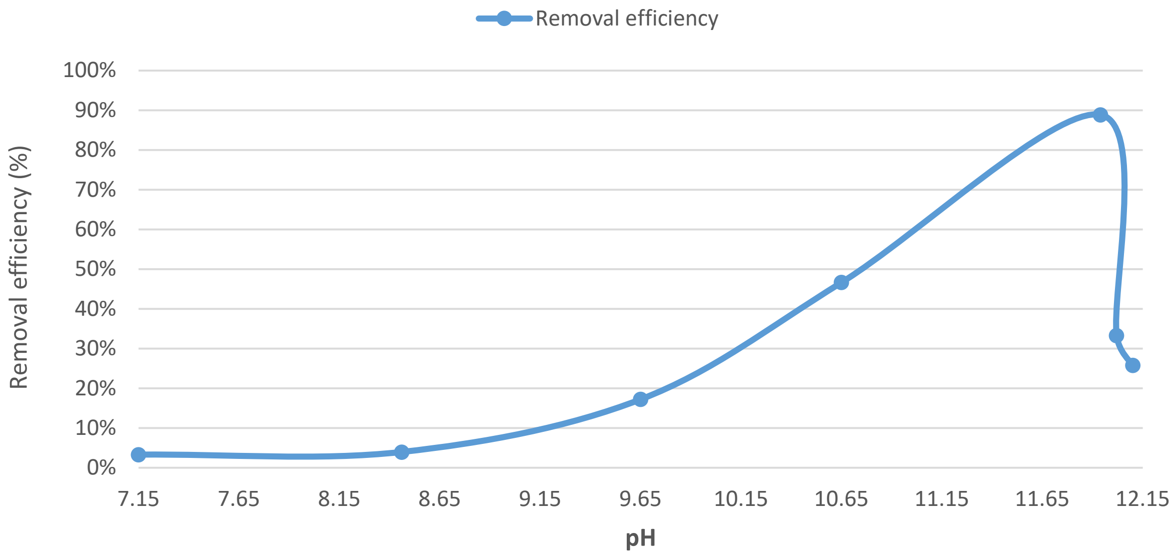


Figure 4.1 Effect of change in pH in removal of colour from wastewater using coagulation-flocculation.

However, from pH 12 upwards, it was noticed that the more the initial pH was increased, the less it would drop after treatment (Figure 4.2). Based on the findings, the pH 11.9 was chosen for the remainder of the experiments.

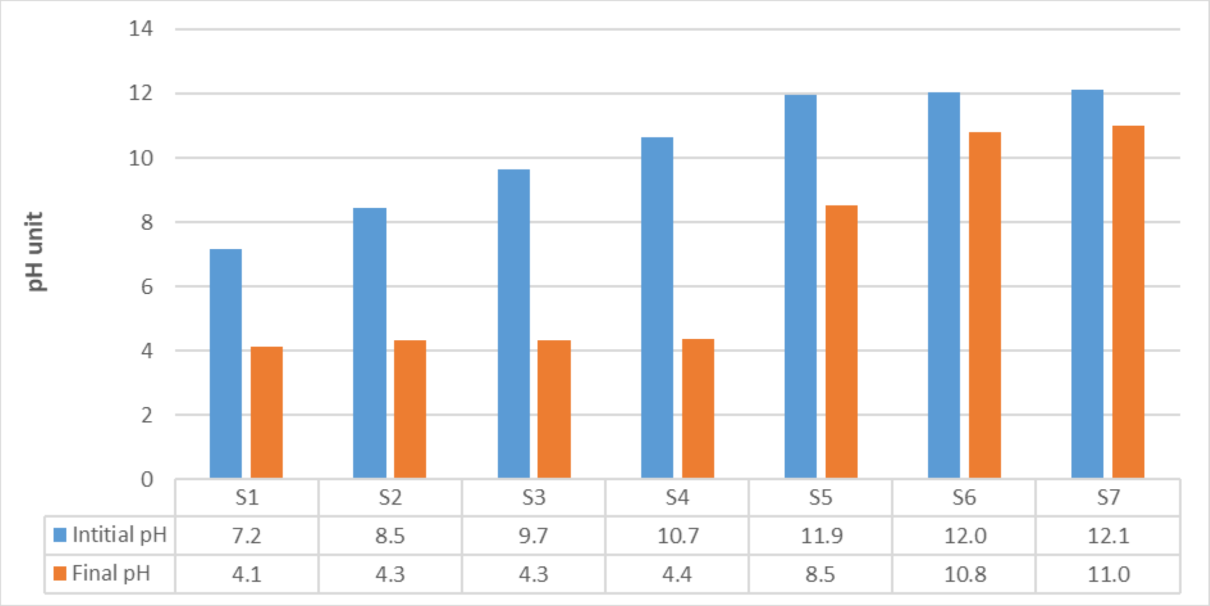


Figure 4.2 Change in pH after coagulation with fresh alum at various pH values.

### 4.2.1.2 Synthetic wastewater characteristics

A fresh batch of synthetic wastewater was made up each day over the 5-day experimental period. The colour, COD and TDS of the synthetic wastewater of each batch were measured in triplicate (Table 4.2). It was found that the synthetic wastewater had an average colour of 133 ± 13 mg/l (range 115-145 mg/l), and the average COD and TDS were evaluated to be 38 ± 4 mg/l (range 32-43 mg/l) and 779 ± 18 mg/l (range 754-804 mg/l), respectively. The average measured COD of the synthetic wastewater aligned with the calculated theoretical COD of the sample evaluated at 31 mg/l (Appendix C, section C.4). The pH of the synthetic wastewater was measured at an approximate range between 11.9 and 12.0. The lowest colour measurement of 115 mg/l with a pH of 11.9 was recorded in Batch 1. The maximum colour concentration of 145 mg/l was measured in Batches 3 and 4 at a pH of 12.0.

Table 4.2 Characteristics of sample synthetic wastewater used in this study

| | **Colour (mg/l Pt/Co)** | **COD (mg/l)** | **TDS (mg/l)** | **pH** |
|---|---|---|---|---|
| **Batch 1 (*n*=3)** | 115 | 32 | 776 | 11.9 |
| **Batch 2 (*n*=3)** | 130 | 37 | 778 | 11.9 |
| **Batch 3 (*n*=3)** | 145 | 36 | 804 | 12.0 |
| **Batch 4 (*n*=3)** | 145 | 41 | 783 | 12.0 |
| **Batch 5 (*n*=3)** | 130 | 43 | 754 | 11.9 |
| **Average ± SD** | **133 ± 13** | **38 ± 4** | **779 ± 18** | **-** |
| **Range** | **115-145** | **32-43** | **754-804** | **11.9-12.0** |

### 4.2.1.3 Analysis of the synthetic wastewater after treatment with coagulation-flocculation.

#### *a) Quality of synthetic wastewater treated with fresh alum as coagulant (Ratio 1:0)*

The synthetic wastewater was treated using coagulation-flocculation with fresh alum. Following this process, a notable decrease in the level of the measured parameters was observed (Table 4.3). A substantial removal of colour was observed as a drop from an average concentration of 133 ± 13 mg/l (range 115-145 mg/l) down to a minimum concentration of 14 ± 1 mg/l (range 5-25 mg/l) (Figure 4.3). An average removal efficiency of 89 ± 2%, with a maximum and minimum value of 96% and 81%, respectively was recorded for colour (Figure 4.3). An average COD removal efficiency of 29 ± 3% (range 19-41%) was recorded, dropping from an average of 38 ± 4 mg/l (range 32-41 mg/l) to 28 ± 4 mg/l (range 21-35 mg) (Figure 4.4). A TDS a concentration of 779 ± 18 mg/l (range 754-804 mg/l) was recorded before treatment, with a drop to 501 ± 25 mg/l (range 367-632 mg/l) after treatment. An average TDS removal efficiency of 36 ± 4% (range 19-59%) was recorded (Figure 4.5).

Table 4.3 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation

| | **Ratio 1:0** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Synthetic wastewater** | | | | **Treated effluent** | | | | **Removal efficiency (%)** | | |
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| Batch 1 (*n*=3) | 115 | 32 | 776.1 | 11.9 | 15 | 23 | 481 | 8.1-8.8 | 85 | 31 | 38 |
| Batch 2 (*n*=3) | 130 | 37 | 778.4 | 11.9 | 15 | 26 | 479 | 8.4-8.6 | 88 | 31 | 38 |
| Batch 3 (*n*=3) | 145 | 36 | 804.5 | 12.0 | 13 | 26 | 488 | 8.4-8.8 | 90 | 28 | 39 |
| Batch 4 (*n*=3) | 145 | 41 | 782.7 | 12.0 | 13 | 30 | 533 | 8.4-8.8 | 91 | 29 | 32 |
| Batch 5 (*n*=3) | 130 | 43 | 754.3 | 12.0 | 15 | 33 | 525 | 8.4-8.6 | 88 | 24 | 30 |
| Average | 133 | 38 | 779 | - | 14 | 28 | 501 | - | 89 | 29 | 36 |
| Deviation | 13 | 4 | 18 | - | 1 | 4 | 25 | - | 2 | 3 | 4 |
| Range | 115-145 | 32-41 | 754-804 | 11.9-12.0 | 5-25 | 21-35 | 367-632 | 8.1-8.8 | 81-96 | 19-41 | 19-59 |

*Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l.

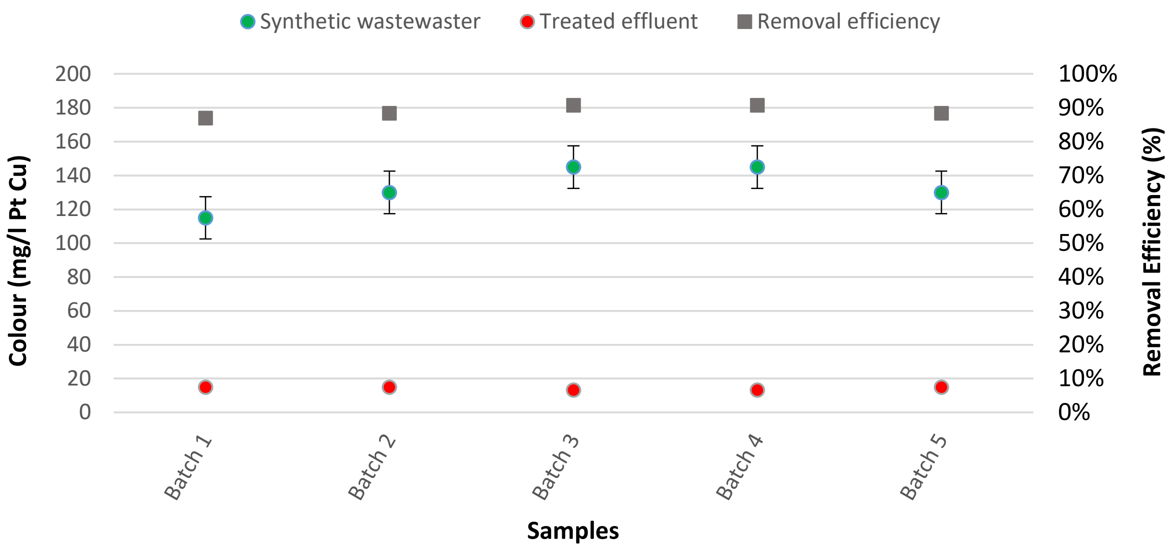


Figure 4.3 Average change in colour and colour removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum (Ratio 1:0)

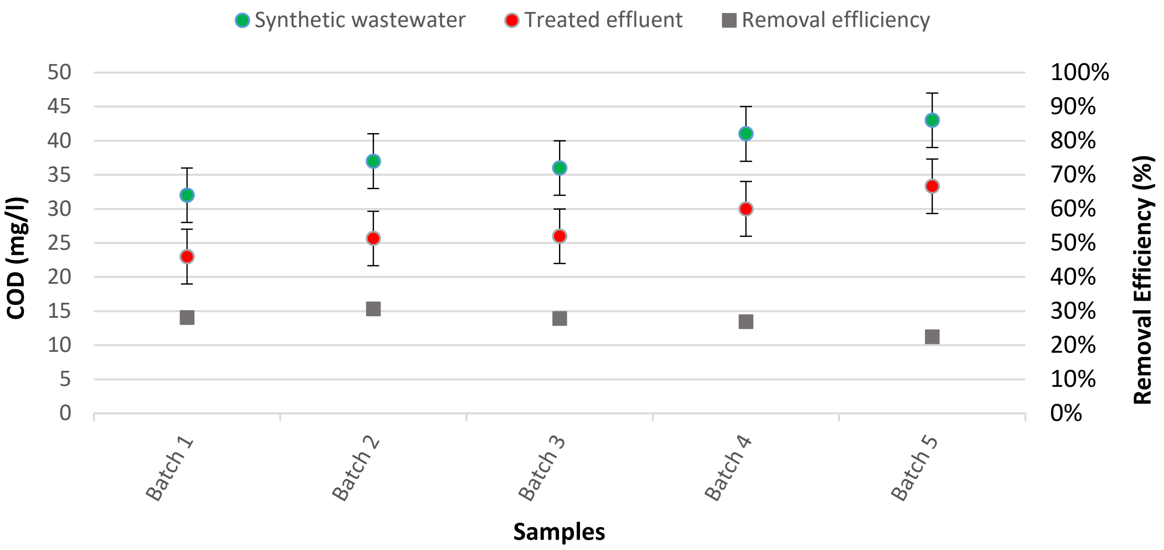


Figure 4.4 Average change in COD and COD removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum (Ratio 1:0)

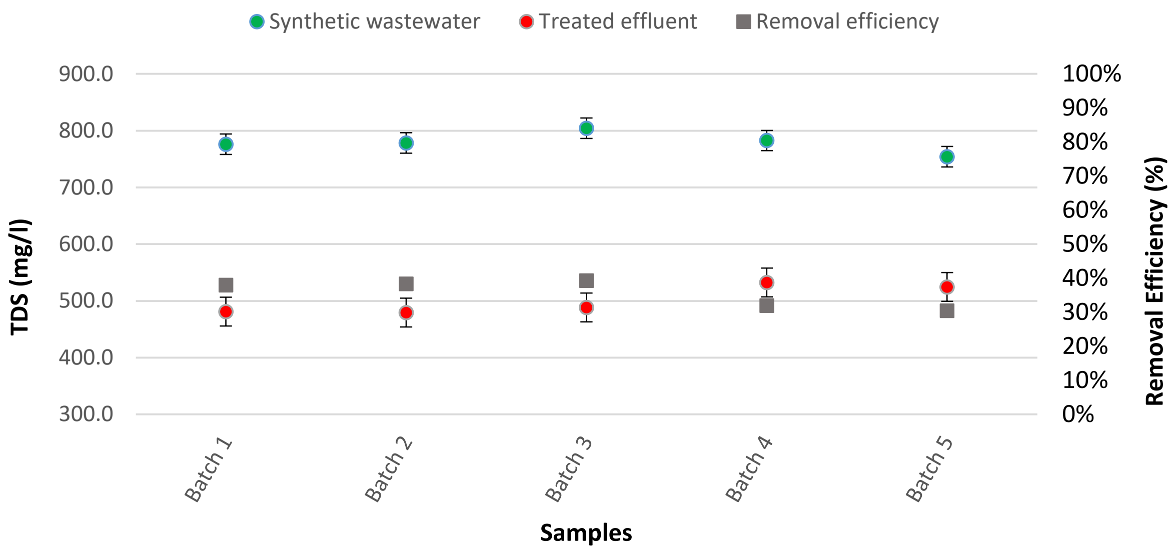


Figure 4.5 Average change in TDS and TDS removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum (Ratio 1:0)

A notable drop in the pH from a maximum of 12.0 in the raw wastewater to a drop of up to 8.1 after treatment was observed (Figure 4.6).

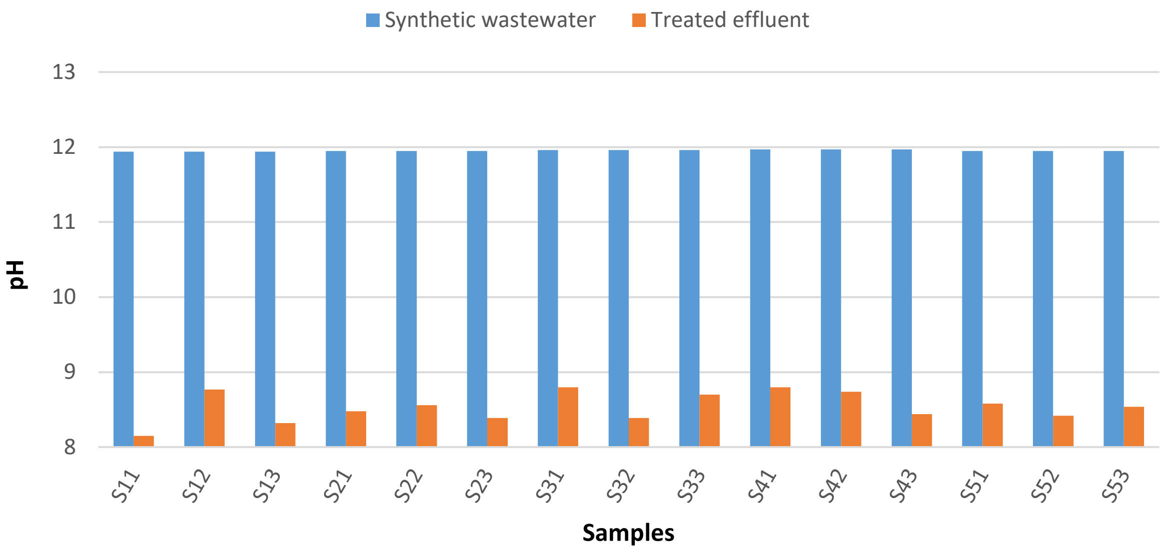


Figure 4.6 Change in pH in synthetic wastewater after coagulation-flocculation with fresh alum (Ratio 1:0)

### b) *Quality of synthetic wastewater treated with RAS as coagulant (Ratio 0:1)*

In this phase of the experimental work, the sludge from the fresh alum coagulation-flocculation experiment was collected and reused as a coagulant, and the results are presented in Table 4.4. A significant colour removal efficiency of 78 ± 3% (range 67-88%) was recorded, with a drop from an average colour concentration of 115 ± 6 mg/l (range 105-120 mg/l) before treatment to 25 ± 2 mg/l (range 15-35 mg/l) after treatment (Figure 4.7). Significant average removal efficiencies of COD and TDS were recorded at 22 ± 3% (range 14-34%) (Figure 4.8) and 32 ± 1% (range 29%-35%), respectively (Figure 4.9). Detailed results can be found in Appendix B (Section 7.4.2).

Table 4.4 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation with RAS

| | **Ratio 0:1** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Synthetic wastewater** | | | | **Treated effluent** | | | | **Removal efficiency (%)** | | |
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| Batch 1 (*n*=3) | 115 | 35 | 750 | 12.0 | 25 | 28 | 505 | 11.5-11.7 | 76 | 20 | 33 |
| Batch 2 (*n*=3) | 120 | 37 | 768 | 11.9 | 23 | 28 | 512 | 11.6-11.7 | 81 | 25 | 33 |
| Batch 3 (*n*=3) | 120 | 34 | 778 | 11.9 | 23 | 27 | 521 | 11.7-11.8 | 81 | 20 | 33 |
| Batch 4 (*n*=3) | 105 | 38 | 753 | 11.9 | 27 | 29 | 515 | 11.6-11.7 | 75 | 25 | 32 |
| Batch 5 (*n*=3) | 115 | 40 | 753 | 12.0 | 28 | 32 | 523 | 11.6-11.7 | 75 | 21 | 31 |
| Average | 115 | 37 | 760 | - | 25 | 29 | 515 | - | 78 | 22 | 32 |
| Deviation | 6 | 2 | 12 | - | 2 | 2 | 7 | - | 3 | 3 | 1 |
| Range | 105-115 | 34-38 | 750-778 | 11.9-12.0 | 15-35 | 25-34 | 502 - 535 | 11.5-11.8 | 67 - 88 | 14-34 | 29-35 |

*Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l.

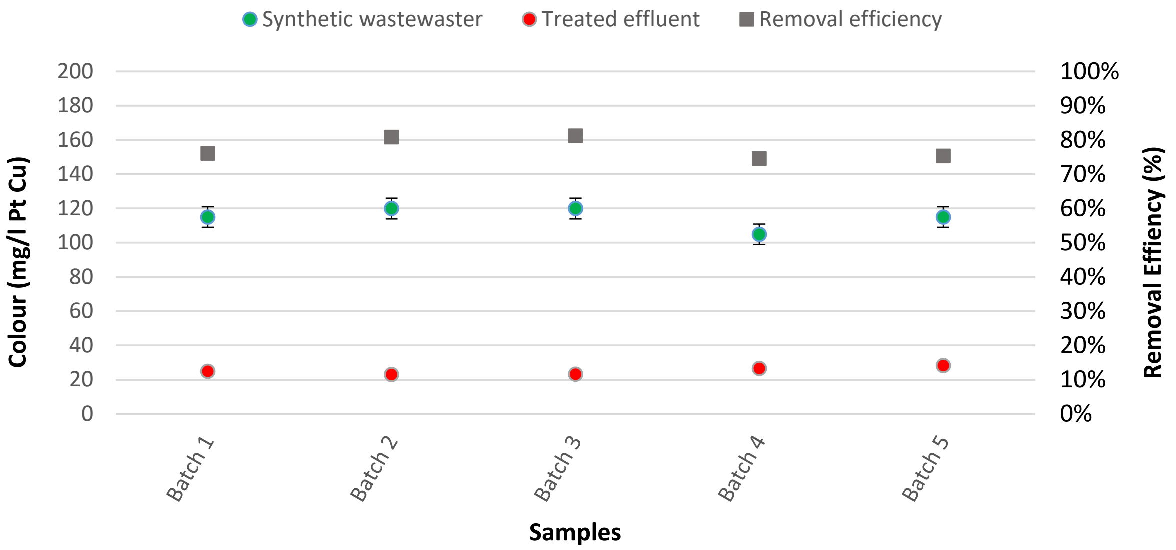


Figure 4.7 Average change in colour and colour removal efficiency of synthetic wastewater after coagulation-flocculation with RAS (Ratio 0:1)

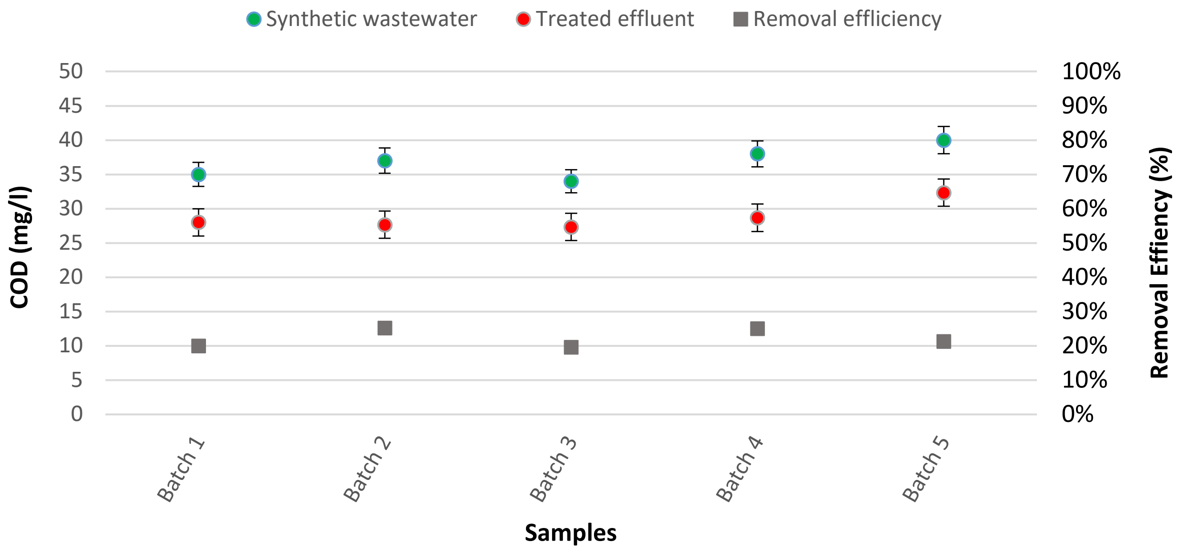


Figure 4.8 Average change in COD and COD removal efficiency of synthetic wastewater after coagulation-flocculation with RAS (0:1)

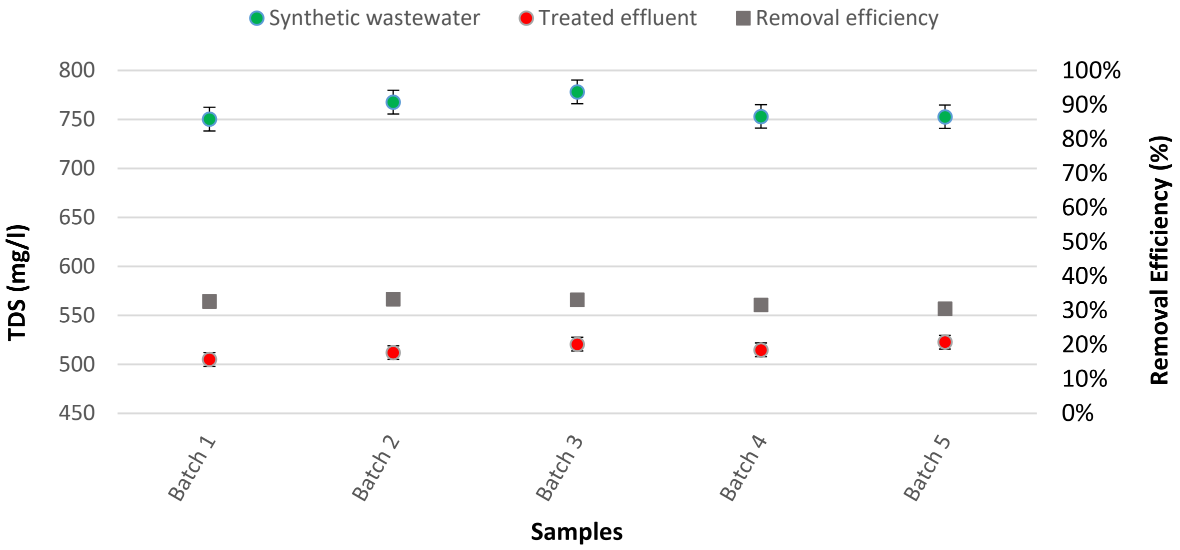


Figure 4.9 Average change in TDS and TDS removal efficiency of synthetic wastewater after coagulation-flocculation with RAS (Ratio 0:1)

The pH dropped slightly from 12.0 in the synthetic wastewater to 11.7 in the treated effluent (Figure 4.10)

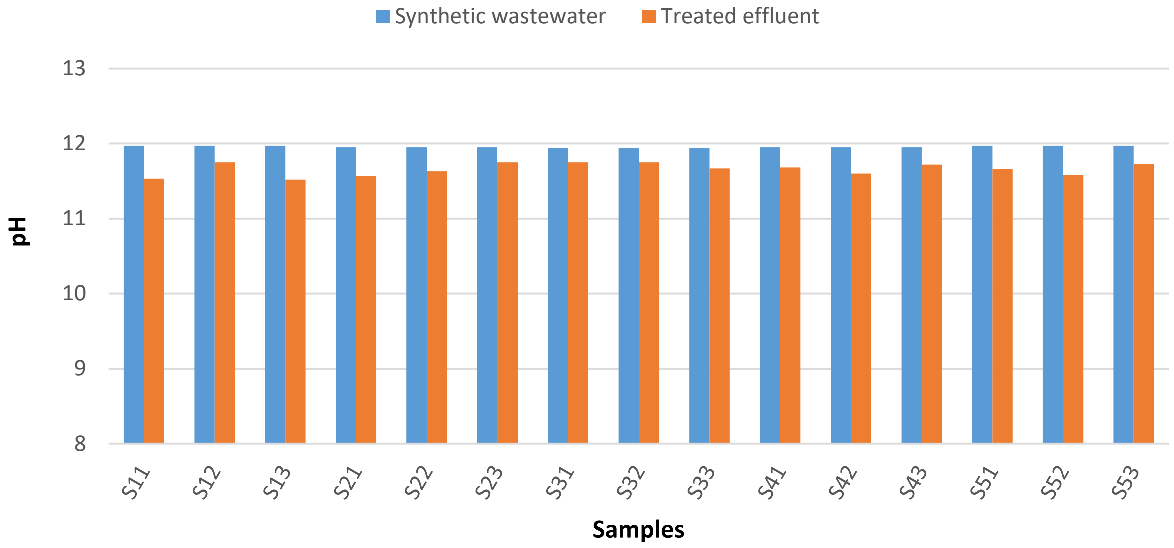


Figure 4.10 Change in pH in synthetic wastewater after coagulation-flocculation with RAS (Ratio 0:1)

### c) *Quality of synthetic wastewater treated with fresh alum and RAS (1:1)*

The characteristics of the final effluent presented in Table 4.5 gives an indication of the quality of the effluent produced by the coagulation-flocculation with fresh alum mixed with RAS at a ratio of 1:1. It was found that a highly notable average reduction of colour of 86 ± 3% (range 83-88%) was achieved, with a drop from an average concentration of 130 ± 4 mg/l (range 125-135mg/l) in the synthetic wastewater down to 18 ± 4 mg/l (range 10-30 mg/l) in the treated effluent (Figure 4.11). A notable average reduction of 37 ± 5% (range 30-50%) of the TDS contained in the water was observed. The TDS concentration was reduced from an average concentration of 724 ± 46 mg/l (range 677-792 mg/l) to an average of 457 ± 21 mg/l (range 393-502 mg/l) (Figure 4.13). Little to no COD removal was recorded after treatment. In most cases, an increase in COD in the treated effluent was observed (Table 4.5).

Table 4.5 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation (ratio 1:1)

| | **Ratio 1:1** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Synthetic wastewater** | | | | **Treated** | | | | **Removal efficiency (%)** | | |
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| Batch 1 (*n*=3) | 130 | 28 | 688 | 11.9 | 17 | 29 | 471.4 | 9.8-10.5 | 87 | -2 | 32 |
| Batch 2 (*n*=3) | 130 | 28 | 745 | 12.0 | 22 | 29 | 470.1 | 10.4-0.6 | 83 | -4 | 37 |
| Batch 3 (*n*=3) | 135 | 34 | 677 | 12.0 | 18 | 35 | 426.9 | 10.4-0.5 | 85 | -2 | 37 |
| Batch 4 (*n*=3) | 130 | 31 | 715 | 11.9 | 15 | 30 | 474.6 | 10.3-10.5 | 88 | 6 | 34 |
| Batch 5 (*n*=3) | 125 | 22 | 792 | 12.0 | 17 | 25 | 444.5 | 10.4-10.5 | 87 | -14 | 44 |
| Average | 130 | 29 | 724 | - | 18 | 29 | 457 | - | 86 | -3 | 37 |
| Deviation | 4 | 4 | 46 | - | 4 | 3 | 21 | - | 3 | 7 | 5 |
| Range | 125-135 | 22-34 | 677-792 | 11.9-12.0 | 10-30 | 22-39 | 393-502 | 9.8-10.6 | 77-89 | -27-11 | 30-50 |

*Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l.

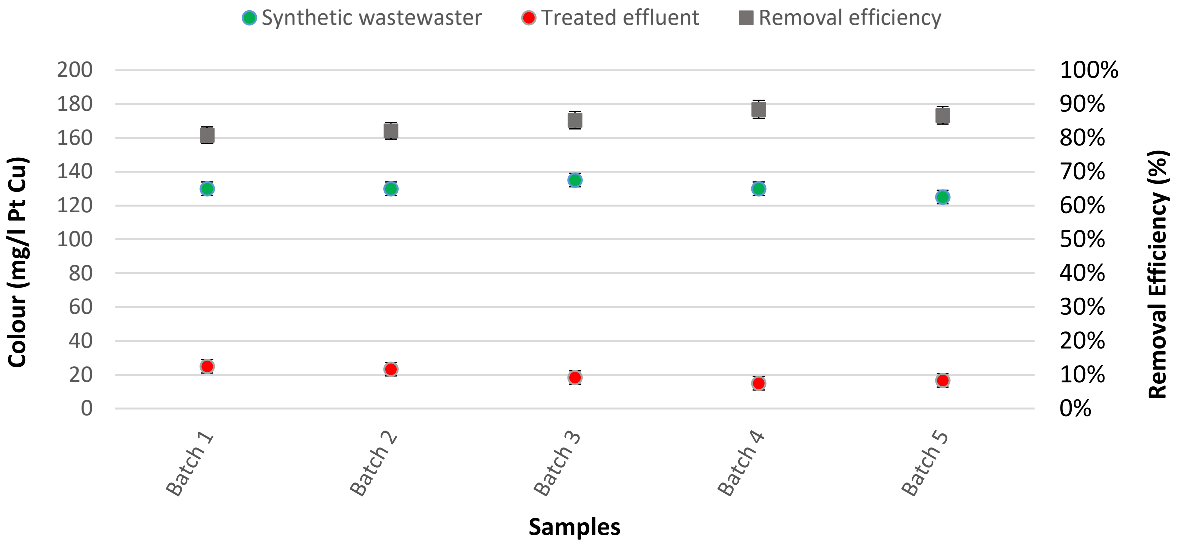


Figure 4.11 Change in colour and colour removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:1)

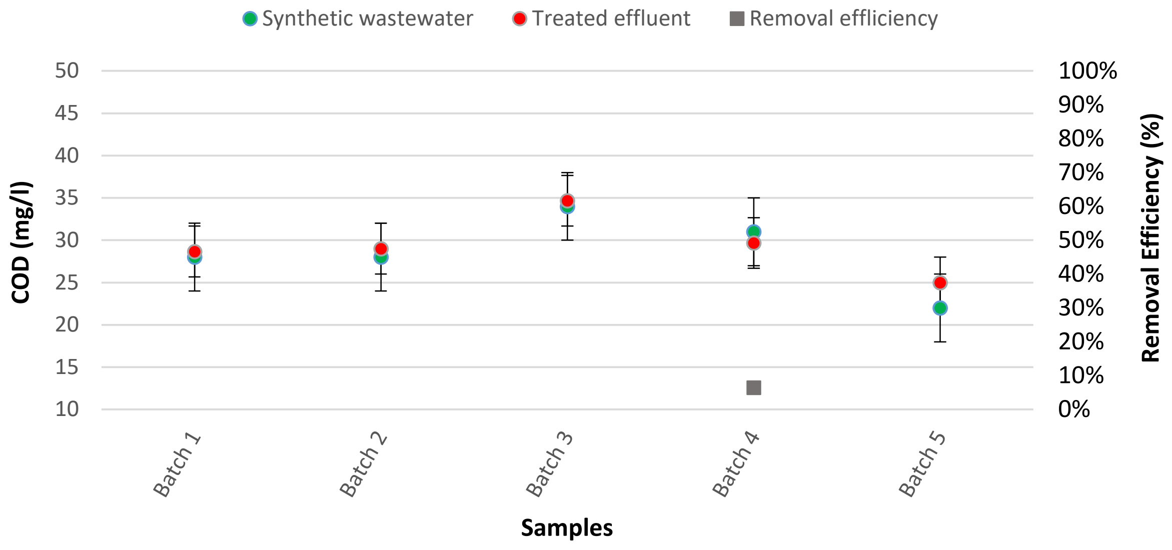


Figure 4.12 Average change in COD and COD removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:1)

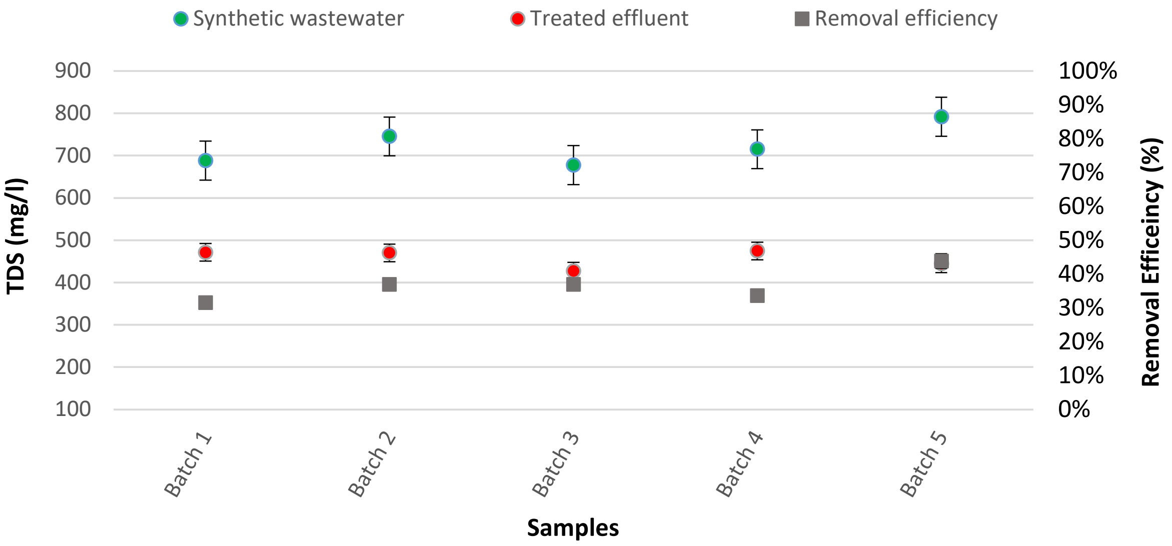


Figure 4.13 Average change in TDS and TDS removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:1)

A change in pH from a range between 11.9 and 12.0 down to a range between 9.8 and 10.6 was recorded, as shown in Figure 4.14.

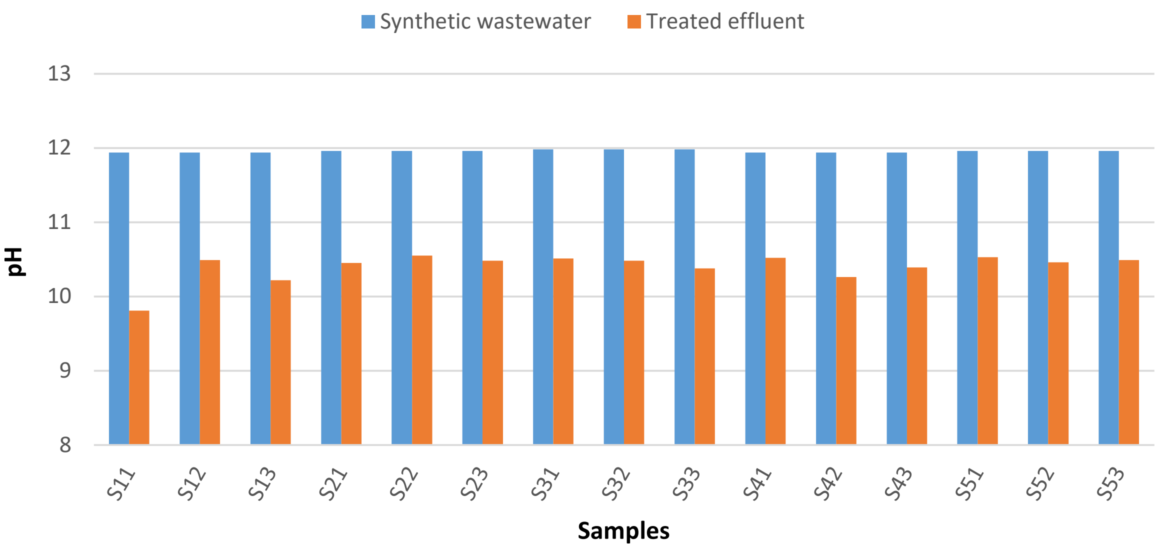


Figure 4.14 Change in pH in synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:1)

*d) Quality of synthetic wastewater treated with fresh alum and RAS (1:2)*

Table 4.6 presents the results of effluent quality achieved by coagulation-flocculation with fresh alum used in combination with RAS at a ratio of 1:2. A notable average reduction of colour from the synthetic wastewater was recorded at 82 ± 2 % (range 80-84%), with a drop from an average concentration of 134 ± 7 mg/l (range 140-125 mg/l) in the raw wastewater down to 25 ± 2 mg/l (range 22-27 mg/l) in the treated effluent (Figure 4.15). An average TDS removal efficiency of 30 ± 5 % (range 22-35%) was achieved. The TDS concentration was reduced from 739 ± 40 mg/l (range 700-786 mg/l) to 515 ± 34 mg/l (range 464-549 mg/l) (Figure 4.16). An increase in COD in the effluent was observed after treatment (Table 4.6).

Table 4.6 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation (ratio 1:2)

| | **Ratio 1:2** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Raw** | | | | **Treated** | | | | **Removal efficiency (%)** | | |
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| Batch 1 (*n*=3) | 140 | 33 | 726 | 11.9 | 23 | 37 | 509 | 11.0-11.1 | 84 | -11 | 30 |
| Batch 2 (*n*=3) | 140 | 35 | 786 | 12.0 | 27 | 38 | 545 | 10.9-11.0 | 81 | -10 | 31 |
| Batch 3 (*n*=3) | 135 | 29 | 700 | 11.9 | 27 | 21 | 464 | 10.7-10.9 | 80 | -7 | 34 |
| Batch 4 (*n*=3) | 130 | 25 | 776 | 12.0 | 25 | 28 | 506 | 11.0-11.1 | 81 | -12 | 35 |
| Batch 5 (*n*=3) | 125 | 28 | 706 | 11.9 | 22 | 29 | 549 | 10.9-11.1 | 83 | -4 | 22 |
| Average | 134 | 30 | 739 | - | 25 | 33 | 515 | - | 82 | -9 | 30 |
| Deviation | 7 | 4 | 40 | - | 2 | 5 | 34 | - | 2 | 3 | 5 |
| Range | 125-140 | - | 700-786 | 11.9-12.0 | 20-30 | - | 460-560 | 10.7-11.1 | 77-86 | - | 21-36 |

*Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l.

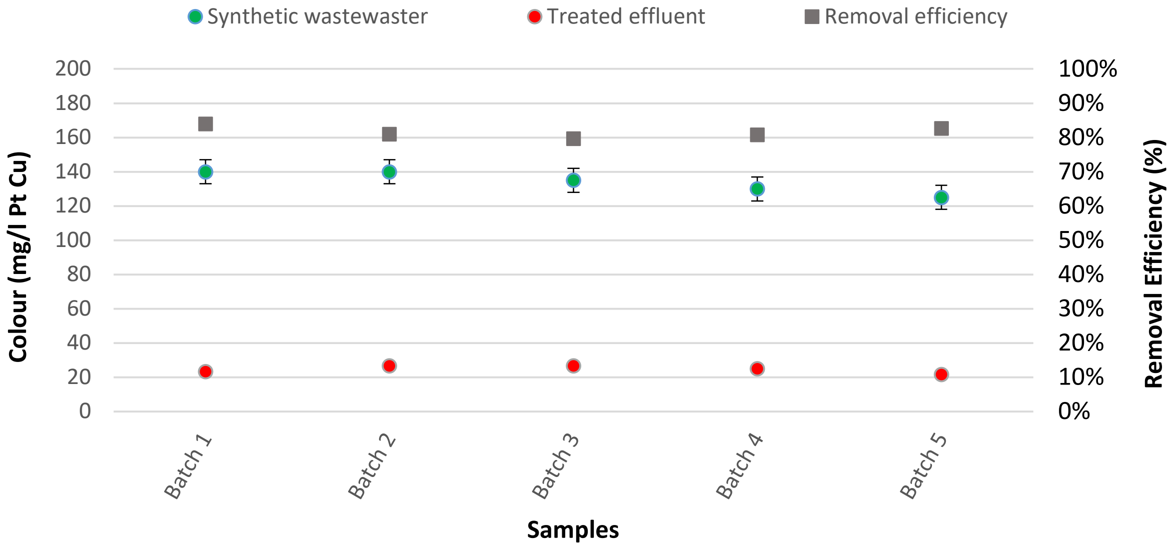


Figure 4.15 Average change in colour and colour removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:2)

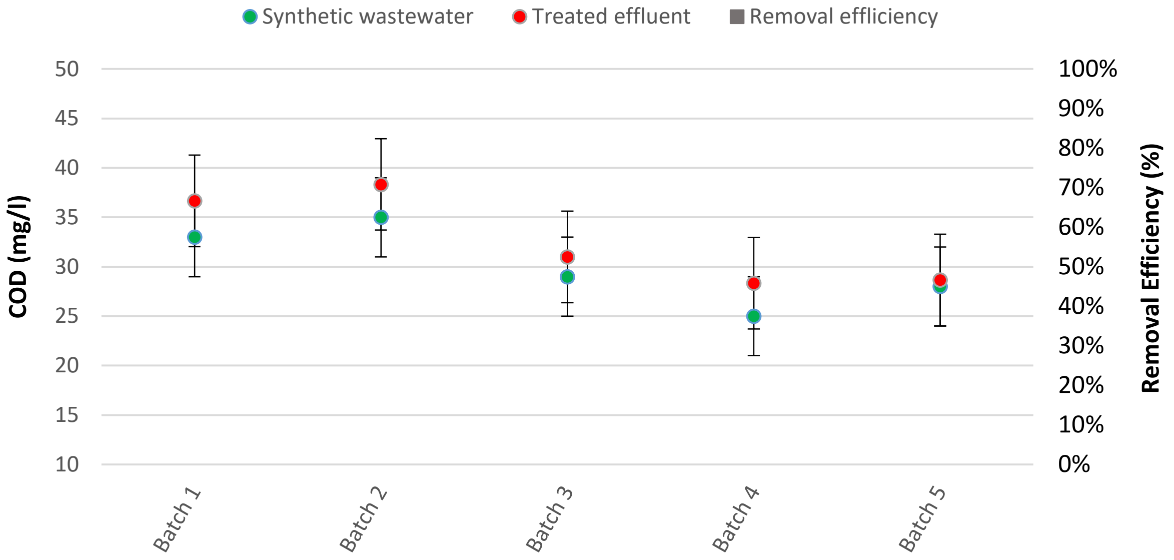


Figure 4.16 Average change in COD and COD removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:2)

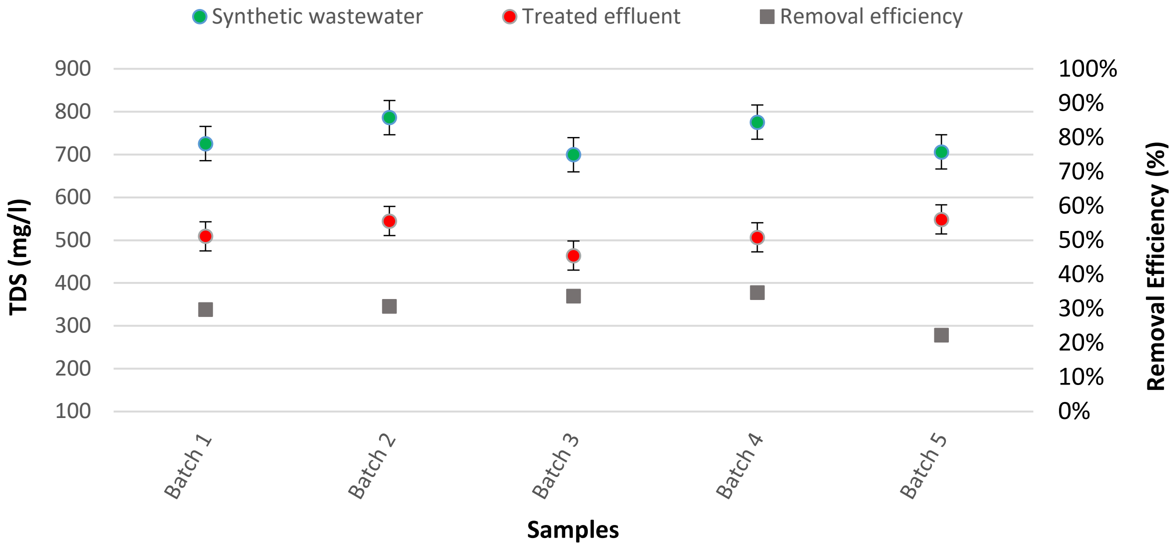


Figure 4.17 Average change in TDS and TDS removal efficiency of synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:2)

The pH slightly dropped from a maximum of 12.0 in the synthetic wastewater down to 10.7 after treatment (Figure 4.17).

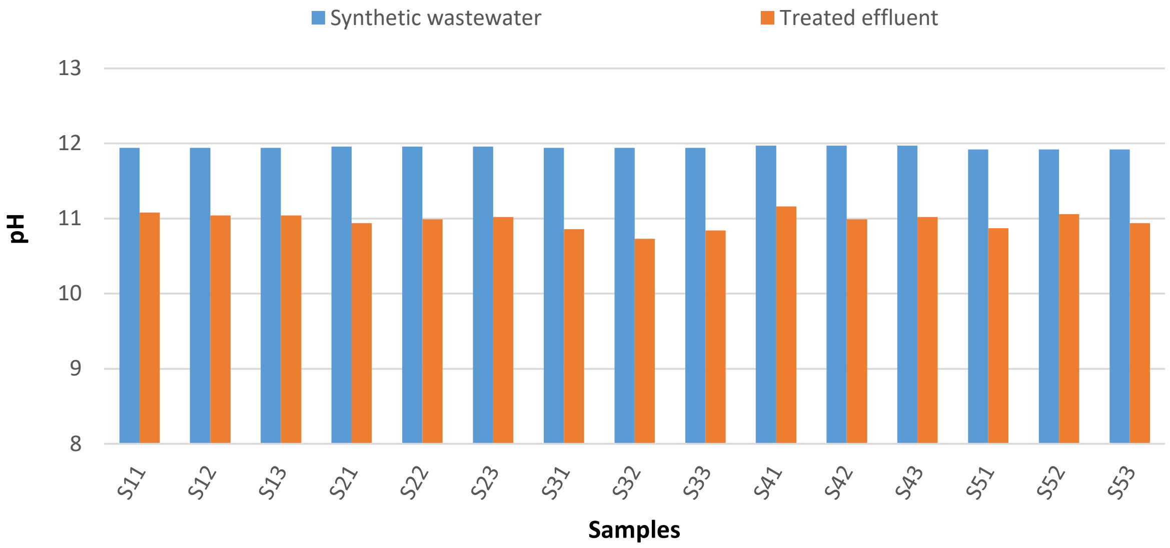


Figure 4.18 Change in pH in synthetic wastewater after coagulation-flocculation with fresh alum and RAS (ratio 1:2)

### 4.2.2 Quality of the synthetic wastewater after treatment with shredded corn cobs

#### 4.2.2.1 Gravimetric test

Table 4.7 presents results of the gravimetric test. The original mass of the corn cobs was 698.5 ± 0.03 g. The cobs were then placed in an oven at 80°C to dry, and the masses were recorded after 1 hour, 1 hour 30 minutes, 2 hours, and 24 hours. The mass of the corn cobs decreased to 432.4 ± 0.02 g after 24 hours.

Table 4.7 Average mass of corn cobs dried over time

| Time | T0 | T1 (1 h) | T2 (1,5 h) | T3 (2 h) | T4 (24 h) |
|---|---|---|---|---|---|
| Mass 1 (g) | 698.5 | 662.9 | 620.0 | 605.0 | 432.4 |
| Mass 2 (g) | 698.6 | 662.9 | 620.0 | 605.0 | 432.5 |
| Mass 3 (g) | 698.5 | 663.0 | 620.0 | 604.8 | 432.4 |
| Average mass (g) ± SD | 698.5 ± 0.03 | 662.9 ± 0.01 | 620.0 ± 0.02 | 604.9 ± 0.07 | 432.4 ± 0.02 |

#### 4.2.2.2 Quality of effluent treated with corn cobs

The results of the laboratory experiments with shredded corn cobs are presented in Table 4.8. The average colour in the treated effluent was 118 ± 3 mg/l (range 115-120 mg/l), with a pH level ranging between 11.9 and 12.0. After treatment, the colour of the effluent was increased to a level above the detection limit of the spectrophotometer (>500 mg/l) in both batch 1, batch 2 and batch 3. The pH of the effluent ranged between 11.0 and 11.2 after treatment with fine particles (≤ 600 µm), between 10.9 and 11.1 in the effluent treated with blended particle mix, and between 11.0 and 11.1 after treatment with coarse particles. Further tests were conducted on COD. A COD of 35 mg/l in batch 1, 37 mg/l in batch 2 and 34 mg/l in batch 3 was recorded in the synthetic wastewater. After treatment, average COD of 14520 ± 516 mg/l (14150 – 15110 mg/l), 14710 ± 419 mg/l (range 14330 – 15460 mg/l) and 10797 ± 869 mg/l (range 10010 – 11730 mg/l) in batch 1, batch 2 and batch 3, respectively, were recorded. The results are discussed in Chapter 5.

Table 4.8 Synthetic wastewater parameters after treatment by adsorption with shredded corn cobs

| | Synthetic wastewater | | | Treated effluent | | |
|---|---|---|---|---|---|---|
| | pH | Colour | COD | pH | Colour | COD |
| Batch 1 (fine) (n=3) | 12.0 | 115 | 35 | 11.0 – 11.2 | >500 | 14520 ± 516 |
| Range | - | - | - | 11.0 – 11.2 | - | 14150 – 15110 |
| Batch 2 (Blend) (n=3) | 12.0 | 120 | 37 | 10.9 – 11.1 | >500 | 14710 ± 419 |
| Range | - | - | - | 10.9 – 11.1 | - | 14330 – 15460 |
| Batch 3 (Coarse) (n=3) | 11.9 | 120 | 34 | 11.0 – 11.1 | >500 | 10797 ± 869 |
| Range | - | - | - | 11.0 – 11.1 | - | 10010 – 11730 |

*Colour expressed in mg/l Pt/Co; COD expressed in mg/l.

## 4.3 Comparison of the quality of effluent achieved using various ratios of fresh alum to RAS

The results for coagulation/flocculation of synthetic wastewater with fresh alum, RAS, and mixtures of the two were compared (Table 4.9). These results were used to select the most suitable approach for the use of RAS in the treatment of wastewater containing disperse dye. This is discussed in detail in Chapter 5.

Table 4.9 Comparison of the quality of effluent achieved using various ratios of fresh alum to RAS

| | Removal efficiency (%) | | | Change in pH | |
|---|---|---|---|---|---|
| Ratio | Colour | COD | TDS | Initial pH | Final pH |
| 1:0 | 89% ± 2% | 29% ± 3% | 36% ± 4% | 11.9 – 12.0 | 8.1 – 8.8 |
| 0:1 | 78% ± 3% | 22% ± 3% | 32% ± 1% | 11.9 – 12.0 | 11.5 – 11.8 |
| 1:1 | 86% ± 3% | -3% ± 1% | 37% ± 5% | 11.9 – 12.0 | 9.8 – 10.6 |
| 1:2 | 82% ± 2% | - | 30% ± 5% | 11.9 – 12.0 | 10.7 – 11.1 |

## 4.4 Summary

A preliminary experiment was conducted to determine the pH at which the highest removal of colour from synthetic textile wastewater containing disperse dye could be achieved using coagulation/flocculation with fresh alum. The synthetic wastewater was formulated based on the optimum pH. The parameters of the synthetic wastewater for pH, colour, COD and TDS were 12.0, 133 ± 13 mg/l, 38 ± 4 mg/l and 779 ± 18 mg/l, respectively. A peak treatment efficiency of 88.9% was found for colour removal at pH 11.9, and a pH of 8.5 was recorded after treatment.

Synthetic wastewater treated with fresh alum as a coagulant/flocculant demonstrated high colour removal efficiencies of up to 96% (Appendix D, Table D.1) in a sample during the actual experiment. Average removal efficiencies of 29 ± 3% for COD and 36% ± 4% for TDS were demonstrated. The pH of the treated effluent was 8.4.

Coagulation-flocculation with recycled sludge achieved average colour, COD and TDS removal efficiencies of 78 ± 3%, 22 ± 3% and 32 ± 1%, respectively. The pH of the treated effluent was 11.7. Fresh alum and RAS were blended at ratios of 1:1 and 1:2 and used as coagulants. For the 1:1 ratio, average colour and TDS removal rates of 86 ± 3% and 37 ± 5%, respectively, were achieved, but there was an average increase in COD of 3 ± 7%. The pH of the treated effluent was 10.4. For the 1:2 ratio, the average removal efficiencies of the colour and TDS were 82 ± 2% and 30 ± 5%, respectively. The COD of the treated effluent was found to be beyond the analytical limit of the test (>150 mg/l). The pH of the treated effluent was 10.7.

Synthetic textile wastewater was treated using three types of shredded corn cobs, classified according to particle size: fine particles (≤600 µm), coarse particles (between 2360 µm and 1180 µm), and blend mix (mix ratio fine-coarse 1:1). An increase beyond the detection limit of the instrument was recorded after treatment (>500 mg/l). Similar results were obtained after treatment with the different media sizes.

The results presented in this chapter were analysed and are critically discussed in Chapter 5.

# 5 Discussion

## 5.1 Introduction

The results and findings obtained during the experimental work, as presented in Chapter 4 are analysed and discussed in this chapter. Results are interpreted, evaluated, and discussed with reference to relevant available literature.

This chapter covers three themes, namely:

- Evaluation of the coagulation-flocculation process,
- Evaluation of the adsorption with shredded corn cobs,
- Comparison of the quality of the treated effluents achieved.

The aim of this study was to assess the capabilities of the RAS as a coagulant to remove disperse dye from textile wastewater. The study was undertaken in the particular context described in the Chapter 3 (Section 3.4.3.2) using synthetic textile wastewater containing disperse dye. The study was conducted using synthetic wastewater based on the fact that it focuses on a particular pollutant at specific concentration while providing controlled conditions, in comparison to actual effluents from textile manufacturing plants that contain chemicals from various processes at concentrations which can constantly vary according to the changing operations of the plant. Although other studies have covered the same topic, the context in which this study was conducted was different in terms of the use of synthetic wastewater instead of actual textile manufacturing effluent (Irfan et al., 2013; Nair et al., 2015; Rana et al., 2017), the choice of coagulants (Verma et al., 2012; Irfan et al., 2013; Rana et al., 2017), the use of coagulant aids (Chu, 2001; Alinsafi et al 2005; Verma et al., 2012; Irfan et al., 2013) and the operating conditions of the coagulation-flocculation process (Xu et al., 2009; Jangkron et al., 2011; Verma et al., 2012; Irfan et al., 2013; Huang et al., 2015; Rana et al., 2017).

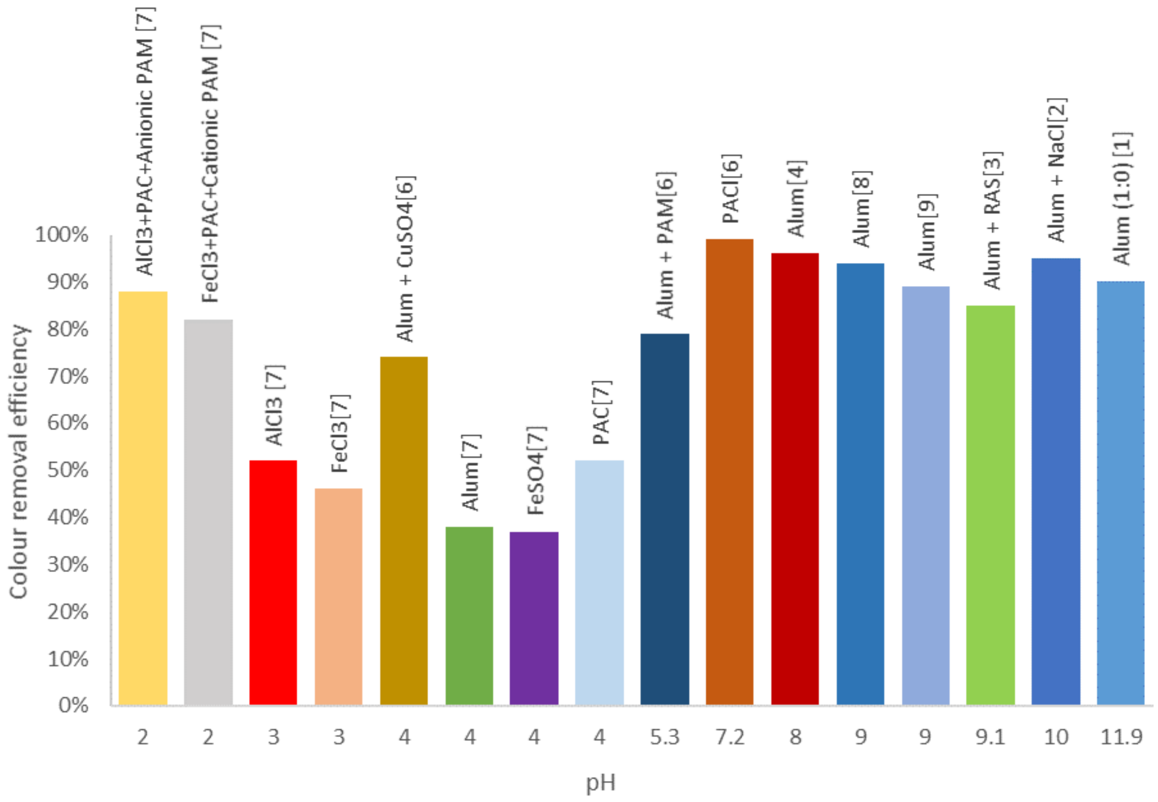
## 5.2 Evaluation of the coagulation-flocculation process

### 5.2.1 Effect of pH on coagulation-flocculation and colour removal

The coagulation-flocculation process achieved the highest colour removal efficiency of 89% of disperse dye at pH 11.9. This was obtained by adding alum [$Al_2(SO_4)_3.18H_2O$] to synthetic wastewater containing potassium hydroxide (KOH) which caused the formation and precipitation of aluminium hydroxide [$Al(OH)_3$] from the wastewater (Equation 5.1). The insoluble $Al(OH)_3$ appeared as a gelatinous floc that settled slowly through the wastewater, sweeping out materials in suspension and colloidal state, as described by Metcalf & Eddy (2004).

$$Al_2(SO_4)_3.18H_2O + 6KOH \longrightarrow 2Al(OH)_3 + 3K_2SO_4 + 18H_2O \qquad (5.1)$$

In this study, higher removal efficiencies were achieved under alkaline conditions (Section 4.1). The alkaline conditions favourable for coagulation-flocculation (Section 3.4.3.2.1) were created by using KOH to provide hydroxide ions (OH-) for the formation of $Al(OH)_3$ (Equation 5.1). These results were supported by findings by Chu (2001), who demonstrated 85% removal efficiency of colour (disperse dye) with 100 mg/l of alum and a cationic polymer as a sludge thickener at a concentration of 32.5 mg/l and a pH of 9.1, Nair et al. (2015), who recorded a colour removal efficiency of 89% when treating synthetic wastewater containing disperse dye with a coagulant mix of alum and RAS at pH 9; and Huang et al. (2015), who achieved 94% removal of colour from a synthetic wastewater containing reactive dye with alum as a coagulant at a pH of 9 (Figure 5.1, Table 5.1). This aligns with the findings from Huang et al. (2015), who showed that dye removal efficiency improves under alkaline conditions due to an increase in the growth rate of alum-based flocs, and Bo et al. (2012) who showed that the coagulation mechanism is transformed to enmeshment with increasing pH because larger flocs with more compact structures are formed in a shorter time. The effectiveness of high pH level of the influent during the coagulation-flocculation process was also demonstrated in the treatment of authentic wastewater: Alinsafi et al. (2005) reported that 95% of colour was removed from the wastewater from a textile manufacturing plant after treatment by coagulation-flocculation with alum and NaCl at a pH of 10; and Xu et al. (2009) reported that when treating tannery wastewater at a pH 8 with alum as a coagulant, a colour removal efficiency 96% can be achieved (Figure 5.1, Table 5.1).



**Coagulation aids as per graph legend**: [1] This study, [2] Alinsafi et al. (2005), [3] Chu (2001), [4] Xu et al. (2009), [5] Jangkron et al. (2011), [6] Verma et al. (2012), [7] Irfan et al. (2013), [8] Huang et al. (2015), [9] Nair et al. (2015), Rana et al. (2017).

Figure 5.1 Assessment of the pH with different coagulation aids in the removal of colour.

In contrast to other researchers, Verma et al. (2012) achieved high removal efficiencies at low pH (79% at pH 5.3 and 74% at pH 4) during the treatment of synthetic wastewater containing disperse dye with alum in conjunction with polyacrylamide (PAM)-based polymer (Figure 5.2) and a catalyst in the form of copper sulphate ($CuSO_4$) (Equation 5.2). However, the findings by Verma et al. (2012) suggested that the effect of pH on the dye (colour) reduction with $CuSO_4$ was explained by the combined effects of (i) the initial catalytic thermal treatment (thermolysis) of the wastewater with $CuSO_4$, (ii) the ionization of amino, hydroxy and sulpho groups in the dye molecules which increases with pH in the acidic range, and (iii) the decrease in the concentration of dissolved hydrolysis products.

$$3CuSO_4.H_2O + 2Al(OH)_3 \longrightarrow 3Cu(OH)_2 + Al_2(SO_4)_3 + H_2O \qquad (5.2)$$

In the case of the use of (PAM)-polymer, it was attributed to the bridging mechanism where the polymer attached at a number of adsorption sites to the surface of the particles found in the wastewater (Verma et al., 2012). A bridge is formed when two or more particles become adsorbed along the length of the polymer (Metcalf and Eddy, 2004). Bridged particles become intertwined with other bridged particles during the flocculation process (Metcalf and Eddy, 2004). The size of the resulting three-dimensional particles grows until they can easily be removed by sedimentation (Figure 5.2). Therefore, under these conditions, the formation of flocs is promoted at lower pH values.

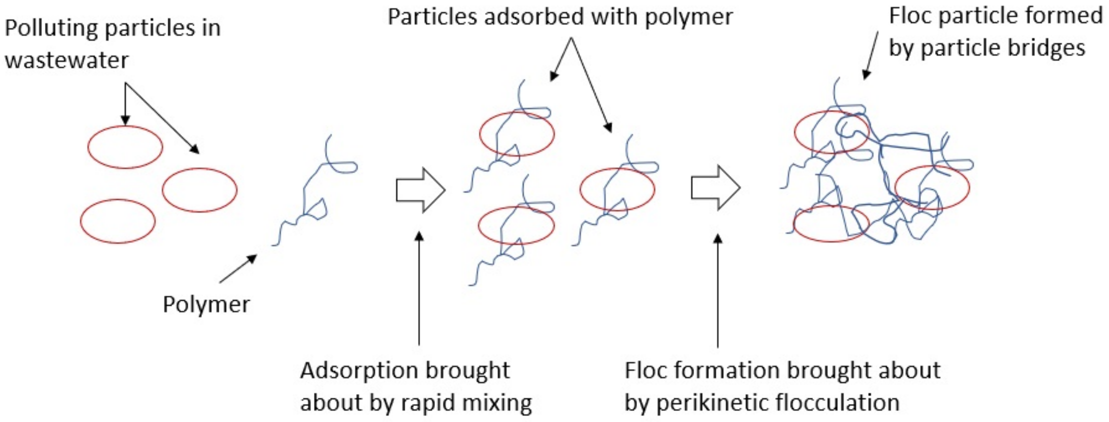


Figure 5.2 Inter-particle bridging mechanism with polymer during coagulation-flocculation process.

### 5.2.2 Performance analysis of coagulation-flocculation with RAS.

The results presented in Chapter 4 Section 4.2.1.3 are analysed in this section and compared with other studies using different dyes and/or coagulants (Table 5.1). Coagulation-flocculation using fresh alum: RAS at ratios 1:0, 0:1, 1:1 and 1:2 are discussed with regard to the effect on colour (Section 5.2.2.1), COD (Section 5.2.2.2), TDS (Section 5.2.2.3) and pH (Section 5.2.2.4). Treatment with fresh alum was used as reference to evaluate the extent of treatment of coagulants containing RAS. The differences in treatment efficiency of each coagulant ratio are discussed and elaborated.

Table 5.1 Efficiency of coagulation-flocculation for the treatment of dye-containing wastewaters: comparison of the results of this study with literature values

| Coagulants | Type of wastewater | Type of dye | Parameters | | | | | | | | Removal efficiency (%) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Synthetic wastewater | | | | Treated effluent | | | | | | |
| | | | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Alum (1:0) [1] | Synthetic | Disperse | 133 | 38 | 779 | 11.9 | 14 | 28 | 501 | 8.8 | 89 | 29 | 36 |
| RAS (0:1) [1] | Synthetic | Disperse | 115 | 37 | 760 | 11.9 | 25 | 29 | 515 | 11.8 | 78 | 22 | 32 |
| Alum + RAS (1:1) [1] | Synthetic | Disperse | 130 | 29 | 724 | 11.9 | 18 | 29 | 457 | 10.6 | 86 | -3 | 37 |
| Alum + RAS (1:2) [1] | Synthetic | Disperse | 134 | 30 | 739 | 11.9 | 25 | 33 | 515 | 11.6 | 82 | -9 | 30 |
| Alum + NaCl[2] | Textile mill | Dye mixture | NM | NM | NM | 10 | NM | NM | NM | NM | 95 | 36 | NM |
| Alum + RAS (1:1)[3] | Synthetic | Disperse | NM | NM | NM | 9.1 | NM | NM | NM | NM | 85 | NM | NM |
| Alum[4] | Tannery | NM | NM | NM | NM | 8 | NM | NM | NM | NM | 96 | 53 | NM |
| Alum[5] | Industrial plant | NM | NM | NM | NM | NM | NM | NM | NM | NM | 98 | 76 | NM |
| Alum + PAM[6] | Synthetic | Disperse | NM | NM | NM | 5.3 | NM | NM | NM | NM | 79 | NM | NM |
| Alum + CuSO4[6] | Synthetic | Disperse | NM | NM | NM | 4 | NM | NM | NM | NM | 74 | NM | NM |
| PACl[6] | Textile mill | Dye mixture | NM | NM | NM | 7.2 | NM | NM | NM | NM | 99 | NM | NM |
| AlCl3 [7] | Paper mill | Dye mixture | NM | NM | NM | 3 | NM | NM | NM | NM | 52 | 13 | NM |
| FeCl3[7] | Paper mill | Dye mixture | NM | NM | NM | 3 | NM | NM | NM | NM | 46 | 16 | NM |
| PAC[7] | Paper mill | Dye mixture | NM | NM | NM | 4 | NM | NM | NM | NM | 52 | NM | NM |
| Alum[7] | Paper mill | Dye mixture | NM | NM | NM | 4 | NM | NM | NM | NM | 38 | NM | NM |
| FeSO4[7] | Paper mill | Dye mixture | NM | NM | NM | 4 | NM | NM | NM | NM | 37 | NM | NM |
| FeCl3+PAC+Anionic PAM [7] | Paper mill | Dye mixture | NM | NM | NM | 2 | NM | NM | NM | NM | 82 | 81 | NM |
| AlCl3+PAC+Cationic PAM [7] | Paper mill | Dye mixture | NM | NM | NM | 2 | NM | NM | NM | NM | 88 | 78 | NM |
| Alum[8] | Synthetic | Reactive | NM | NM | NM | 9 | NM | NM | NM | NM | 94 | NM | NM |
| Alum[9] | Synthetic | Disperse | NM | NM | NM | 9 | NM | NM | NM | NM | 89 | 74 | NM |
| Alum[10] | Textile mill | Dye mixture | NM | NM | NM | 4 | NM | NM | NM | NM | NM | 40 | NM |
| FeCl3[10] | Textile mill | Dye mixture | NM | NM | NM | 6 | NM | NM | NM | NM | NM | 35 | NM |
| FeSO4[10] | Textile mill | Dye mixture | NM | NM | NM | 4 | NM | NM | NM | NM | NM | 32 | NM |
| PAC[10] | Textile mill | Dye mixture | NM | NM | NM | 6 | NM | NM | NM | NM | NM | 26 | NM |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l; NM= Not mentioned

[1] This study, [2] Alinsafi et al. (2005), [3] Chu (2001), [4] Xu et al. (2009), [5] Jangkron et al. (2011), [6] Verma et al. (2012), [7] Irfan et al. (2013), [8] Huang et al. (2015), [9] Nair et al. (2015), [10] Rana et al. (2017).

### 5.2.2.1 Colour

The hydrophobic nature of disperse dye keeps the particles in a colloidal state when in an aqueous solution, so that addition of pure (fresh) alum promotes high adsorption rates of suspended and/or colloidal states from the body of water (Verma et al., 2012). Although fresh alum achieves good dye removal, copious amounts of sludge are generated (Jangkron et al., 2011). In this study, an average colour removal efficiency of 89 ± 13% (maximum 96%) was achieved with fresh alum. On macroscopic visual observation, virtually no suspended particles were observed. These findings were supported by studies from Huang et al. (2015), who demonstrated that coagulation-flocculation was effective in the decolourisation of textile wastewater containing dye. Similar results of treatment with fresh alum were also obtained in studies conducted by Nair et al. (2015) where fresh alum demonstrated an average colour removal efficiency of 89% during the treatment of a synthetic textile waste wastewater containing disperse dye; and Alinsafi et al. (2005), where an average removal efficiency of 95% was recorded during treatment of the wastewater from a textile manufacturing plant.

The performance of the RAS that was not mixed with fresh alum [alum: RAS (0:1)] in the treatment of synthetic textile wastewater was the lowest of the all the coagulants used in the study, with an average removal efficiency of 78 ± 3%. It was assumed that the removal of dye from the wastewater was made possible by the presence of ‘active’ aluminium particles in the alum sludge. Theoretically, disperse dyes in most cases have an extremely low solubility in water, and they can be treated as ‘colloidal particles’. Upon coagulation at suitable doses, agglomeration occurs, and dye particles are destabilized and can be removed by gravity settling. However, studies conducted by Chu (2001) showed that if there is an overdose of alum, a repulsive force is established between the disperse dye particles due to the accumulation of positive charges on the particle surface, and this causes restabilisation. During the restabilisation stage, the agglomerated particles (i.e. dye–alum particles) are suspended in solution and cannot be removed by gravity settling (Figure 5.3). However, the agglomerated and restabilised particles can still be removed by filtration.

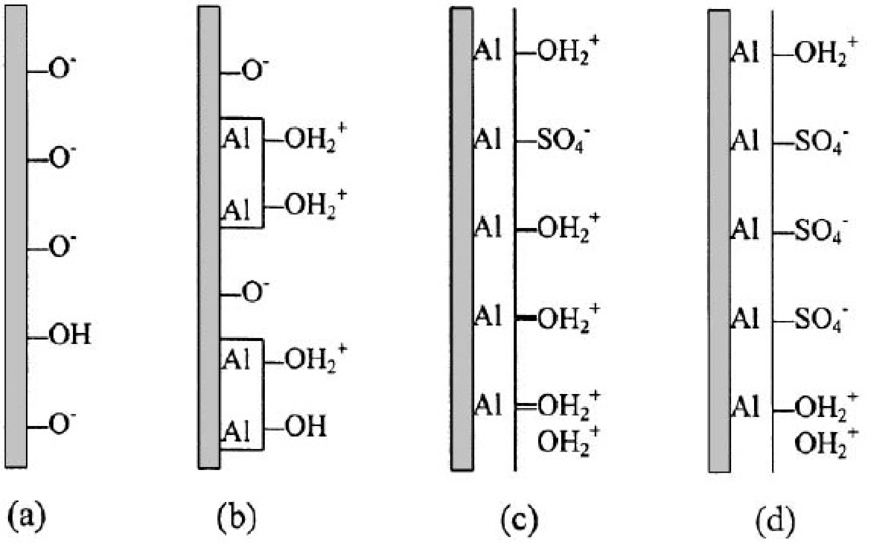
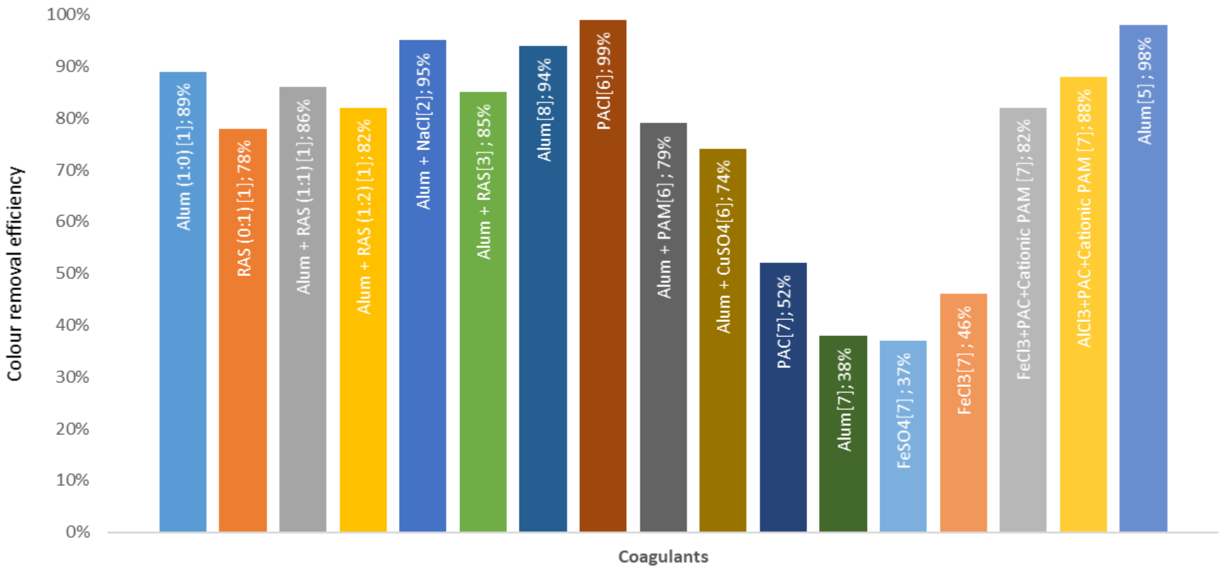


Figure 5.3 Schematic diagram of alum-treated dye particles. (a) Negatively charged dye particle; (b) particle destabilized by charge neutralization; (c) particle restabilised by excess alum hydrolyses species; and (d) destabilization by adsorption of sulphate ions.

Aluminium ions contained in the sludge also enhances the processes of adsorption and chemical precipitation that helps to remove pollutants from wastewater (Yang et al., 2006). The results obtained in this study were similar to those found in a study conducted by Verma et al. (2012) under acidic conditions. The authors showed colour removal efficiencies of 79% and 74%, respectively, at pH 5.3 with PAM as a catalyst, and 74% with $CuSO_4$ as an add-on at a pH level of 4 when treating dye-containing synthetic wastewater with alum.

The physical evidence highlighted the limitations of the RAS as a coagulant, as the presence of thick particles in suspension were observed in the effluent after treatment. The finding was also supported by results from a study conducted by Chu (2001), who stated that the reduction in colour removal efficiency of alum by recycled alum was due to a limited amount of available alum particles being present in the RAS. This caused rapid saturation of the alum particles and consequently promoted the release of some of the dye particles back into the wastewater [Figure 5.3 (c)]. Therefore, although the RAS still possessed adsorption capacity, the study demonstrated that it does not provide the best alternative as a coagulant for the removal of dye from wastewater.



[1] This study, [2] Alinsafi et al. (2005), [3] Chu (2001), [4] Xu et al. (2009), [5] Jangkron et al. ( 2011), [6] Verma et al. (2012), [7] Irfan et al. (2013), [8] Huang et al. (2015), [9] Nair et al. (2015), [10] Rana et al. (2017).

Figure 5.4 Comparison of colour removal efficiencies at the studied fresh alum: RAS mix ratio.

The treatment with the coagulant mix ratio of 1:1 fresh alum to RAS demonstrated high removal capabilities of colour from the synthetic textile wastewater, recording an average removal of 86 ± 3%. Visual observations indicated that the quality of flocs in terms of number and size, were superior to those obtained with unmixed RAS. It was therefore conclusively demonstrated that the coagulant with a coagulant mix ratio of 1:1 was highly effective in the removal of colour from the synthetic wastewater. When the synthetic textile wastewater was treated using fresh alum to RAS in a ratio of 1:2 (i.e. high concentration of RAS), high colour removal was still demonstrated, with an average removal of 82 ± 2% being recorded (Section 4.2.1.3.4). Once again, it was shown (as with the 1:1 ratio), that the addition of fresh alum to the RAS improved colour removal, albeit at slightly lower efficiency [Figure 5.3 (d)].

These findings are supported by a study conducted by Chu (2001), who achieved a colour removal efficiency of 85% when treating synthetic textile wastewater with RAS supplemented by fresh alum at a ratio of 1:1. Nair et al. (2015) attributed the improved colour removal to the fact that the particles of fresh alum found in the coagulant mix remove not only the dye in the aqueous phase, but also any dye particles that may have diffused back into the water from the RAS. Yang et al. (2006) demonstrated that the presence of aluminium ions in the alum sludge improved the processes of adsorption and chemical precipitation, thereby assisting in the removal of pollutants from wastewater. However, when the alum/RAS ratio was decreased, particles were found suspended in the effluent after treatment. Similar results were found by Nair et al. (2015), who claimed that this was due to an excess of RAS in the coagulant mix which promoted the release of particles back into the wastewater. This may explain the 3% decrease in colour removal efficiency obtained when the RAS to fresh alum ratio was increased from 1:1 to 1:2 in this study.

In summary, fresh alum particles can achieve high adsorption rates of pollutants in suspended and/or colloidal states from bulk water (Verma et al, 2012). Therefore, as expected, the highest colour removal efficiency of 89 ± 2% was achieved after coagulation/flocculation with fresh alum. Conversely, treatment with unmixed RAS resulted in the lowest average removal efficiency of 78 ± 3%. This was improved to > 80% by the addition of fresh alum to the RAS (1:1 and 1:2 ratios).

### 5.2.2.2 COD

The COD concentrations in the synthetic textile wastewater were very low (32-43 mg/l), and well below the range (0-75 mg/l) for discharge of effluent into municipal wastewater sewer (DWA, 2010). Nevertheless, treatment with fresh alum demonstrated poor removal of COD from the synthetic textile wastewater, as average removal efficiencies ranged between 22% and 31%. Similar results were obtained in the study conducted by Alinsafi et al. (2005) where a COD removal efficiency of 36% was observed during the treatment of textile manufacturing plant wastewater using coagulation-flocculation with alum and NaCl. Findings from Rana et al. (2017) also demonstrated COD removal efficiency ranging from 26 to 40% could be achieved by treating textile industry wastewater with coagulants such alum, $FeCl_3$, PAC or $FeSO_4$. It was hypothesised that the poor COD removal with fresh alum was caused by the increase in the dissolved content in the wastewater after adding the coagulant. Although no Al was found in the fresh synthetic wastewater, it was detected after coagulation/flocculation (Table 5.2). The TN concentration was measured as an indicator of the presence of remaining dye in the effluent (Figure 5.5, Table 5.2, Appendix A). The results were also supported by findings of Verma et al. (2012) who showed that the low COD treatment rates in the coagulation-flocculation using fresh alum was due to the fact that some of the coagulant particles remained dissolved in the effluent after treatment thereby resulting in an increase in the dissolved constituent in the wastewater. Therefore, in this study fresh alum has demonstrated poor capabilities in the treatment of COD from the synthetic textile wastewater.

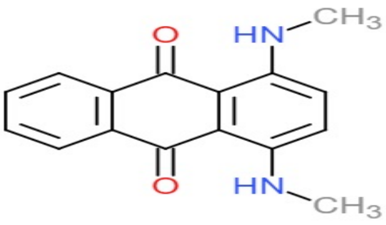
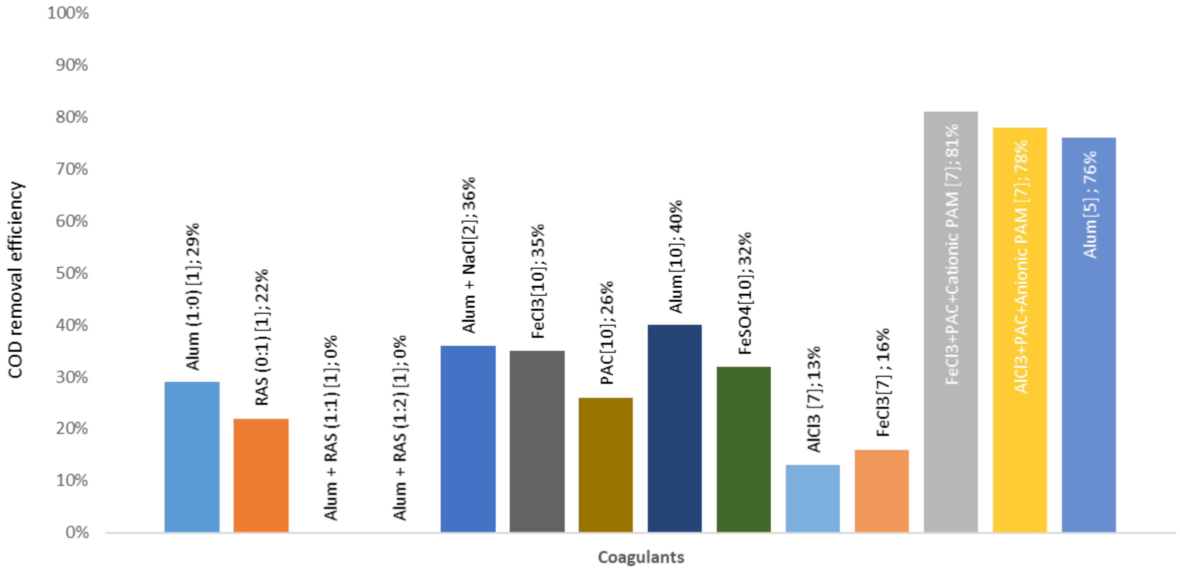


Figure 5.5 Chemical structure of Disperse Blue 14 dye

RAS also demonstrated poor treatment capabilities, with average removal efficiency of 22 ± 3%. Since RAS was the only potential component added in the wastewater during the treatment, the low efficiency of the treatment was mainly due to the pollutant found in the sludge (Table 5.2). Chu (2001) also claimed that the poor treatment efficiency of RAS is due to the release of the polluting particles previously trapped in the RAS back to the aqueous phase causing deterioration of the effluent quality. Therefore, coagulation-flocculation with RAS does not present an attractive alternative for the removal of COD from textile wastewater.



[1] This study, [2] Alinsafi et al. (2005), [3] Chu (2001), [4] Xu et al. (2009), [5] Jangkron et al. ( 2011), [6] Verma et al. (2012), [7] Irfan et al. (2013), [8] Huang et al. (2015), [9] Nair et al. (2015), [10] Rana et al. (2017).

Figure 5.6 Comparison of COD removal efficiencies at various fresh alum: RAS mix ratio.

The coagulation flocculation treatment with fresh alum/RAS of mix ratio of 1:1 also have displayed very poor treatment capabilities in the removal of COD from the synthetic textile wastewater, with a highest removal efficiency was of 6% being recorded. However, increases in COD of up to 14 % in the effluent after treatment were observed. The increase in COD was mainly attributed to the excess of dissolved chemicals from the fresh coagulant in the wastewater, and also to the dye particles released by the RAS with saturated binding sites (Chu, 2001; Yang et al., 2007; Verma et al., 2012). An average increase in COD of 9 ± 2% was also recorded during the treatment with the coagulant of fresh alum/RAS of mix ratio of 1:2. In the same light as during the treatment of coagulants of ratios 0:1 and 1:1, the increase in COD was mainly caused by the release of polluting particles from the sludge back in the water. This claim was confirmed by the analysis of TN content as a proxy of the dye where changes from 97 ± 17 mg/l in the synthetic wastewater to 40 ± 10 mg/l of TN in the effluent treated with the coagulant of mix ratio 1:1; and 64 ± 17 mg/l of TN in the effluent treated with the coagulant of mix ratio 1:2 were recorded (Table 5.2). These results indicated the presence of the dye particles remained in the effluent after treatment with both 1:1 and 1:2 coagulant mixes. This was due to the excess saturated dye particles trapped in the sludge that are restabilised when the coagulant has a ratio of RAS in the sludge higher than the fresh alum (Chu, 2001; Yang et al., 2007; Verma et al., 2012). Yang et al. (2007) and Verma et al. (2012) also supported the claim by stating that the polluting particles that were trapped the sludge can be released back into aqueous phase during the treatment process. In the study conducted by Nair et al. (2015), it was stated that when the amount of contaminant released by the sludge in the solution exceeds the removal by coagulation, the COD removal efficiency is reduced. This implies that the coagulation flocculation treatment with fresh alum/RAS of mix ratio of 1:2 has very poor treatment capabilities in the removal of COD from the synthetic textile wastewater containing disperse dye.

Table 5.2 Comparison of the quality of effluent achieved using various ratios of fresh alum to RAS (1:0, 0:1, 1:1, 1:2)

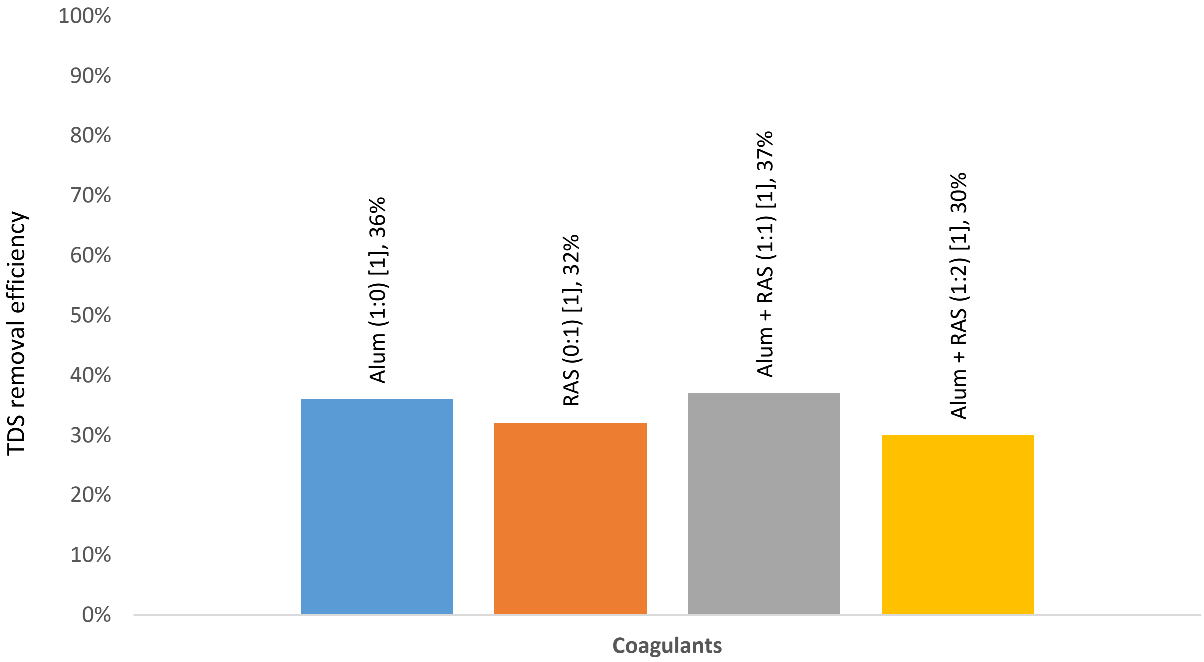
| **Samples** | **Synthetic wastewater** | | **Treated effluent** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **1:0** | | **0:1** | | **1:1** | | **1:2** | |
| | **Al** | **TN** | **Al** | **TN** | **Al** | **TN** | **Al** | **TN** | **Al** | **TN** |
| **Batch 1** | - | 110 | 0.23 | 50 | 0.20 | 40 | 0.76 | 30 | 2.16 | 50 |
| **Batch 2** | - | 70 | 0.22 | 40 | 0.16 | 40 | 0.57 | 40 | 2.27 | 70 |
| **Batch 3** | - | 93 | 0.26 | 20 | 0.18 | 20 | 0.59 | 50 | 3.07 | 90 |
| **Batch 4** | - | 100 | 0.22 | 40 | 0.22 | 30 | 0.65 | 40 | 2.00 | 50 |
| **Batch 5** | - | 110 | 0.24 | 40 | 0.18 | 40 | 0.62 | 50 | 2.50 | 60 |
| **Average** | - | 97 | 0.24 | 38 | 0.18 | 34 | 0.64 | 40 | 2.50 | 64 |
| **Deviation** | - | 17 | 0.02 | 11 | 0.02 | 9 | 0.10 | 10 | 0.50 | 17 |

Al expressed in mg/l Al and TN expressed in mg/l.

In summary, the main focus of this study was on colour and TDS removal because the COD concentrations in the synthetic textile wastewater were so low that treatment to reduce the COD concentration would theoretically not be required. Nevertheless, poor COD removal efficiencies were recorded. coagulant mixes of fresh alum and RAS (1:1 and 1:2). Poor COD removal was supported by evidence from other studies that have also shown that coagulation-flocculation with alum and/or RAS had very low treatment capabilities.

### 5.2.2.3 TDS

Poor removal of TDS (<40%) was achieved with fresh alum sludge, RAS, and mixtures of the two (Figure 5.6). Residual Al was found in the treated effluent (Table 5.2), which was also demonstrated in a study by Verma et al. (2012). It was hypothesised that this inability of the coagulant to effectively remove TDS was due to the fact that some of the dye and/or alum particles trapped in the sludge may have been released back into the aqueous phase (Chu, 2001; Verna et al., 2012). The highest TDS removal efficiency was recorded at 37 ± 5% in the effluent treated with the coagulant mix ratio of 1:1, and 30 ± 5% was the removal efficiency obtained after treatment with the coagulant mix ratio of 1:2. The treatment with fresh alum removed 36 ± 4% of pollutant from the wastewater and a removal efficiency of 32 ± 1% was achieved with RAS. The consistency in low removal efficiencies highlighted ineffectiveness of coagulation-flocculation in the reduction of TDS in the wastewater. This limitation was caused by the fact that some the particles of coagulant such Al are dissolved in the wastewater during the treatment process, as indicated in Table 5.2. This was also supported by findings by Chu (2001) who stated that ‘‘in the case of coagulant containing RAS, some polluting particles are released from the saturated coagulant pores back to the wastewater during the treatment process’’. Furthermore, although the coagulation-flocculation in wastewater treatment involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation, a net increase in the dissolved constituent can be observed in the effluent as a result of chemical addition (Verma et al., 2012).



[1] This study

Figure 5.7 Comparison of TDS removal efficiencies at various fresh alum: RAS mix ratio.

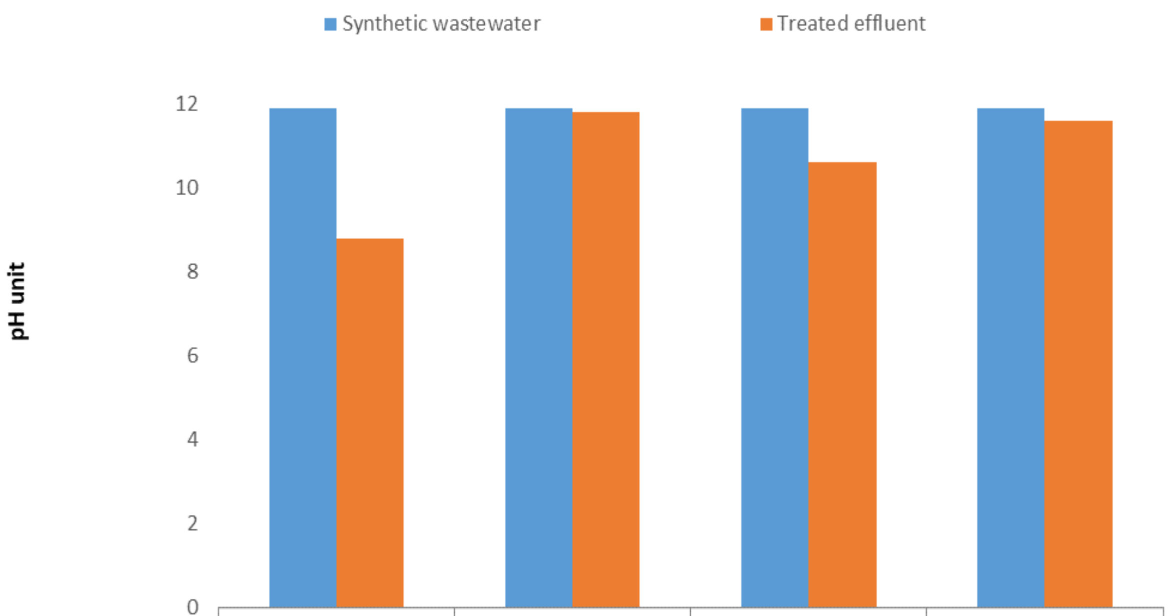
In summary, RAS with and without added fresh alum was used for the treatment of TDS, and limited treatment capabilities were found. Likewise, very poor TDS removal efficiencies were demonstrated with coagulant mixes of fresh alum and RAS (1:1 and 1:2). Findings therefore show that coagulation/flocculation with RAS did not provide a good option for the removal of TDS from textile wastewater.

#### 5.2.2.4 pH

When using fresh alum as a coagulant, a drop in pH from a maximum of 12 in the raw wastewater down to a pH ranging between 8 and 9 in the treated effluent was recorded. This notable change in pH was attributed to the alum in the wastewater that forms sulphuric acid in contact with water (Equation 5.3) as indicated by Verma et al. (2012), as alum was the only chemical constituent added during the treatment process.

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4 \tag{5.3}$$

However, very little change was in pH was recorded when RAS was incorporated into the coagulant mix, as it dropped from a maximum of 12.0 in the raw wastewater down to a pH range between 10.6 and 11.8 in the treated effluent. This relatively small change was attributed to the limited amount of free alum particles be available to produce sulphuric acid (Huang et al., 2015). According to Metcalf and Eddy (2004), an excessive amount of coagulant may be required to lower the pH to the optimal pH ranges in highly alkaline water.



| | Alum (1:0) [1] | RAS (0:1) [1] | Alum + RAS (1:1) [1] | Alum + RAS (1:2) [1] |
|---|---|---|---|---|
| ■ Synthetic wastewater | 11.9 | 11.9 | 11.9 | 11.9 |
| ■ Treated effluent | 8.8 | 11.8 | 10.6 | 11.6 |

[1] This study

Figure 5.8 Comparison of changes in pH during treatment of synthetic wastewater with fresh alum and different fresh alum: RAS mix ratios.

It was demonstrated that the treatment with coagulant mix ratio of 1:2 provided little change in the pH as a decrease from a range between 11.9 and 12.0 in the raw synthetic wastewater down to a pH ranging between 10.7 and 11.1 in the treated effluent was recorded. Findings from Chu (2001) and Huang et al. (2015) suggested that although fresh alum promoted the drop in the pH level by producing sulphuric acid in contact with water, its effect was limited due to the important amount RAS in the coagulant mix ratio which promoted a considerable release and/or restabilisation of dye particles back in aqueous form and therefore limiting the drop in pH.

### 5.2.2.5 Summary

In this study, treatment of synthetic wastewater with fresh alum and fresh alum:RAS showed that high removal of colour can be achieved, implying that these coagulants are highly effective in the treatment of wastewater containing disperse dye. Treatment with alum:RAS demonstrated particularly poor COD and TDS removal efficiencies. It was postulated that this was mainly due to the release of particles previously trapped in the sludge back into the bulk water.

Based on the results of this comparative study, the coagulant containing fresh alum and RAS at a ratio of 1:1 was found to offer the best alternative to fresh alum for the removal of colour and TDS from the synthetic textile wastewater containing disperse dye.

## 5.3 Evaluation of the adsorption with corn cobs

### 5.3.1 Analysis of adsorption with corn cobs effluent

This section primarily focuses on the treatment capabilities of corn cobs as a natural medium in the removal of colour from synthetic wastewater containing dyes.

Studies have demonstrated that various other agricultural wastes and other biomass can effectively remove dyes from textile wastewater via biosorption (da Rosa et al., 2008; Rangabhashiyan et al., 2013; Adegoke & Belo, 2015; Singh et al., 2017). The most important parameters affecting the efficiency of the biosorbents are the pH of the influent wastewater and type of dye (Section 5.3.1.1), the concentration of dye (Section 5.3.1.2), the biosorbent dosage and particle size (Section 5.3.1.3), and the time of contact between the wastewater and the biosorbent (Section 5.3.1.4). The type of biosorbent, in terms of effectiveness is also important to consider when assessing this type of technology (Section 5.3.1.5).

Figure 5.9 Disperse dye particles trapped in the media after adsorption with shredded corn cobs during experimental work (this study)

In this study, after treatment of synthetic wastewater with shredded corn cobs, colour concentrations exceeding the limit of the spectrophotometer (>500 mg/l) were recorded in the effluent. It was hypothesised that this was due to high concentrations of starch or other molecules released from the shredded corn cobs that was significantly affecting the turbidity of the effluent (Figure 5.6). This was supported by the fact that notable increases in COD were also found after treatment with shredded corn cobs. Increases from 35 mg/l in batch 1, 37 mg/l in batch 2 and 34 mg/l in batch 3 to 14520 ± 516 mg/l, 14710 ± 419 mg/l and 10797 ± 869 mg/l, respectively, were recorded. To confirm whether the increased COD was from organic molecules from the corn cobs, the total organic carbon (TOC) concentration in the samples was measured. Increases from 348 mg/l in batch 1, 330 mg/l in batch 2, and 344 mg/l in batch 3 to 6633 ± 391 mg/l, 5333 ± 431 mg/l and 4692 ± 118 mg/l, respectively, were recorded (Table 5.3). The study was conducted in light of previous research, where Nigam et al. (2000) reported good removal of mixed dye using shredded corn cobs. Release of organics such as starch release was not mentioned in the manuscript.

Table 5.3 TOC analysis test results of synthetic wastewater treated with shredded corn cobs

| Average ± SD | Synthetic wastewater<br>TOC | Treated effluent<br>TOC |
|---|---|---|
| Batch 1 (fine) (n=3) | 348 | 6633 |
| Range | 9 | 391 |
| Batch 2 (Blend) (n=3) | 330 | 5333 |
| Range | 9 | 431 |
| Batch 3 (Coarse) (n=3) | 344 | 4692 |
| Range | 5 | 118 |

TOC expressed in mg/l.

#### 5.3.1.1 Effect of pH in the adsorption process

The pH has been reported as an important factor for biosorption of dyes. The pH can affect the surface charge and the extent of dissociation of functional groups on the active sites of biosorbents, as well as the degree of ionization, structural stability, and colour intensity of the dye molecules (Oguntimein, 2015). A number of studies have shown that high dye removal rates can be achieved under alkaline conditions (da Rosa et al., 2008; Rangabhashiyan et al., 2013; Adegoke & Belo, 2015; Singh et al., 2017). Temesgen et al. (2018) demonstrated that the removal of reactive dye with banana peels and orange peels increased by >20% when the pH was increased. According to da Rosa et al. (2018), when the solution pH is increased, the surface of the biosorbent becomes negatively charged due to deprotonation caused by binding with $OH^-$ molecules in the bulk liquid, thus improving biosorption by electrostatic attraction. However, Robinson et al. (2002) performed preliminary investigations on the effect of pH on dye adsorption by apple pomace and demonstrated that there was no significant difference between pH ranges of 6–12 (Table 5.4).

Contradictory results are found because dye removal efficiencies are related to the properties of the biosorbent and the particular dye. For example, at high pH, the negatively charged surface on a biosorbent does not favour the sorption of anionic dyes because of electrostatic repulsion between the anionic dye molecules and the adsorbent surface (Temesgen et al., 2018). This is supported by the results obtained by Akar et al. (2015) who treated synthetic wastewater containing Congo red with rice husks and found that as the pH of the aqueous medium decreased, the biosorption capacity of the biomass increased. The maximum dye uptake capacity of the adsorbent was found to be 49.5mg/g at an initial pH value of 2.0. Under strongly acidic conditions, the surface of the biosorbent becomes positively charged, increasing the attraction for negatively charged dye molecules. In addition, competition between excess $OH^-$ and the negatively charged dye ions for the binding sites can decrease biosorption rates under alkaline conditions (Akaret al., 2009). The effect of pH was not considered in this study. However, the removal colour under alkaline conditions (pH=11.9) was expected as the experimental parameters were designed in alignment with the previous studies (section 3.4.3.3).

#### 5.3.1.2 Concentration of dye

Reports have shown that an increase in initial dye concentration can lead to an increase in adsorption capacity. According to Oguntimein (2015), increasing the dye concentration causes an increase in the driving force between the solution and biosorbent and reduces the mass transfer resistance between the dye and the biosorbent. In other words, the increase of the initial dye concentration increases the likelihood of contact between dye molecules and the adsorbent (da Rosa et al., 2018). However, intraparticle diffusion can be reduced and a lack of available biosorption sites can occur at high dye concentrations (Deniz & Kepecki, 2016). Thus, the percentage of dye removal is dependent upon the initial dye concentration. The concentration of dye was not taken into consideration in this study as one formulation of synthetic wastewater was used throughout the experimental phase.

#### 5.3.1.3 Biosorbent dosage and particle size

During biosorption of dyes, with the same mass of adsorbent, the highest removal of dye was expected with the batch of shredded corn cobs containing fine particles, followed by the mixed-size and coarse particles, due to the increase in surface area with smaller particle size. This was supported by the study conducted by Robinson et al. (2002), where an apple pomace adsorption media of 600 mm particle size showed an increase in percentage of dye removal at all substrate weights, in comparison to the amount removed by particles 2 mm x 4 mm.

During biosorption, the removal rates are typically higher initially and at higher sorbent concentrations due to high availability of free adsorption sites (Oguntimein, 2015). As the process proceeds, the available sites are gradually occupied by the dye species, and the adsorption rate decreases. Temsgen et al. (2018) demonstrated that by increasing the concentration of carbonised banana and orange-peel powder from 0.2 g to 1 g, dye removal increased from 34.8% to 89.8% and 31.5% to 70.2%, respectively. However, the increase in adsorption at higher biosorbent concentrations can be countered if the concentration of biosorbent becomes so high that particles agglomerate – this can decrease the accessibility to free adsorption sites by the dye molecules (Akar et al., 2019; Oguntimein, 2015; da Rosa et al., 2018).

#### 5.3.1.4 Effect of contact time

According to evidence from previous studies, biosorption occurs rapidly. Using Chlorella spp., da Rosa et al. (2018) found that 82-95% of saturation was attained within the first 30 min, with the rate gradually decreasing thereafter until equilibrium was reached. This can be explained by the fact that initially all active sites on the adsorbent surface are free, resulting in rapid initial biosorption (Akar et al., 2009). The analysis of the contact time did not form part of the scope of this study.

#### 5.3.1.5 Type of biosorbent

A number of studies have been conducted using different type of biosorbents for dye removal, achieving removal rates of >70% (Table 5.4 & Table 5.5).

Table 5.4 Comparison of biosorption test results with previous studies

| Adsorbent | Dye<br>Type | Initial concentration (mg/l) | pH | Contact time (min) | Removal efficiency | Reference |
|---|---|---|---|---|---|---|
| Apple pomace | Dye mixture | 200 | NM | 48 h | 96% | Robinson et al. (2002) |
| Banana peel | Reactive | 25 | 4 | 100 | 70% | Temesgen et al. (2018) |
| Chlorella pyrenoidona | Rhodamine B | 1000 | 8 | 240 | 89% | da Rosa et al. (2008) |
| Citrus limetta peel | Methylene Blue | 25 | 12 | 60 | 90% | Signh et al. (2017) |

Table 5.5 Comparison of biosorption test results with previous studies (continued)

| Adsorbent | Dye<br>Type | Initial concentration (mg/l) | pH | Contact time (min) | Removal efficiency | Reference |
|---|---|---|---|---|---|---|
| Corn cobs (1) | Disperse | 12.5 | 12 | 48 h | - | This study |
| Corn cobs (2) | Disperse | 12.5 | 12 | 48 h | - | This study |
| Corn cobs (3) | Disperse | 12.5 | 12 | 48 h | - | This study |
| Corn Cobs | Dye mixture | 500 | NM | 48 h | 70% | Nigam et al. (2000) |
| Grapefruit peel | Crystal violet | NM | NM | 60 | 96% | Rangabhashiyan et al. (2013) |
| Meranti sawdust | Methylene Blue | 600 | 6 | 240 | 73% | Rangabhashiyan et al. (2013) |
| Nostoc Linckia | Reactive | 100 | 2 | 2 | 94% | Mona et al. (2011) |
| Orange peel | Reactive | 25 | 4 | 100 | 89% | Temesgen et al. (2018) |
| Proteus vulgaris | Reactive Red 198 | NM | 2 | 20 | 99% | Akar et al. (2009) |
| Pine cone | Acid Black 7 | NM | 12 | NM | 95% | Rangabhashiyan et al. (2013) |
| Pine cone | Acid Black 26 | NM | 12 | NM | 94% | Rangabhashiyan et al. (2013) |
| Pine cone | Acid Black 25 | NM | 12 | NM | 95% | Rangabhashiyan et al. (2013) |
| Pistachio shell | Reactive | 50 | 6 | 10 | 89% | Deniz et al. (2016) |
| Ricinus communis | Malachite Green | 25 | 7 | NM | 99% | Rangabhashiyan et al. (2013) |
| Rice husk | Congo Red | NM | 8 | 30 | 96% | Adegoke & Belo (2015) |
| Sunflower seed (Dried) | Direct | NM | 2 | NM | 92% | Oguntimein (2005) |

Shredded corn cobs: (1) Particles ≤600 µm, (2) Particles from 2360 µm to ≤600 µm, (3) Particles between 2360 µm and 1180 µm; NM= Not Mentioned

#### 5.3.1.6 Summary

This study showed that adsorption with shredded corn cobs was not was not a viable treatment method for dye removal. Although the effluent was visibly decolourised, high concentrations of organic carbon leached from the cobs, resulting in a turbid effluent with increased concentrations of COD. This finding was contrary to that published by Nigam et al. (2000), which suggested that corn cob shreds could be used for decolourising textile effluents.

### 5.3.2 Comparison of effluents achieved with coagulation-flocculation and adsorption with shredded corn cobs

For the coagulation-flocculation study, a coagulant mix ratio of 1:1 (fresh coagulant: RAS) was selected as it demonstrated the best overall dye removal. Due to the poor results obtained for biosorption with shredded corn cobs, coagulation-flocculation was compared with literature findings for biosorption with agricultural wastes (Table 5.6). The main advantages of coagulation-flocculation are that it requires notably shorter contact time and no pre-treatment is required. It was therefore concluded that this was the better alternative for the removal of dye from synthetic wastewater.

Table 5.6 Evaluation of methodologies for dye removal

| Coagulation-flocculation (1:1) | Adsorption with shredded corn cobs |
|---|---|
| High colour removal efficiency | High colour removal efficiency |
| Performs in alkaline environment | Performs in both alkaline and acidic environments |
| Water and wastewater treatment plant waste | Agricultural waste |
| Low cost | Low cost |
| Operation time up to 2 h | Contact time up to 48 h |
| Can be used directly | Requires pre-treatment before use |
| Requires fresh alum for higher efficiency | Produced wastewater during pre-treatment |

# 6 Conclusions and recommendations

This chapter summarises the findings and discussions detailed in previous chapters. It highlights the importance of the study by providing answers to the research problem and objectives. This section also outlines the outcomes of the research and provides recommendations for further study.

## 6.1 Conclusions

Textile industries are high consumers of water in South Africa. Wastewater generated from the textile industry is very complex and poorly degradable. Dye has been a major issue in the treatment of textile mill effluent as colour is the most noticeable component, even at low concentrations and is not easily degradable. Many methods have been developed to treat textile effluent; however, factors such as the composition of the effluent and the conditions of the site determine the choice of technology.

This study involved the performance assessment of the RAS as a coagulant in the treatment of synthetic textile wastewater containing disperse dye by evaluating removal efficiencies of selected physiochemical parameters at fresh alum: RAS mix ratios of 1:0, 0:1, 1:1 and 1:2. The selected treatment process was also compared to the adsorption with shredded corn cobs.

### 6.1.1 Determination of the quality of effluent achieved by the coagulation-flocculation process

The mix ratio of fresh alum: RAS of 1:1 achieved a colour removal rate close to that of fresh alum sludge (86 ± 3% v/s 89 ± 2%). Removal rates of 36 ± 4%, 32 ± 1%, 37 ± 5%, 30 ± 5% of TDS were achieved after treatment with fresh alum, RAS, and coagulants of mix ratios (fresh alum: RAS) of 1:1 and 1:2, respectively. Coagulation-flocculation displayed poor removal of COD. The highest COD removal efficiency of 29 ± 3% was recorded with fresh alum, followed by RAS (0:1) with 22 ± 3%. However, increases in COD (i.e. negative removal efficiencies) were observed in the effluents treated with lower fresh alum: RAS mixes (-3 ± 1% and -9 ± 2% at ratios of 1:1 and 1:2, respectively). The increase was assumed to be due to the low concentration of COD in the fresh synthetic wastewater, and also saturation of the adsorption capacity of the coagulant and subsequent release of dye molecules previously trapped within the RAS.

In summary, the coagulant fresh alum and RAS mix ratio of 1:1 offered the best alternative to fresh alum in the removal of disperse dye from the synthetic textile wastewater.

### 6.1.2 Comparison of effluents achieved with coagulation-flocculation and adsorption with shredded corn cobs

Although previous studies have demonstrated that agricultural wastes can effectively remove dye from textile wastewater, in this study, adsorption with shredded corn cobs experiments was not effective. Visual observations suggested that substantial amounts of dye were removed from the synthetic wastewater and trapped in the shredded corn cobs bed. However, the effluent became extremely turbid due to the release of organic matter from the shredded corn cobs. This interfered with the analytical method for colour measurement and rendered the treated effluent unsuitable for direct discharge.

## 6.2 Recommendations

The coagulation-flocculation with coagulant containing RAS is viewed as a promising technology for the treatment of textile wastewater. However, due to the findings and shortfalls obtained in the study, recommendations on the variance of treatment efficiency are suggested.

The following recommendations are based on the use of coagulation-flocculation in the treatment of synthetic wastewater and possible future studies and investigations based on experience with actual textile industry effluent:

- In order to achieve the maximum efficiency for the removal of colour with coagulation-flocculation with RAS, the effect of cationic polymer in the production of thicker sludge during the treatment process should be determined.

- The extent of treatment capability of coagulation-flocculation with regards to wastewater quality parameters that were not considered in the study should be investigated.

- Further investigations on the applications of the treatment method selected in this study in actual textile industry effluent should be considered.

In light of the outcomes of the study, the following topics should be considered:

- Performance assessment of coagulant containing RAS in the treatment of textile wastewater using a pilot plant with continuous flow.

- The effect of sludge thickener in the treatment of textile wastewater with RAS.

- Critical assessment of the biosorption of dye from textile wastewater using agricultural waste.

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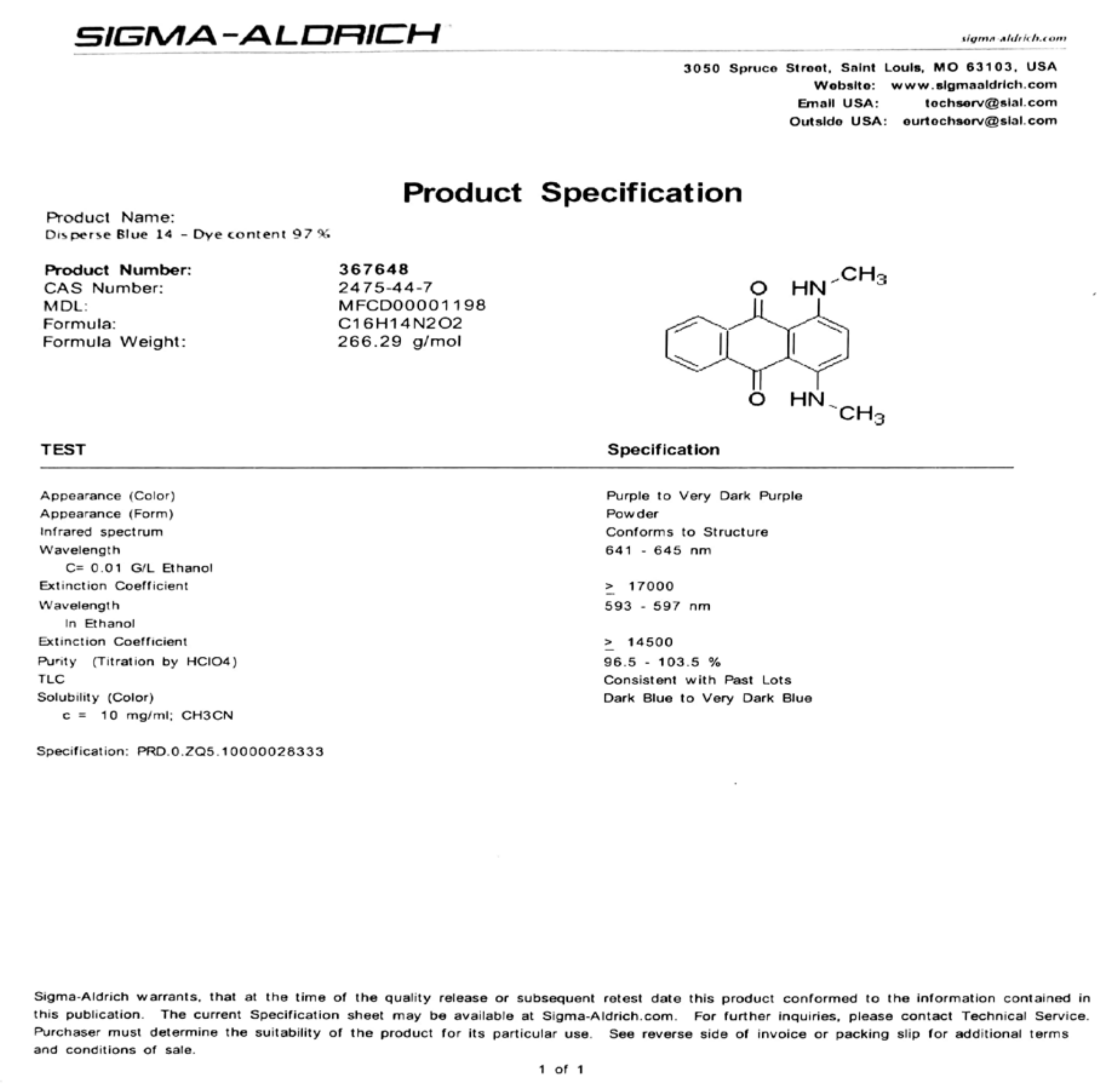
# Appendices

## Appendix A. Products specifications

### *A.1 Disperse Blue 14*



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**Product Specification**

Product Name:
Disperse Blue 14 - Dye content 97 %

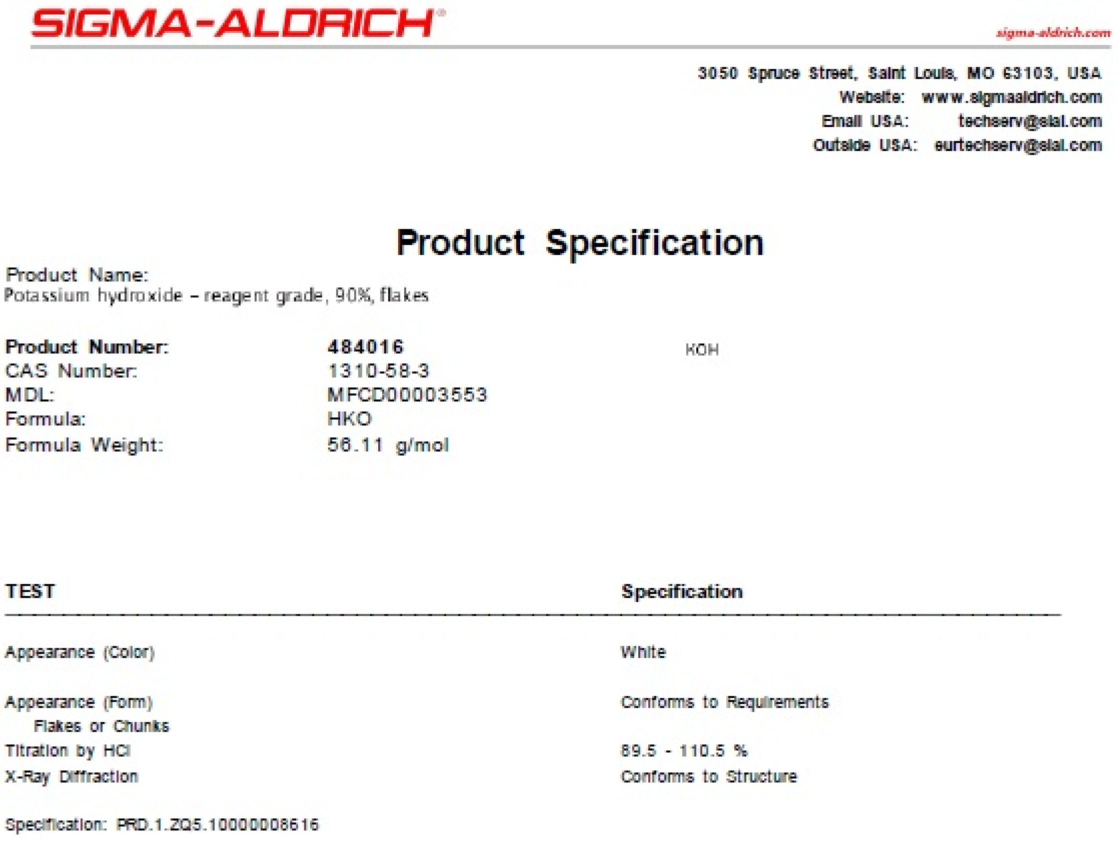
| | |
|---|---|
| **Product Number:** | **367648** |
| CAS Number: | 2475-44-7 |
| MDL: | MFCD00001198 |
| Formula: | C16H14N2O2 |
| Formula Weight: | 266.29 g/mol |

| **TEST** | **Specification** |
|---|---|
| Appearance (Color) | Purple to Very Dark Purple |
| Appearance (Form) | Powder |
| Infrared spectrum | Conforms to Structure |
| Wavelength<br>C= 0.01 G/L Ethanol | 641 - 645 nm |
| Extinction Coefficient | ≥ 17000 |
| Wavelength<br>In Ethanol | 593 - 597 nm |
| Extinction Coefficient | ≥ 14500 |
| Purity (Titration by HClO4) | 96.5 - 103.5 % |
| TLC | Consistent with Past Lots |
| Solubility (Color)<br>c = 10 mg/ml; CH3CN | Dark Blue to Very Dark Blue |

Specification: PRD.0.ZQ5.10000028333

1 of 1

### *A.2 Potassium hydroxide*



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Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

## Product Specification

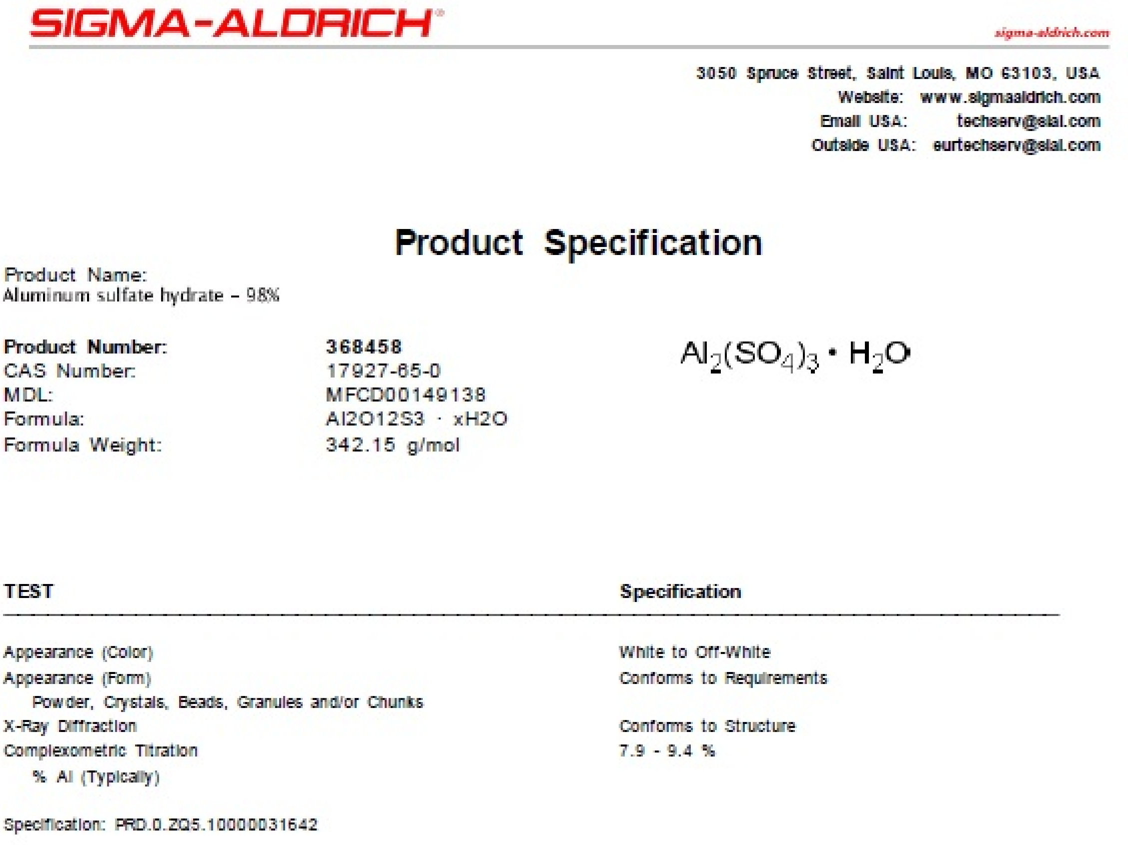
Product Name:
Potassium hydroxide – reagent grade, 90%, flakes

| | | |
|---|---|---|
| **Product Number:** | **484016** | KOH |
| CAS Number: | 1310-58-3 | |
| MDL: | MFCD00003553 | |
| Formula: | HKO | |
| Formula Weight: | 56.11 g/mol | |

| **TEST** | **Specification** |
|---|---|
| Appearance (Color) | White |
| Appearance (Form)<br>Flakes or Chunks | Conforms to Requirements |
| Titration by HCl | 89.5 - 110.5 % |
| X-Ray Diffraction | Conforms to Structure |

Specification: PRD.1.ZQ5.10000008616

### *A.3 Aluminium sulphate*



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## Product Specification

Product Name:
Aluminum sulfate hydrate – 98%

| | |
|---|---|
| **Product Number:** | **368458** |
| CAS Number: | 17927-65-0 |
| MDL: | MFCD00149138 |
| Formula: | Al2O12S3 · xH2O |
| Formula Weight: | 342.15 g/mol |

$Al_2(SO_4)_3 \cdot H_2O$

| **TEST** | **Specification** |
|---|---|
| Appearance (Color) | White to Off-White |
| Appearance (Form)<br>Powder, Crystals, Beads, Granules and/or Chunks | Conforms to Requirements |
| X-Ray Diffraction | Conforms to Structure |
| Complexometric Titration<br>% Al (Typically) | 7.9 - 9.4 % |

Specification: PRD.0.ZQ5.10000031642

# Appendix B. Analytical procedures

B. Wastewater characteristics

### *B.1 Colour*

The colour was determined photoelectrically using the Palintest (Gateshead, United Kingdom) Photometer 7100. The colour was expressed using the platinum/cobalt colour scale. Each unit was equivalent to the colour produced by 1 mg/l platinum in the form of chloroplatinic acid in the presence of 2 mg/l cobaltous chloride hexahydrate. These units are identical with the "Hazen" units, which have been traditionally used to express the results from the visual estimation of water colour.

The following procedures were used to determine the colour:

- The test tube was filled with the sample to the 10ml mark.
- 10ml of deionised water was fill in a test tube and retain for use as the "blank" tube.
- Option Phot. 47 was selected on the photometer.
- The blank test tube was then inserted in the photometer for "blanking" of the apparatus.
- Finally, the test tube containing was inserted and the value was read on the display.

### *B.2 Chemical oxygen demand*

Merck Spectroquant analyser was used for the analyses of COD. The samples were oxidised with a hot sulphuric solution of potassium dichromate that reacts with the oxidisable substances contained in 1l of water under the working conditions of the specified procedure.

The following procedures were used to determine the COD:

- Cells test 14541 were used for this study.
- The cells were swirled to suspend the bottom sediment.
- 3 ml of the sample were carefully pipetted into the reaction cell. The cell was then closed tightly with the screw cap, mixed vigorously, producing exothermal reactions in the process.
- The reaction cells were then heated in the thermoreactor at 148 degrees Celsius for 2 hours.
- The cell was then removed from the thermoreactor and placed in test-tube rack to cool.
- After 10 minutes the cells were swirled then replaced in the rack for complete cooling to room temperature.
- The cells in the spectroquant compartment for reading of the value indicated

### *B.3 Total dissolved solid*

A TDS was measured by determining the concentration of dissolved ionized particles, such as salts and minerals, in the samples. The TDS was measured in part per million.

The TDS was determined using the following procedures:

- The TDS of samples was determined by TDS meter Eutech Cond610 with glass calomel electrode.

- The electrode rinse with distilled water and air dried before use to remove any impurities.
- The TDS count of water samples was determined by dipping the tip of the electrode in the samples and the stabilised value indicated was recorded.

### *B.4 pH*

The pH was measured by change in potential of glass standard calomel electrodes in comparison with approved standard buffers of different pH values.

Analytical procedures:

- The pH of wastewater samples was determined by pH meter Eutech model 700 with glass calomel electrode.
- The pH meter was first standardized by 3 standard buffer solutions of 4, 7 and 9 to verify the linear response of the electrode.
- The pH of water samples was determined by immersing the tip of the electrode in the samples and read the value indicated.

### *B.5 Total Nitrogen*

Merck Spectroquant analyser was used for the analyses of total nitrogen. Organic and inorganic nitrogen compounds are transformed into nitrate according to Koroleff's method by treatment with an oxidizing agent in a thermoreactor.

The following procedures were used to determine the total nitrogen:

- Pipetted 10 ml sample into an empty cell.
- Added 1 level of reagent N-1K to into the cell and mixed.
- Added 6 drops of reagent N-2K into the cell and mixed.
- Heated the cell at 120 degrees in the preheated thermoreactor for 1 hour.
- Allowed the cell to cool to room temperature then shake the cell after 10 min.
- Added 1 level of reagent N-3K into a reaction cell and shake and shake vigorously for 1 min.
- Pipetted the sample the sample into the reaction cell and mix briefly.
- Left the hot cell to stand for 10 min.
- Measured the sample in the photometer.

### *B.6 Total Organic Carbon*

Merck Spectroquant analyser was used for the analyses of total organic carbon. By digestion with sulfuric acid and peroxodisulfate, carbon-containing compounds were transformed into carbon dioxide. This reacted with an indicator solution, the colour of which was determined photometrically.

The following procedures were used to determine the total organic carbon:

- Pipetted 1 ml sample into an empty cell.
- Added 9 ml of distilled water and mix.
- Added 2 drops of reagent TOC-1K into the cell and mix.

- Ensured that the pH is below 2.5.
- Stirred for 10 min at medium speed.
- Pipetted 3 ml sample into a reaction cell.
- Added 1 level of reagent TOC-2K into the reaction cell, close with a steel cap and shake
- Heated the cell standing on its at 120 degrees in the preheated thermoreactor for 2 hours.
- Allowed the cell to cool to room temperature for 60 min.
- Cooling the cell upright.
- Measured the sample in the photometer.

### *B.7 Aluminium*

The test is carried out by adding the 2 Palintest Aluminium test tablets the sample of water. The first tablet acidified the sample to bring any colloidal aluminium into solution and the second buffered the solution to provide the correct conditions for the test. The intensity of the colour produced in the test was proportional to the aluminium concentration and was measured using a Palintest Photometer. Expressed in mg/l Al.

Test procedure:

- Filled the test tube to the 10 ml mark.
- Added one Aluminium No 1 tablet, crushed and mixed to dissolve.
- Added one Aluminium No 2 tablet, crushed and mixed gently to dissolve. Avoid vigorous agitation.
- Stood for 5 min to allow full colour development
- Selected Phot 3 on Photometer
- Took Photometer reading in usual manner

### *B.8 Iron*

The test was carried out by adding the Palintest Iron test tablet the sample of water. The decomplexing/reducing agent broke down weakly complexed forms of iron and converted the iron form from ferric to ferrous form. The ferrous iron reacted with 3-(2-Pyridyl)-5, 6-bis(4-phenyl-sulphonic acid)-1, 2, 4-triazine (PPST) to form a pink colouration. The intensity of the colour produced in the test was proportional to the iron concentration and was measured using a Palintest Photometer. Expressed in mg/l Fe.

Test procedure:

- Filled the test tube to the 10 ml mark.
- Added one Iron LR tablet, crush and mix to dissolve.
- Stood for 1 min to allow full colour development
- Selected Phot 18 on Photometer
- Took Photometer reading in usual manner

# Appendix C. Laboratory experiments guideline

## C. Laboratory experiments

### C.1 Experiment 1: Production of synthetic wastewater

A stock solution of 1000 mg/l was prepared by adding 1000 mg of dye in 1 litre distilled water. The stock was then diluted to the working concentration of 12.5 mg/l.

### C.2 Experiment 2: Coagulation-flocculation

Optimum pH test

- Conducted coagulation-flocculation experiments on the synthetic wastewater with an initial pH of 9.13.
- Added Aluminium Sulphate [Al2(SO4)3.18H2O] and a cationic polymer to the wastewater at a concentration of 100 mg/l and coagulant aid at a concentration of 31.25 mg/l.
- Immediately mixed the liquor at an initial speed of 80 rpm for 1 min.
- Reduced the rotating speed to 30 rpm and maintain for a period of 20 min.
- Stopped the machine and allow the settling of particles in the wastewater for 60 min
- Collected the supernatant and take for analysis of its characteristics.
- Repeated experiments with synthetic wastewater pH values of 7, 8, 9, 10, 11, 12 and 13.

Coagulation-flocculation

- Conducted coagulation-flocculation experiments on the synthetic wastewater with an initial pH of 9.13.
- Added Aluminium Sulphate [Al2(SO4)3.18H2O] and a cationic polymer to the wastewater at a concentration of 100 mg/l and coagulant aid at a concentration of 31.25 mg/l.
- Immediately mixed the liquor at an initial speed of 80 rpm for 1 min.
- Reduced the rotating speed to 30 rpm and maintain for a period of 20 min.
- Stopped the machine and allow the settling of particles in the wastewater for 60 min.
- Collected the supernatant and take for analysis of its characteristics.
- Collected the settled wet sludge will be collected, dewater using the standard method for total dissolved solids (ASTM D5907).
- Dried sludge in an oven at 105$^{o}$C.
- Collected the dried sludge and its mass will be measured using an electronic scale.
- Used dry sludge as a coagulant in conjunction with fresh alum at ratios (fresh alum: RAS) of 1:1, 2:1, 1:2, 0:1.
- Handled the effluent and sludge produced in the same manner as during the treatment with fresh alum.

### C.3 Experiment 3: Adsorption with corn cobs

- Shredded corn cobs using a blender and sieve to particles of sizes of approximately 3×3×2 mm3 and oven dry it.
- Placed the substract and the synthetic wastewater in a 50 ml cell test at a ratio of 10 g: 100 ml.
- The mixture was allowed to stand for 48 h.

- Centrifuged samples at 10 000 g for 5 min
- Collected samples for analysis.

### C.4 Determination of theoretical COD

- Oxidation of dye:

$$2C_{16}H_{14}N_2O_2 + 41O_2 \rightarrow 32O_2 + 14H_2O + 4NO_2 \qquad \text{(D.1)}$$

- Quantity of dye = 12.5 mg = 12.5 $10^{-3}$ g

- Molar mass of dye: 266.29 g/mol

- Molar mass of $O_2$: 16 g/mol × 2 = 32 g/mol

- $COD^{th} = \frac{12.5\times41\times32}{2\times1000\times266.29}$ = 0.0308 g/l ≈ 31 mg/l

## Appendix D. Laboratory experiment results

Table D.1 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation with fresh alum

| | | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | S11 | 115 | 32 | 776.1 | 11.94 | 15 | 21 | 490.4 | 8.15 | 87% | 34% | 37% |
| | S12 | 115 | 32 | 776.1 | 11.94 | 10 | 25 | 631.8 | 8.77 | 91% | 22% | 19% |
| | S13 | 115 | 32 | 776.1 | 11.94 | 20 | 23 | 321.3 | 8.32 | 83% | 28% | 59% |
| Average | | 115 | 32 | 776.1 | 11.94 | 15 | 23 | 481.2 | 8.41 | 87% | 28% | 38% |
| Batch 2 | S21 | 130 | 37 | 778.4 | 11.95 | 20 | 25 | 483.7 | 8.48 | 85% | 32% | 38% |
| | S22 | 130 | 37 | 778.4 | 11.95 | 15 | 28 | 503.0 | 8.56 | 88% | 24% | 35% |
| | S23 | 130 | 37 | 778.4 | 11.95 | 10 | 24 | 451.7 | 8.39 | 92% | 35% | 42% |
| Average | | 130 | 37 | 778.4 | 11.95 | 15 | 26 | 479.5 | 8.48 | 88% | 31% | 38% |
| Batch 3 | S31 | 145 | 36 | 804.5 | 11.96 | 15 | 27 | 367.4 | 8.80 | 90% | 25% | 54% |
| | S32 | 145 | 36 | 804.5 | 11.96 | 15 | 26 | 546.0 | 8.39 | 90% | 28% | 32% |
| | S33 | 145 | 36 | 804.5 | 11.96 | 10 | 25 | 551.8 | 8.70 | 93% | 31% | 31% |
| Average | | 145 | 36 | 804.5 | 11.96 | 13 | 26 | 488.4 | 8.63 | 91% | 28% | 39% |
| Batch 4 | S41 | 145 | 41 | 782.7 | 11.97 | 15 | 24 | 515.2 | 8.80 | 90% | 41% | 34% |
| | S42 | 145 | 41 | 782.7 | 11.97 | 10 | 32 | 565.1 | 8.74 | 93% | 22% | 28% |
| | S43 | 145 | 41 | 782.7 | 11.97 | 15 | 34 | 517.5 | 8.44 | 90% | 17% | 34% |
| Average | | 145 | 41 | 782.7 | 11.97 | 13 | 30 | 532.6 | 8.66 | 91% | 27% | 32% |
| Batch 5 | S51 | 130 | 43 | 754.3 | 11.95 | 15 | 30 | 588.1 | 8.58 | 88% | 30% | 22% |
| | S52 | 130 | 43 | 754.3 | 11.95 | 5 | 35 | 493.7 | 8.42 | 96% | 19% | 35% |
| | S53 | 130 | 43 | 754.3 | 11.95 | 25 | 35 | 491.9 | 8.54 | 81% | 19% | 35% |
| Average | | 130 | 43 | 754.3 | 11.95 | 15 | 33 | 524.6 | 8.51 | 88% | 22% | 30% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.2 Average readings of synthetic wastewater treated by coagulation-flocculation with fresh alum

| | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | 115 | 32 | 776.1 | 11.9 | 15 | 23 | 481.2 | 8.4 | 87% | 28% | 38% |
| Batch2 | 130 | 37 | 778.4 | 12.0 | 15 | 26 | 479.5 | 8.5 | 88% | 31% | 38% |
| Batch3 | 145 | 36 | 804.5 | 12.0 | 13 | 26 | 488.4 | 8.6 | 91% | 28% | 39% |
| Batch4 | 145 | 41 | 782.7 | 12.0 | 13 | 30 | 532.6 | 8.7 | 91% | 27% | 32% |
| Batch5 | 130 | 43 | 754.3 | 12.0 | 15 | 33 | 524.6 | 8.5 | 88% | 22% | 30% |
| Average | 133 | 38 | 779.2 | 12.0 | 14 | 28 | 501.2 | 8.5 | 89% | 27% | 36% |
| Deviation | 13 | 4 | 18 | - | 1 | 4 | 25 | - | 2% | 3% | 4% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.3 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation with RAS

| | | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | S11 | 115 | 13 | 750.4 | 11.97 | 25 | 30 | 505.6 | 11.53 | 78% | 14% | 33% |
| | S12 | 115 | 35 | 750.4 | 11.97 | 20 | 28 | 504.5 | 11.75 | 83% | 20% | 33% |
| | S13 | 115 | 35 | 750.4 | 11.97 | 30 | 26 | 505.2 | 11.52 | 74% | 26% | 33% |
| Average | | 115 | 35 | 750.4 | 11.97 | 25 | 28 | 505.1 | 11.60 | 76% | 20% | 33% |
| Batch 2 | S21 | 120 | 37 | 767.8 | 11.95 | 15 | 28 | 518.8 | 11.57 | 88% | 24% | 32% |
| | S22 | 120 | 37 | 767.8 | 11.95 | 29 | 25 | 501.7 | 11.63 | 76% | 32% | 35% |
| | S23 | 120 | 37 | 767.8 | 11.95 | 25 | 30 | 515.7 | 11.75 | 79% | 19% | 33% |
| Average | | 120 | 37 | 767.8 | 11.95 | 23 | 28 | 512.1 | 11.65 | 81% | 25% | 33% |
| Batch 3 | S31 | 120 | 34 | 778.3 | 11.94 | 25 | 25 | 517.5 | 11.75 | 79% | 26% | 34% |
| | S32 | 120 | 34 | 778.3 | 11.94 | 20 | 29 | 528.9 | 11.75 | 83% | 15% | 32% |
| | S33 | 120 | 34 | 778.3 | 11.94 | 25 | 28 | 515.5 | 11.67 | 79% | 18% | 34% |
| Average | | 120 | 34 | 778.3 | 11.94 | 23 | 27 | 520.6 | 11.72 | 81% | 20% | 33% |
| Batch 4 | S41 | 105 | 38 | 753.2 | 11.95 | 20 | 32 | 517.2 | 11.68 | 81% | 16% | 31% |
| | S42 | 105 | 38 | 753.2 | 11.95 | 35 | 29 | 505.2 | 11.60 | 67% | 24% | 33% |
| | S43 | 105 | 38 | 753.2 | 11.95 | 25 | 25 | 521.8 | 11.72 | 76% | 34% | 31% |
| Average | | 105 | 38 | 753.2 | 11.95 | 27 | 29 | 514.7 | 11.67 | 75% | 25% | 32% |
| Batch 5 | S51 | 115 | 40 | 752.8 | 11.97 | 25 | 34 | 520.9 | 11.66 | 78% | 15% | 31% |
| | S52 | 115 | 40 | 752.8 | 11.97 | 35 | 34 | 535.4 | 11.58 | 70% | 15% | 29% |
| | S53 | 115 | 40 | 752.8 | 11.97 | 25 | 29 | 511.8 | 11.73 | 78% | 28% | 32% |
| Average | | 115 | 40 | 752.8 | 11.97 | 28 | 32 | 522.7 | 11.66 | 75% | 21% | 31% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.4 Average readings of synthetic wastewater treated by coagulation-flocculation with RAS

| | **Synthetic wastewater** | | | | **Treated effluent** | | | | **Efficiency** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| **Batch 1** | 115 | 35 | 750.4 | 12.0 | 25 | 28 | 505.1 | 11.6 | 76% | 20% | 33% |
| **Batch2** | 120 | 37 | 767.8 | 12.0 | 23 | 28 | 512.1 | 11.7 | 81% | 25% | 33% |
| **Batch3** | 120 | 34 | 778.3 | 11.9 | 23 | 27 | 520.6 | 11.7 | 81% | 20% | 33% |
| **Batch4** | 105 | 38 | 753.2 | 12.0 | 27 | 29 | 514.7 | 11.7 | 75% | 25% | 32% |
| **Batch5** | 115 | 40 | 752.8 | 12.0 | 28 | 32 | 522.7 | 11.7 | 75% | 21% | 31% |
| **Average** | **115** | **37** | **760.5** | **12.0** | **25** | **29** | **515.0** | **11.7** | **78%** | **22%** | **32%** |
| **Deviation** | **6** | **2** | **12** | **-** | **2** | **2** | **7** | **-** | **3%** | **3%** | **1%** |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.5 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation with fresh alum and RAS (ratio 1:1)

| | | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | S11 | 130 | 28 | 688.4 | 11.94 | 20 | 32 | 465.4 | 9.81 | 85% | -14% | 32% |
| | S12 | 130 | 28 | 688.4 | 11.94 | 25 | 29 | 473.2 | 10.49 | 81% | -4% | 31% |
| | S13 | 130 | 28 | 688.4 | 11.94 | 30 | 25 | 475.7 | 10.22 | 77% | 11% | 31% |
| Average | | 130 | 28 | 688.4 | 11.94 | 25 | 29 | 471.4 | 10.17 | 81% | -2% | 32% |
| Batch 2 | S21 | 130 | 28 | 745.4 | 11.96 | 20 | 31 | 460.2 | 10.45 | 85% | -11% | 38% |
| | S22 | 130 | 28 | 745.4 | 11.96 | 25 | 28 | 453.6 | 10.55 | 81% | 0% | 39% |
| | S23 | 130 | 28 | 745.4 | 11.96 | 25 | 28 | 496.6 | 10.48 | 81% | 0% | 33% |
| Average | | 130 | 28 | 745.4 | 11.96 | 23 | 29 | 470.1 | 10.49 | 82% | -4% | 37% |
| Batch 3 | S31 | 135 | 34 | 677.4 | 11.98 | 25 | 34 | 419.6 | 10.51 | 81% | 0% | 38% |
| | S32 | 135 | 34 | 677.4 | 11.98 | 15 | 31 | 393.2 | 10.48 | 89% | 9% | 42% |
| | S33 | 135 | 34 | 677.4 | 11.98 | 15 | 39 | 467.9 | 10.38 | 89% | -15% | 31% |
| Average | | 135 | 34 | 677.4 | 11.98 | 18 | 35 | 426.9 | 10.46 | 85% | -2% | 37% |
| Batch 4 | S41 | 130 | 31 | 715.1 | 11.94 | 15 | 33 | 502.5 | 10.52 | 88% | -6% | 30% |
| | S42 | 130 | 31 | 715.1 | 11.94 | 20 | 31 | 468.4 | 10.26 | 85% | 0% | 34% |
| | S43 | 130 | 31 | 715.1 | 11.94 | 10 | 25 | 452.8 | 10.39 | 92% | 19% | 37% |
| Average | | 130 | 31 | 715.1 | 11.94 | 15 | 30 | 474.6 | 10.39 | 88% | 6% | 34% |
| Batch 5 | S51 | 125 | 22 | 791.6 | 11.96 | 15 | 22 | 483.2 | 10.53 | 88% | 0% | 39% |
| | S52 | 125 | 22 | 791.6 | 11.96 | 20 | 25 | 398.7 | 10.46 | 84% | -14% | 50% |
| | S53 | 125 | 22 | 791.6 | 11.96 | 15 | 28 | 451.5 | 10.49 | 88% | -27% | 43% |
| Average | | 125 | 22 | 791.6 | 11.96 | 17 | 25 | 444.5 | 10.49 | 87% | -14% | 44% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.6 Average readings of synthetic wastewater treated by coagulation-flocculation with fresh alum and RAS (ratio 1:1)

| | **Synthetic wastewater** | | | | **Treated effluent** | | | | **Efficiency** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** | **pH** | **Colour** | **COD** | **TDS** |
| **Batch 1** | 130 | 28 | 688.4 | 11.9 | 25 | 29 | 471.4 | 10.2 | 81% | -2% | 32% |
| **Batch2** | 130 | 28 | 745.4 | 12.0 | 23 | 29 | 470.1 | 10.5 | 82% | -4% | 37% |
| **Batch3** | 135 | 34 | 677.4 | 12.0 | 18 | 35 | 426.9 | 10.5 | 85% | -2% | 37% |
| **Batch4** | 130 | 31 | 715.1 | 11.9 | 15 | 30 | 474.6 | 10.4 | 88% | 6% | 34% |
| **Batch5** | 125 | 22 | 791.6 | 12.0 | 17 | 25 | 444.5 | 10.5 | 87% | -14% | 44% |
| **Average** | **130** | **29** | **723.6** | **12.0** | **20** | **29** | **457.5** | **10.4** | **85%** | **-3%** | **37%** |
| **Deviation** | **4** | **4** | **46** | **-** | **4** | **3** | **21** | **-** | **3%** | **7%** | **5%** |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.7 Results of physico-chemical analyses of synthetic wastewater treated by coagulation-flocculation with fresh alum and RAS (ratio 1:2)

| | | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | S11 | 140 | 33 | 725.6 | 11.94 | 20 | 38 | 506.4 | 11.08 | 86% | -15% | 30% |
| | S12 | 140 | 33 | 725.6 | 11.94 | 25 | 37 | 512.8 | 11.04 | 82% | -12% | 29% |
| | S13 | 140 | 33 | 725.6 | 11.94 | 25 | 35 | 508.4 | 11.04 | 82% | -6% | 30% |
| Average | | 140 | 33 | 725.6 | 11.94 | 23 | 37 | 509.2 | 11.05 | 84% | -11% | 30% |
| Batch 2 | S21 | 140 | 35 | 786.5 | 11.96 | 25 | 40 | 555.3 | 10.94 | 82% | -14% | 29% |
| | S22 | 140 | 35 | 786.5 | 11.96 | 30 | 38 | 542.5 | 10.99 | 79% | -9% | 31% |
| | S23 | 140 | 35 | 786.5 | 11.96 | 25 | 37 | 536.4 | 11.02 | 82% | -6% | 32% |
| Average | | 140 | 35 | 786.5 | 11.96 | 27 | 38 | 544.7 | 10.98 | 81% | -10% | 31% |
| Batch 3 | S31 | 135 | 29 | 699.7 | 11.94 | 30 | 29 | 459.8 | 10.86 | 78% | 0% | 34% |
| | S32 | 135 | 29 | 699.7 | 11.94 | 25 | 31 | 461.4 | 10.73 | 81% | -7% | 34% |
| | S33 | 135 | 29 | 699.7 | 11.94 | 25 | 33 | 471.2 | 10.84 | 81% | -14% | 33% |
| Average | | 135 | 29 | 699.7 | 11.94 | 27 | 31 | 464.1 | 10.81 | 80% | -7% | 34% |
| Batch 4 | S41 | 130 | 25 | 775.6 | 11.97 | 20 | 29 | 495.3 | 11.16 | 85% | -16% | 36% |
| | S42 | 130 | 25 | 775.6 | 11.97 | 25 | 29 | 506.1 | 10.99 | 81% | -16% | 35% |
| | S43 | 130 | 25 | 775.6 | 11.97 | 30 | 27 | 518.2 | 11.02 | 77% | -8% | 33% |
| Average | | 130 | 25 | 775.6 | 11.97 | 25 | 28 | 506.5 | 11.06 | 81% | -12% | 35% |
| Batch 5 | S51 | 125 | 28 | 706.2 | 11.92 | 20 | 30 | 549.6 | 10.87 | 84% | -7% | 22% |
| | S52 | 125 | 28 | 706.2 | 11.92 | 25 | 28 | 536.4 | 11.06 | 80% | 0% | 24% |
| | S53 | 125 | 28 | 706.2 | 11.92 | 20 | 28 | 559.8 | 10.94 | 84% | 0% | 21% |
| Average | | 125 | 28 | 706.2 | 11.92 | 22 | 29 | 548.6 | 10.96 | 83% | -4% | 22% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.8 Average readings of synthetic wastewater treated by coagulation-flocculation with fresh alum and RAS (ratio 1:2)

| | Synthetic wastewater | | | | Treated effluent | | | | Efficiency | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Colour | COD | TDS | pH | Colour | COD | TDS | pH | Colour | COD | TDS |
| Batch 1 | 140 | 33 | 726 | 11.9 | 23 | 37 | 509 | 11.1 | 84% | -11% | 30% |
| Batch2 | 140 | 35 | 787 | 12.0 | 27 | 38 | 545 | 11.0 | 81% | -10% | 31% |
| Batch3 | 135 | 29 | 700 | 11.9 | 27 | 31 | 464 | 10.8 | 80% | -7% | 34% |
| Batch4 | 130 | 25 | 776 | 12.0 | 25 | 28 | 507 | 11.1 | 81% | -12% | 35% |
| Batch5 | 125 | 28 | 706 | 11.9 | 22 | 29 | 549 | 11.0 | 83% | -4% | 22% |
| Average | 134 | 30 | 739 | 11.9 | 25 | 33 | 515 | 11.0 | 82% | -9% | 30% |
| Deviation | 7 | 4 | 40 | - | 2 | 5 | 34 | - | 2% | 3% | 5% |

Colour expressed in mg/l Pt/Co; COD and TDS expressed in mg/l

Table D.9 Fe, Al and TN experiments results for effluents treated with coagulation-flocculation

| Samples | Synthetic wastewater | | | Treated effluent | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1:0 | | | 0:1 | | | 1:1 | | | 1:2 | | |
| | Fe | Al | TN | Fe | Al | TN | Fe | Al | TN | Fe | Al | TN | Fe | Al | TN |
| Batch 1 | 0.00 | 0.00 | 110 | 0.00 | 0.23 | 50 | 0.01 | 0.20 | 40 | 0.01 | 0.76 | 30 | 0.01 | 2.16 | 50 |
| Batch 2 | 0.00 | 0.00 | 70 | 0.01 | 0.22 | 40 | 0.01 | 0.16 | 40 | 0.00 | 0.57 | 40 | 0.00 | 2.27 | 70 |
| Batch 3 | 0.00 | 0.00 | 93 | 0.00 | 0.26 | 20 | 0.00 | 0.18 | 20 | 0.01 | 0.59 | 50 | 0.01 | 3.07 | 90 |
| Batch 4 | 0.00 | 0.00 | 100 | 0.00 | 0.22 | 40 | 0.00 | 0.22 | 30 | 0.01 | 0.65 | 40 | 0.00 | 2.00 | 50 |
| Batch 5 | 0.00 | 0.00 | 110 | 0.01 | 0.24 | 40 | 0.00 | 0.18 | 40 | 0.01 | 0.62 | 50 | 0.00 | 2.50 | 60 |
| Average | 0.00 | 0.00 | 97 | 0.00 | 0.24 | 38 | 0.01 | 0.18 | 34 | 0.01 | 0.64 | 40 | 0.01 | 2.50 | 64 |
| Deviation | 0.00 | 0.00 | 17 | 0.00 | 0.02 | 11 | 0.00 | 0.02 | 9 | 0.01 | 0.10 | 10 | 0.01 | 0.50 | 17 |

Fe expressed in mg/l Fe; Al expressed in mg/l Al, TN expressed in mg/l

Table D.10 Adsorption with shredded corn cobs experiments results

| | | Synthetic wastewater | | | Treated effluent | | |
|---|---|---|---|---|---|---|---|
| | | Colour | COD | pH | Colour | COD | pH |
| Batch 1 | C11 | 115 | 33 | 12.0 | >500 | 14150 | 11.1 |
| | C12 | 115 | 33 | 12.0 | >500 | 14300 | 11.0 |
| | C13 | 115 | 33 | 12.0 | >500 | 15110 | 11.0 |
| Average | | 115 | 35 | - | >500 | 14520 | - |
| Batch 2 | C21 | 120 | 35 | 12.0 | >500 | 15460 | 10.9 |
| | C22 | 120 | 35 | 12.0 | >500 | 14330 | 10.9 |
| | C23 | 120 | 35 | 12.0 | >500 | 14340 | 11.0 |
| Average | | 120 | 37 | - | >500 | 14710 | - |
| Batch 3 | C31 | 120 | 29 | 11.9 | >500 | 10010 | 11.0 |
| | C32 | 120 | 29 | 11.9 | >500 | 11730 | 11.1 |
| | C33 | 120 | 29 | 11.9 | >500 | 10650 | 11.0 |
| Average | | 120 | 34 | - | >500 | 10797 | - |

Colour expressed in mg/l Pt/Co; COD expressed in mg/l

Table D.11 TOC and TN experiments results for effluents treated with corn cobs

| | | Synthetic wastewater | | Treated effluent | |
|---|---|---|---|---|---|
| | | TOC | TN | TOC | TN |
| Batch 1 | C11 | 348 | 113 | 6575 | 60 |
| | C12 | 348 | 113 | 7050 | 70 |
| | C13 | 348 | 113 | 6275 | 50 |
| Average | | 348 | 113 | 6633 | 60 |
| Batch 2 | C21 | 330 | 127 | 5250 | 50 |
| | C22 | 330 | 127 | 4950 | 70 |
| | C23 | 330 | 127 | 5800 | 90 |
| Average | | 330 | 127 | 5333 | 70 |
| Batch 3 | C31 | 344 | 119 | 4600 | 50 |
| | C32 | 344 | 119 | 4825 | 70 |
| | C33 | 344 | 119 | 4650 | 50 |
| Average | | 344 | 119 | 4692 | 70 |

TOC and TN expressed in mg/l