Utilizing Coagulants from Industrial Waste for Treating Stone Cutting Wastewater: Technical Feasibility and Parametric Optimization

By

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Abstract

Treating waste by waste is an important concept in environmental sustainability. In treating wastewater containing suspended mineral particles (e.g. stone cutting and tile industries), flocculation sedimentation process is widely used, utilizing a commercial flocculent. Utilizing coagulant from other natural sources and industrial wastes can assist in waste management and in reducing the treatment cost.

This study aims at utilizing coagulants from wastewater (released by leather and aluminum coating industries) for treating stone cutting wastewater. A full literature review indicates that this innovative approach has not been investigated in previous research work.

After characterizing the wastewater, the effects of various operating parameters on wastewater treatment efficiency were investigated experimentally. Wastewaters (from the two sources) were mixed, then jar test experiments were performed. The effects of changing wastewater mixing ration and pH on the removal efficiency were investigated by turbidity meter and UV-spectrophotometry.

The optimum mixing ratio for treating stone cutting wastewater with wastewater from leather manufacturing (liming step) was found to be close 10%. It achieved a turbidity removal efficiency of 98.8%. A similar optimum value was obtained when wastewater from aluminum coating was utilized as a coagulant. However, the obtained removal efficiency was 90%. The removal efficiency changes with pH of the system. The best efficiency was obtained at alkaline conditions (with an optimum value of 9.5).

These experimental results were compared with similar experiments utilizing a commercial lime solution. A lower removal efficiency (91%) was obtained.

For the purpose of comparison, a lain sedimentation test was performed (without adding a coagulant). The obtained removal efficiency was 75%. Such a comparison emphasizes the technical feasibility of this novel process (utilizing wastewater as a coagulant).

الإهداء

بسم الله الرحمن الرحيم

" وقل اعملوا فسيرى الله عملكم ورسوله والمؤمنون "

إلهي لا يطيب الليل إلا بشكرك، ولا يطيب النهار إلا بذكرك . . . الله جل جلاله

إلى من بلغ الأمة وحمل الرسالة وأدى الأمانة إلى حبيب الله محمد صلوات ربي عليه

إلى بلدي موطني وارضي فلسطين

***

إلى الشمس المضيئة في حياتي . . . إلى من ركع العطاء أمام قدميها

إلى الظل الذي آوي إليه في كل حين . . . إلى القلب الناصع بالبياض " أمي الغالية"

***

إل من كلله الله بالهيبة والوقار . . . إلى الذي أحمل اسمه بكل افتخار

إلى من حصد الأشواك عن دربي ليمهد لي طريق العلم . . . إلى القلب الكبير "والدي العزيز"

***

إلى أولئك المخلصين الذين أضاؤوا لنا الطريق . . . إلى أساتذتي الأفاضل

إلى صديقاتي ورفيقات دربي . . . إلى قسم هندسة تكنولوجيا البيئة

إليكم نهدي هذا البحث

الشكر

الحمد لله الذي بفضله تتم الصالحات

لله الشكر أولا وأخرا الذي فتح لنا أبواب رحمته فأنار بصرنا وبصيرتنا ومن علينا بإنجاز هذا العمل المتواضع .

والدينا الكرام نشكركما بحجم الحب الذي أكننتموه في قلوبكم لنا فكان نورا نهتدي به . نشكركم بحجم الدعم الذي وهبتمونا إياه لإنجاز هذا العمل .

مشرفنا أستاذنا الكريم الدكتور ماهر الجعبري نشكرك بحجم الأمل الذي منحتنا إياه طيلة أيام دراستنا . نشكرك بحجم الصبر الذي تحليت به لنكون الأفضل دائماً .

أساتذتنا الأعزاء نشكركم بحجم الإخلاص الذي رافقكم طوال مسيرتنا الأكاديمية بحجم الجهد الذي بذلتموه لنكون بالصدارة دائماً .

كما ونتقدم بخالص الشكر الى كل من ساهم بإنجاز هذا العمل ونخص بالذكر

المهندستان هبة سليمية و ناريمان زاهدة في قسم هندسة تكنولوجيا البيئة

الأستاذة دعاء سدر في قسم الكيمياء التطبيقية

العم ابو النور والسيد عامر الزعتري في مدبغة الزعتري

المهندس حسان عرمان في مصنع نابكو

وإلى كل الأحبة الذين كانوا معنا بقلوبهم ودعواتهم نشكركم كل الشكر .

ولن نضيع هذه الفرصة لنصل ونسلم على رسولنا الكريم "معلمنا الأول " عليه الصلاة وأتم التسليم .

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Chapter One

Research Concept

1.1 Introduction

Industrial sector is the most important economic sector in Palestine; it includes stone and marble, metals, glasses, leather and other industries.

Stone cutting industry is a type of mining industries, it plays a major role in terms of production, employment and export. The total number of facilities in Palestine are about 1124 facilities [1].

In Palestine there is a limited number of metal factories such as steel and aluminum, but also it contributes in the Palestinian economic growth.

When raw materials pass through manufacturing and operation process, it releases many waste that could be solid, liquid or gases. It classified as non-hazardous or hazardous waste, which leads to a serious health and environmental problem.

Industrial wastewater is one of the major problems; wastewater from stone cutting industry has a high concentration of calcium carbonate powder. Metal industry releases acidic or alkaline wastewater including heavy metals and high concentration of suspended solid, which causes serious impacts on human health and environment.

Wastewater treatment could be physical, chemical or biological. Flocculation sedimentation is a type of physicochemical wastewater treatment used to separate suspended solid or colloidal particle from wastewater. Flocculation process currently used in stone cutting plants.

Coagulation process neutralizes the negative charges of contaminated suspended particle in wastewater by the addition of coagulating agents, these coagulants could be organic or inorganic based on aluminum or iron salts.

Coagulant could be natural or synthetic, natural coagulants available in many natural sources such as starch, cellulose, guar gum, palm oil and chitosan. Inorganic coagulants could be available in industrial waste streams such as metal industry.

Minimization environmental adverse effects of metal and stone cutting wastewater industry and achieve lower treatment costs investigated by applying 3R principle through reuse, recycle metal industry wastewater and replace commercial coagulants.

In this project wastewater from aluminum industry will be utilized to replace the commercial coagulant to treat stone cutting wastewater.

1.2 Scientific Background

Many researchers studied flocculation sedimentation process to treat wastewater containing fines or suspended solid. Flocculation by bridging is the most important mechanism in treatments which has high efficiency in suspension destabilization [2]. Others studied the types and usage of natural flocculants as coagulant, which needed large dosage to achieve treatment [3].

Flocculation sedimentation process for tile wastewater treatment was studied by Al-Rjoub and Talahmeh [4]. They used the typical conical sedimentation tank for treatment tile wastewater with commercial flocculating agent. The separation efficiency reached 97% at 100mg/L.

Coagulation aims to change surface charge then aggregate the particles together [5]. Several coagulant types are used for suspension wastewater, Stone cutting wastewater was treated by lime and alum; 100 PPM alum was the best dosage for turbidity and TS removal [6].

Iron-based coagulants and alum get many studies because they are effective in treating wastewater that have organic substance and colloidal particles [7]. For example $AL_2(SO4)_3$ (alum) was generally used for pulp mill and paper wastewater treatment [6, 7]. Several research teams investigated optimum conditions for these coagulants such as dosage and pH, which have importance effect on treatment behavior [7].

Several researchers investigate the potential utilizing of coagulants from waste and wastewater. For example poly-Al-Zn-Fe coagulant was prepared from galvanized aluminum slag. It has great ability for turbidity and organic matter removal [4]. Other coagulant prepared by waste from aluminum industry has a similar capacity with commercial coagulants (alum, ferric sulfate, ferric chloride) [8].

In recent year's natural resource investigated success in treatment. These include chitosan and rice starch, which were used to treat palm oil mill effluent [9-11]. Also Gums and mucilage used for treating tannery and sewage effluent [3].

1.3 Problem Statement

Main problem

Experimental investigation of utilizing alternative coagulants from industrial wastewater for replacing commercial polymeric coagulant for stone cutting wastewater treatment.

Sub-Problems

1. What are the potential coagulants available in local industrial waste/wastewater?
2. Is it technically feasible to use these potential coagulants to treat stone cutting wastewater?
3. What are the relevant characteristics of wastewater from metal surface treatment?
4. What are the optimum operating conditions for the selected coagulant?

1.4 Goal and Objectives

The main goal of the present study is to utilize the concept of "treating waste by waste "***to replace*** the commercial coagulant with coagulants from available waste to treat stone cutting wastewater in the existing flocculation sedimentation treatment process to reduce the environmental impacts.

The Objectives of the project are:

1. Reviewing previous research studies that utilize natural coagulants or industrial waste as coagulant.
2. Investigating the available Palestinian industrial waste that contains coagulants.
3. Analyzing the characteristic of a selected industrial wastewater that contains coagulants.
4. Establishing an experimental procedure for investigated the technical feasibility of utilizing industrial wastewater.
5. Confirming technical feasibility of utilizing industrial wastewater as coagulant to treat stone cutting wastewater.
6. Optimizing the dosage and pH of the selected potential coagulant from waste.

1.5 Project Importance

Wastewater is the main pollutant in stonecutting industry, it contains high amounts of lime stone powder, which is released from various unit operations in high concentration. The discharge of these untreated wastewater causes reduction in soil quality and change the characteristic of surface and groundwater.

Contaminated drinking water bodies with metal particles such as aluminum and iron causes human health problems, such as nerve damage, cancer and reach to kidney damage if high concentration of suspended particles found. Aquatic life also is highly affected by suspended solids reduce visibility and light absorbent in water, which can increase stream temperatures and reduce photosynthesis. Reduction of plant photosynthesis reduces the amount of food, habitat and dissolved oxygen available for other species. Fish is one example express the pollution from fine aluminum particles, it could clog fish gills and erodes its tissue, it will also interfere with egg and larval development and fish gill functions.

Stone cutting powder and metal particle appears as solid waste or concentrated in wastewater, but they are very wealthy so some of these wastes must be exploited as a source in unit operation treatment. Water is the first compound in our life which forms 60% of the human body, it is the basic factor for bioprocess in all different organism.

Wastewater treatment is a very important process to preserve water quality and quantity, it reducing organic and inorganic matter, minimizing pathogenic and reduce risks to human and environment. Flocculation sedimentation treatment is a traditional method using commercial flocculants/coagulants. Using coagulants from available waste is a new and unique approach in the wastewater treatment processes, which lowers cost with high efficiency.

This project implements one of the most important environmental principles, it is aim to apply treatment waste by waste concept. Aluminum industry wastewater will be used as coagulant to treat stone cutting wastewater to contribute the minimization of both aluminum and stone cutting wastewater.

1.6 Methodology

The project has two main stages. In the first stage a review report will be prepared based on description research approach, in the second stage, the research approach for this project is based on the experimental methodology, for confirming and optimizing the use of a potential waste for treating stonecutting wastewater.

The main activities are as follows:

1. Literature review about coagulant sources.
2. Identify potential waste that could be used as coagulants.
3. Collecting industrial wastewater sample.
4. Preliminary testing on model coagulant solutions.
5. Investigating the efficiency of different model coagulates solutions.
6. Select the optimum model solution to treat stone cutting wastewater via batch flocculation sedimentation treatment process.
7. Investigating the utilized wastewater as coagulant on stone cutting wastewater.
8. Appling different test for coagulant performance.
9. Various parameters were studied such as pH and dosage.

Research Requirements (Materials and Equipment)

1. Wastewater samples from stone cutting, tile, aluminum etching and leather liming industries.
2. Commercial coagulant solution (Aluminum chloride $AlCl_3$, Aluminum sulfate $Al_2(SO_4)_3$ and Lime coagulant CaO).
3. Laboratory equipment (flasks, bottle, funnel, burette , etc.), stirrer, turbidity meter.
4. Chemical materials (H_2SO_4 and $NaOH$)

1.7 Budget

The estimated total cost for this project is 400 Nis as listed in table1.1.

Table 1.1: Budget.

Requirement	***Unit***	***cost***	***Contribution***		***Requirement***
			Department	***R.C granting***	
laboratory equipment	NIS	100	100%	0	0%
Cost of experiment	NIS	100	100%	0	0%
Materials	NIS	200	20%	0	80%
Transportation	NIS	200	0	0	100%
Total cost	NIS	**400**	40%	0	60%

1.8 Action plan

The action plan during the first semester is shown in Table 1.1, and the action plan for the next semester is shown in Table 1.2.

Table 1.2: Action plan for the first semester

Tasks	*September*				*October*				*November*				*December*			
	Wk 1	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*
Project Identification																
Literature Review																
Material collection																
Experiment work																
Preliminary tests using coagulant Model																
Preliminary Results analysis																
Report preparation																

Table 1.3: Action plan for the second semester

Tasks	*January*	*February*				*March*				*April*				*May*
	Wk 4	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*	*Wk 2*	*Wk 3*	*Wk 4*	*Wk 1*
Real Wastewater Sample Collection														
Experimental work														
Results Analysis														
Report Preparation														

Chapter Two

Literature Review for Coagulants Types, Sources and Flocculation Treatment for Stone Cutting Wastewater

2.1 Introduction

The characteristics of industrial wastewater depend on the production process and the types of the raw materials used: Stone industry is based on the extraction and transportation of huge stone blocks from quarries to stone cutting plants, where they are processed (mainly mechanically) to produce building stones. These processes need large volumes of water for cooling, cleaning, lubrication and for dust reduction. Thus it generates large volume of wastewater contaminated with suspended particle.The particles content ranges from (5-12)g/L [12, 13]. Approximately 25–40% of the weight of the block is released as fine particles in wastewater [14]. Tile industry is based on the mixing of grit, sand, cement and limestone. After forming tiles, water is used to clean and polish the tile surface. This generates wastewater contaminated with mineral suspended particle. Waste suspension from marble, granite and ceramic tile industries contain cement, fine grits and lime stone particles. Discharging these untreated wastewater to open area alters soil, surface water and groundwater characteristics.

Flocculation sedimentation using conical sedimentation tank is a type of physicochemical wastewater treatment, it is used to separate suspended solids or colloidal particles from wastewater [15-17]. Enhancing settling of particles is achieved using various types of agents, through increasing the particle size. Flocculation by particle-particle bridging, using long branched polymers is the most important mechanism in treatment, with a high efficiency in suspension destabilization [2]. In addition, the used polymers may neutralize the surface charge of the particles.

Particles aggregation is obtained by minimizing repulsive forces and maximizing attraction forces (e.g. electrostatic force) [18]. Coagulation process is based on neutralizing the negative charges of contaminated suspended particle in wastewater by the addition of coagulating agents, and thus enhances particle aggregation [5]. Coagulants include natural and synthetic types, using metal or pre-polymerized coagulants [3, 19]. Flocculation of fine particles is based on using large molecular weight polymers to bridge between the particles [14].The usage of natural materials as coagulant received noticeable research interest [3].

There are various industrial wastes that are potential coagulants for wastewater treatment: Metal industry releases acidic and alkaline wastewater including heavy metals and high concentration of suspended solid. Aluminium powder coating apply cleaning, etching, anodizing, colouring, and sealing processes. In galvanization industry, metal surface are protected against corrosion by coating with paint, oil, grease or coating with non-corrosive metals such as tinning [20]. Both industries result in acidic and alkaline wastewaters contaminated with metallic compounds that causes coagulation. In tanning industry, various waste and wastewater are generated. Among these is the lime contaminated wastewater [21]. Highly acidic/alkaline wastewater are also released from graphite and coal extraction industries [22]. A solid waste from coal mine processing include coal gangue and ash [23]. Effluents streams from pulp and paper industry contain high concentrations of organic matter, organic chlorides, suspended solids, biological oxygen demand (BOD) and chemical oxygen demand (COD) [24]. Waste from palm oil industry composes nearly 40%, which is known as activated bleaching earth [25, 26]. These industrial wastes are considered in various previous works to treat wastewater by coagulation/flocculation method [15].

This chapter summarizes the results of an extensive literature review for various types and sources of coagulants. It concludes with highlighting and recommending alternative coagulants from industrial wastes for replacing commercial polymeric coagulant, for wastewater treatment from stone cutting and other similar industries (e.g. tile industry). It capitalizes on the concept of "treating waste by waste", and the cleaner production concept of "replacing" the commercial coagulant. It also analyzes the available industrial wastes (particularly in Palestine) to propose new potential coagulants.

2.2 Methodology - Literature Review

The methodology of this study is based on the description research approach. The required references were obtained from scientific databases available on Sciencedirect, Google Scholar and ResearchGate. The search was made using subject keywords including “stone cutting”, “flocculation sedimentation”, “natural coagulant”, “flocculent” and ”prepared coagulant”. The increased research interest in these aspects was analyzed based on number of papers published appeared in recent years. The results are presented in a graphical form.

The selected papers are screened and classified into four groups. The classification was based on the treatment approach, sources and types of coagulants. The obtained results are shown in tables 1-4.

These tables were structured around the experimental methods that have been used by the researchers in order to investigate the efficiency of treatment. The various experimental parameters, methodology and tests, and the main results are listed in these tables.
Based on these information, the treatment methods were analyzed and compared in graphical form (Figures 3-5), in order to highlight the optimized coagulants that achieved the best treatment efficiency.

2.3 Experimental Research Approach

Papers in this field focused on the coagulant performance and on analyzing the characteristics of coagulants structure, through a unified experiment research approach.

The experimental approach for investigating the technical feasibility of the various potential coagulants was mainly based on mixing the selected coagulant with the wastewater, then observing the settling behaviour of the system. The performance of these coagulants was the main research object, i.e. optimizing the solid-liquid separation process. This was done mainly by measuring the removal or residual turbidity, suspended solids (SS) and phosphate removal, using mainly jar test and sedimentation test. In sedimentation test without coagulant, long times for settling were observed (e.g. 2 hours), and consequently, the interval for measurements was usually taken as 10 minutes [6, 22, 27].

The coagulants was added at certain dosage for stone cutting wastewater in a testing cylinder. The cylinder was sealed and inverted (top-bottom) four times to obtain good mixing. Then it was left for 15 min to allow sedimentation of the aggregated particles. Then, a sample from the supernatant was taken from the top, for measurement (e.g. residual turbidity) [28]. Experiments with jar test involved three main stages: rapid mixing (of coagulant and wastewater), slow mixing and settling. After settling, supernatant samples were taken from a point 2–3 cm below the surface of the water sample cylinder for analysis [22].

The experimental variables for studying coagulant performance included measurements for the followings:

- Residual turbidity measured using Turbidimeter.
- pH by using pH-Meter.

- The absorbance, color removal and Natural Organic Matter (NOM) using a UV/Vis spectrophotometer.[29]
- Total phosphorus (TP) using ammonium molybdate spectrophotometry.
- Electrical conductivity (EC) using EC meter.
- Temperature using a thermometer.
- Zeta-potential using a laser zee meter and micro-electrophoretic mobility detector.

The analytical methods for determining the concentration of pollutants included:
- Residual aluminum concentration using eriochrome cyanine R method [29].
- The concentration of phosphates using the ascorbic acid method [29].
- Chemical oxygen demand using a colorimetric closed reflux method [26].

For analyzing the characteristics of coagulants structure, various analytical devices and methods were used such as scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD), X-ray fluorescence and transmission electron microscope (TEM). They were used to find out micro-properties during preparation, and for investigating the crystalline phases [6-8]. Some researchers used inductively coupled plasma (ICP) spectroscopy and molybdenum blue photometry for analyzing components and metals, for prepared coagulants [3].

2.4 Results and Discussions

The obtained review results are summarized in tables 2.1, 2.2, 2.3 and 2.4: The first group of papers are listed and summarized in Table 2.1. It highlights the treatment methods for stone cutting and marble wastewater. The second group is shown in Table 2.2. It summarizes research efforts on various commercial coagulants to treat suspension wastewater. The third group is shown in Table 2.3. It reviews the use of natural coagulants in various wastewater treatment application. Finally, the fourth group of search results is shown in Table 2.4. It summarizes utilizing coagulants from industrial waste to treat wastewater.

Table 2.1: Wastewater treatment process in stone cutting industry

Treatment Process	Wastewater source	Note on Equipment &Technique	Result	Ref Year
Filtration	Stone cutting	ceramic membranes	membranes were suitable for stone cutting wastewater treatment (if flocculation was used as a pre-treatment)	[30] 2001
Ultrafiltration	Stone cutting	-silica-modified alumina (100 nm) membrane γ-alumina membrane (10nm)	-very fine suspended solids was removed -The permeate flux achieved with the 100 nm membrane decreased and continued to decline even after 24 h of filtration, the permeate flux achieved with the 10 nm membrane was stable	[31] 2002
Filtration (Recycle System)	Stone cutting	-air pump -storage tank -high pressure filter-filter pump	Produced "crystal clear water" used for stone cutting fabrication, operations and polishing processes	[32] 2009
Flocculation Sedimentation	Stone cutting	-conical cylindrical -sedimentation vessel-impinging disk -polymer and stirring tanks	88.5% separation efficiency was found with 300 mg/l and 100 mg/l polymer dosage	[17] 2002
Flocculation	Natural stone suspensions (marble and travertine)	anionic polymers addition	34%,28% anionic polymer for marble, travertine suspension respectively gave the best flocculation performance -At high pH the settling rate increased	[33] 2005
Aggregation	Marble (cutting and equalization processes)	Metal Coagulant-flocculent addition	High efficiencies for turbidity removal	[34] 2005
Coagulation/ flocculation/ Sedimentation	Marble Industry	hydrated metal salts addition	High turbidity removal	[35] 2015
Proposing a central water treatment plant	stone cutting	wastewater collection pond, filtration, clean water collection basin	-Recycling easier -More economic	[15] 2002
Novel wastewater cleaning system	Stone cutting (Stone-crushing and sand-making process)	hydro-cyclone separation followed by screening, clarification and filtration	Recovering fine sand and clean wastewater for recycling	[36] 2012
Solid liquid separation process	Mining processing	microfiltration with ion exchange flocculation -Sedimentation tank with microfiltration followed by chlorination	-Removed suspended solid and dissolved impurities -Reuse water for gardening, agricultural and forestry application	[37] 1995

2.4.1 Characteristics of the Stone Cutting Wastewater

In general, wastewater from mining industry has high concentrations of total suspended solid (TSS), high hardness, high conductivity, high apparent color, but low BOD, and low COD. Also, it has a neutral pH value close to that of the tap water. The suspension characteristics of wastewater from stone cutting industry has been investigated by many researchers. In general, it contains high TS, TSS and TDS[6]. Table 2.2 summarizes the values of some characteristic parameters for mining wastewater [37].

Table 2.2: Mining and Stone cutting wastewater characteristics

Parameter	Mining Range	Stone Cutting Value	Unit
Total dissolved solids(TDS)	500 - 2000	7500	mg/L
Electrical conductivity(EC)	600 - 10,000	12500	µs /cm
pH	7 - 9.5	7.2	--
Turbidity		390	NTU
Temperature		20	°C
Suspended solids(SS)	10 – 100		mg/L
Hardness	500 - 2000		mg/L as $CaCO_3$
Biochemical Oxygen Demand (BOD)	5		mg/L
Chemical Oxygen Demand (COD)	10 – 100		mg/L

These suspended particles have a negative charge. Their surface charge results in distributing them in wastewater, causing high turbidity and electrical conductivity [14]. Figure 2.1 shows the zeta potential of natural stone powder wastewater. No zero zeta potential value is observed, indicating the isoelectric point occura at a different pH value other than those oin the figure [14].

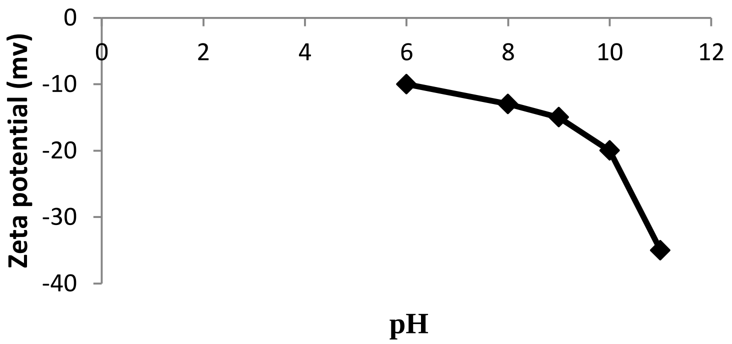


Figure 2.1: Zeta potential of natural stone cutting wastewater as a function of pH [14].

These characteristics have direct effects on treatment methods and efficiency. For examples, the surface charge that stabilizes the suspension (by obtaining a mono-dispersed suspension), and thus increasing the settling time (reducing separation efficiency). The particle size has a direct effect on the settling velocity. In laminar flow region, the settling velocity is proportional to the square of the particle size.

2.4.2 Types of Wastewater Treatments in Stone Cutting Industry

Table 2.1 summarizes the reviewed literature from the prospective of wastewater treatment approach. It includes studies on wastewater from stone cutting and marble industries. There are three main methods; filtration, flocculation-sedimentation and sedimentation basin. These processes are used for treating stone cutting wastewater, and other wastewater containing high concentration of suspended solid, such as those from tile and marble industries. The literature indicates that there are other potential treatment methods, such as microfiltration, ultrafiltration, hydro-cyclone and ion exchange.

The usage of these treatment varies in the concentration of suspended solids in wastewater, volume of wastewater and treatment cost. Sedimentation pools is the oldest method used in small plants. It is less expensive than flocculation sedimentation and filtration. Flocculation sedimentation appeared after sedimentation basin to achieve highest treatment efficiency.

Table 2.1 indicates that flocculation sedimentation is the most repeated process with the best treatment efficiency compared to other treatments. These research papers are published within the period of 1995 and 2015, indicating a rising interest in this process.

2.4.3 Types of Agents for Flocculation/Coagulation Process

The flocculation/coagulation process involves the use of various chemicals for destabilization the particles [3, 38], and thus enhancing the settling. Parameters affecting the process include pH, temperature and specific coagulant dosage to destabilize the particles. The coagulant is added in a specific dosage. Any excess dosage may result in a negative effect on treatment process such as 'sweep flocculation' where extensive and amorphous metal hydroxide precipitation occurs [39]. This is achieved though the rapid mixing between coagulant in short time, cussing collision to achieved the first step of treatment by provide the desired size of collide. Then long time period is needed to control collision and grow flocs [7]. With electrolyte materials, the negatively charged suspended particles are neutralized. The repulsion force between the particles is eliminated and the van der Waals force dominates [3, 19]. The following subsections summarize the reviewed types of coagulants.

2.4.3.1 Commercial Coagulants

Various coagulants are used in industrial wastewater treatment and in water purification. Table 2.3 summarize the various types of coagulants investigated in the reviewed literature for different types of wastewater (including wastewater from stone cutting industry). Most of these publications were published in recent years, indicting an increased research interest in this field. These include aluminium chloride and sulfate, poly aluminium chloride, alum, ferric chloride and lime. The synthetic polymeric coagulants included (1) polyanionic polymers resulting from anionic properties due to the presence of carboxyl groups, and (2) polycationic resulting from cationic properties (derivatives of polyacrylamide). Polycationic polymers has advantages of low cost, effectiveness in treatment, less sludge production and less dependence on temperature [40, 41]. The optimum operating conditions for synthetic coagulants were investigated in previous literature. Coagulant dosage is the main parameter.

Table 2.3 also summarizes testing approaches for investigating treatment efficiency. In these studies, the treatment efficiency was monitored and investigated based on various variables. These include:

- Turbidity.
- Total suspended solid (TSS), total solid (TS) and suspended solid(SS).
- Total phosphate (TP).
- Chemical oxygen demand (COD) and dissolved organic carbon (DOC).
- Electrical conductivity (EC).

The experimental tests included mainly sedimentation and jar test followed by turbidity measurement. The treatment efficiency was optimized by measuring the percentage particle removal and reduction in turbidity.
In most of the cases in stone cutting industry, the coagulant dosage was in the range of 100-300 ppm. The process efficiency was high (over 90%).

Table 2.3: Commercial coagulants utilized for treating wastewater

Coagulant	Chemical Formula	Wastewater	pH	Test	Dosage (PPM)	Removal factors	Optimum Result	Ref. /year
Aluminium chloride	$AlCl_3$	Natural stone (travertine) wastewaters	6	classical sedimentation test	300	Turbidity	21 NTU	[28] 2009
Lime	CaO	Stone cutting	7.2	Jar Test	25 100 100	Turbidity TSS TS	99.8% removal 79.3% removal 99.1% removal	[6] 2013
Aluminium Sulfate	$Al_2(SO_4)_3$	Surface water (river)	6	Jar Test	15 15	Turbidity DOC	94.5% removal 53.5% removal	[42] 2010
		Surface water (river)	7	Jar Test	2 2	Turbidity Organic Matter	80% removal 25% removal	[39] 2005
		Marble-cutting	10.2	Jar Test	200 200 200 200	Turbidity TS SS COD	99.3% removal 89.5 % removal 92.5 % removal 20% removal	[34] 2005
poly aluminium chloride (PAC)	PAC	Stone cutting	7.2	Jar Test	75 100 100	Turbidity TSS TS	99.2% removal 70.7% removal 94.1% removal	[6] 2013
		surface water (river)	6	Jar Test	15 15	Turbidity DOC	96.3% removal 32.7% removal	[42] 2010
		Tile making	7	Jar Test	250 250 250	Turbidity TSS COD	99.9% removal 99.9% removal 75% removal	[43] 2016
	PAC-18	Surface water (river)	7	Jar Test	2 2	Turbidity Organic Matter	86% removal 45% removal	[39] 2005
	PAC-14,	Surface (river) water	7	Jar Test	2 2	Turbidity Organic Matter	87% removal 45% removal	
	PAC-HB	Surface (river) water	7	Jar Test	2 2	Turbidity Organic Matter	86% removal 44% removal	
Alum	$KAl(SO_4)_2$	Stone cutting	7.2	Jar Test	200 100 100	Turbidity TSS TS	98.6% removal 82.5% removal 97.1% removal	[6] 2013
Ferric chloride	$FeCl_3$	Stone cutting	7.2	Jar Test	500	Turbidity TSS TS	99.4% removal 80% removal 94.3% removal	
		Beverage Industrial	9	Jar Test	300	COD TP TSS	73% removal 95% removal 97% removal	[44] 2007
		Marble-cutting	10.2	Jar Test	200	Turbidity TS SS COD	98.9% removal 89.9% removal 96.2% removal 10% removal	[34] 2005

2.4.3.2 Coagulants from Natural Sources

Natural coagulants and bio-flocculants emerged in recent research works as alternative materials to replace the conventional and commercial coagulants in wastewater treatment. Figure 2.2 shows the number of new published studies on natural coagulants in a function of time (years). Natural coagulants have lower cost and ability to achieve high treatment efficiency. Natural coagulants are safe, biodegradable and available from agricultural resources without pollution impacts.

Table 2.4 summarized the reviewed research work utilizing natural coagulants. These coagulants include ipomoea dasysperma seed gum, chitosan (liquid and solid), mallow and okra mucilage, moringaoleifera seed (MOC), gure gum, rice starch and starch. The functional mechanisms for coagulation include charge neutralisation or flocculation by bridging, with high molecular weight and its particular macromolecular structures (carboxyl and hydroxyl groups)[3].

These natural coagulants were not used so far in threatening wastewater from stone cutting industry. The investigated applications included decolorization of textile dye solutions and distillery spent wash, treatment of palm oil mill effluent, dairy wastewater and rubber washing tank.

Table 2.4 indicates that the testing approaches for investigating treatment efficiency was mainly based on jar test. It also included the use of response surface methodology (RSM). The investigated experimental parameters included settling time, dosage, pH, mixing speed. The treatment efficiency was optimized by measuring percentage (color) removal and reduction in turbidity.

2.4.3.3 Coagulants from Industrial Wastes

In the recent years the concept of "treating waste by waste" received a great research interest. Figure 3 shows that most of the obtained previous studies were published after 2008. It also compares that to the number of publications per year on coagulants from natural sources.

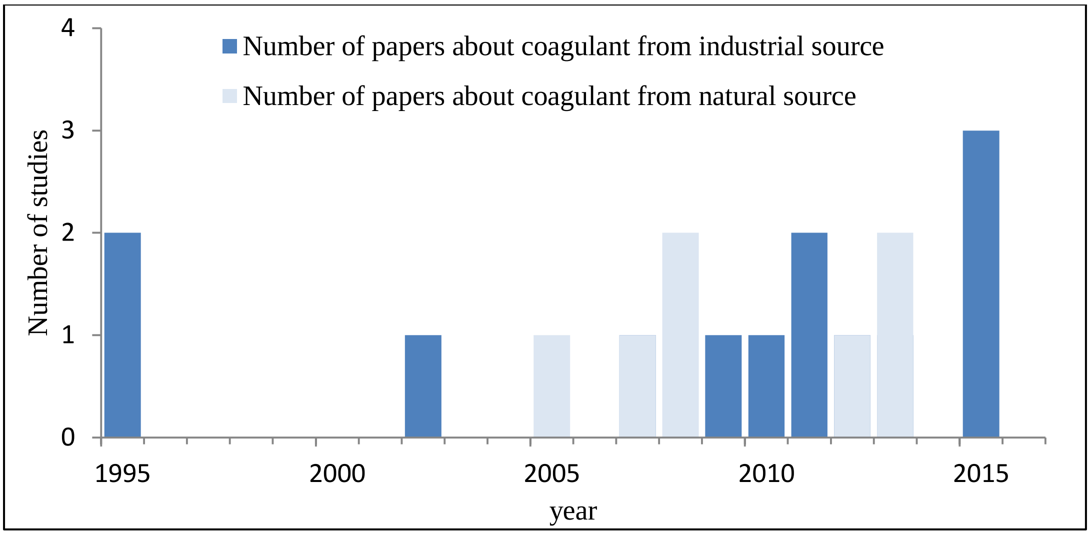


Figure 2.2: Chronological order of publication of the reviewed papers for potential coagulants from natural source and industrial waste.

Various components from industrial wastes were utilized as coagulants as listed in Table 2.5. Their industrial sources include metal industries including aluminium industries and galvanizing, purifying graphite, coal mine processing, palm Oil and pulp and paper mills. The used coagulants were either prepared from waste such as modified cellulose from pulp and paper industry and ployaluminum chloride (PAC) from aluminium industry, or were used directly like the etching wastewater from galvanization processing.

The treatment efficiency was optimized by measuring the residual turbidity, zeta-potential, removal of phosphates, COD, SS, Nitrogen (NH3–N), oil, color, and chromaticity. The experimental approach in these studies was mainly based on jar test. The investigated parameters included mainly the coagulant dosage and pH.

Table 2.4: Natural coagulants utilized for treating industrial wastewater

Natural Coagulant	Coagulant Characteristics	Treatment Application	Investigated Parameters for Treatment Efficiency	Tests	Optimum Result	Ref/ year
Ipomoea dasysperma seed gum	- Biodegradable -Non-toxic Soluble in water - High molecular weigh	Decolorization of textile dye solutions	- pH - Settling time - Dosage	Jar-Test	(96.3-97.4%)optimum turbidity removal at 12 mg/L dosage	[45] 2006
Chitosan liquid and solid	- Non toxic - Linear cationic polymer - High molecular weight - Soluble in acidic solution	Treatment of palm oil mill effluent	- Settling time - Dosage	Jar-Test	- 80% oil and 97% turbidity reduction for 6.0% liquid dosage -Chitosan liquid was more efficient than solid Chitosan	[10] 2008
Mallow and Okra mucilage	-Have five neutral sugars -Non toxic -Biodegradable	Treatment of synthetic wastewater	- Settling time - Dosage	Jar-Test	-mallow and okra mucilage had a significant flocculation properties -okra was as efficient as mallow in removing turbidity at lower doses	[46] 2009
Moringaoleifera seed (MOC).	-Biodegradable - Non-toxic	Color removal from the distillery spent wash.	- Storage duration - Temperature - pH - Dosage	Response Surface Methodology (RSM)	-The dosage: 60 ml at pH 8.5 color removal was 67% -The coagulation efficiency was at room temperature for 3 days	[47] 2009
Gure gum	-Biodegradable -Non-toxic-Long chain polymer	Treatment of rubber washing tank	- pH - Settling time - Mixing speed	Response Surface Methodology (RSM)	-Guar gum removed 88.1%turbidity -it has a flocculent structure pattern, produces porous and strong flocs	[48] 2013
Rice starch	-Biodegradable -Non-toxic	Palm oil mill treatment	-PH - Settling time - Stirring speed - Dosage	Jar-Test	88.4% TSS was removed at 0.55 g/L dosage with 0.2 g/L alum in short settling time	[11] 2014
Starch	-Non-toxic -Biodegradable -Composed of two homopolymers of D-glucose	Treatment of Dairy Waste Water	-Stirring speed - Settling time - Dosage	Jar-Test	- the optimum turbidity removal was at 40 mg/l dosage (Starch +alum) -TDS is reduced to 30.7% -TSS reduction is 30. 6% and 48.3% total nitrogen reduction	[9]/2014

Table 2.5: Coagulants from industrial wastes (IW) utilized for treating industrial wastewater

Coagulant industrial Source	Type of (IW) used as coagulant	Type of pollutant in waste source	coagulant	characterization methods	Treatment Application	Test	Factor	Results: Removal efficiency	Results: Optimum	Ref/ year
Aluminium processing Secondary Industries	Granular Aluminium Metal	Aluminium Suspended Solids	Ployaluminum chloride (PAC) [preparation]	-Al content - Basicity (%) - Density - Al distribution - Reactive Al species with time	Tap water Clarification	Jar Test	Dosage pH	Residual Turbidity	< 0.025 NTU	[29] 2010
								Zeta-potential	> -18(mV)	
								Phosphates concentration	under 1 mg/L at dosage 100	
								Residual aluminium Concentration	250 μg/L	
			Polyaluminum Chloride (PAC) [preparation]	- AL_2O_3 content - Basicity %	Water with FTU=30 Turbidity	Jar Test	Dosage	Residual Turbidity	16 FTU	[49] 2012
					water with FTU=150 Turbidity			Residual Turbidity	16 FTU	
					water with FTU=150 Turbidity			Residual Turbidity	16 FTU	
Aluminium industry	Red mud	- strongly alkaline - oxides of iron - aluminium, silicon &titanium	- Coagulant solution [preparation] - Solid Coagulant [preparation]	- The metals' and other cations' concentrations - Ferrous ($Fe^{2+)}$ and ferric (Fe^{3+}) iron contents - crystalline phases	synthetic effluents containing phosphorus concentrations ranging from 5 to 100 mg P/L.	Dephosphatat-ion Test	pH	Phosphate removal	98%	[8] 2008
					solution containing 5 mg P/L			Phosphate removal	70%	

Aluminium Industry	Red mud	-strongly alkaline oxides of iron, aluminum, silicon &titanium	composite coagulant with red mud and bauxite [preparation]	-pH effect - ionic strength - water temperature	municipal sewage and eutrophic water treatment	Jar Test	pH	Phosphate Residual phosphate removal	0.02 mg/L 4.9% - 10.4%	[50] 2011
Aluminium Coating	Etching and rinsing alkaline wastewater	- Chemical element (AL,Na,$NaAlO_2$,$AlSO_4$,Cr) -Suspended solids	Use of Etching water [Direct]	- Iron and Mg contents - Calcium content - pH	Treatment of final tannery wastewater	-Jar Test -Bench Scale Test	Dosage	COD removal SS removal	95% 95%	[20] 2016
Galvanizion industry	aluminium slag	Metallic zinc, aluminium and alloy.	poly-Al–Zn–Fe coagulant (PAZF) [preparation]	The PAZF structure	Fountain water	Jar Test	Dosage pH	COD removal Nitrogen (NH_3–N) removal	82% 89%	[27, 51, 52] 2016 2014 2012
					Pharmaceutical wastewater			Turbidity removal COD removal	79.5% 16%	
					dyeing wastewater			Turbidity removal COD removal	26.5% 8.1%	
					pesticide wastewater			Turbidity removal COD removal	40% 13.4%	
					Deep blue acidic waste			Chromaticity removal Turbidity removal COD removal	93.8% 83.32% 62.19%	
					Palm scattered processing wastewater			Chromaticity removal Turbidity removal COD removal	97.84% 84.44% 66.01%	
					Landscape wastewater			Chromaticity removal Turbidity removal COD removal	86.98% 82.39% 86.82%	

purifying graphite	acidic and alkaline wastewater	silicon, iron, aluminium, sodium carbonate hydraulic acid and sodium hydroxide	Polyaluminum ferric silicate chloride (PAFSC) [preparation]	- Metal analyses - silicon dioxide Content -Determination of TP - Sodium hydroxide and sodium carbonate contents	Yellow River	Jar Test	PH Dosage	Residual turbidity	2 mg/L	[22] 2011
					Municipal wastewater		Dosage	Total phosphate removal	95%	
								COD removal	> 95%	
Coal mine processing	Gangue	Aluminium oxide ferric oxide.	Polysilicatealuminium (PSA) [preparation]	- The structure of PAS	-Dyeing - Steelworks wastewater	-	Dosage	Turbidity removal color removal suspended substance (SS) removal	Removal rates of color and SS increase by 20%-40% compared with traditional coagulant	[53] 1996
			Polyaluminum ferric chloride (PAFC) [preparation]	The structure of PAFC	-coal-mine ww - oilfield ww	Jar Test	Dosage	COD Removal SS Removal Oil Removal	80% 90% 90%.	[54] 1996
				$-Fe_2O_3$ content $- Al_2O_3$ content - Density - Color	general characterization wastewater	Jar Test	pH dosage	Red waste removal	98%	[55] 2003
								light yellow waste removal	96%	
								bright red waste removal	38%	
					Petrochemical plant WW			COD removal Oil removal	> 80% > 90%	
					Coal mining processing WW			COD removal SS removal	80% 90%	
					Iron and steel plant WW			SS removal	> 90%	

Palm Oil	-Solid bleaching waste - oily wastewater	Flammable waste bleaching earth	acid based coagulant agent from WABE [preparation]	- specific analysis of metals and non-metals	Soaking paper mill	-	Dosage	Turbidity removal COD removal TSS removal	99.90% 50% 50%	[26] 2013
					Palm oil mill effluent treatment			Turbidity removal COD removal TSS removal	91.67% 95.77% 52%	
Paper and pulp mills	Solid waste	-sand, wood residues -sludge -chemical and metals	modified cellulose [preparation]	-elemental analysis (EA) - static light scattering (SLS) for molecular weight evaluation	waste water that contained 5mg/L of dye	-	Dosage	Color removal	cationic cellulose 98%	[56] 2016

2.4.4 Research Trends and Applications

This review indicates that flocculation sedimentation process was widely used in recent years. Mostly, it was used to treat stone cutting wastewater. The experimental results indicated a high treatment efficiency was obtained, with low cost compared to other treatment methods.

Previous studies focussed on utilizing various inorganic and coagulants (e.g. $AlCl_3$, CaO, $AL_2(SO_4)_3$, PAC and $FeCl_3$) for treating various types of wastewater [6, 21, 39, 45, 51, 52]. Lime and alum were used for treating stone cutting wastewater [6]. Iron-based coagulants were found to be effective in treating wastewater with organic substance and colloidal particles [7]. Alum ($AL_2(SO4)_3$) was used for treating pulp and paper wastewater [6, 7]. Aluminium sulphate coagulant $AL_2(SO_4)_3$ was used to remove particles and organic matter from water river [42]. Research efforts focused on investigating the optimum conditions for treatment, mainly dosage and pH [7]. The treatment efficiency (turbidity removal) at different dosages, obtained from these previous publications, is compared in Figure 2.3.

Obviously, high treatment efficiency was obtained with these coagulants. In general, increasing the dosage increased the treatment efficiency, due to faster coagulation and larger particle aggregates. In these cases, the coagulation mechanism is based on coating the particles with a chemical layer to enhance aggregation and then enhancing settling within a short time period [57]. Lime seemed to be the most efficient coagulant.

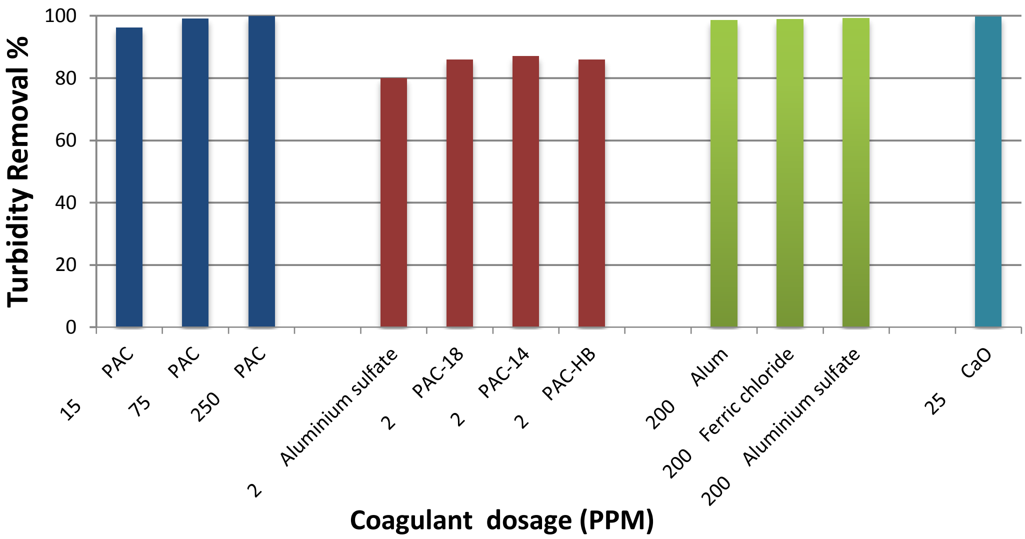


Figure 2.3: Treatment efficiency (turbidity removal) using various commercial coagulants indicated in the figure for treating various types of wastewater [6, 34, 39, 42-44].

Coagulants used for treating wastewater from marble and stone cutting industry and from tile industry included $Al_2(SO_4)_3$, $KAl(SO_4)$, $FeCl_3$, CaO and PAC. The effects of different dosages of alum, polymer and ferric chloride coagulants were investigated using jar test technique [6]. A high efficiency of TSS and turbidity removal using ferric chloride coagulant for stonecutting wastewater treatment was obtained [58]. Wastewater from marble industry was treated using commercial flocculation reagent [59]. In addition, the technical feasibility of using the commercial polymer flocculating agent (used in stone cutting) for treating wastewater from tile industry (in a similar flocculation-sedimentation process) was confirmed recently [4]. The obtained treatment efficiency (turbidity removal and reduction in TSS), from these publications, are compared in Figure 2.4. For the treatment of wastewater from stone cutting and marble industry, $Al_2(SO_4)_3$ was more efficient than $KAl(SO_4)$ and $FeCl_3$ (for the same dosage of 200 ppm). It resulted in a turbidity removal of 99.3% [6, 39, 51].

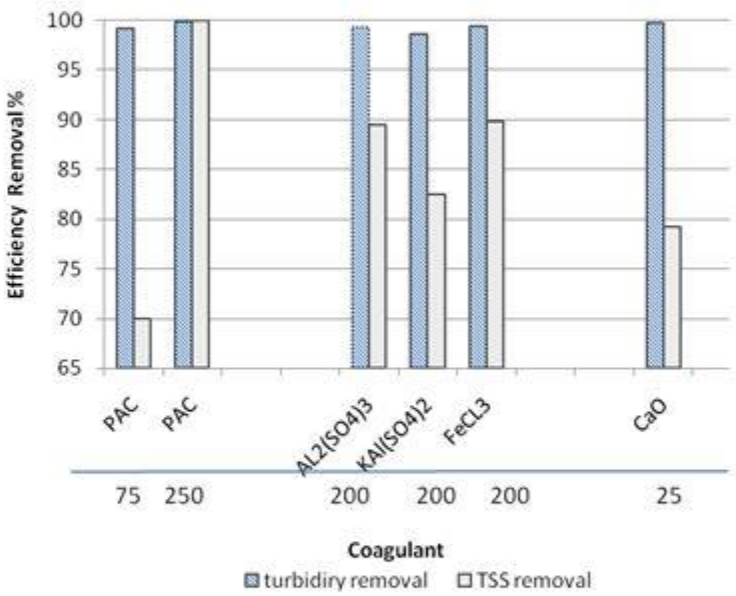


Figure 2. 4: Treatment efficiency (turbidity removal and reduction in TSS) for wastewater from marble and stone cutting industry and from tile industry using commercial coagulants[6, 34, 43].

Previous studies also confirmed that replacement of the commercial coagulant with natural coagulants was efficient in treating industrial wastewater. The investigated natural coagulants included starch, cellulose, guar gum, palm oil and chitosan. Chitosan and rice starch were used to treat palm oil mill effluent [9-11], gums and mucilage which were used to treat tannery and sewage effluent [3]. No application was found for using these natural coagulants for treating wastewater from stone cutting industry. This trend can be investigated in future research work. The obtained results indicated a high wastewater treatment efficiency (turbidity removal) at different dosage, time and pH. Their performance was nearly efficient as that of the commercial polymers and inorganic coagulants.

Coagulants obtained from various industrial wastes and wastewater were also efficient in wastewater treatment. Metal coagulants were generated from metal industrial wastewater streams. Few recent studies investigated the technical feasibility of utilizing coagulants from waste to treat different types of wastewater [27, 49, 51-53, 55, 56]. For example poly-Al-Zn-Fe coagulants were prepared from galvanized aluminum slag. This was shown to have large ability for reducing the turbidity and the organic matter [4]. Other coagulants prepared from aluminum industry waste was found to have a similar removal capacity as the commercial coagulants (i.e. alum, ferric sulfate, ferric chloride) [8]. Poly aluminium chloride (PAC) coagulant was prepared from aluminium industrial waste to clarify tap water [29]. Also, poly-Al–Zn–Fe(PAZF) coagulant was prepared from galvanization industrial waste for pharmaceutical and dyeing wastewater treatment [51]. Wastewater from etching process in aluminium industry was utilized directly to treat tannery wastewater [20]. Red mud waste from primary aluminium industry was prepared and converted to solid /liquid coagulants for phosphorus removal. It had similar characteristics as that of the commercial coagulant. Treatment efficiency reached 98% for phosphorus removal [5]. Aluminium suspended solids from secondary aluminium industry were converted to Poly aluminium chloride (PAC) coagulant for water clarification. The obtained residual turbidity was less than 0.025 nm [45].

In aluminium coating industry, sulfuric acid (H_2SO_4) or hydrochloric acid(HCL) are used in anodizing tank. These result in forming $AL_2(SO_4)_3$ and$AlCl_3$ compounds in the resulting wastewater. These compounds are similar to the commercial coagulant compounds. No studies were found on utilizing these industrial wastewaters from coagulation. Their use can be investigated in future research work.

2.4.5 Potential New Application

This study identified various new research problems in the two directions of (1) utilizing industrial wastewater and (2) utilizing natural coagulants, for treating wastewater from stone cutting and Tile industries. Identifying new industrial waste as a coagulant must be based on analysing the production process, raw materials and the waste from various industries.

Samples of the identified new research problems which are committed for further research work include:

Problem 1: Investigating the technical feasibility of utilizing wastewater from the liming step in leather industry for treating stone cutting wastewater. The excess lime (released in the wastewater) will coagulate particles and enhance settling.

Problem 2: Generalizing problem 1 for treating wastewater contaminated with mineral particles from other industries such as tile industry and marble industry.

Problem 3: Investigating the technical feasibility of utilizing $AL_2(SO_4)_3$ and $AlCl_3$ from anodizing wastewater from the aluminum industry for treating stone cutting wastewater.

Problem 4: Generalizing problem 1 for treating wastewater contaminated with mineral particles from other industries such as tile industry and marble industry.

Problem 5: Investigating the technical feasibility of utilizing a selected natural coagulant (Table 3) (e.g. rice starch from rice washing) for treating wastewater stone cutting, tile industry and marble industries.

Other new research problems can be identified from careful reading of Table 4, i.e. granular aluminum waste from aluminum workshop.

In these proposed research problems, the experimental procedure is well defined as established in these previous publications (e.g. mixing and then observing sedimentation performance in jar test). The technical feasibility of these applications can be investigated by determining the removal efficiency (based mainly on turbidity removal). The experimental parameter may include dosage (or mixing ratio between the two types of wastewater) and pH.

2.4.6 Concluding Remarks and Recommendation for Future Research Work

There is an increasing research interest in the flocculation-sedimentation process for treating wastewater contaminated with mineral particles such as that from stone cutting industry. Treating waste by waste can be utilized to source new potential coagulants and flocculants from industrial wastes.

In previous studies. Flocculation-sedimentation , the types of investigated coagulating agents included commercially available coagulants such as aluminum sulfate, poly aluminum chloride, alum, ferric chloride, lime and synthetic polymeric coagulants (poly-cationic and poly-anionic). It also included coagulants from natural sources such as ipomoea dasysperma seed gum, chitosan (liquid and solid), mallow and okra mucilage, moringaoleifera seed (MOC), gure gum, rice starch and starch. Coagulants from the industrial wastes were either prepared from wastes (such as modified cellulose from pulp and paper industry and ployaluminum chloride (PAC) from aluminum industry), or were used directly like etching water from galvanization processing.

Based on this review, sample new research problems are recommended. These include experimental work for investigating the potential use of new coagulating agents sourced from industrial wastes and natural sources. The following industrial waste are proposed as new possible sources for coagulants:

- Wastewater containing lime(CaO) from liming step in leather industry
- Wastewater containing aluminum sulfate $AL_2(SO4)_3$ or aluminum chloride ($ALCL_3$) from anodizing tank in aluminum finishing industry.
- Coagulants from natural sources for stone cutting wastewater.
- Granular aluminum waste from aluminum workshop.

There is also a research need for developing mathematical models for flocculation sedimentation processes based on coagulation kinetics. Such models can assist in characterizing the coagulants, and in process control and operation. The proposed models may also assist in interpreting the effects of various parameters on separation efficiency.

Chapter Three

Experimental Analysis

3.1 Introduction

Stone cutting and tile wastewater contain a small suspended particles, which cannot be settled or removed naturally due to their light weight and stability. These particles cause stability and turbidity of water. The discharge of untreated wastewater affect human, soil quality, agriculture, surface and groundwater.

Leather industry producing large volume of wastewater from liming step containing lime and other chemical compounds. The discharge of untreated liming wastewater causes reduction in soil quality and change the characteristics of surface and groundwater [60], also aluminum coating industry producing an acidic wastewater contains aluminum compounds. To exploited these wastewater, aluminum and liming wastewater can be reused in order to utilize the concept of treating waste by waste to replace the commercial coagulant for treating stone cutting and tail wastewater in coagulation sedimentation treatment process. Coagulation process is used to destabilize suspended particles by the addition of these wastewater. Different characteristics such as pH, temperature (T), total dissolve solid (TDS), lime content and electrical conductivity (EC) are usually measured for analysis the wastewater.

Testing performance of coagulation sedimentation process in stone cutting and tile wastewater treatment was determined using jar test and classical sedimentation test as many studies indicated [2-5]. Also the influences of pH and coagulant mixing ratio on the effectiveness of removal efficiency was studied

This chapter summarizes the methods and procedures used in the experiments including the characteristics of wastewater used and estimate the optimum mixing ratio and pH of leather liming and aluminium etching wastewater.

3.2 Experimental work

This work is based on experimental work. it started from analysis of the characteristics of stone cutting, tile, leather liming and aluminum etching wastewater samples. These include measuring pH, electrical conductivity (EC), and total dissolved solid (TDS), turbidity, UV absorbance and mass fraction of wastewater sample. The lime content of leather liming wastewater was determined. Spectrophotometric calibration curve for leather liming wastewater and prepared lime coagulant solution were prepared at 291 nm and 285 nm wavelengths respectively. The applicability of classical sedimentation test and jar test were confirmed. The effects of pH and wastewater mixing ratio were also investigated. The turbidity and UV absorbance for the supernatant of stone cutting and tail wastewaters were analyzed by turbidity meter and UV-Visible Spectrophotometer at 425 nm wavelengths.

3.3Materials and Equipment

3.3.1Materials

Real samples of stone cutting wastewater were collected from local factory (Al-Sharabaty company, Al Fahs, Hebron, Palestine), tile wastewater samples were collected from (Sunokrot Company, Al Fahs, Hebron, Palestine). For wastewater used as coagulants two types were used, which is leather liming and aluminium etching wastewater. Leather liming wastewater and commercial lime were obtained weekly from a local tanning leather factory (Al Zatari Company, Al Fahs, Hebron, Palestine). Aluminium etching wastewater sample was collected from (Nabco factory, Nablus, Palestine), also aluminium granular solid waste was collected from workshop (Hebron, Palestine).

Hydrochloric acid (HCl) 97%, sucrose, phenolphthalein indicator, anhydrous sodium carbonate and methylorange indicator were used for lime content analysis experiment. Commercial coagulants (lime, $Al_2(SO_4)_3$, $AlCl_3$) were used in classical sedimentation test. One molar (sulphuric acid H_2SO_4 and NaOH) were used for pH adjustment.

3.3.2 Equipment

The used analytical apparatus included: turbidity meter (Waterproof Portable TN100 meter), UV-Visible spectrophotometer (BOECO, Hamburg, Germany), Hotplate magnetic stirrer (300 degC-HS4), pH meter (PCE-228 pH-meter), electric conductivity meter (EE002) and laboratory equipment (mechanical shaker, analytical balance, graduated cylinder, beakers, dropper …etc.).

3.4 Methods

3.4.1Characterization of Wastewater

The characteristics of stone cutting, tile making, leather liming and aluminium etching wastewater samples were analysed by measuring total dissolved solid (TDS), temperature (T), electrical conductivity (EC), pH, turbidity and mass fraction of solid content. Mass fraction of stone cutting and leather liming wastewater were determined by taking 100 ml of real samples, then drying in an oven at 100°C. The obtained characteristics of wastewater from leather liming, aluminium etching, stone cutting and tiles industries are shown in table 3.1.

Table 3.1:characteristics of wastewaters

Wastewater Source	Parameters				
	Turbidity (NTU)	pH	Electrical conductivity (ms/cm)	Total dissolved solid (mg/L)	Mass fraction %
Stonecutting	730	8.35	411	246	2.6
Tile making	900	12.83	13.29	7.98	2.47
Leather liming	855	12.53	6.44	3.95	0. 19
Aluminium etching	400	6.5	482	290	0

3.4.2 Stability of Lime Wastewater

The stability of leather liming wastewater with time was determined by measuring turbidity, acidity (pH), temperature, electrical conductivity (EC) and total dissolved solids (TDS) for two months. The samples were stored at room temperature.

3.4.3 Lime Content of Leather Liming Wastewater

Sucrose (10 g) weight was mixed with 50 ml leather liming wastewater on a shaker for 15 minutes, then it was filtered by buchner filter using a vacuum pump. The sample was titrated with HCl (0.1 N) using phenolphthalein indicator. For HCl standardization, 0.15 g of anhydrous sodium carbonate was dissolved in 25 ml distilled water, then it was titrated with 0.1 N HCl using methylorange indicator [61]. Calcium oxide percent in wastewater was calculated according to equation 3.1 and 3.2.

$$N\ HCl = \frac{1000 \times mass\ Na2\ CO3\ (g)}{53\ \times Av.titre\ ml} \quad (3.1)$$

$$lime\% = \frac{0.5 \times A\ \times N \times 56.08}{B} \quad (3.2)$$

Where, A is a volume of standard HCl used in titration in liter, N normality of HCl mol/L while B is the weight of sample in g.

3.4.4 Preparation of Calibration Curve for Leather Liming Wastewater

3.4.4.1 Leather Liming Wastewater Spectra

Wavelength scanning was made for leather liming wastewater sample using UV-visible spectrophotometer for determining the suitable wavelength in order to measure the absorbance. The obtained UV spectra for leather liming wastewater is shown in figure 3.1.

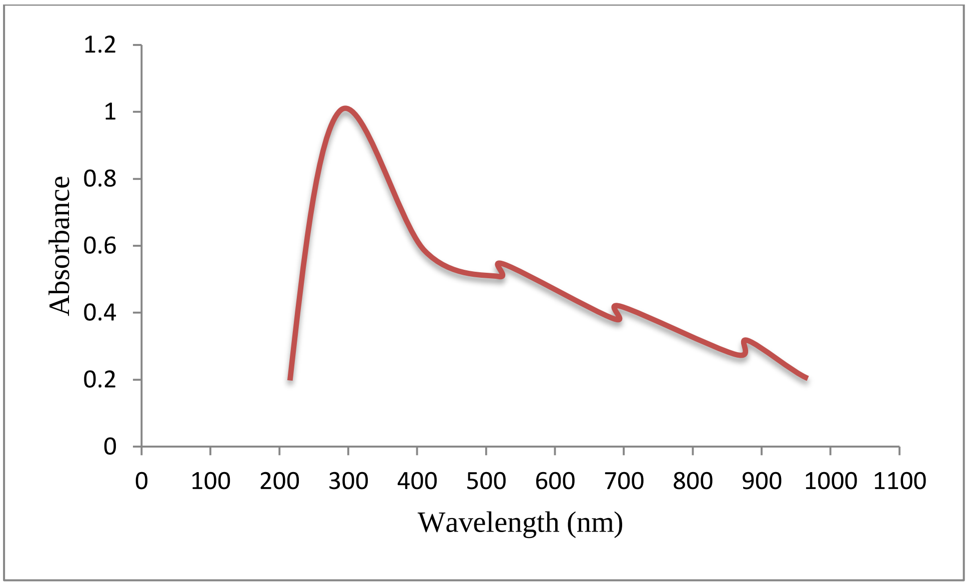


Figure 3.1 Measured spectra for wastewater.

Clearly the maximum wavelength is 291 nm. The reported maximum wavelength for lime solution is 285 nm

3.4.4.2 Calibration Curve for Real Wastewater Sample

A sample of 50 ml leather liming wastewater was diluted to different concentrations (2.1–1.6×10^{-2}) g/l in order to determine the UV absorbance at wavelength 291 nm. Figure 3.2 shows the relationship between concentration and UV absorbance.

3.4.4.3 Calibration Curve for Lime Solution Sample

Lime coagulant solution was prepared by dissolving 0.1 g commercial lime in 50 ml distilled water according to lime content experiment. The solution then diluted to obtain a concentrations ($2.1 - 1.6\times10^{-2}$) g/l in order to determine the absorbance at wavelength 285 nm. Figure 3.2 shows the relationship between concentration and absorbance for lime coagulant solution. Obviously, a linear relationship is obtained.

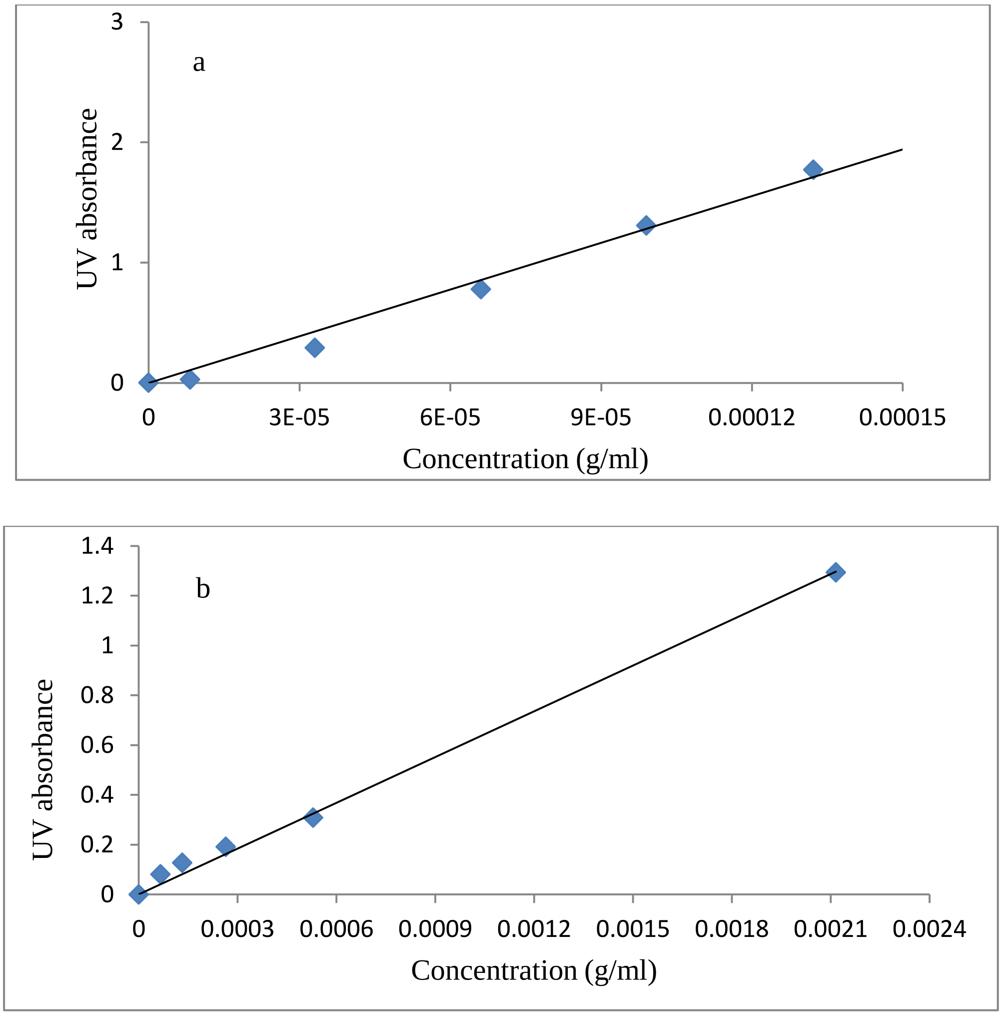


Figure 3.2: UV spectrophotometric calibration curve for (a) leather liming wastewater at a maximum wavelength 291 nm and (b) prepared lime coagulant solution at a maximum wavelength 285 nm.

3.4.5 Plain Sedimentation Test of Stone Cutting Wastewater

One liter of stone cutting wastewater was placed in 1000 ml graduated cylinder 30 cm in height. The cylinder was then sealed and inverted twice to obtain good mixing and left 90 minutes for settle, for plain sedimentation test using coagulants, the selected commercial coagulants (lime, $Al_2(SO4)_3$ and $AlCl_3$) was added to the cylinder (at 300 mg/L dosage), which was again sealed and inverted four times for 15 minutes to settle the aggregated particles. An aliquot from the supernatant water was obtained at a depth of 10 cm, and its residual turbidity was measured using UV-Visible spectrophotometer according to several scientific paper [6, 27].

3.4.6 Jar Test

A jar test experimental procedure was used to evaluate the coagulation performance of aluminium wastewater and lime wastewater (as a sources of coagulants) in comparison with lime standard solution for treating 100 ml stone cutting and tile wastewater. The mixing ratios of aluminium wastewater were (4, 8, 9, 10, 10.5, 11, 12 and 20%) and for leather liming wastewater and lime standard solution were (4, 8, 10, 12, 15, 20, 25 and 30 %). The wastewater containing coagulants was mixed with stone cutting wastewater (70 rpm) for 1 minute and at 10 rpm for 6 minutes. The settling time was 10 minutes and the supernatants then analysed by measured the turbidity, UV absorbance and pH [37]. Also a control sample (without a coagulant) was subordinated to the test. Jar test with 10% mixing ration was carried out at different pH values. In all tests the coagulation was examined at the following pH values: 7, 7.5, 8, 8.5, 9.0, 9.5, 10.0, 10.5,11, 11.5, and 12.5. Adjustment of pH of the samples was performed by adding 1M of H_2SO_4 or NaOH to the system. The supernatant was withdrawn to measure turbidity and absorbance using turbidity meter and UV spectrophotometer. Then, the removal efficiency for the samples was measured by equation 3.3.

$$Removal\ Effecincy\ = 100\% \times (1 - \frac{c_f}{c_i}) \qquad (3.3)$$

Where c_f is the final value of absorbance or turbidity, and c_i is the initial value.

3.4.7 Preparation of Poly-aluminium Chloride (PAC)

Poly-aluminium chloride (PAC) coagulant was prepared by dissolving 9.5 g granular aluminium waste in 33 ml pure Hydrochloric acid (HCl 37%). The solution was heated to 70 °C then filtered and dried. Than 3.3 g of the obtained aluminium chloride particles was dissolved in 100 ml distilled water and heated at 80°C for 20 minutes. Then 0.25 M sodium hydroxide solution was added slowly under continues stirring.

For evaluation of PAC coagulant performance, 1ml PAC coagulant was added to 7g/100 ml stone cutting wastewater. Then, the system was stirred by rapid mixing at 70 rpm for 1 minutes and slow mixing at 10 rpm for 6 minutes. The system is left to settle by gravity for 10 minutes. good turbidity removal efficiency was investigated.

Chapter Four

Treatment Performance of Stone Cutting and Tile Wastewater Utilizing Industrial Wastewater from Leather Liming and Aluminium Etching

4.1 Plain Sedimentation

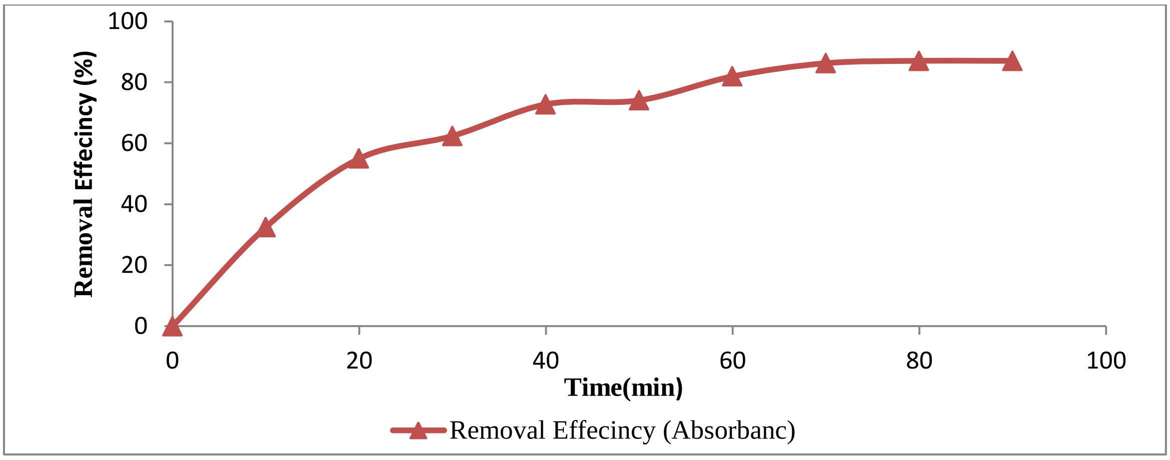


Figure 4.1: Effect of settling on stone cutting wastewater without coagulants on removal efficiency.

Figure 4.1 shows the obtained results from jar test for the case of plain sedimentation (without coagulant). The removal efficiency increase with increase time, however long time period (e.g. 70 minute) is required to obtain 86% removal efficiency. This is in agreement with previous results obtained by Mohammad et al [6]. They indicated that 2 hours were needed to obtain 95% removal efficiency when no coagulant used. Stone cutting effluent contains significant concentrations of very fine suspended particles have a negative charge. Their surface charge results in distributing them in wastewater, causing high turbidity, electrical conductivity and longing time for settling [14].

4.2 Performance Evaluation of Stone Cutting Wastewater Treatment with Commercial Coagulants.

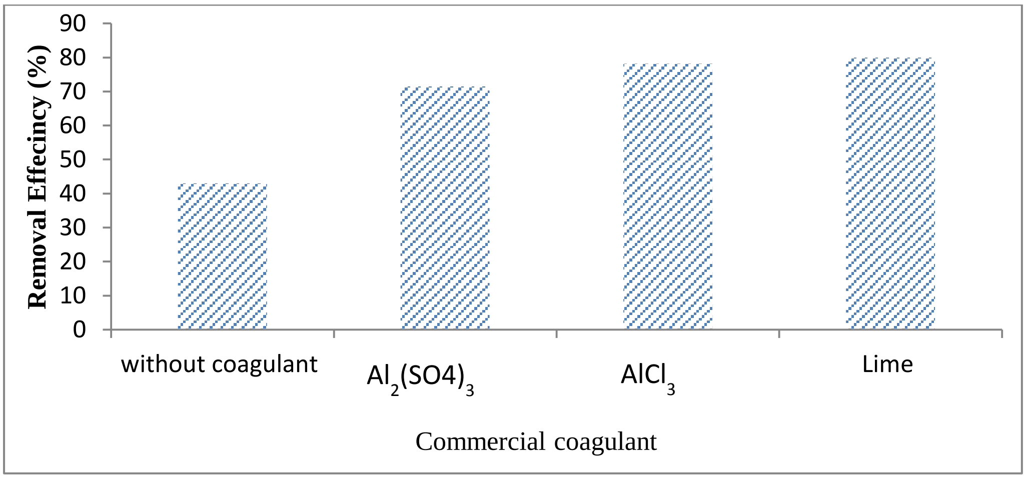


Figure 4.2: The removal efficiency of stonecutting wastewater using different commercial coagulants at dosage 300mg/L after sedimentation test after 15 min.

Figure 4.2 shows the obtained removal efficiency of various coagulants (from commercial sources) after sedimentation test for 15 min. High removal efficiencies were obtained (71%, 78% and 80%) for $Al_2(SO4)_3$, $AlCl_3$ and lime respectively. This indicates a higher settling velocity than settling without coagulant and lime performance was the best coagulant for treating stone cutting wastewater.

4.3 Performance Evaluation of Stone Cutting Wastewater Treatment with Aluminium Etching Wastewater

4.3.1 Effect of Mixing Ratio on Turbidity and Absorbance.

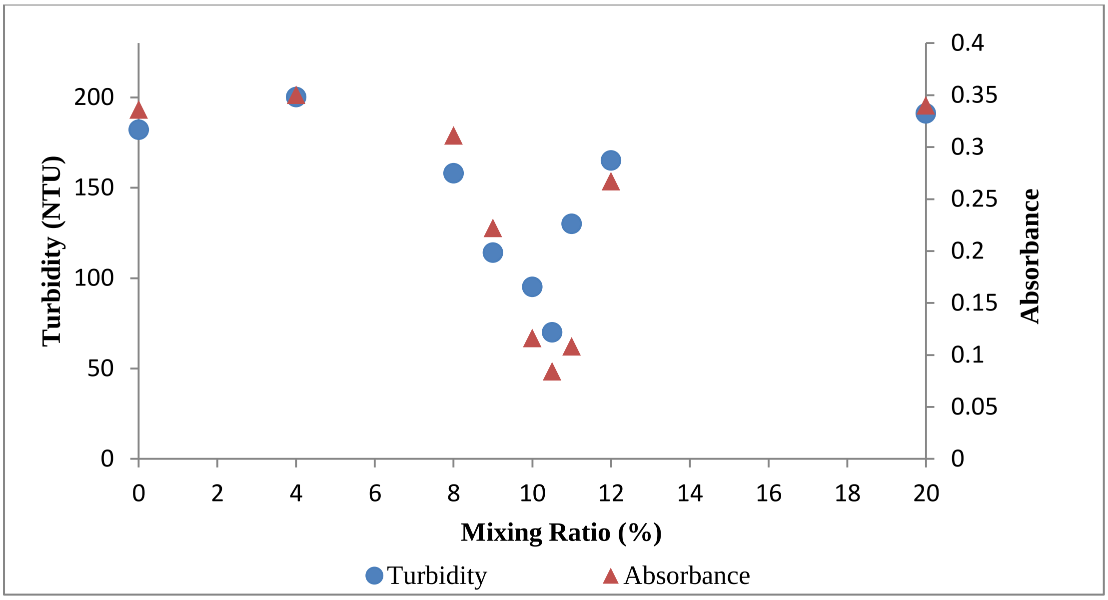


Figure 4.3 Variation of turbidity and absorbance for stonecutting wastewater with different Aluminium etching wastewater mixing ratio (%).

Figure 4.3 shows the turbidity and absorbance values of the supernatant liquid as a function of wastewater coagulant mixing ratio, it obtained by UV/V spectrophotometeric technique and turbidity meter to evaluate the removal efficiency of stone cutting wastewater according to equation 3.3. Which many studies confirmed the validity of using UV/V spectrophotometeric technique and turbidity meter for monitoring variations in removal suspend solid [18, 33, 62, 63]. The turbidity and absorbance decreases with increasly wastewater mixing ratio, further increase leads to an increase turbidity and absorbance again owing to the redispersion of colloidal particles, it results from the insufficient free suspended particles surface for coating contacts, which cause steric repulsion force [33].

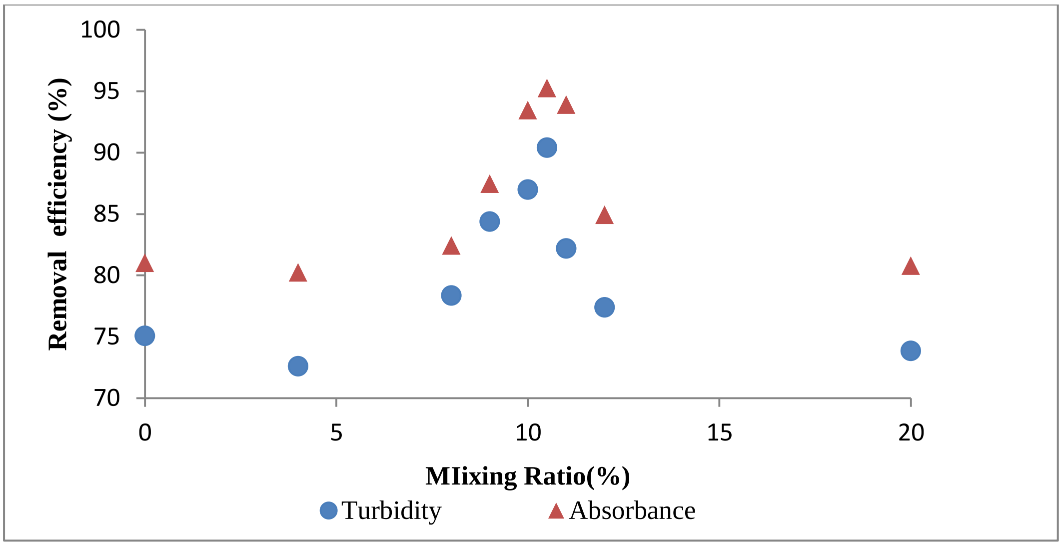


Figure 4.4 Variation of turbidity and absorbance removal efficiency for stonecutting wastewater with different aluminium etching wastewater mixing ratio(%).

Figure 4.4 shows the turbidity and absorbance removal efficiency of the supernatant liquid as a function of wastewater coagulant mixing ratio for stone cutting wastewater. The removal efficiency increase with an increase of wastewater to a certain mixing ratio (4.0 - 10.5), further increase leads to decrease removal efficiency again. Maximum removal efficiency reach to 95% and 90% for absorbance and turbidity respectively.

4.3.2 Effect of pH on Turbidity and Absorbance.

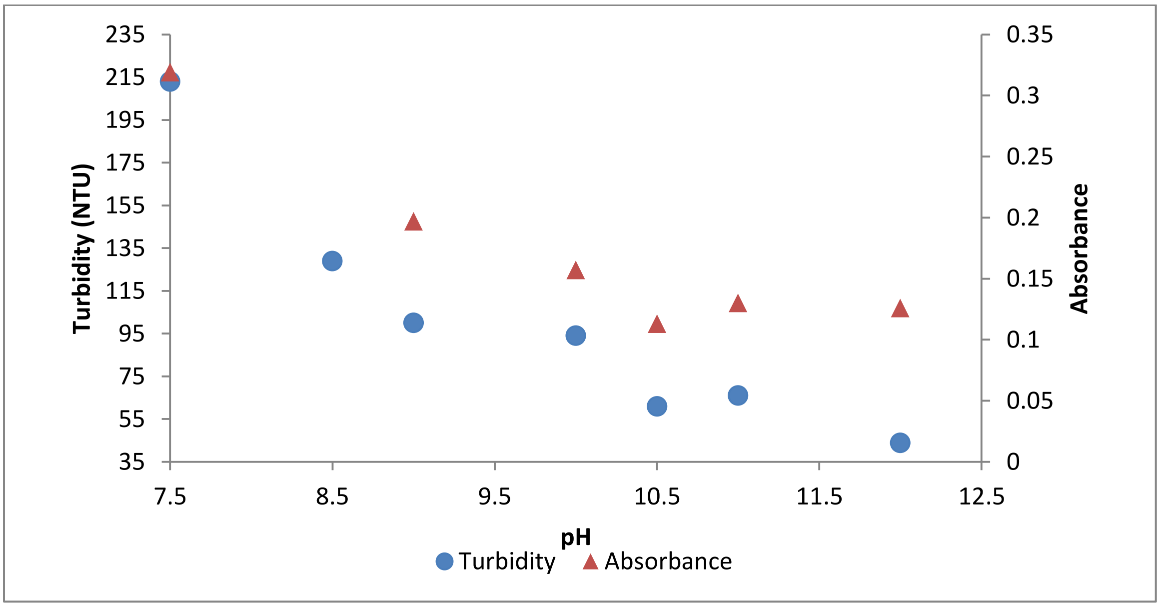


Figure 4.5: Variation of turbidity and absorbance for stone cutting wastewater with different aluminium etching wastewater pH at mixing ratio (10 %).

Figure 4.5 shows the effect of stone cutting wastewater pH on the turbidity and absorbance of the supernatant liquid, after jar test by 10% mixing ratio. It is clearly seen that pH 10.5 have good performance for turbidity and absorbance, which only 61 NTU and 0.113 respectively. While pH 7.5 gave the maximum turbidity for wastewater reach (220 NTU). This may be attributed to zeta potential of colloidal stone cutting particles [33].

At (6-10) pH the zeta potential of stone cutting particles are in the aggregation(or coagulation) limits (-15 to +15 mV) [33], while at pH above 11 their zeta potentials are in the dispersion limits (<15 mV) Therefore, at pH range (7.5-10) the turbidity and absorbance in the supernatant liquid decreases [33].

4.4 Performance Evaluation of Stone Cutting Wastewater Treatment with leather Liming Wastewater and Lime Solution

4.4.1 Effect of Mixing Ratio on Turbidity and Absorbance

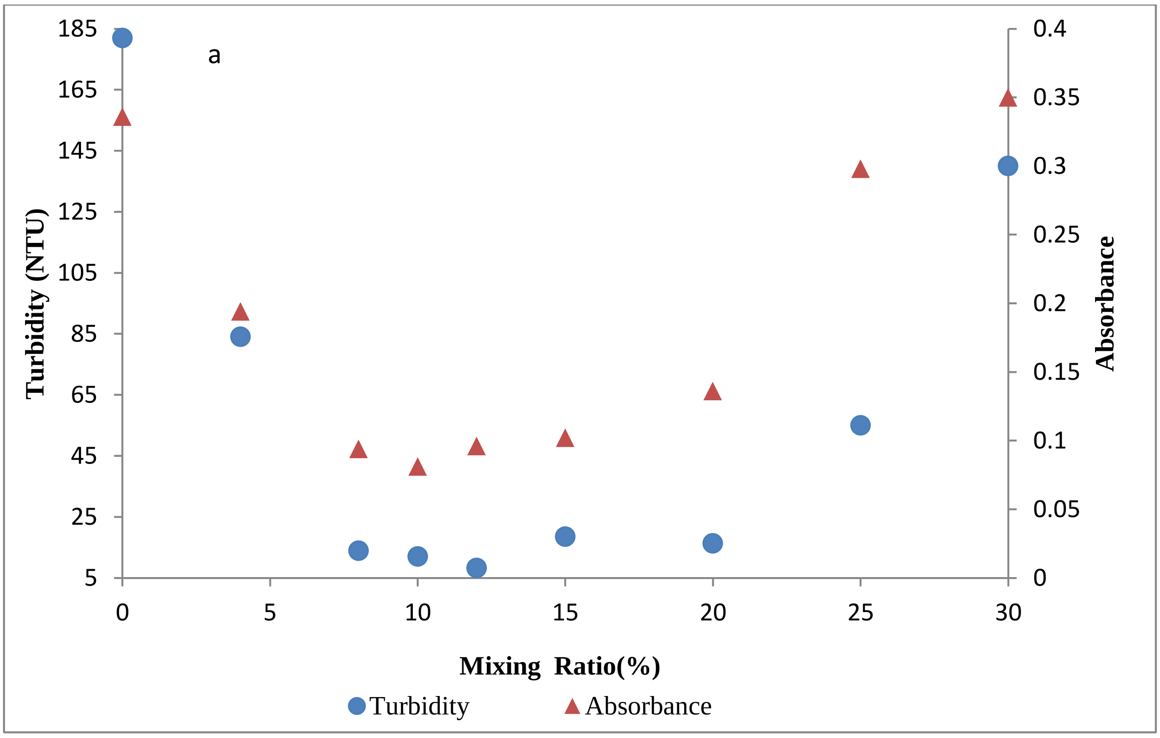


Figure 4.6 Variation of turbidity and absorbance for stonecutting wastewater with different liming wastewater mixing ratio (%)

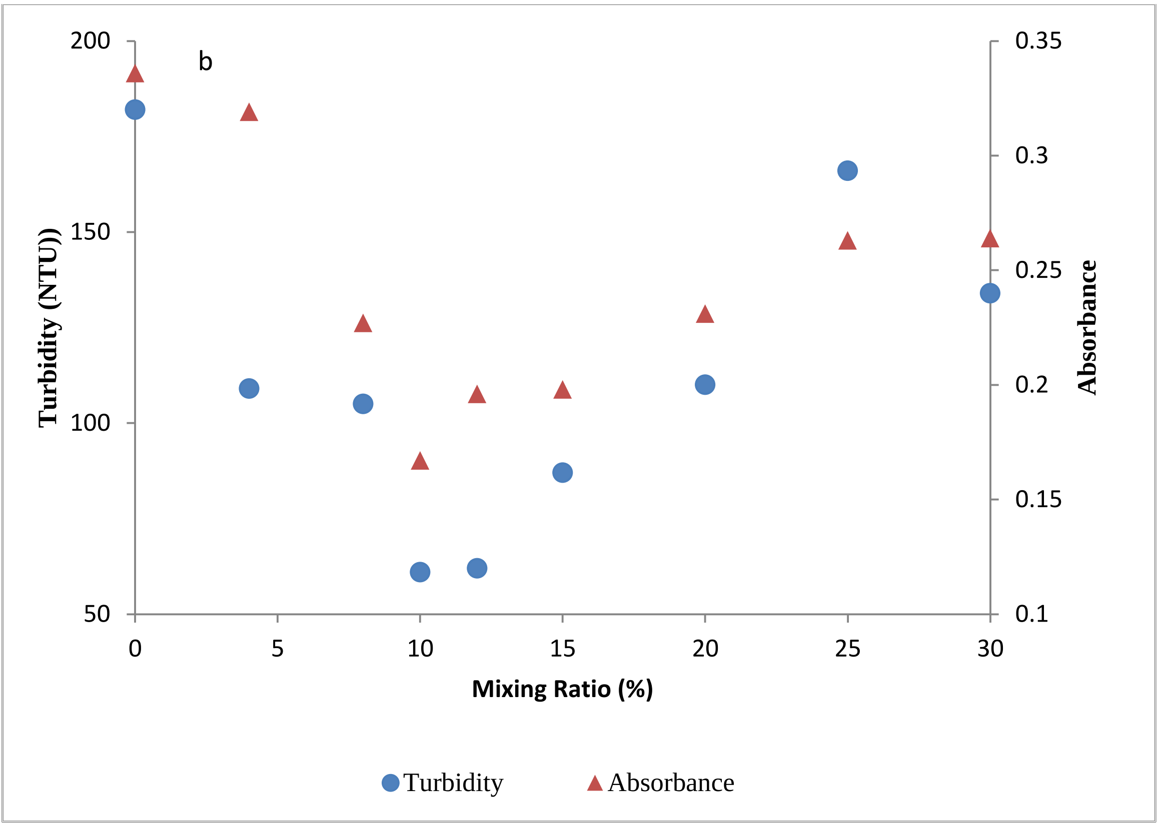


Figure 4.7 Variation of turbidity and absorbance for stone cutting wastewater with different standard lime solution mixing ratio (%).

The results in Figure 4.6 and 4.7 are shown the mixing ratio of leather liming wastewater and standard lime solution had a good effect on turbidity and absorbance, decrease significantly first with increase mixing ratio, further increase leads to increase turbidity and absorbance value again.

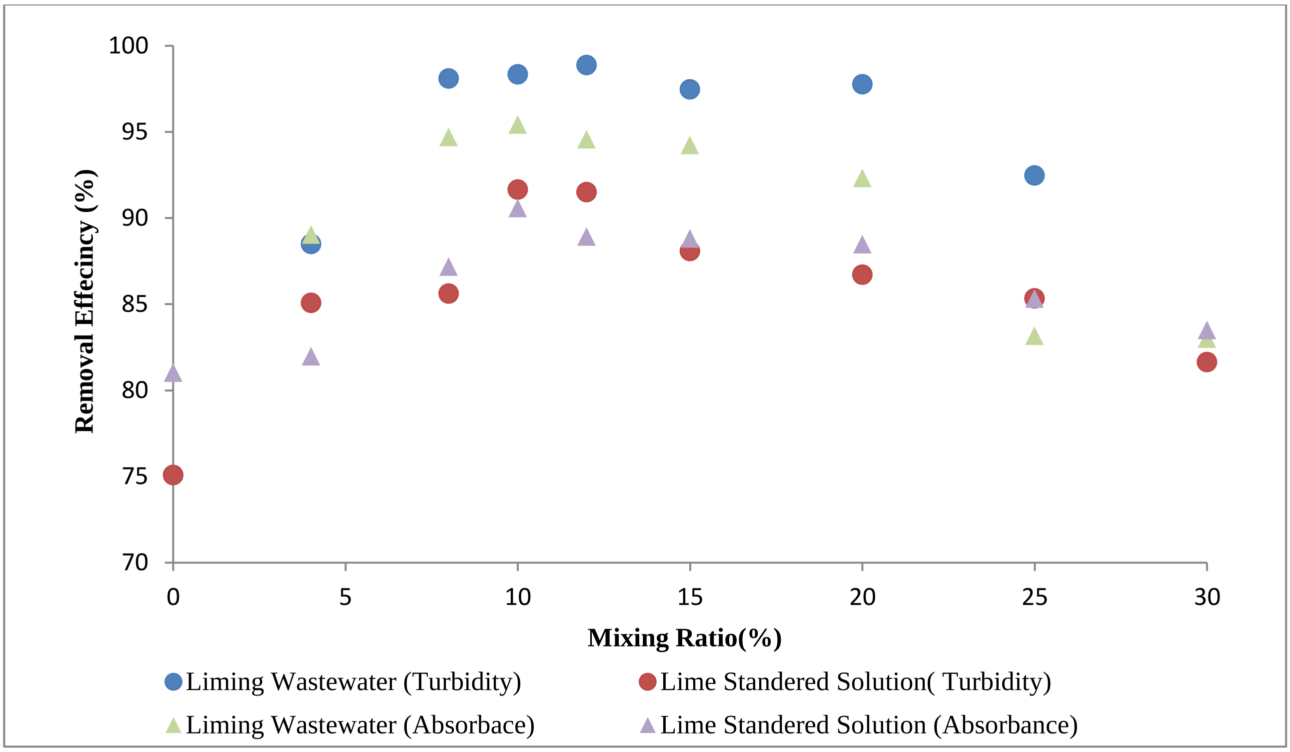


Figure 4.8 Variation of the removal efficiency for stone cutting wastewater with different liming wastewater/standard solution mixing ratio.

Leather liming wastewater was used to investigate the effect of mixing ratio on coagulation performance for stone cutting wastewater in comparison with lime solution. The results are shown in figure 4.8, which indicate that treatment efficiency of (turbidity and absorbance) firstly increase by increasing the mixing ratio to reach the optimum value of (10%) for both, after that, it was decreased. Also it indicate that liming wastewater exhibited lower residual turbidity than lime standard solution at the same mixing ratio. At the optimum mixing ratio, the removal efficiency of liming wastewater reach to 98% compared with lime solution which reach to 91%. These results demonstrate that the removal efficiency of liming wastewater was higher than that of lime standard solution. Result appear from (4% to 10 %) mixing ratio the $Ca(OH)_2$ magnitude the surface charge by decreased negative charge drastically; owing to preferential coagulation and disequilibrium stone cutting particles. The buildup of Ca^{+2} ions on particle of stone cutting wastewater resulted from excess mixing ratio. This increasing surface charge [64, 65].

4.4.2 Effect of Mixing Ratio on pH

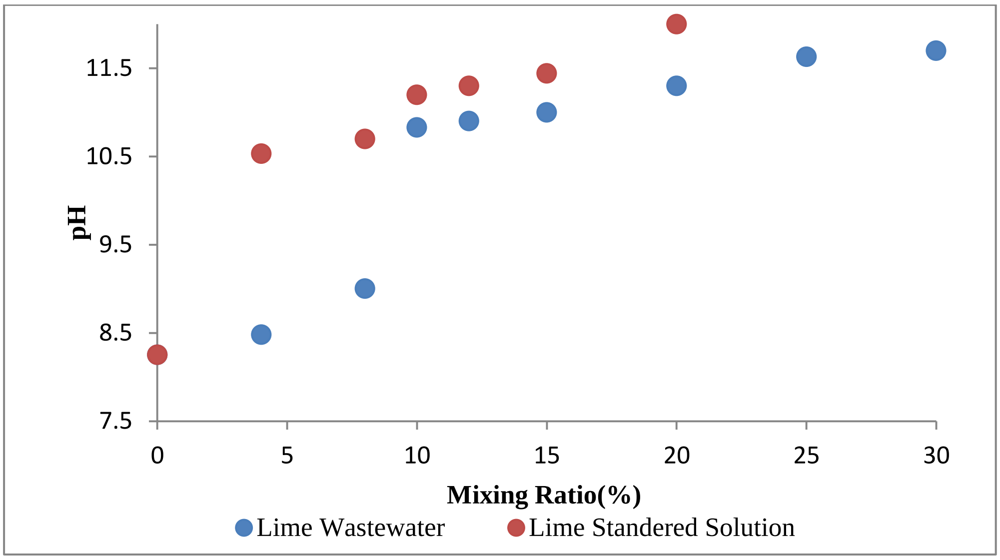


Figure 4.9 Effect of mixing ratio for stone cutting wastewater pH with different lime wastewater and lime standard solution mixing ratio (%).

Figure 4.9 shows that the progressive addition of lime wastewater resulted in increased pH from 8.25 to 12. On the other hand, the rate of reduction of turbidity and absorbance increases in completely basic area [64, 66]. This result confirm as the mixing ratio of lime increases during treatment, addition of excess OH^- ions raises pH of wastewater .[65, 67].

4.4.3 Effects of pH on Turbidity

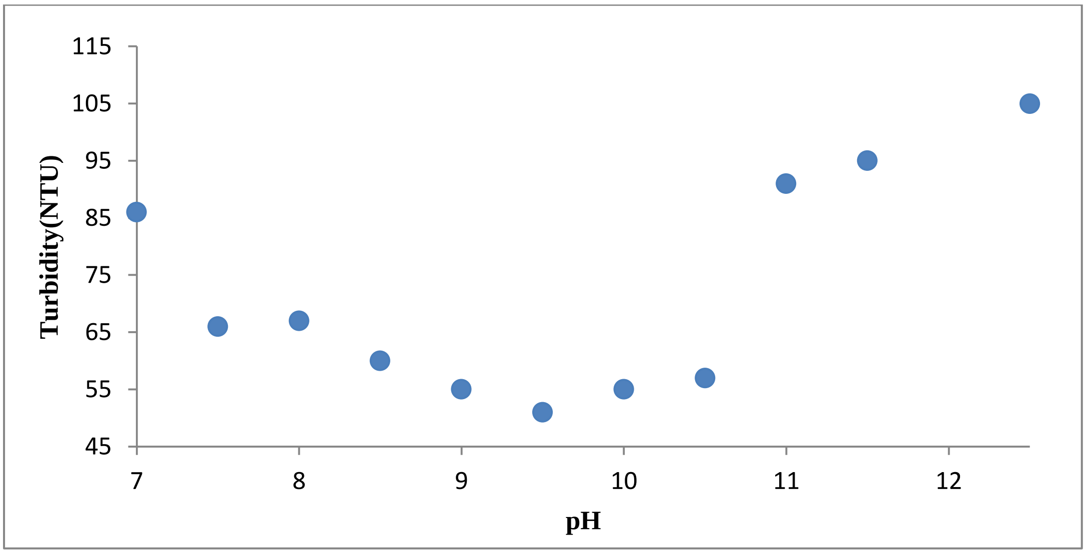
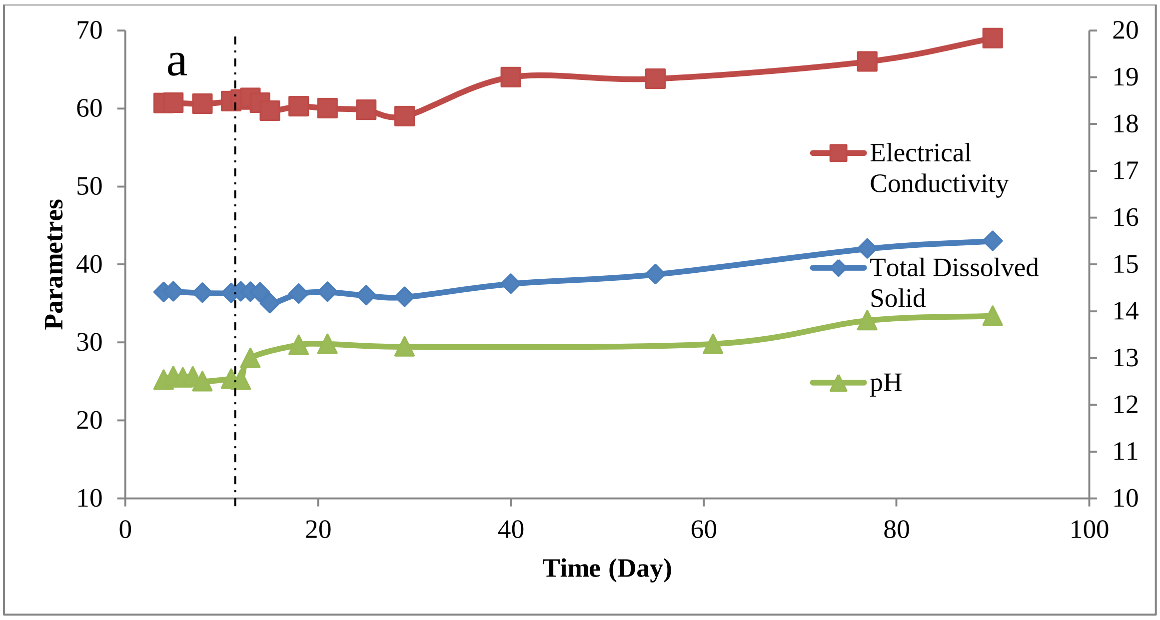


Figure 4.10 Variation of turbidity for stone cutting wastewater with different lime wastewater pH at mixing ratio (10 %).

Figure 4.10 shows the turbidity removal was correlated with the pH of the system. pH is a main factor that influence gelation time and on coagulation performance. To investigate optimum operation condition, the pH of system varied between 7.0 and 12.0, the mixing ratio of examined coagulants was 10.0%. When pH between 7.0 and 9.5, the turbidity decreased gradually to reach the optimum removal at pH around 9.5.When pH is higher than 9.5, the suspension system is difficult to destabilize due to excess OH^-, increasing negative charge and zeta potential unstable [65].

4.4.4 Coagulant Stability



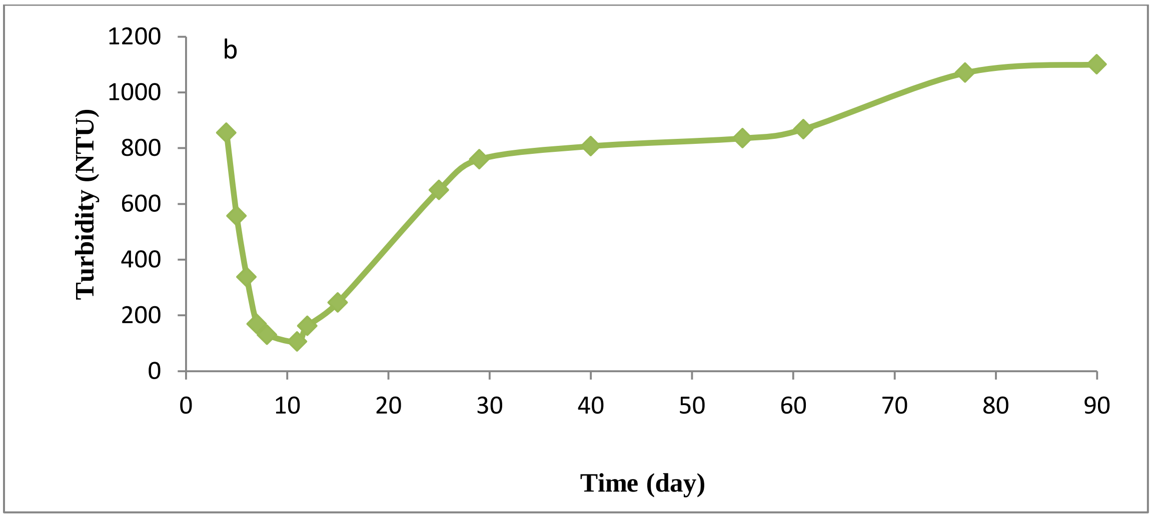


Figure 4.11 Investigations on the stability of liming wastewater. (a) total dissolved solid, electrical conductivity and pH variation with time and (b) turbidity variation with time.

Coagulant stability is an important parameter; it effects treatment performance [22]. Coagulant still effective on coagulation in specific period. After this period treatment process can deteriorate. Three month were enough to appear changes in liming wastewater. Figure 4.11 is show the total dissolve solid (TDS), electrical conductivity (EC), pH and turbidity variations with time for liming wastewater. Coagulant is quite stable at the first 20 days, the turbidity tended to decrease at the beginning, but with longer time the turbidity values increase followed by decrease in coagulation efficiency. pH variation over time, a slight increase was observed. TDS and EC were increased with time. In other study, coagulants that prepared from the wastewater are quite stable at specific period, after that the efficiency for coagulant was deteriorate [27].

4.5 Performance Evaluation of Tiles Wastewater Treatment with Lime Wastewater

4.5.1 Effect of Mixing Ratio on Turbidity and Absorbance

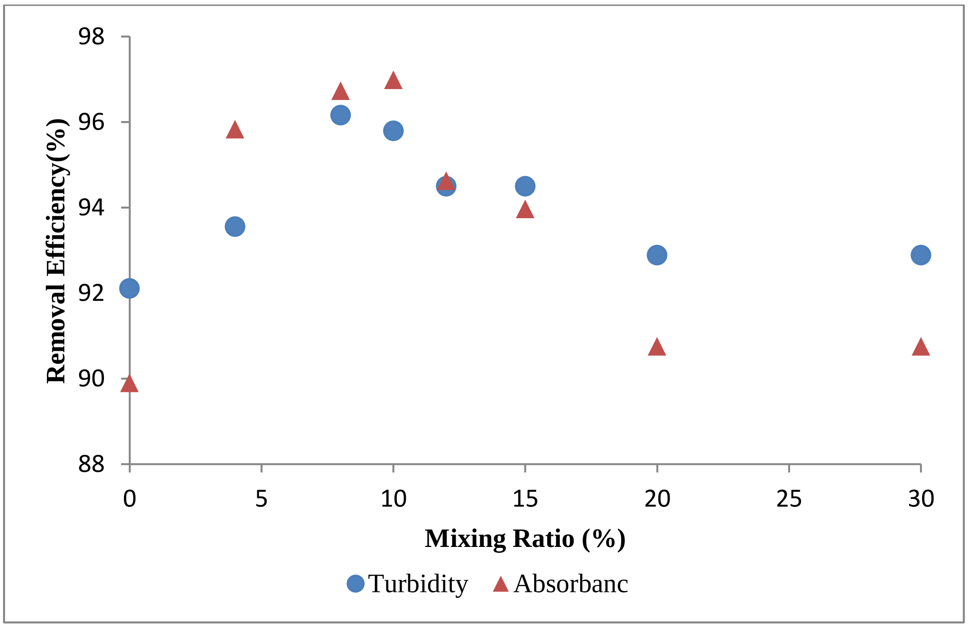


Figure 4.12 Variation of removal efficiency for tiles wastewater with different liming wastewater mixing ratio.

Figure 4.12 describes the removal efficiency of (turbidity and absorbance) as a function of mixing ratio (%), the turbidity removal rate for tiles wastewater ranged between 92%-95%. The highest removal efficiency was gained in mixing ratio of 8%. These results confirm the expectations about the possibility of using liming wastewater as coagulant for treating tiles wastewater

Conclusion

According to the results that were obtained from study, batch coagulation sedimentation process using aluminium etching and leather liming wastewater as coagulants is an effective method to reduce suspended particles and replace commercial coagulants. Jar tests were carried out in the presence of two types of wastewater at different mixing ratios and pHs. Coagulation behaviour of stone cutting and tile suspensions were studied by determining the residual turbidity and absorbance values. It was found that type of treated wastewater, mixing ratio of the coagulant wastewater and the solution pHs has an important effect on the turbidity removal. Each two types of wastewater used in the coagulation sedimentation tests, substantially reduced the turbidity and absorbance of stone cutting and tile wastewater with an increase in coagulant mixing ratio, further increase leads to an increase in turbidity and absorbance again. However, the best performance for both aluminium etching and leather liming wastewater on stone cutting wastewater was found around 10% mixing ration, for aluminium etching wastewater, it reach 70 NTU and 0.084 with removal efficiency reach to 90% and 95% for turbidity and absorbance respectively. For leather liming wastewater the turbidity and absorbance value was 8.25 NTU and 0.081 with removal efficiency reach 98.8% and 95.4% for turbidity and absorbance respectively. A lower removal efficiency (91%) was obtained when using a commercial lime solution coagulant. The removal efficiency changes with pH of the system. The best efficiency was obtained at 10.5 and 9.5 for aluminum etching and leather liming wastewater, lain sedimentation test was also performed, without adding a coagulant. The obtained removal efficiency was 87%.

Recommendation

1. Treating stone cutting and tile wastewater by coagulation sedimentation process using wastewater as coagulants is an effective and inexpensive method to replace commercial coagulants, reduce suspended particles and recycle stone cutting and tile wastewater.
2. All safety measures must be taken during wastewater treatment.
3. Applying cleaner production practices between aluminum coating and stone cutting industries by combination etch wastewater in percentage of 10%.
4. Applying the cleaner production practices between leather, stone cutting or tile industries by combination etch wastewater in percentage of 10%.

Appendix A.1 Calculations

Calculation

$$N\ HCL = \frac{1000\times\ mass\ Na2\ CO3\ (g)}{53\ \times Av.titre} = \ 0.108\ mol/L$$

$$lime\ \% = \frac{0.5 \times A\ \ \times N \times 56.08}{B}$$

$$lime\% = \frac{0.5\times 35\times\ 10^{-3}\times .108\times 56.08}{47.82}\times 100\% = 0.22\ \%$$

Mass of CaO= n× M = (0.5 ×0.108× 35× $10^{-3}\ \times 56$) = 0.1058 g in 50 ml

0.22 % < 1.5% , losses in tanning process

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