EFFECT OF COAGULATION-FLOCCULATION AND SEDIMENTATION PRE-TREATMENT STEPS ON FLOC CHARACTERISTICS IN DRINKING WATER TREATMENT

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APPROVAL CERTIFICATE

It is certified that the contents and forms of the thesis entitled

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Has been found satisfactory for the requirements of the degree of Master of Science in Environmental Sciences

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Dedication

This research is dedicated to my loving, caring, and industrious parents and my siblings whose efforts and sacrifice have made my dream of having this degree a reality. words cannot adequately express my deep gratitude to them.

"O My Sustainer, Bestow on my parents your mercy even as they cherished me in my childhood"

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AFFIFA AQDAS

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List of Abbreviation

DBPs	Disinfectant By Products
D*f*	Fractal dimensions
DLA	Diffusion Limited Aggregation
HA	Humic Acid
HDL	Highest Desirable Level
IUCN	International Union on Conservation of Nature
MPL	Maximum Permissible Limit
NOM	Natural Organic Matter
PCRWR	*Pakistan Council of Research in Water Resources*
RLA	Reaction Limited Aggregation
SDGs	Sustainable Development Goals
SFWs	Synthetic Feed Waters
T	Temperature

Abstract

Humic substances are major part of NOM (Natural Organic Matter) contamination in surface water. It adds color to water, transports heavy metals, precursor of carcinogenic DBPs formation and also act as a substrate for bacterial growth in water distribution system. Many advance technologies and disinfection procedures are being practiced for removing humic acid and pathogens from drinking water, but they are costly and posing severe environmental effects. Conventional water treatment process includes coagulation-flocculation using alum as chemical coagulant due to its cost effectiveness and easy availability. To improve efficiency of coagulation-flocculation and sedimentation, it is necessary to study floc properties in detail. In this study two synthetic feed waters (SFWs) have been prepared, one with humic acid (SFW-1) and other with humic acid incorporating *E. coli* (SFW-2). Optimum coagulant dose of 70 and 60 mg/L has been found for SFW-1 at pH 10.25±0.5 before coagulation and SFW-2 at pH 7.5±0.5 respectively. Floc characteristics i.e., floc size and fractal dimensions (*Df*) have been studied on coagulation at 150 rpm for 2 minutes with three flocculation regimes of high, medium and low Gt_{mix} conditions for both SFWs i.e., 117660, 57564, 16713 respectively. After that settling time of 30 minutes has been provided in each condition. Largest average floc size was 395.1± 44.8 µm for SFW-1 and 498.2±29.7 µm for SFW-2 and highest *Df* was 2.64±0.04 for SFW-1 and 2.70±0.05 for SFW-2 achieved at medium Gt_{mix} condition before 30 minutes of settling for both SFWs. This study may ultimately beneficial for improving water quality in treatment plants that plays a main role in achieving SDG 6 ‘clean water and sanitation’ target 6.1 ‘safe and affordable drinking water for all’.

Chapter 1

Introduction

1.1 Background

Water is the most important component needed for the survival of all kinds of living organisms and ultimately development of ecosystem. Although Pakistan is an agricultural country, but it has already been declared as water scarce country. According to IMF Pakistan is at third number on the list of countries having water scarcity (on the water scarcity index which compares national annual water availability with the total annual withdrawals percentage) (Zhang, 2021). According to PCRWR (Pakistan Academy of Science and Council of Research in Water Resources) Pakistan will be facing severe water shortage by 2025.

On global scale the groundwater volume that is available is restricted with limited recharge that is around ~ 12,600 Km^3/yr while the groundwater extraction that has been recorded is ~ 1500Km^3/yr (Akter and Ahmed, 2021).

Hence water is very limited and in Pakistan, 70% of water is used for agricultural purposes furthermore many people are now shifting towards urban locations for getting better living standards, that exerting additional pressure on water resources especially clean water for drinking purpose. This serious competition requiring extra groundwater to be pumped to meet the needs but its depleting groundwater resources severely (Tariq *et al.,* 2020).

Fortunately, Pakistan is blessed with adequate surface water resources as shown in Fig no.1.1 and it is easily accessible as well. Usage of surface water for drinking purpose requires proper treatment. Main cause of surface water pollution is when toxic material, chemical or biological contamination intermix with water bodies. Poor treatment facilities cause spreading of harmful diseases from drinking water (Patoli *et al.,* 2010).

Whenever water comes from surface water resources it is very important to make it safe for drinking because surface water get contaminated easily. Drinking water must be without any color, odor and turbidity, it should be esthetically pleasant. Pakistan National Conservation Strategy reported that less rain causes drought and other water resources are not well developed hence it is causing serious reduction in water availability. Improper or poorly treated water supply causes many health issues to public.

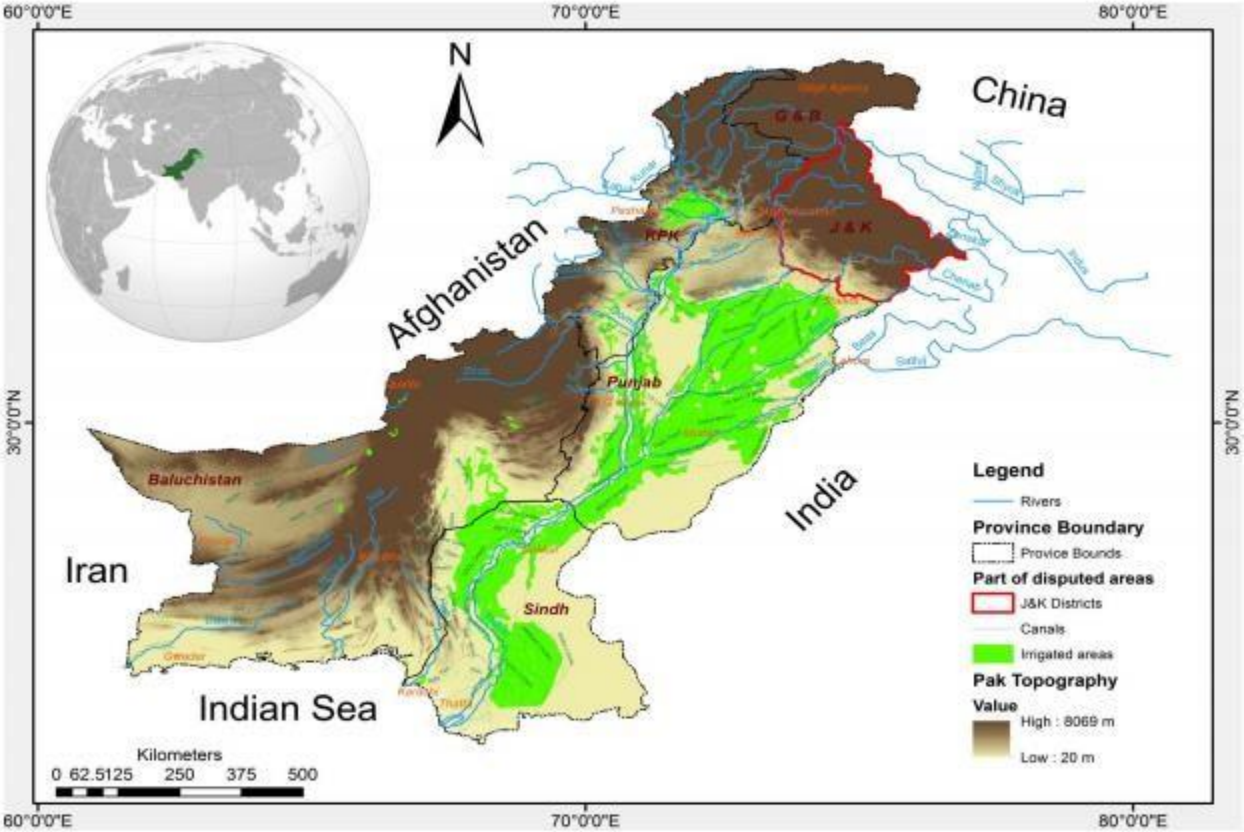


Figure 1.1: Surface water resources in Pakistan (Tariq *et al.*, 2020)

Many industries and urban communities release toxic compounds without any prior treatment into water bodies that worsen the water quality and ultimately adverse health impacts on human beings. Water and Sanitation Agency of Pakistan is mainly focused on increasing the water quantity, because of over population and their requirements, as compared to water quality. As well as there is lack of awareness, proper equipments and personnel for treatment technology and quality monitoring. In developing countries their significant population that is facing health issues just because of unsafe drinking water.

Around five million children in developing countries die because of supply of contaminated drinking water. As population is increasing day by day causing intensification in this situation that ultimately resulting in poor management for water quality (Huang and Xia, 2001). It is assessed that in Pakistan 40% of all deaths and 30% of all diseases are caused because of bad quality of water. Water related diseases are containing 40% of communicable diseases as reported by Pakistan National Conservation Strategy. Typhoid, diarrhea, giardiasis, gastroenteritis, and cryptosporidium infections are the most common water borne diseases in Pakistan. International

Union on Conservation of Nature (IUCN) estimated that diarrhea caused by low quality water causing 60% deaths of infants in Pakistan which is highest ration in whole Asia. According to United Nation International Children Emergency Fund (UNICEF) around eighty thousand cases related to water borne diseases are only in Rawalpindi and overall, 20–40% of hospitals are filled with people that are having some kind or water borne illness.

Over population is a main reason for over burdening the pressure on water resources. Almost 50 percent of world's population living in water stressed areas. The term water stressed is defined as when the demands of water surpasses the available supply either because lack of resources or poor quality. Figure 1.2 represents that water availability and population are two inversely proportional parameters.

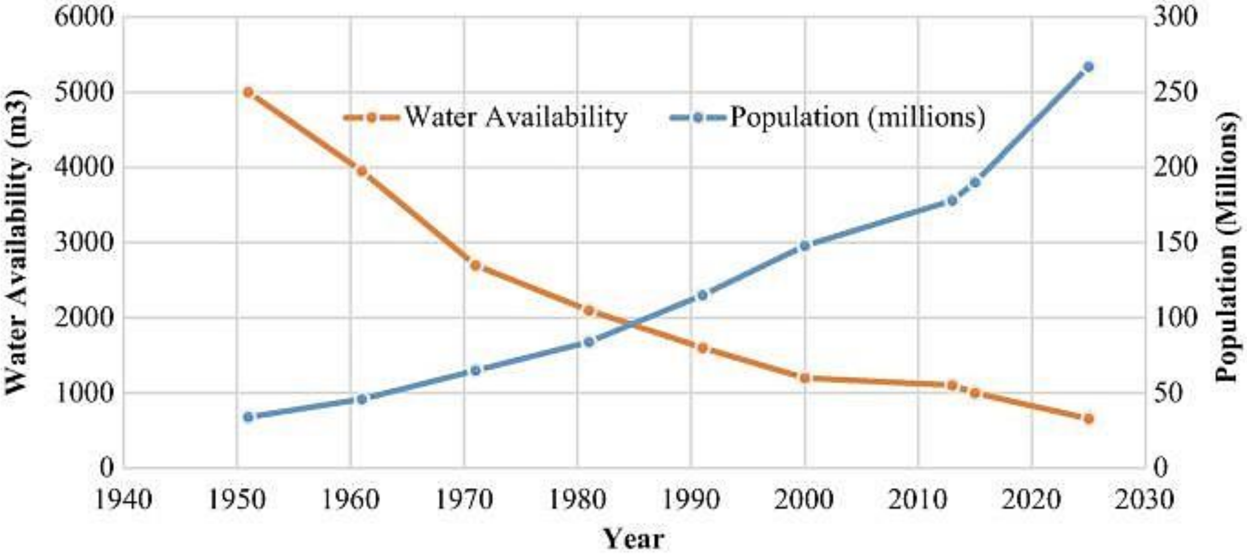


Figure 1.2: Water availability and population scenario of Pakistan

Due to climate change the intrusion of natural organic matter (NOM) in surface water demands modifications in dosing approaches and selection of hydrodynamic conditions in pretreatment system. NOM not only adds color to the water, but it is also transporter of heavy metals and toxic contaminants. It is also precursor of carcinogenic DBPs (Disinfection by-products) formation when chlorine is utilized as disinfectant (Ghernaout, 2018). It also acts as a substrate for bacterial growth in distribution systems (Matilainen *et al.,* 2010; Jacangelo *et al.,* 1995). Figure 1.3 represents the possible reasons of increasing NOM in surface waters.

NOM can change the productivity of coagulation flocculation units because of its fluctuating nature in terms of both quality and quantity (Sillanpää *et al.*, 2018). Humic substances are basic component of NOM. The humic substances constitute 60–90% of NOM (Sachse *et al.,* 2005). Figure 1.3 demonstrates the possible reasons for increasing NOM in drinking water. From the perspective of water treatment, humic acid is the most important component. It is large molecule that carry a negative charge. Humic acid has a hypothetical molecular structure and important functional groups (Duan and Gregory, 2003; Ulu *et al.*, 2014).

The optimized removal of humic substances take place at slightly acidic pH. Acidifying the water for that purpose can increases the corrosivity of water and it also requires high amount of base to counter the corrosive tendency of water before distribution which is very costly and labor-intensive (Jiao *et al.,* 2017).

Therefore, it is necessary to optimize the removal of humic acid at alkaline pH efficiently. The presence of humic acid in treated water causes re-growth of pathogenic microorganisms in water distribution networks (Maleki *et al.*, 2015).

Hence it is very important to not only remove humic acid from water efficiently but also removal of pathogenic bacteria is very crucial. Low removal efficiency of pathogens during water treatment is very common thus impacting society immensely. It causes disease outbreaks and contributing in increasing the background disease rates globally, that severely effecting the developing world. Although disinfection is one of the most significant water treatment process for removing pathogens, but it has adverse effects on human health as disinfection by products can cause cancer and reproductive/developmental abnormalities.

Establishing appropriate methods for the treatment of water and preventing the growth of pathogens in drinking water treatment system is of paramount importance for human health (Tsitsifli & Kanakoudis, 2018).

E.coli as a model organism taken in this study because of its environmental significance. It is disease causing pathogen for example serious illness related to diarrhea and kidney damage etc. It is also indicator of fecal contamination in drinking water, it grows and spread faster too. Therefore, the waterborne pathogen should be removed efficiently to ensure safe water supply (Sha'arani *et al.*, 2019).

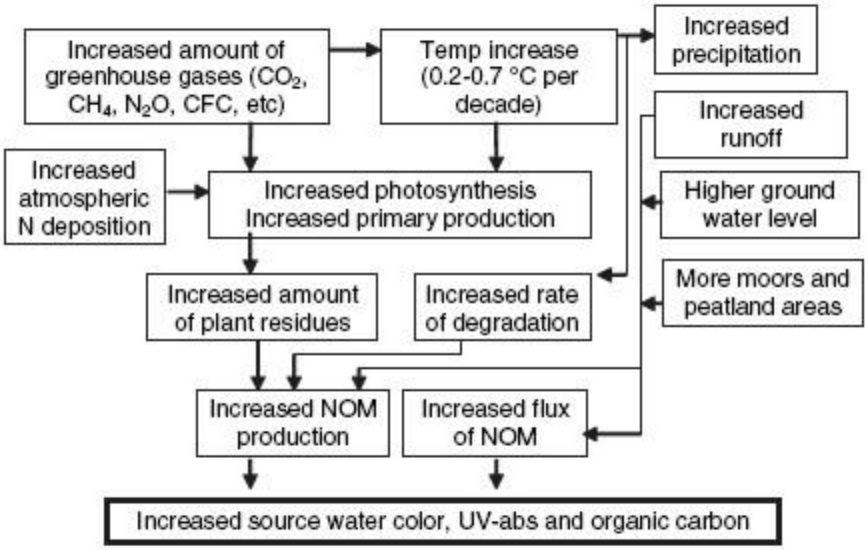


Figure 1.3: Possible reasons for increasing NOM in surface waters (Eikebrokk & Liltved, 2004)

Drinking water treatment require critical steps of coagulation and flocculation. Flocs are very complex in their structures and behavior that's why effect of these features must be understood clearly in order to predict their sedimentation effect with accuracy. Surface area, mass, morphology and number of flocs is the functions of time and shear stress in the whole dynamic process of floc aggregation. Moreover, aggregates can be of same sizes with different structures because of diverse particle arrangements during flocculation. These variations in surface area and mass can significantly changes floc behavior specifically in terms of their collisions and efficiency of aggregation (Vahedi & Gorczyca, 2012). Porous structure and irregular shape of these aggregates can create hinderance in the predicted rate of settling behavior. These characteristics can change porosity and density that subsequently changes the drag forces on the surface of floc that can slow down velocities as compare to the ones that stocks law predicted. Floc size and D_f are the most important properties of flocs as it is directly related to the settling velocity. The D_f gives an idea of the irregularity of flocs and has been popularly used for estimating the compactness of flocs. It is related to the rate of aggregation i.e., reaction-limited aggregation (RLA) and diffusion-limited aggregation (DLA). In DLA repulsive forces between particles are very weak hence causing them to aggregate by the process of diffusion which is very time-consuming forming porous and fragile flocs. In RLA the repulsive forces are very strong causing particle to aggregate in less time by overcoming repulsive barrier through thermal activation, forming compact and denser flocs (Amjad & Khan 2016).

In any water treatment facility, it is very fundamental to optimize the particle size for successful operation. Media filtration include size and concentration of particle as well as their surface chemical properties. These can typically get effected by pre-treatment methods (Jiao *et al.,* 2014). There is certain amount of flocs that are not settle down easily because of their size and weak strength that can causes their breakage by hydraulic shear forces, in most of the cases sizes between range of 1–10 μm are very challenging to get removed in media filters, because they can straight pass through the filter and get detached from filter media and causing overloading of the filter.

That's why it is very important to develop those flocs that are having good characteristics so that efficient filtration subsequently results in high quality drinking water (Fabrizi *et al.,* 2010).

1.2 Problem statement

For human consumption all waters need proper treatment technology, and surface water is more vulnerable to contamination as compared to groundwater. And for treatment system it is very important to know what is in the water so that appropriate technology will be designed. It is equally important to sustain proper monitoring system so that each step manage properly. Floc characteristics are very important to study because overall aggregate formation must get settle in sedimentation process that causes less load on membrane that subsequently leads to less back washing and media replacement. Larger flocs make membrane cake that can be remove by backwashing easily. If flocs size is smaller and of fragile in nature then it got stuck in inner pores of membrane that causing difficulty in back washing and we need to replace whole media, stronger flocs would not break in filtration media. That is why this study is established for making flocs characteristics easily removable from the water to make it purify in less time period and in inexpensive way. It can help in improving water quality of treatment plants.

1.3 Objectives

1) Effect of coagulation-flocculation and sedimentation pre-treatment steps on removal percentage of HA and HA-*E. coli* complex from drinking water.
2) Effect of velocity gradient on the characteristics of flocs i.e., size and fractal dimension.
3) Quantify floc size and fractal dimensions of HA and HA-*E. coli* complex flocs using light microscopy and ImageJ

Chapter 2

Literature Review

Water is an essential factor for the whole life and the human survival and, having an important role for both drinking as well economic sectors. Therefore, protecting this source against any pollution has become necessary (Witek & Jarosiewicz, 2009, Reza & Singh, 2010; Sojobi, 2016). Population growth, economic development, changing lifestyles and the industrialization have led to emerging of a wide range of physical and chemical pollutants threatening the environment. In many areas, providing adequate water has become increasingly difficult, both for drinking, industrial, and environmental purposes (Saxena & Brighu, 2020).

In the last century, the availability and quality of ground waters have been changing, mainly due to urbanization, industrialization etc., it leads to the use of surface water for drinking purpose because it is easily available but more vulnerable to contamination than ground water. Surface waters often have a frequently changing chemistry or composition due to seasonal changes or after a dilution with rain. This is a disadvantage for precipitation processes, which require an enhanced system control (Katrivesis *et al.*, 2019).

Water that does not infiltrate into the ground called as surface water. It is either a direct runoff that flowing over saturated or impermeable surfaces that eventually collected in large reservoirs or it is also flowing to the ground from surface openings. It is very conspicuous water source as every stream, river, or lake around is a surface water body. Surface water is also highly contaminated because when rainwater flows across different surfaces, it picks up many harmful contaminants and carries them to surface water sources. As it is already mentioned that for using surface water for drinking purpose, the source must be well protected or collected water should be treated very well to make it free from any dangerous pollutants and pathogens. There are many places on Earth where there are abundant sources of water but drinking water is scarce. Many people living in equatorial rain forests or surroundings suffer from "water, water everywhere, but not a drop to drink".

2.1-Occurrence of contaminants and drinking water quality standards

Groundwater moving through sedimentary rocks and soils may pick up a wide range of compounds, such as magnesium, calcium, and chloride, arsenate, fluoride, nitrate, and iron; thus, the effect of these natural contaminations depends on their types and concentrations. The natural occurring elements present at unacceptable levels can contaminate water as well (Liu *et al.*, 2020; Mulligan *et al.*, 2001; Ghrefat *et al.*, 2014).

Other contaminants are man-made by-products of industry, and agriculture, including heavy metals like mercury, copper, chromium, lead, and hazardous chemicals, dyes and compounds like insecticides and fertilizers. Surface water can be used for drinking purpose, but it requires proper treatment technology because it is more prone to contamination than ground water.

Water pollution basically occur when from any industry or waste site, some toxic chemical or microorganisms meet water bodies it can be run off or leach in to ground water site or freshwater resource. Technological development causes various impurities in drinking water that are of different kinds i.e. physical, chemical and biological from which nutrients and microorganisms can transported from one place to another as well (Park & Latrubesse, 2015).

If treatment facilities are in poor condition it causes spread of waterborne diseases and in Pakistan drainage lines and drinking water sanitation system runs in a parallel way that causing leakages with intermixing results in worsening of water quality (Patoli *el al.*, 2010).

As already mentioned, whenever water comes from surface water resources it is very important to make it safe for drinking because surface water get contaminated easily. Drinking water must be without any color, odor and turbidity, it should be esthetically pleasant.

Table 2.1: Drinking water quality standards (Khan *et al*., 2012; WHO, 1996; PCRWR, 2005; WHO, 2006).

“GUIDELINE/STANDARD VALUES FOR PAKISTAN					
Serial no.	Properties/ Parameters	Unit	HDL (Highest Desirable Level)	MPL (Maximum Permissible Level)	WHO Standards
1	pH	---	7.0-8.5	6.5-9.2	6.5-9.2
2	Electrical Conductance	µS/cm^3	1000.00	1200.00	1200.00
3	Total Solids	mg/L	1000.00	1500.00	1000.00
4	Total Dissolved Solids	mg/L	1000.00	1500.00	995.00
5	Total Suspended Solids	mg/L	05.00	05.00	05.00
6	Total Hardness as $CaCO_3$	mg/L	200.00	500.00	500.00
7	Calcium Hardness as $CaCO_3$	mg/L	75.00	200.00	250.00
8	Magnesium Hardness as $CaCO_3$	mg/L	30.00	150.00	150.00
9	Total Alkalinity as $CaCO_3$	mg/L	400.00	500.00	500.00
10	Chloride as Cl^{-1}	mg/L	200.00	600.00	250.00
11	Sodium (Na)	mg/L	150.00	200.00	200.00
12	Potassium (K)	mg/L	50.00	75.00	75.00
13	Lead (Pb)	mg/L	0.01	0.05	0.01
14	Selenium (Se)	mg/L	0.01	0.01	0.01
15	Arsenic (As)	mg/L	0.01	0.05	0.01”

2.2-Sources and types of contaminants in water

Fundamentally, the contaminants are of four types associated with water pollution

1) Inorganic contaminants

2) Organic contaminants
3) Biological contaminants,
4) Radiological contaminants.

2.2.1-Inorganic contaminants

Chemical parameters are great indication towards the presence of contaminants. For example, hardness in drinking water is because of naturally occurring contaminant that depend upon the geography. Calcium and magnesium components are the main cause of hardness in water. Hardness is divided into two categories i.e. carbonate and non-carbonate hardness. 300-400 mg/L hardness in water is appropriate for drinking but prolonged consumption of water containing these salts with TDS 500 mg/L may causes kidney stone.

There are many other inorganic contaminants that causes water to be destructive for drinking purpose i.e. fluoride, lead, arsenic, mercury, copper, antimony, cyanide and chromium. Sources of fluoride in drinking water is basically because of weathering of rocks containing minerals of fluoride e.g. fluorspar, fluorite, fluorapatite etc. on the earth causes high level of this substance in groundwater. Some pharmaceutical products, toothpaste, disinfectants, preservatives and vitamin supplements are also sources of fluoride in drinking water. It can be a great cause of dental and skeletal fluorosis that is significantly connected with dementia and Alzheimer's diseases (Sharma & Bhattacharya 2017; Fawell et al. 2006).

One of the biggest mass poisoning case in world is contamination by arsenic, it causes several lifethreatening diseases for example arsenicosis, toxicity of arsenic is depending upon its oxidation state Arsenate (As V) and Arsenite (As III). It has been analyzed that As (III) stays ten times more toxic as compare to As(V) (Pontius *et al.*, 1994). Mercury (MCL 0.002 mg/L) (EPA US, 2006) comes into the drinking water mainly by run off from agricultural activities, seepage from landfills and from some kind of industries causing severe issues in nervous systems of consumers. Copper (MCL 1.3 mg/L) (EPA US, 2006) comes into drinking water by rocks and soil as well as corrosions in plumbing structure mainly.

Gastrointestinal distress can cause by short term exposure to wards this substance, long term exposure causes permanent kidney and liver damage. Usage of different fertilizers are the main source of nitrate contamination in water. Asbestos comes from mineral and can be present in the form of fibers in drinking water. Barium is another inorganic contaminant that occurs naturally in aquifers while beryllium contamination comes from mining operations and from improper disposal of waste (Sharma & Bhattacharya 2017).

2.2.2-Organic contaminants

Organic contamination mainly comes through pesticides, industrial waste and domestic waste. Public hygiene sources and agriculture is the main source of pesticides. Pesticides used for agricultural purpose, if handled in improper way causes adverse effects to the environment. Pesticides are basically designed to intermingle with the different chemical mechanisms of pest's body. Hence there is great chance that pesticides can interact with non-targeted organisms' metabolism. Environmental agencies have fixed MCL's for pesticides (EPA US 2009).

Some solvents and organic chemicals like benzene, toluene, styrene, vinyl chloride and trichloroethylene etc. called as volatile organic chemicals are also very important organic contaminants plus adhesives, degreasers, gasoline additives etc. Dyes now a days having major concern of damaging water quality. Release of dyes in environment causes eutrophication that can produces very hazardous by products through different chemical mechanisms like hydrolysis, oxidation and other reactions occurring in wastewater phase waste (Sharma & Bhattacharya, 2017).

Apart from these contaminants there are other compounds responsible for causing potential adverse effect on ecosystems and subsequently to the human beings, called as emerging contaminants, mostly organic in nature (Lapworth *et al.*, 2012).

It comprises of mainly pharmaceuticals i.e. erythromycin, codeine, carbamazepine, ibuprofen, ciprofloxacin, Tamiflu etc., industrial compounds like chlorinated solvents, the fuel oxygenate methyl tertiary butyl ether, petroleum hydrocarbons, plasticizers/resins bisphenols etc., personal care products for example, alkyl esters of p-hydroxy benzoic acid, N,N diethyl meta toluamide, triclosan), fragrances, water treatment by products i.e. trihalomethanes, N-nitroso dimethyl amine, flame retardants, plasticizers, as well as surfactants waste (Sharma & Bhattacharya, 2017).

2.2.3-Biological contaminants

Living organisms in water causes biological contaminants to emerge for example bacteria, virus, algae and protozoa (Ashbolt, 2004). Pathogenic bacteria are very harmful causing huge contamination in water while there are some non-pathogenic bacteria that causes taste and odor issues (Nwachcuku & Gerba, 2004).

Virus are minutest living creature capable of causing deadly diseases through contamination for example polio virus and corona virus. Algae is very abundant and easily growing depending upon availability of nutrients. It can grow excessively in water body causing clogging in filters, unwanted odor and taste. Blue green algae i.e. Aphanizomenon and Anabaena can produce toxic chemicals that can damage nervous system (Hitzfeld *et al.,* 2000).

Similarly, some of protozoa commonly present in surface water, if it is contaminated with feces which collect water from sewage treatment plants, for example Cryptosporidium and Giardia.

2.2.4-Radiological contaminants

Radioactive material from rocks, soils and industrial processes discharge radioactive contaminants. Certain radioactive minerals when get erode naturally, emit radioactive radiations

i.e. α, β. Radioactive elements (U^{226}, Ra^{226}, Ra^{228} and Rn^{228}) cause more problems in ground water as compare to surface water and they are very dangerous for human exposure(Sharma & Bhattacharya, 2017).

2.3-Human health risk concerns due to water contamination

It has been recorded that approximately 51% of world's population take water from centralized system while 32% from protected sources but 17% of world's population uses water from totally unprotected and vulnerable sources. As already discussed, water isn't safe if it's from contaminated source.

Table 2.3 demonstrates selected contaminates with the potential health risks they are causing in human beings. There is great need of risk assessment for ensuring better water quality and averting contaminants of all kinds that transmit over public water supplies.

Table 2.2: Health risks of common contaminants in drinking water (Adipah, 2018)

“Drinking water contaminants	**Health risk concerns**
Arsenic	Carcinogenic, peripheral neuropathy, oxidative stress
Antibiotic resistance genes	Pathogen resistance to antibiotic
Alkylphenol Polyethoxylates (APEOs)	Cause toxicity
Alachlor	Carcinogenic
Asbestos	Intestinal polyps
Benzene	Neurological damage, anemia, leukemia
Chlordane	Carcinogenic
Cyanotoxins	Adverse effect on nervous system and liver
Disinfection by-products	Cause toxicity
3,3,7,8-TCDD or Dioxins	Carcinogenic
Endocrine disrupting compounds and personal care products	Disrupt endocrine system in humans
Fluorinated alkyl surfactants (FASs)	Cause toxicity
Lead	Gastrointestinal discomfort
Methyltertbutylether (MTBE)	Cause toxicity
Methylmercury	Adverse effects on CNS and renal effects
Perchlorate	Thyroid disruption
PAHs	Carcinogenic and reproductive effects
PCBs	Carcinogenic, developmental toxicity”

2.4-Natural organic matter

NOM is present in all kind of surface waters; it is basically a complex composition of different organic compounds came from biological and chemical degradation of animal and plant residues (Metsämuuronen et al. 2014). NOM is complex mixture of humic acid, fulvic acid, proteins and polysaccharides causes’ growth of bacteria and viruses (Vepsäläinen *et al.*, 2012).

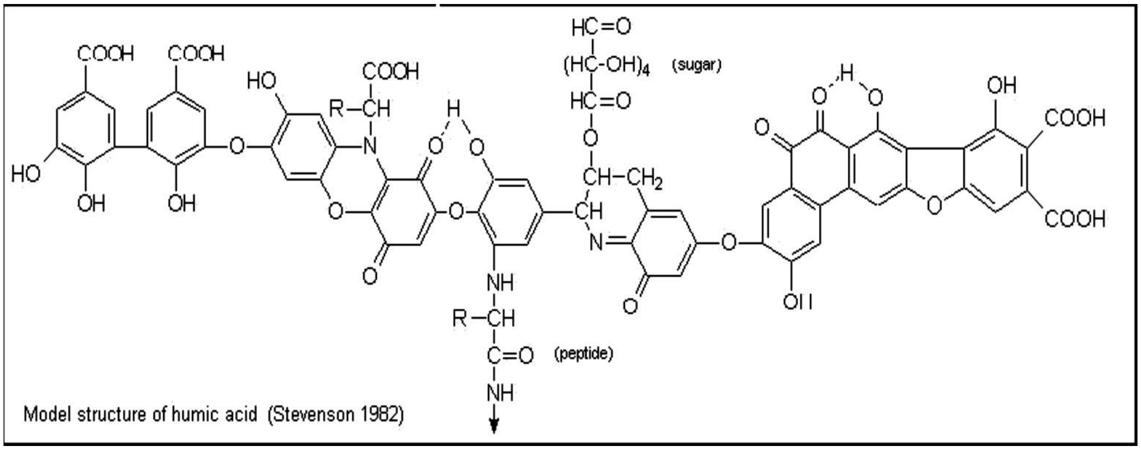
If NOM is present in drinking water, then it causes many problems in water treatment process. It is extremely important to remove it from drinking water. It is primarily comprising of components with various properties and molecular sizes ranging between small to macromolecules and large particles. It is separated into particulate organic matter that can retained through filter paper and dissolved organic matter that cannot retained on filter paper in fact it can easily pass through the filter. Removing dissolved organic matter is difficult than particulate organic matter. Huge difference in molecular sizes of NOM makes it very problematic for its complete removal from water through any single process especially because of seasonal variation that causes boundless impact on its quality and concentration. Organic compounds of NOM divided into two categories i.e., hydrophilic fraction and hydrophobic fraction. Hydrophilic fraction of NOM is consisting of mainly aliphatic carbon and nitrogenous compound for example carboxylic acids, proteins and carbohydrates. While hydrophobic fraction of NOM primarily contained humic and fulvic compounds that are rich in aromatic carbons, conjugated double bonds and phenolic structures (Metsämuuronen *et al.*, 2014; Vepsäläinen *et al.*, 2012; Ashery *et al.*, 2010).

2.5-Humic substances

NOM is primarily composed of humic substances and humic substances usually accounts for over half of dissolved organic matter (Metsämuuronen *et al.*, 2014; Vepsäläinen *et al.*, 2012). Aliphatic and aromatic structures, amino and quinone groups, carboxylic and phenolic-OH are the main constitutes of humic substances. Humic substances are categorize into three main fractions. A completely insoluble fraction called as humin, humic acid which is soluble at high pH range and insoluble in acidic pH range, then third fraction is fulvic acid that can solubilize at any pH (Lowe & Hossain, 2008).

Humic acid formation is mainly result of condensation and polymerization reaction, interaction of amino acids and sugar, and microbiological degradation of surrounding animal decay and vegetation. Humic acid enters into surface waters by means of rainwater run-off from the surrounded lands (Lowe & Hossain, 2008). Although humic substances studied a lot by researchers but still there is not enough information regarding their accurate structure. There is not any single structural formula that be sufficient for them (Lu *et al.*, 2001).

They are considered as complex molecules with amino acids, peptides, amino sugars and aliphatic compounds that are accompanying with aromatic groups. Figure 2.1 is demonstrating the hypothetical model of a typical molecular structure of humic acid. It contains bounded and free phenolic hydroxyl groups, quoin structures, oxygen and nitrogen as a bridge unit and COOH are arbitrarily placed on aromatic groups (Vepsäläinen et al., 2012).



Model structure of humic acid (Stevenson 1982)

Figure 2.1: Typical molecular structure of humic acid

Hence, we can accept that composition of humic substances for example humic acid is very complicated and complex. Moreover, it is highly dependent on area making it problematic to consistently recognize and find any process to characterize and quantify the humus content for instance the results of sea water and degraded sediments are very different from each other. Table 2.4 showed the percentage of humic substances depending on place from where the samples were taken.

Table 2.3: Comparison of humus content in waters of Australia (Lu *et al.,* 2001).

“Places	**Mass percentage of NOM (%)**
Sea waters	10-30
Rivers and streams	40-70
Lakes	~50
Degraded sediments	60-70
Highly degraded sediments	90”

2.6-Pathogenic bacteria

As its already mentioned that biological contamination in surface water mainly comprises with pathogenic bacteria that are responsible for many harmful diseases in living organisms and need to be treated. Generally greatest microbial risk is linked with taking drinking water that is not treated well and contaminated with animal or human feces. Main source of fecal contamination in drinking water is wastewater discharge and coastal sea water intrusion in fresh water, causes pathogenic microorganism to grow. Hence safe drinking water is one of a main challenge of 21st century. So microbiological control, especially in drinking water should be norm everywhere. Bacteriological quality of drinking water must be proficiently checked and treated before sending it to consumer end (Cabral, 2010).

2.7-Pathogenic *Escherichia coli*

Escherichia coli (E. coli) is single cell organism, a kind of bacteria that is utilize as an indicator of bacteriological water quality. Whenever there is existence of *E.coli* in surface water it means that water has been contaminated by feces. Presence of *E.coli* is also an indicator of other disease-causing bacterial communities in water. They can infect human beings by ingestion and through skin contact. It can cause gastroenteritis, hepatitis, cholera and giardiasis. Most potential and common sources of *E.coli* contamination differentiated by location. Sources in urban area are different than rural areas. There is huge livestock setting in rural farm type areas and people mainly relies on septic systems. Under these kinds of circumstances animal and human sewage is possible source in surface water (Sasakova *et al.*, 2018).

2.8-Treatment of surface water for drinking purpose

Drinking water should be safe for the consumers it must contain all of the elements that make it perfect for drinkable purpose, e.g. pH must be correct, mineral concentration must be accurate and it must be free from any kind of micro-organisms. The quality of water should be guaranteed and certified by the authorities of water treatment plants, as it is most important indicator of health and well-being of a society. Drinking water from any source especially from surface water (rivers, streams, lakes) must be prudently and thoroughly process before sending it to consumer end. The characterization of raw water is highly dependent upon the amount of dissolved inorganic and organic material, gases and existence of any microorganisms in the water. Most conspicuous properties of raw water and treated water are concentration of organic and inorganic matter, turbidity, color, temperature, pH, hardness, electric conductivity, and presence of microorganisms (pathogenic and non-pathogenic) (Hoslett *et al.,* 2018).

Nature and origin of water along with demands established by end use plays a vital role for selecting suitable treatment process for raw water. Ground water as compare to surface water is clean enough. It only requires reagents for the disinfections process to protecting it from pathogenic bacteria. While seas water is treated by the process of nano-filtration and reverse osmosis in order to remove the salinity from the water. Surface water are most commonly utilized source of water for drinking purpose because of overpopulation ground water sources are diminishing. Surface water can effectively treat for making it free from contamination. It involves a collective arrangement of physicochemical processes. It involves subsequent steps of coagulation flocculation, sedimentation, filtration in gravity or through pressure filters and disinfection processes.

2.9-Coagulation-flocculation

Coagulation flocculation are two subsequent successive steps meant to overcome the forces that are stabilizing the suspended particles in the solution. Coagulation refers as a most important physicochemical procedure in potable water treatment in which a coagulant is added for the reduction of electric charge between the suspended particles and formation of flocs in flocculation.

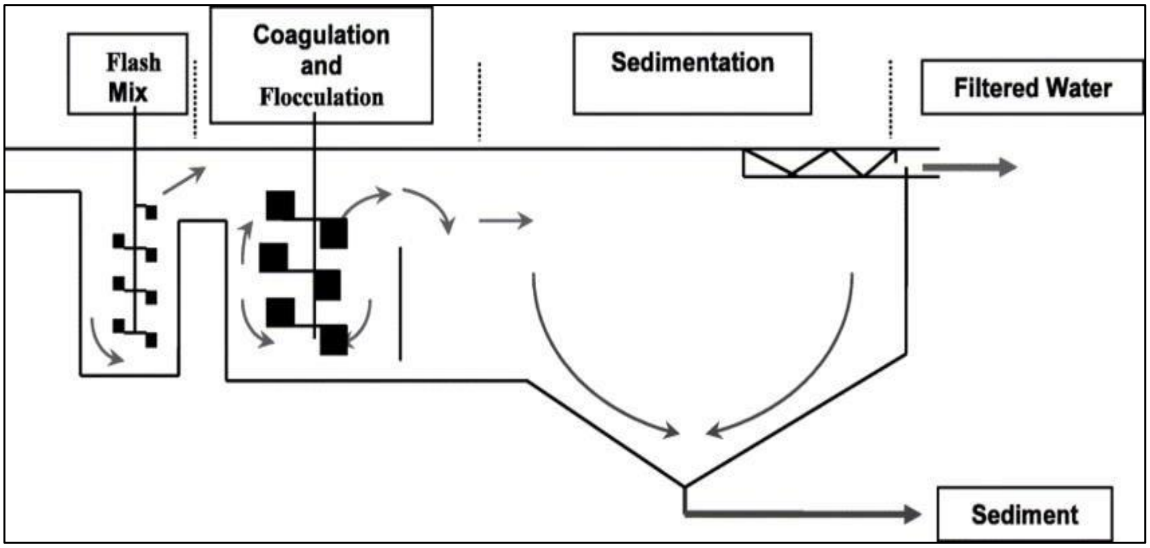


Figure 2.2: Typical drinking water treatment system

2.10-Chemical Coagulation

Chemical coagulation is accomplished by the addition of inorganic salts called as coagulants for example aluminium and iron salts. The choice of coagulant is depending upon the characteristics (pH, NOM content, and alkalinity) of water that need to be treated. Most common coagulant utilized for the treatment of water and wastewater are aluminium salts. They are very effective and can be used for treating wide range of water types. They are also easily available and are also very cost effective. Conventional aluminium salts for example alum, $AlCl_{3,}$ and pe-hydrolyzed aluminium coagulants (Feng *et al.,* 2015).

They also perform very fast in the process of floc formation and give good performance even at low temperatures. That’s why their usage is very famous in Nordic countries. For humic substances removal from water the efficacy of coagulation relies on many factors for example coagulant type, coagulant dosage, mixing condition that need to be optimum slow mixing conditions causes small size floc formation while high mixing conditions may cause floc breakage. pH is another very important parameter to be observed during coagulation flocculation, properties of humic substances must be known for example their size, charge, functionality and hydrophobicity along with concentration of destabilizing anions such as bicarbonate, sulfates and chlorides and divalent cations.

It has been researched that humic substances carry high quantity of negative charges because of presence of ionized groups for instance phenolic and carboxylic functional groups. It has also been observed that fraction with higher charge are easier for removal. That’s why the nature of humic substances are significantly impacts on dosage of coagulant (Matilainen *et al.,* 2010).

As its already mentioned that mixing speed in coagulation flocculation is divided into two steps first one is the process of coagulation in which rapid or flash mixing is provided so that coagulant will mix properly. When coagulant mix properly in the water it starts promoting the particle collisions that causes chemical interactions between them. After this step, the process of flocculation will start. Flocculation requires slow mixing providing opportunities to the particles to get in contact and form flocs time provided at this stage for slow mixing is also higher that coagulation because it causes flocs to form and grow in size. However, it must be optimum otherwise time being too high for flocculation can cause floc breakage (Vepsäläinen *et al.,* 2012).

2.11-Flocculation

Aggregation of particles for the formation of flocs is very important stage in various solid-liquid separation processes. The flocculation process generally involves some kind of chemical destabilization and a stage in which particles collides with each other and form dense flocs. The process of destabilization is very simple it requires overcoming the repulsive forces among particles with coagulants and bridging between them through polymeric flocculants or formation of precipitated metal hydroxides that appreciates the process of sweep flocculation with coagulants i.e., aluminium and iron salts (Watanabe, 2017).

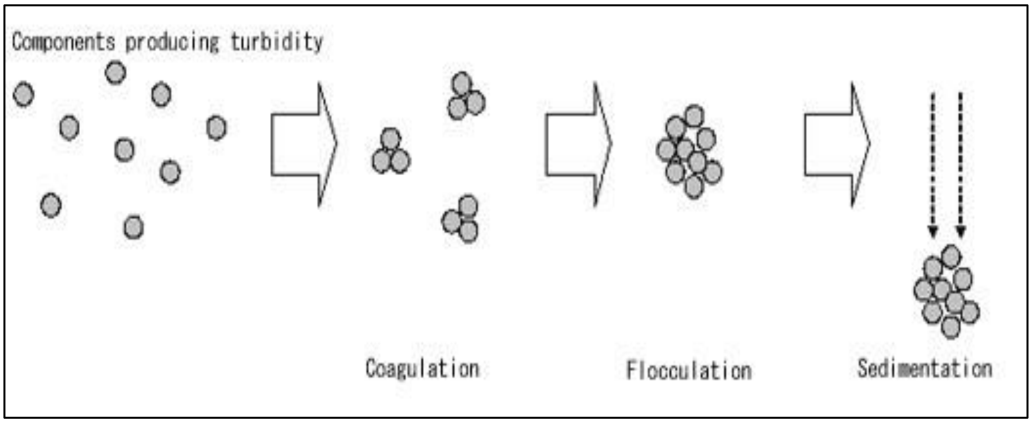


Figure 2.3: Coagulation flocculation and sedimentation

2.12-Floc morphology

Floc morphology is very important parameter to be studied after flocculation for efficient contaminants removal. Floc morphology mainly explored by floc size and fractal dimensions. Fractal dimensions of flocs increases with the compactness of flocs or we can say that compact flocs have large fractal dimension. Small sized spherical flocs with compact nature is formed when there is low collision efficiency. Because low collision efficiency can sufficiently hinder the flocculation rate.

When there is adequate collision efficacy and non-limiting flocculation kinetics, flocs with less fractal dimensions will be formed. Mechanically, floc breakage will occur if tensile energy between particles exceeds the bonding energy called large scale fragmentation. Or it may also slough the small particles from the surface because of tangential shear called as surface erosion (Jarvis *et al.*, 2005).

Flocs that are larger in size and irregular in shape having low fractal dimensions undergo large-scale fragmentation and small sized highly compact flocs undergo surface erosion. Floc size distribution is the most common parameter used to analyze the sizes of flocs in a particular water treatment system. Not only size but its fractal dimension also very important property that is directly proportional to the subsequent sedimentation process. Fractal dimensions of flocs actually gives an idea of flocs shape and it has been used enormously for quantifying floc's compactness (Saxena & Brighu, 2020).

2.13-Velocity gradient

Physical properties or morphology of flocs are extremely dependent on given hydrodynamic conditions during the process of coagulation and flocculation. Hydrodynamic conditions are mainly comprising on mixing conditions that are global velocity gradient, mixing time and distribution of velocity field (Pivokonsky *et al.,* 2011). During coagulation or rapid mixing conditions, applied velocity gradient must lies in the range of 100–400 s^{-1}. During slow mixing or flocculation stage velocity gradient typically ranged from 20 to 100 s^{-1} (Vašatová *et al.,* 2020; Polasek 2007).

Rotation frequency of impellers mainly considered for mixing conditions that are applied in rpm or revolution per minutes. But rpm cannot deliver the information regarding hydrodynamic. It is always very crucial to get the value of global velocity gradient (G) for proficient flocculation process (Camp & Stein 1943; Vašatová *et al.,* 2020). Global velocity gradient can be found out with derivation of equation (1) (2) and (3) mentioned below:

$$G = \sqrt{[P/\mu V]} \qquad (1)$$

G - mean velocity gradient, dv/dz, (s^{-1})

P - power input (W) or (ft lb/s); ($P=K_T n^3 D^5 \gamma/g_c$)

μ - dynamic viscosity (N s/m^2) or (lb s/ft^2) and

V - volume of tank (m^3) or (ft^3)

$$P = K_T \rho n^3 D^5 \qquad (2)$$

K_T - impeller constant

ρ - density of liquid, (kg/m^3)

n - impeller speed, (rps)

D - impeller diameter, ft(m)

$$\rho = \gamma / g_c \qquad (3)$$

γ- specific weight of liquid, lb/ft^3 (N/m^3)

g_{c-} acceleration due to gravity 32.17ft/s^2 (9.806m/s^2)

2.14-Fractal Dimensions

As already mentioned, that term fractal dimension defines the various features of floc morphology. The fractal dimension of a distinct particle, that may be a prime particle or a complex particle such as an aggregates or floc, explains the irregularity and self-similarity of the particles. It is basically measure of complexity of flocs external shape. Fractal dimension also excessively used for the determination of population of flocs in many studies in which it is indicated that how the shape of smaller flocs related to the large sized flocs (Bunde & Havlin, 2013).

2.15-Floc size and fractal dimension study by image analysis

Microscopy is the most economical, useful and simple technique to study the structural characteristics of flocs. Using optical microscope can help anyone to analyze individual flocs on high magnification. This technique can evade underestimation of floc structure by measuring only solid area but not the effective area involving pores and water in the floc body. Although this technology is pain staking but very accurate and utilized in many researches.

Images can easily capture through microscope with the help of many software. Micro-eye is a supporting software used to capture images from microscope after that captured images exported to another software named ImageJ (Saxena & Brighu, 2020).

2.16-ImageJ

ImageJ is an image processing program based on java. It is developed by NIH (National Institute of Health) and “Laboratory for Optical and Computational Instrumentation (LOCI, University of Wisconsin)” in 1997. The first version of this software was developed in public domain. While other new versions incorporating related projects were licensed with permissive BSD-2 license.

This software was designed in an open architecture format that facilitates extensibility through extensive macros and java plugins.

It also has built in java compiler and editor. User-written plugins can resolve many image processing and analyzing issues. It can capture three-dimensional live cell imaging with radiological image processing. In this study it has been utilized for quantifying floc size and fractal dimensions (Abràmoff et al., 2004).

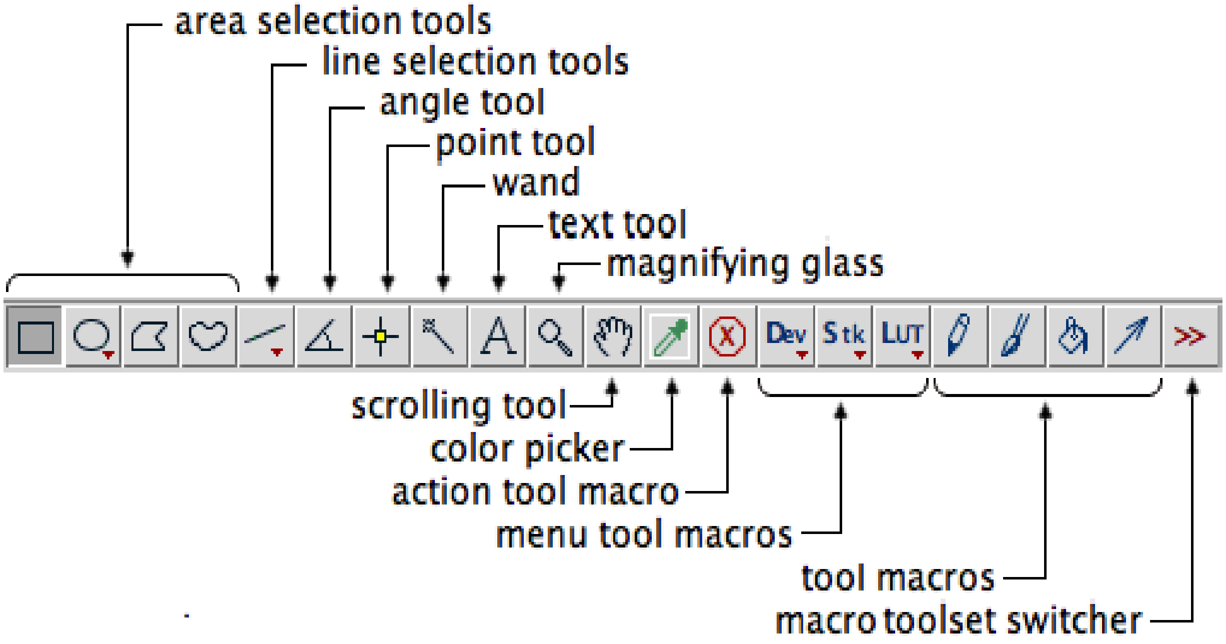


Figure 2.4: Common functions of ImageJ

Chapter 3

Methodology

The work has been planned and implemented in two segments by preparing two synthetic feed waters. SFW-1 is prepared for studying removal efficiency and floc morphology of humic acid. While SFW-2 has been prepared by intrusion of E.coli in humic acid feed water. Effect of pretreatment on both SFWs is studied and interpreted in terms of structural characteristics of flocs by same methods. Six sets of pretreatment condition span for three flocculation regimes (Low, medium, and high Gt_{mix}) and the before and after settling of flocculated suspensions has been illustrated.

3.1- Equipments and instruments

A list of equipment and instruments that has been utilized for this research is mentioned down below:

- **Sonicator (JAC-ultrasonic 1505)**

  Sonicator or ultra-sonic bath is a device that use to homogenize samples by utilizing ultrasonic waves. In this study it used for homogenizing stock solution. It also includes accessories, support devices and other probes. It comes with temperature option and time range that need to be set for a particular suspension to get homogenized completely. It uses water bath inside to transmit ultrasonic energy.

Figure 3.1: Sonicator (JAC-ultrasonic 1505)

- **Magnetic stirrer**

  This device used in laboratories for easy mixing purpose. It works by a magnet bar that need to be put inside the sample then through magnetic field it provides the stirring action.

In this study it is used to stir the synthetic feed waters. The stir bar or magnet bar motion is driven by another assembly of electromagnets in the stirring device beneath the vessel. The whole process in accomplished by electromagnetic field generated by both magnets.

- **Jar test apparatus- JLT 6 VELP SCIENTIFICA**

  In this study a jar test apparatus model (JLT 6 VELP SCIENTIFICA) was used for the coagulation-flocculation experimentations. It is assembly of 6 stirrers with automatic time and rpm adjustments. Multiple stirrers and their reproducible stirring rpms allow the standard conditions for the tests to be done, which is a basic condition for reliable results. Jar tests mainly employed for optimizing coagulant dose, and mixing conditions along with pH variation study for exploring the removal efficiency of selected sample.

Figure 3.2: Jar test apparatus (JLT 6VELP SCIENTIFICA)

- **UV-Spectrophotometer**

  UV-spectrophotometer is derived from ultraviolet-visible spectroscopy or ultraviolet-visible spectrochemistry. It is a quantitative method that used for measuring how much a chemical suspension or a sample absorbs light. It is accomplished by determining the intensity of light that passes through the sample with respect to the intensity of light that passes through a blank or reference sample.

Figure 3.3: UV-spectrophotometer

- **pH meter**

  This instrument use excessively in many laboratories for measuring the hydrogen ion activity in the liquid samples. Or we can say this instrument measures the alkalinity and acidity of a liquid sample. pH level is basically degree of hydrogen ions activity. pH meter gives values ranges from 1 to 14. Values lies in the range of 1 to 6 considers as acidic pH while 7 is neutral and from 7 to 14 the pH is alkaline.

- **Autoclave**

  Autoclave is used for sterilization purpose. It generally operates at very high temperature and pressure in order to destroy spores and microorganisms. Its purpose is to decontaminates and sterilize the lab ware, media and instruments.

- **Laminar flow hood**

  Laminar flow hood designed to use media for preparing petri plates or several other microbiological experimentations on biological samples or any microbes sensitive materials. It is used to prevent contaminations. It has air drawn system by HEPA filters installed inside. It also has UV-C germicidal lamp, used for sterilizing the interior of laminar flow hood. UV-C germicidal lamps must be kept on for at least fifteen minutes before starting to work on it. The lamps must be switch off after fifteen minutes before its usage.

- **Hot air Oven (UN-110)**

  Hot air oven is designed for removing moisture from the glassware, after they has been sterilized from autoclave, that need to be utilized for experiments. Drying oven or hot air oven introduces fresh air that removes the moisture. Its airflow system provides high performance of drying and heating.

- **Incubator (IN-110)**

  Incubator is very essential equipment used for microbiological experiments. It is used for supporting bacterial growth by providing them a temperature-controlled environment.

- **Optical Microscope**

  Optical microscope or light microscope is commonly using visible light and a system of lenses for creating magnified view of images from the glass slides. Optical microscope used in this study is containing four magnifications i.e., 4x, 10x, 40x and 100x convex lenses. Only images from 10x lens has been captured and analyzed for comparison in this study.

- **IDS-Digital camera**

  This camera is immensely used for educational purposes in research and development activities. This camera can easily mount over microscope and its data cable need to be attached with a computer system that presents the view of "eye piece" to the computer screen through a supporting software that is "micro-eye". The software must be installed in the computer system for the view.

Figure 3.4: Assembly of optical microscope, IDS-digital camera and computer system

- **Colony counter (SUNTEX-560)**

  Colony counter is used for estimating the no. of colonies present, based on their ability to continue growth under certain conditions like temperature and nutrient medium. It can also help us to find general bacterial content in any aqueous sample by serial dilution and spreading.

Figure 3.5: Colony counter (SUNTEX-560

3.2- Flow Chart for Schematics of study

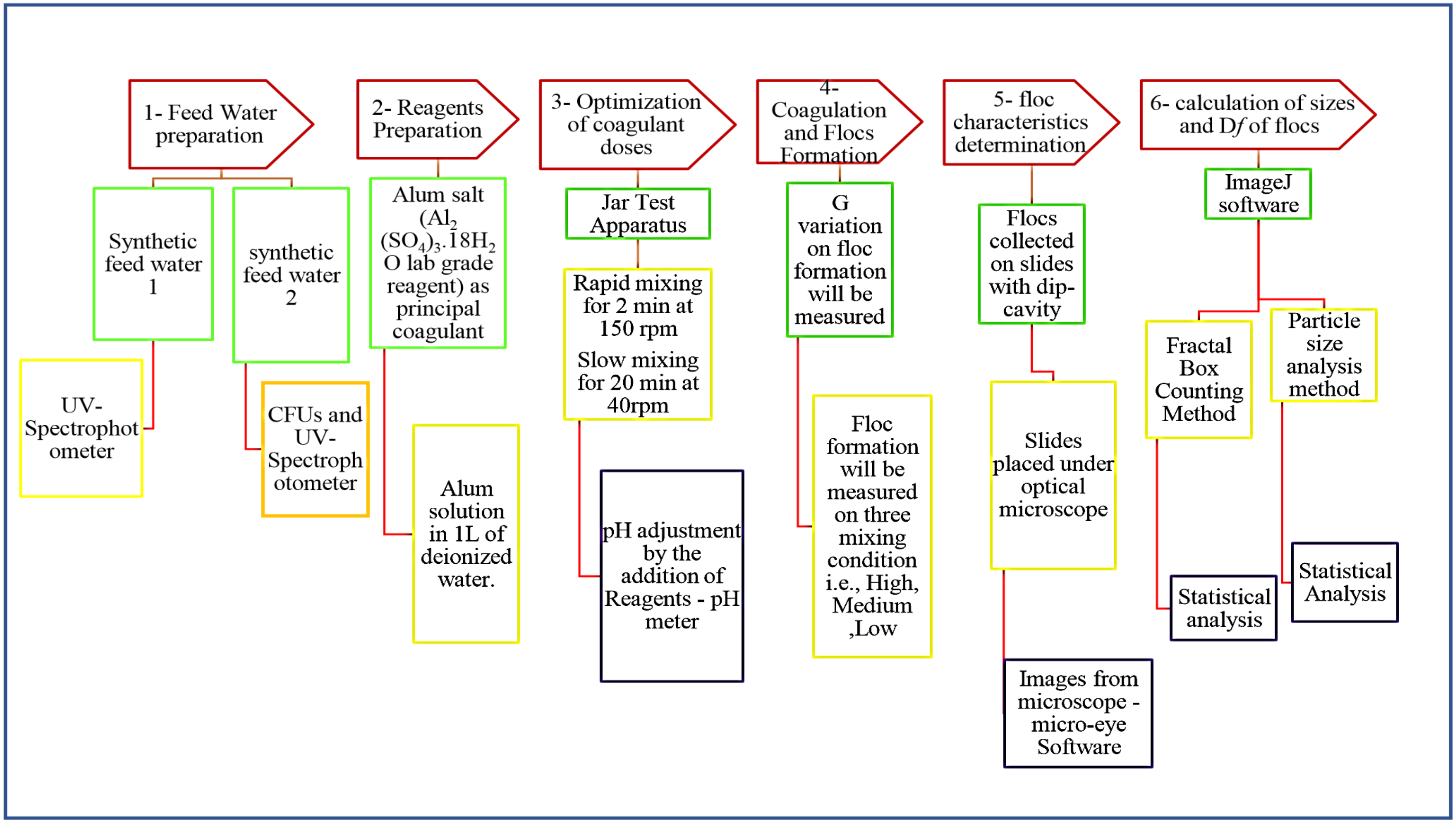


Figure 3.6: Flow chart demonstrating schematics of study

3.3- Research Design

The research has been designed in three phases

1) Phase-I: Preparation of synthetic feed waters (SFWs)
2) Phase-II: Coagulant Dose optimization
3) Phase-III: Floc morphology study at different velocity gradient (G) and time (t) by ImageJ i.e., Floc Size and Fractal dimensions

3.3.1- Phase-1: Preparation of synthetic feed waters

3.3.1.1- Synthetic feed water 1 (SFW-1)

10mg of humic acid dissolved in aqueous solution of 5 mL of 2M NaOH and treated with ultrasound in a sonicator for 30 min. The solution was diluted with deionized water to 100 mL and stirred for 30 min in a magnetic stirrer. The concentration of HA in the stock solution was, thus, 100 mg/L, the concentration of NaOH was 0.1 M and pH was 11-12. This method is similar to the one used by Sakarinen, 2016. The synthetic feed water was prepared by diluting the right amount of HA stock solution with deionized water to get concentration of 20mg/L humic acid in each beaker. The concentration of humic acid has been taken 20mg/L in both SFWs because maximum concentration of NOM that can be found in surface water is from 0.1 mg/L to 20 mg /L (Rodrigues *et al.,* 2009). The stock solution was stored in dark at 4˚C. pH of synthetic feed water has been adjusted to 10.25 by adding 0.1M HCl. UV_{254} nm wavelength is directly proportional to the concentration of humic acid. The possible effect of NaOH on the spectra was excluded by a comparison of NaOH and H_2O spectra, NaOH did not have peaks in a range of 300-0 nm. Linear relationship indicated that UV spectrophotometry is a suitable method for quantifying the removal efficiency of HA.

Figure 3.7: SFW-1 Stock solution

Figure 3.8: Floc formation in SFW-1

3.3.1.2- Synthetic feed water 2 (SFW-2)

E. coli (Escherichia sp. NCCP-1755) was collected and assayed on eosin methylene blue (EMB) agar. Prior to seeding into synthetic feed water, a culture from the agar plate was inoculated into 25 mL of sterile Luria Bertani broth until the optical density OD_{600} reached 1.0.To evaluate the removal of the bacteria, a 1 L beaker containing synthetic feed water 1 was spiked with bacteria (*E. coli*, ~ 10^{6} CFU/mL) without coagulant. The other beakers were injected with alum doses. The same coagulation standard procedure was performed. pH of synthetic feed water 2 has been adjusted to 7.5 to get optimum growth of *E. coli* for experimentation. Spread plate method has been used to measure the removal efficiency of *E .Coli*. Method for preparing SFW-2 is similar to the method used by Sha'arani et al 2019 (Sha'arani *et al.*, 2019).

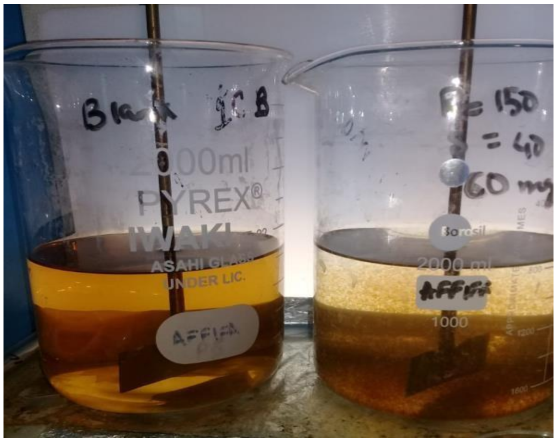


Figure 3.9: Floc formation in SFW-2

Figure 3.10: Colony count of *E.coli* (SFW-2)

3.4- Reagents Preparation

Aluminium sulphate or alum ($Al_2(SO_4)^3$. $18H_2O$, reagent grade, Sigma Aldrich) has been utilized as a principal coagulant. Stock solution of coagulant was made by dissolving 10g of alum in 1 L of deionized water. For pH adjustment 2mM $NaHCO_3$ solution has been prepared by dissolving 16.8mg of $NaHCO_3$ in 100 mL of Deionized water.

3.4.1- Phase-2: Optimization of coagulant dose

Alum solution as a coagulant prepared by dissolving 10g of alum (Alum salt ($Al_2(SO_4)_3.18H_2O$) in 1L of deionized water. Coagulant dose was optimized by diluting humic acid stock solution to concentration, 20mg/L. A jar test apparatus (JLT 6 VELP SCIENTIICA) with 2L cylindrical beakers was used. For dose optimization a range of coagulant dosages has been tested to get maximum removal efficiency in both synthetic feed waters (SFWs) 1 and 2. The optimum and standard coagulation procedure involves rapid mixing for 2 min at 150 rpm, flocculation at 40 rpm for 20 min and settling at 30 min. pH was adjusted to ~ 10.25 for SFW-1 and ~ 7.5 for SFW-2. Alum dose was tested in range from 10-100mg/L. after the process of coagulation flocculation suspension was allowed to settle for 30 minutes. A sample of 40mL has been collected with the help of micropipette from approximately 2 cm below the water surface and tested for humic acid removal efficiency by UV-spectroscopy method and for E.coli removal efficiency by spread plate method.

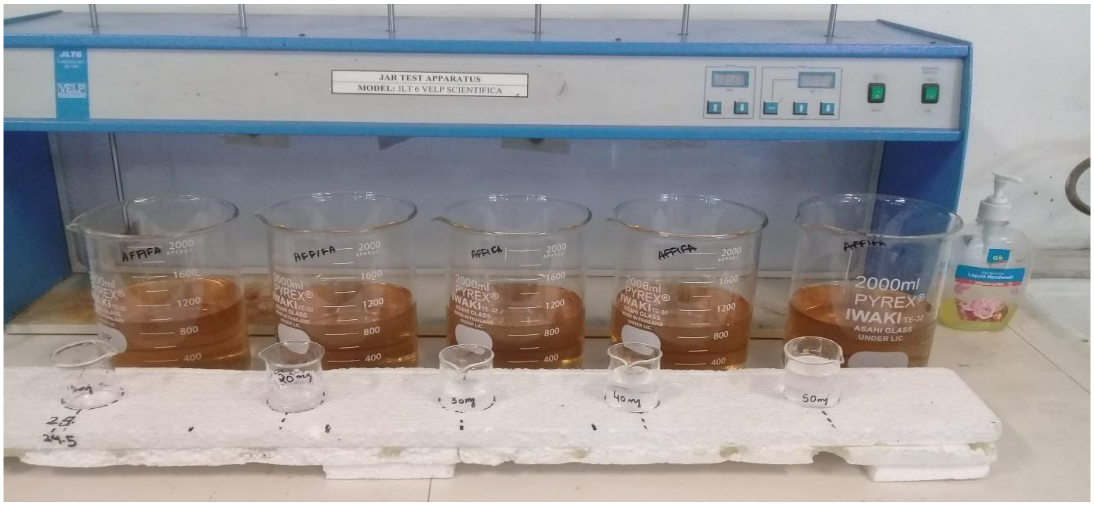


Figure 3.11: SFW-1 before coagulation-flocculation and sedimentation process

Figure 3.12: SFW-1 after coagulation-flocculation and sedimentation process

3.5- Phase-3: Floc Morphology/Characteristics study at different velocity gradient and time

Optimized dosages were further extended and optimized for varied velocity gradient (G) and time (t) to study floc morphology/characteristics. Three flocculation conditions were tested with different values at high, medium, and low Gt_{mix} conditions, mentioned in Table 3.1, where G is the mean velocity gradient and t_{mix} is the duration of mixing.

Table 3.1: Experimental scheme for varied *Gt_{mix}*

Experimental Code	**Pre-treatment Step 1 → Coagulation**				**Pre-treatment Step 2 → Flocculation**				**Pre-treatment Step 3 → Settling**
	rpm	**G (s^{-1})**	**t (s)**	**Gt_{mix}**	**rpm**	**G (s^{-1})**	**t (s)**	**Gt_{mix}**	
High Gt_{mix} →D	150	137.04	120	16440	120	98.05	1200	117660	0
High Gt_{mix} → S									30
Medium Gt_{mix} →D					80	53.3	1080	57564	0
Medium Gt_{mix} →S									30
Low Gt_{mix} →D					40	18.57	900	16713	0
Low Gt_{mix} →S									30

3.5.1- Determination of floc size and fractal dimensions (D_f)

The floc sizes were analyzed by using an optical microscope and a digital camera mounted over the microscope, similar to the method used by Saxena and Brighu (2020). Only two-dimensional sizes of the flocs can be evaluated by this technique.

Flocs were collected before 30 minutes of settling and after 30 minutes of settling by collecting sample from 2cm below the water surface through glass pipette. Dip cavity slides has been used for collecting flocs that has been sealed with coverslips. 10X objective lens was used to view and capture the images.

For image processing and analysis two software has been employed i.e., micro-eye and ImageJ (National Institutes of Health, USA). Micro-eye was supporting software that helps in capturing the images from microscope to laptop. In ImageJ, the sizes are calculated by measuring the area covered by pixels (figure 3.15), as per described by Saxena and Brighu 2020.

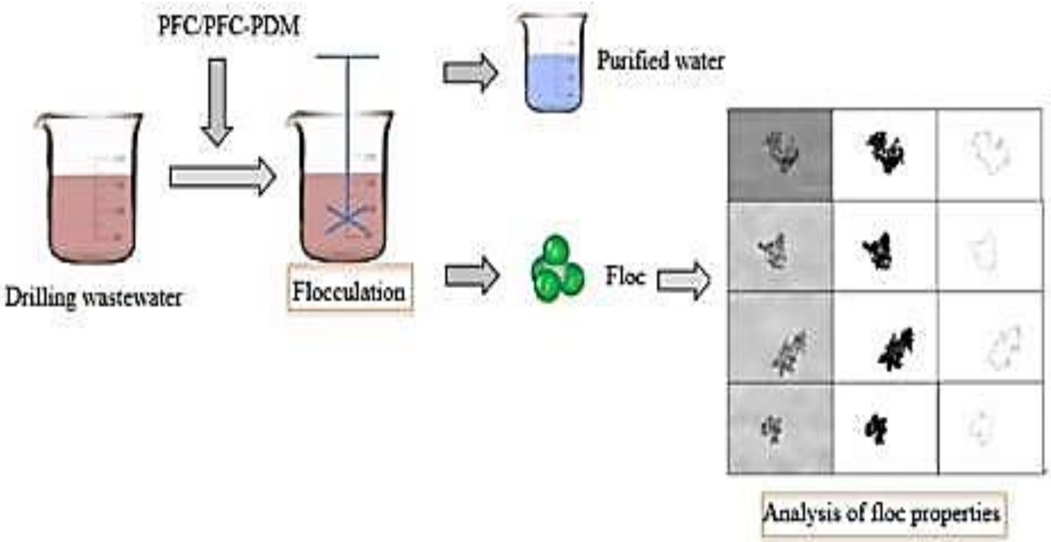


Figure 3.15: Example of schematic diagram of floc size measurement

The D_f of flocs has been analyzed by fractal box counting method as mentioned in figure: 3.16 and 3.17. The values of D_f range from 0 to 3. As it is already mentioned that high values of D_f implies for compact flocs called reaction limited aggregates (RLA) while lower D_f shows more porous structure of flocs that comes in the category of diffusion limited aggregates (DLA).

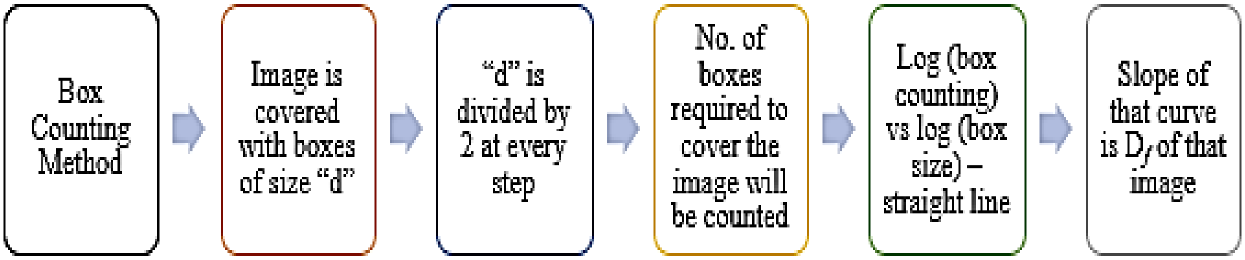


Figure 3.16: Box counting method

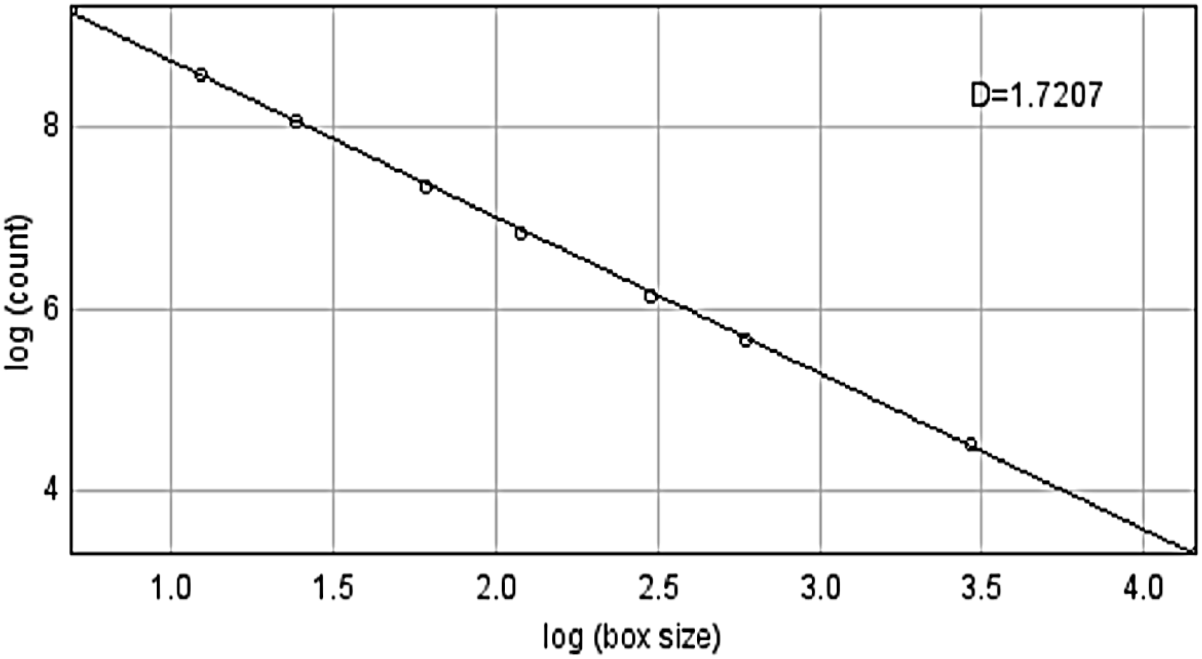


Figure 3.17: Slope of fractal dimension value

4-Results and Discussions

4.1- Phase-1: Calibration of HA concentrations by UV absorbance

A concentration series of humic acid solution ranged between 0 to 100 mg/L has been measured by UV-vis Spectroscopy in order to find the relationship between UV_{254} and the concentration of tested humic acid. The concentrations were attained by dissolving the known concentration of humic acid in 0.1M NaOH. Figure 4.1 demonstrating the empirical relationship between the UV-absorbance and Humic acid concentration. It has been observed that UV_{254} is directly proportional to the concentrations of humic acid. The possible effect of NaOH was excluded from the spectra by comparing it from H_2O spectra. And it showed that NaOH did not have peaks in between range of 300-0 nm. Hence it has been assessed that according to linear relationship UV-spectrophotometry is appropriate method for quantification of humic acid removal efficiency.

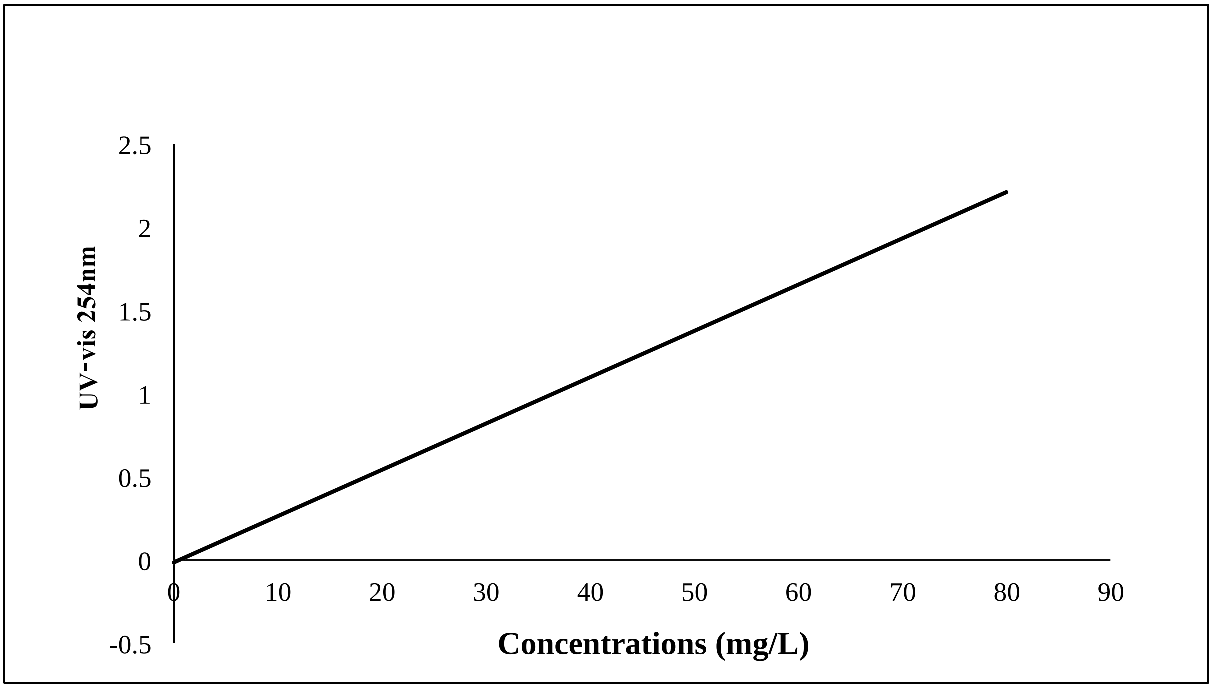


Figure 4.1: Absorbance of 254 nm UV light as a function of humic acid concentration for the humic acid concentration series used to calibrate the spectrophotometric method.

4.2-Phase-2: Coagulant Dose Optimization for SFWs

Coagulant dose optimization tests were performed to determine the optimum alum dose required for the maximum removal of humic acid from SFW-1. From 10 to 120 mg/L of alum dose, optimum coagulant dosage was 70 mg/L for treating SFW-1. pH before coagulation was adjusted to 10.25 and after treatment pH of SFW-1 was 6.3 at optimum coagulant dose (Table 4.1). Similar results as been demonstrated by Mensah-Akutteh, 2022 by optimizing aluminium coagulation treatment through response surface methodology. They have investigated alum dose, pH and alkalinity for removal of turbidity, color by NOM, residual aluminium and phenanthrene, for maximum color removal optimum values were pH 6.5, alum dose 70.0 mg/L and alkalinity 90.0 mg/L.

Table 4.1: Dose optimization for SFW-1

Alum dose (mg/L)	**% Removal**	**pH**	
		Initial	**Final (Avg)**
10	0.54	10.25± 0.5	10.16±0.08
20	0.94		10.02±0.23
30	29.4		9.99±0.65
40	34		9.78±0.04
50	86.8		6.95±0.25
60	91.3		6.64±0.50
70	97.15		6.37±0.04
80	97.3		5.95±0.28
90	96.9		5.62±0.54
100	96.25		5.07±0.02

Trend for alum dose optimization in SFW-1 has been demonstrated in Figure 4.2 and it has been shown there that after 70 mg/L of alum dose the removal efficiency of humic acid in prepared feed water has started decreasing with decreased pH after coagulation causing acidification of effluent. Figure 4.3 and 4.4 are the microscopic images of flocs at optimum dose, recorded by optical microscope through micro-eye software utilizing 10X objective lens.

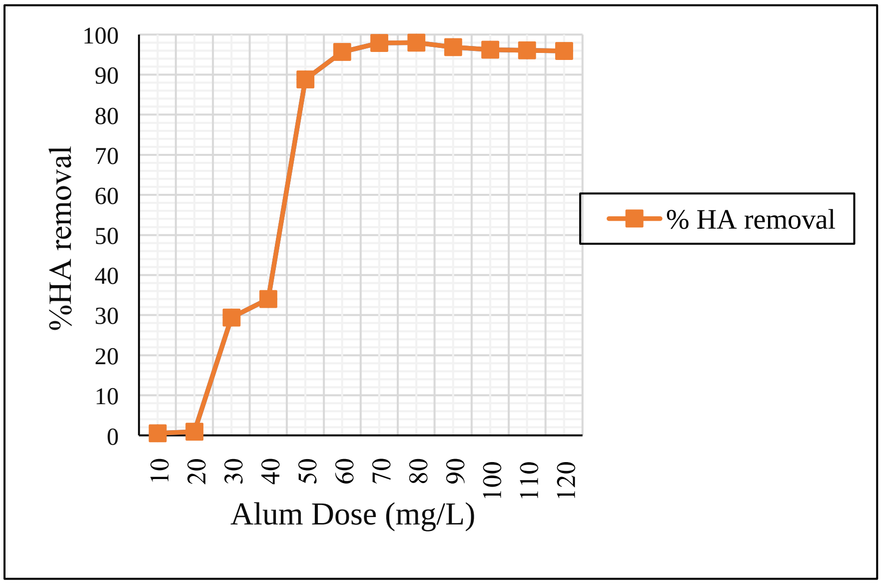


Figure 4.2: Trend for alum dose optimization for SFW-1

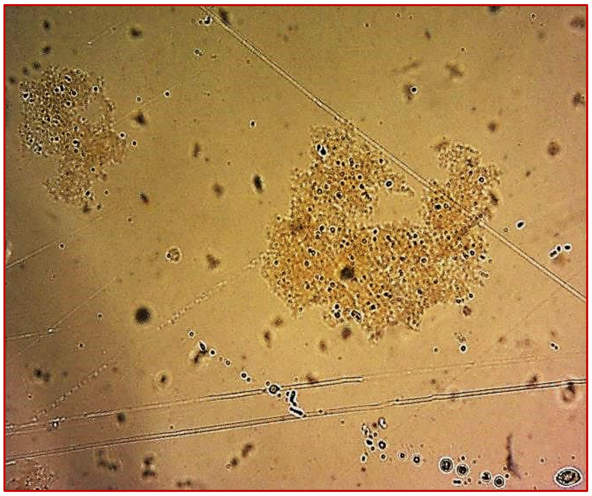


Figure 4.3: Floc before settling (Direct)

Figure 4.4: Floc after settling (supernatant)

Table 4.2 demonstrates the optimum dose for treating SFW-2. Same steps were followed for determination of optimum coagulant dose like in SFW-1, but the pH of SFW-2 was adjusted to 7.5 ± 0.5 for the optimal growth of E.coli and attainment of its maximum removal in the presence of humic acid. Coagulant dose tested was from 10 to 90 mg/L.

Table 4.2: Dose optimization for SFW-2

Alum dose (mg\L)	**E-coli % removal efficiency**	**HA% removal efficiency**	**pH**	
			Initial	**Final (Avg)**
10	7.14	16.7	7.5±0.5	6.92± 0.06
20	26.47	62.5		6.29±0.10
30	10.36	86.6		6.18±0.14
40	42.85	93.7		6.05±0.12
50	47.20	97.8		5.86±0.04
60	50.138	98.15		5.71±0.05
70	47.89	98.42		5.49±0.14
80	49.03	99.63		5.09±0.06
90	47.9	99.71		4.93±0.10

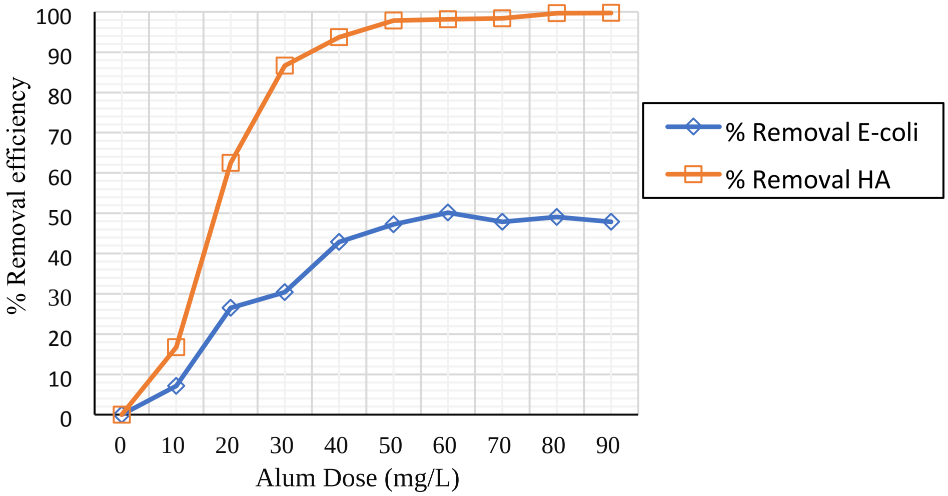


Figure 4.5: Trend of Alum dose optimization for SFW-2

Trend for alum dose optimization in SFW-2 has been demonstrated in figure 4.5 and it has been revealed there that after 60 mg/L of alum dose the removal efficiency of humic acid as well as *E.coli* in prepared feed water has started decreasing with reduced pH after coagulation causing acidification of effluent. Figure 4.6 and figure 4.7 are the microscopic images of flocs at optimum dose, taken by optical microscope through micro-eye software utilizing 10X objective lens.

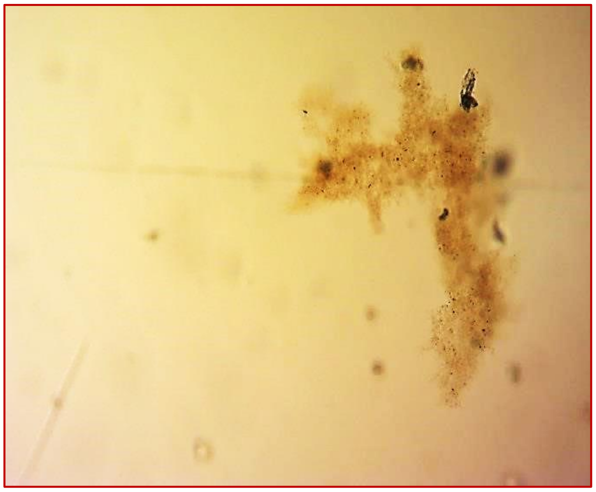


Figure 4.6: Floc before settling (Direct)

Figure 4.7: Floc after settling (Supernatant)

As it's already mentioned that humic substances including humic acid shows negative charge in the spectrum of pH values. Maximum removal of humic acid is found to occur at acidic to neutral pH values in the range of 4–7.5, depending on coagulant/humic ratio. Many studies set this range as an efficacious pH by using ferric and aluminium coagulants. Because in this range the leading coagulation mechanism is charge neutralization amongst positively charged ferric or aluminium hydroxopolymers and ionized phenolic and carboxylic groups in humic substances. Beyond this range of pH, coagulation mechanism is mainly dominated by adsorption of humic substances to ferric or aluminium precipitate but this does not produce satisfactory DOC removal (Bernhardt *et al.*, 1985; Stumm & Morgan 1996; Newcombe *et al.*, 1997; Cheng 2002; Duan *et al.*, 2003; Liu *et al.*, 2009; Pivokonsky *et al.*, 2015; Naceradska *et al.*, 2019). That is why we can see that for SFW-1 pH was adjusted to 10.25 causes maximum removal of humic acid (20mg/L) at 70mg/L of alum dose that was 97.15. And for SFW-2 pH was adjusted to 7.5 and maximum removal of humic acid along with *E.coli* inclusion optimum dose of alum was 60 mg/L that was 98.15 for humic acid removal and 50.13 for *E.coli* removal efficiency. Similar trend has been shown by Sha'arani *et al.*, 2019 by giving comparison of alum with diatomite performance for removal efficiency of gram-positive and gram-negative bacteria i.e., *Staphylococcus* sp. and *E. coli* in clay suspension. Figure 4.8 represents the assessment of *E.coli* removal efficiency by CFU method

Figure 4.8: CFUs of *E.coli* on EMB by a range of alum doses

4.3- Phase-3: Optimized Mixing conditions for SFWs in terms of floc size

As demonstrated earlier in experimental scheme that High, medium and Low Gt_{mix} conditions has been employed for studying floc properties. At all three conditions the floc size has been analyzed directly right after flocculation without giving any time for settling (Gt_{mix}-D) and after 30 minutes of settling as well (Gt_{mix}-S) as demonstrated in table 4.3 for SFW-1 and table 4.4 for SFW-2. Low velocity gradient taken in this study was 18.57 s^{-1} for 900 s for SFW-1. Average floc size at this condition was 371.0 ± 43.0μm without settling and 135.6 ± 26.9 μm after 30 minutes of settling. For SFW-2 average floc size at low Gt_{mix} condition was 412.3±20.7 μm before settling and 153.09±47.2 μm after 30 minutes of settling. After that the value of velocity gradient has been increased along with time to upsurge the treatment efficiency. G value 53.3 s^{-1} has been provided for 1080 s for treating both SFWs, called it as medium Gt_{mix} condition.

Table 4.3: Floc size and at optimized mixing conditions (SFW-1)

Experimental Code	**Pre-treatment Step 1 → Coagulation**			**Pre-treatment Step 2 → Flocculation**			**Pretreatment Step 3 → Settling (min)**	**Floc size (μm)**
	Gt_{mix}	**Dose (mg/L)**	**pH**	**G (s^{-1})**	**t (s)**	**Gt_{mix}**		
High Gt_{mix} →D	16440	70	10.25± 0.5	98.05	1200	117660	0	162.5±14.8
High Gt_{mix} → S							30	42.2±11.3
Medium Gt_{mix} →D				53.3	1080	57564	0	395.1±44.8
Medium Gt_{mix} →S							30	155.9±29.6
Low Gt_{mix} →D				18.57	900	16713	0	371±43.0
Low Gt_{mix} →S							30	135.6±26.9

Floc size eventually increased in both SFWs. In SFW-1 the average floc size was 395.1 ± 44.8 µm before settling and 155.9 ± 29.6 µm after settling. In SFW-2 floc size was 498.2±29.7 µm before settling and 140.75± 23.8 µm after settling.

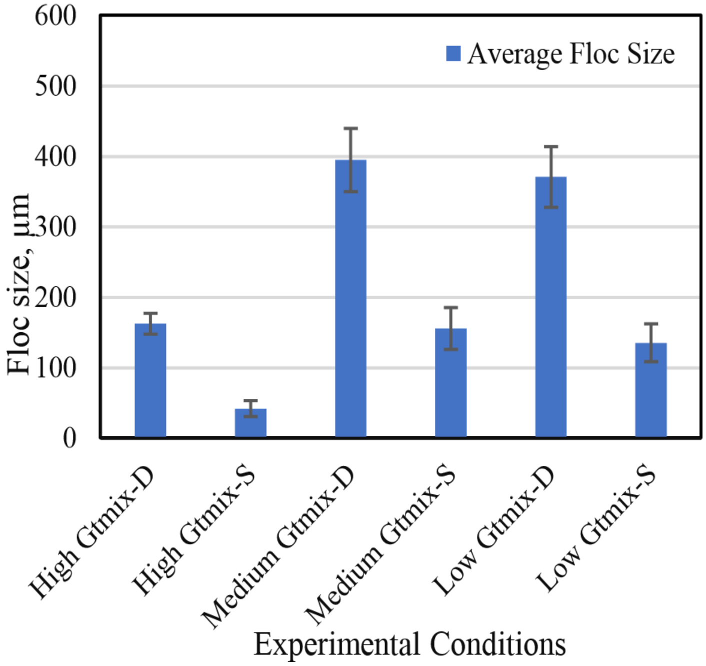


Figure 4.9: Average floc size at varied G (SFW-1)

After experimentation on medium Gt_{mix} condition the velocity gradient has been further increased to 98.05 s^{-1} for 1200 s. but at this condition floc sizes were not increased by increasing velocity gradient in fact, at this condition floc breakage has been occur and floc size has been reduced drastically. As figure 4.9 demonstrated that for SFW-1 Average floc size at high Gt_{mix} condition before settling was 162.5 ± 14.8 µm and after settling average floc size was 42.24 ± 11.3 µm.

Table 4.4: Floc size at optimized mixing conditions (SFW-2)

Experimental Code	**Pre-treatment Step 1 → Coagulation**			**Pre-treatment Step 2 → Flocculation**			**Pretreatment Step 3 → Settling (min)**	**Floc size (µm)**
	Gt$_{mix}$	**Dose (mg/L)**	**pH**	**G (s^{-1})**	**t (s)**	**Gt$_{mix}$**		
High Gt$_{mix}$ →D	16440	70	10.25 ± 0.5	98.05	1200	117660	0	196.6±25.6
High Gt$_{mix}$ → S							30	58.8±8.19
Medium Gt$_{mix}$ →D				53.3	1080	57564	0	498.2±29.7
Medium Gt$_{mix}$ →S							30	140.7±23.8
Low Gt$_{mix}$ →D				18.57	900	16713	0	412.3±20.7
Low Gt$_{mix}$ →S							30	153.0±47.2

In SFW-2 average floc size before settling was 196.65 ± 25.6 µm and after settling average floc size was 58.8 ± 8.19 µm. Hence it can be assessed that medium Gt_{mix} conditions giving maximum size of flocs in term of both before and after 30 min of settling while in low Gt_{mix} conditions floc sizes are also rational while in high Gt_{mix} conditions, due to floc breakage floc size has been decreased.

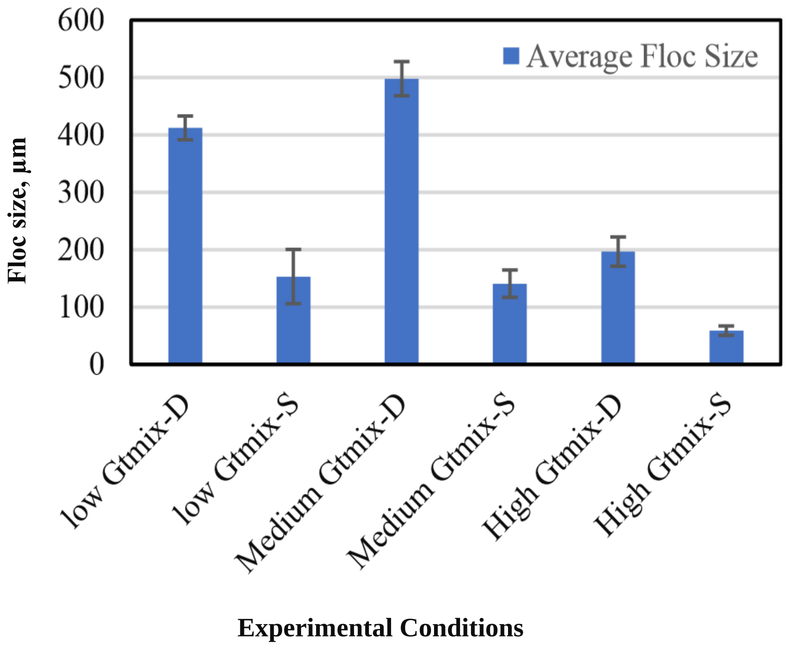


Figure 4.10: Average floc size at varied G (SFW-2)

The floc size of SFW-2 is overall higher than SFW-1, as it is already mentioned that alum works best in neutral to acidic pH. The results are consistent with the trend showed by study of Shihab & Hamad., 2018. They treated samples of surface water with alum as a coagulant with velocity gradient range from 30 s^{-1} to 60 s^{-1} and it has been demonstrated that efficiency of water treatment was highest at 60s^{-1}. Moruzzi & Silva, 2018 conducted a study regarding floc breakage and reversibility by preparing humic acid synthetic feed water with alum as a coagulant and applied velocity gradient ranged between 20s^{-1} to 120s^{-1}. It has been presented by authors that diameter of flocs starts decreasing by applying very high velocity and after breakage sizes of flocs wide ranging from 157 to 132 µm. At 100s^{-1} stable dimeter or values during the steady state of flocculation was 156± 08 µm and after breakage it was 141± 07 µm, that were fragile with loosely bound structure. Hence not only optimization of mixing speed is very important, but breakage of previously formed aggregates should be avoided as much as possible.

4.4- Phase-3: Optimized Mixing conditions for SFWs in terms of D_f

Second property that has been studied in this study is D_f for the determination of compactness of flocs. Compactness is very important characteristic of flocs. If flocs are not compact, they can easily breakdown by the turbulence of high shear during the transfer from one system to the other or by localized vortices. Porous flocs will not be settling down easily during process of sedimentation. hence quantification of compactness of flocs are very important to optimize them for better removal. D_f can be estimated by 2D or 3D method. In this study D_f has been analyzed by 2D fractal box counting method.

Table 4.5: Fractal dimensions of flocs at varied Gt*mix* (SFW-1)

Experimental Code	**Pre-treatment Step 1 → Coagulation**			**Pre-treatment Step 2 → Flocculation**			**Pretreatment Step3 → Settling (min)**	**D*f***
	Gt*mix* (s-1)	**Dosage (mg/L)**	**pH**	**G**	**t (s)**	**Gtmix**		
High Gt_{mix} →D	16440	70	10.25 ± 0.5	98.05	1200	117660	0	1.82±0.06
High Gt_{mix} → S							30	1.60±0.05
Medium Gt_{mix} →D				53.3	1080	57564	0	2.64±0.04
Medium Gt_{mix} → S							30	2.35±0.07
Low Gt_{mix} → D				18.57	900	16713	0	2.54±0.07
Low Gt_{mix} → S							30	2.31±0.02

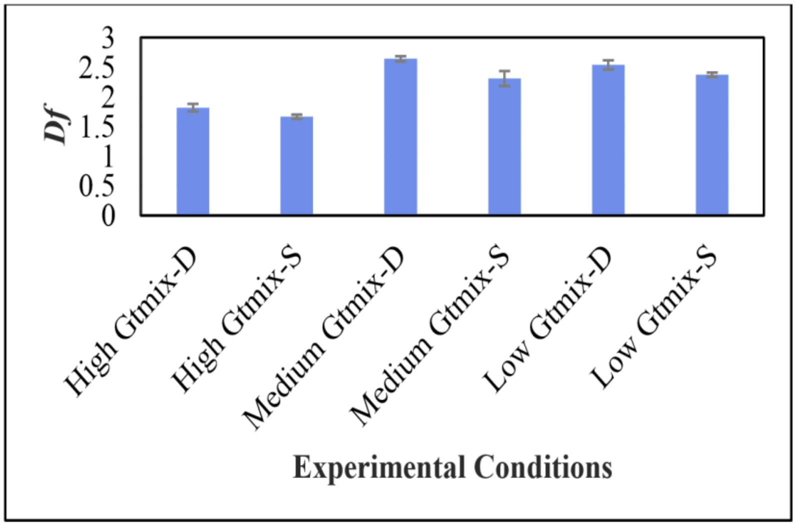


Figure 4.11: Trend of fractal dimension for SFW-1

It has been demonstrated by figure 4.11 that for SFW-1 D_f at low Gt_{mix}-D was 2.5 and after 30 min of settling it was 2.3 at medium Gt_{mix}-D it was 2.6 and at medium Gt_{mix}-S it was 2.3 at high Gt_{mix} conditions it was 1.82 before settling and 1.6 after settling. For SFW-2 (figure 4.12) D_f at low Gt_{mix}-D was 2.6, after settling it was 2.3. At medium Gt_{mix}-D it was 2.7 and after settling it was 2.3. At high Gt_{mix} it was 1.8 before settling and 1.6 after settling.

Table 4.6: Fractal dimensions of flocs at varied Gtmix (SFW-2)

Experimental Code	**Pre-treatment Step 1 → Coagulation**			**Pre-treatment Step 2 → Flocculation**			**Pretreatment Step3 → Settling (min)**	**D*f***
	Gtmix (s-1)	**Dosage mg/L**	**pH**	**G**	**T (s)**	**Gtmix**		
High Gt_{mix} →D	16440	60	7.5 ± 0.5	98.05	1200	117660	0	1.83±0.01
High Gt_{mix} → S							30	1.64±0.04
Medium Gt_{mix} →D				53.3	1080	57564	0	2.70±0.05
Medium Gt_{mix} → S							30	2.35±0.02
Low Gt_{mix} → D				18.57	900	16713	0	2.66±0.05
Low Gt_{mix} →S							30	2.31±0.04

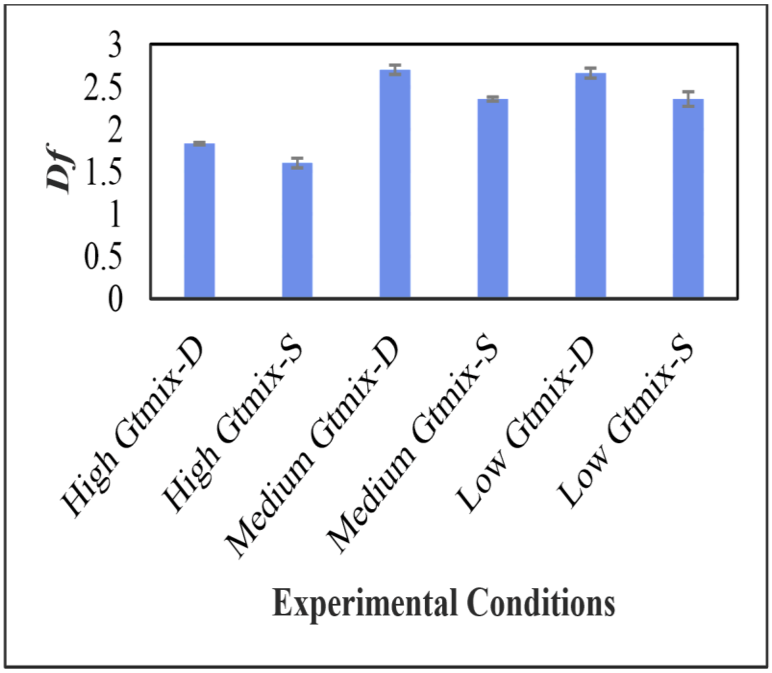


Figure 4.12: Trend of fractal dimension for SFW-2

It has been formulated from above results that medium Gt_{mix} conditions i.e., 57564 is best for application. Because D_f values at low and medium Gt_{mix} conditions were under domination of RLA D_f, giving them higher strength to settle down in less time while at high Gt_{mix} conditions in both SFWs values lies under domination of DLA D_f, making them fragile and suspended requiring higher period of time for settling. However, fractal dimensions of SFW-2 were higher than SFW1. Similar trend has been showed by Moruzzi *et al.*, 2017 that value of D_f has been increase by increasing the time of flocculation at certain limit. Applied velocity gradient in their study was 20 and 60 s^{-1} and flocculation times of 2, 3, 4, 5, 10, 20, 30, 60, 120, and 180 min, giving D_f range from 1.1 to 1.8 in prepared kaolin feed water. However, Many *et al.*, 2019 presented D_f of Rhône estuary water flocs that lies between ∼2.0–2.5. Amjad 2015 presented range of D_f from 2.12 to 2.73 of suspended humic acid flocs by processing images from confocal microscopy.

4.5-Comparison of flocs morphology for SFWs

It has been demonstrated by the figure 4.13 Floc size and fractal dimension is higher in SFW-2 in all Gt_{mix} conditions by providing optimum dose of alum with pH adjusted to 7.5±0.5 before coagulation. And it has been demonstrated that medium Gt_{mix} is suitable for application in both

SFWs. Floc characteristics are comparatively improved and lies under domination of reaction limited aggregation giving them higher strength to settle down in less time.

Table 4.7: Comparison of floc morphology in SFWs

Experimental Code	Floc Morphology SFW-1		Floc Morphology SFW-2	
	Size	Df	Size	Df
High Gt_{mix} →D	162.5±14.8	1.82±0.06	196.6±25.6	1.83±0.01
High Gt_{mix} →S	42.2±11.3	1.60±0.05	58.8±8.19	1.64±0.04
Medium Gt_{mix} →D	395.1±44.8	2.64±0.04	498.2±29.7	2.70±0.05
Medium Gt_{mix} →S	155.9±29.6	2.35±0.07	140.7±23.8	2.35±0.02
Low Gt_{mix} →D	371±43.0	2.54±0.07	412.3±20.7	2.66±0.05
Low Gt_{mix} →S	135.6±26.9	2.31±0.02	153.0±47.2	2.31±0.04

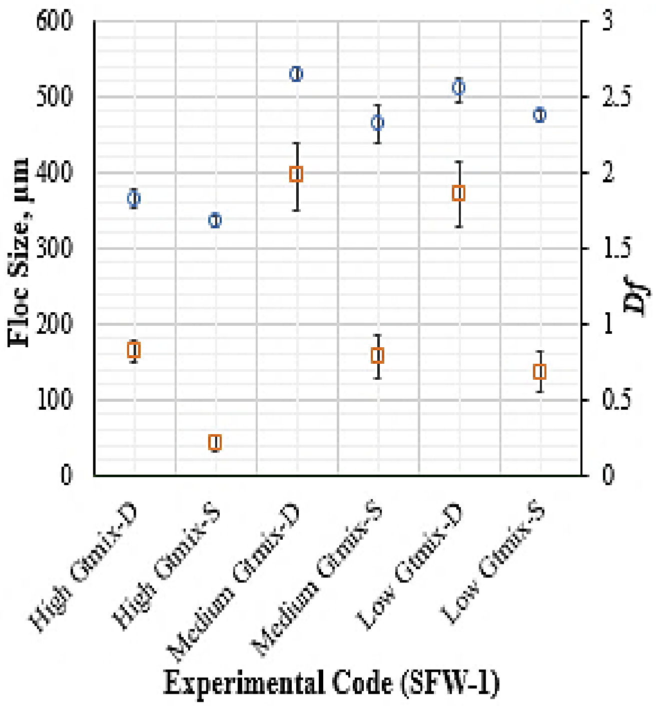


Figure 4.13: Comparison SFW-1

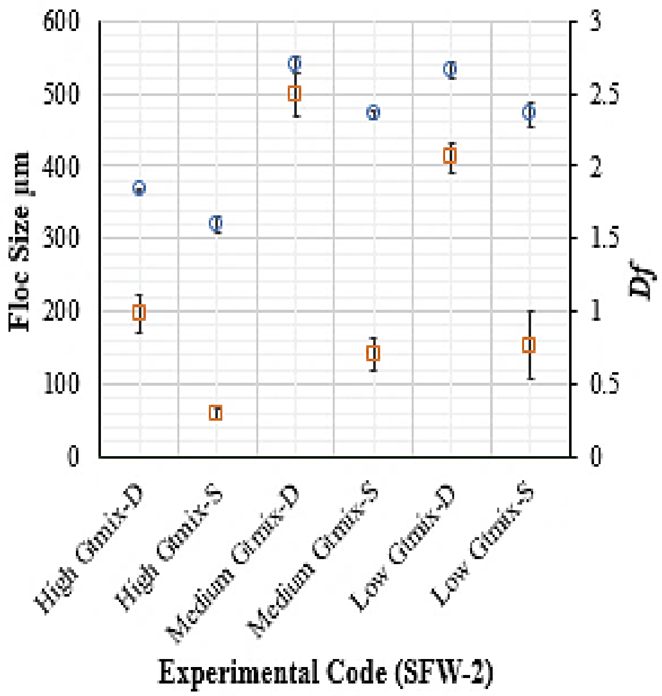


Figure4.14: Comparison SFW-2

This graph shows the comparison between floc morphology or characteristics at applied velocity gradients and it has been assessed that under certain mixing conditions fractal dimensions of flocs are increasing with increasing floc sizes. A broader range of floc size is found to map on to narrow range of fractal dimensions

Microscopic images of floc formation from 10X objective lens of optical microscope has been illustrated in Figure 4.15 for SFW-1 and Figure 4.16 for SFW-2. The images of flocs have been taken by supporting software Micro-eye.

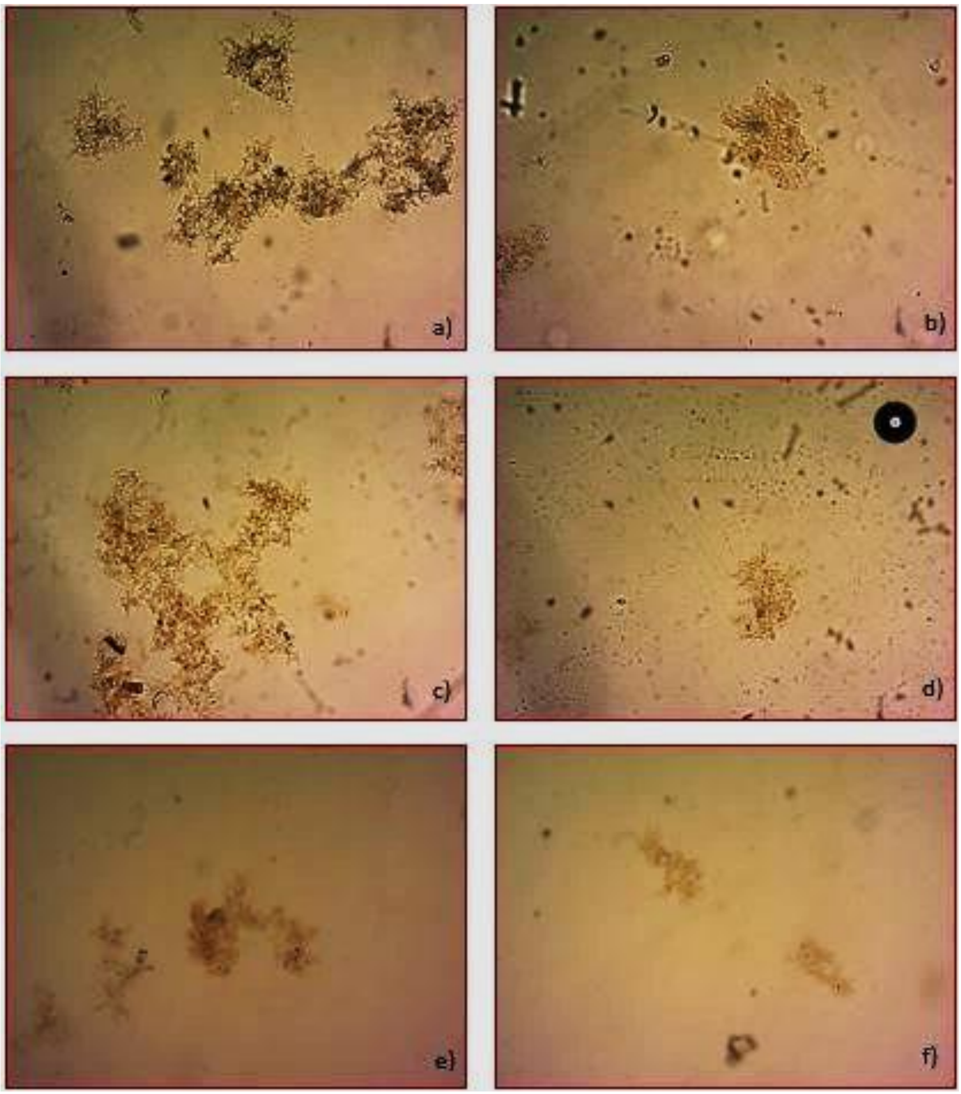


Figure 4.15: Microscopic images of flocs in SFW-1 (a)Low Gt_{mix}-D (b)Low Gt_{mix}-S (c)Medium Gt_{mix}-D (d)Medium G_{tmix}-S (e)High Gt_{mix}-D (f)High Gt_{mix}-S

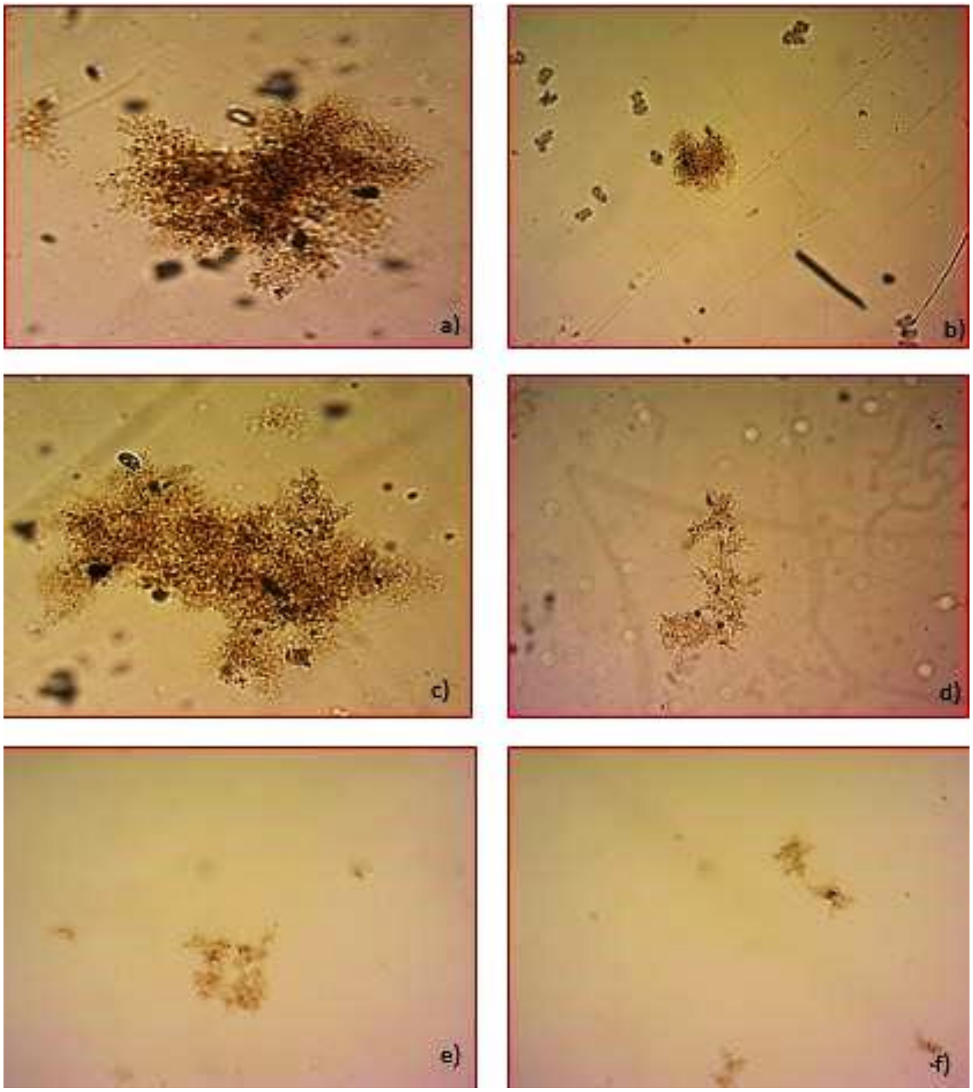


Figure 4.16: Microscopic images of flocs in SFW-2 (a)Low Gt_{mix}-D (b)Low Gt_{mix}-S (c)Medium Gt_{mix}-D (d)Medium Gt_{mix}-S (e)High Gt_{mix}-D (f)High Gt_{mix}-S

Chapter 5

Conclusions

It has been concluded from the above study that optimization of coagulant dose and optimization of velocity gradient in flocculation process is an important dynamic process that helps in improving floc structure for better settling manner. 70 mg/L of Alum dose for maximum removal of HA from SFW-1 is optimum at pH 10.25 before coagulation, while for SFW-2, 60 mg/L was an optimum dose for removing HA and *E.coli* at pH 7.5 before coagulation, because alum works best at neutral to acidic pH. Floc characteristics has been studied on three Gt_{mix} conditions i.e., high (117660), Medium (57564) and Low (16713). Medium Gt_{mix} condition i.e., 57564 before 30 min of settling give maximum floc size and D_f as compared to low and high Gt_{mix} condition in terms of both SFW-1 and SFW-2. In SFW-1 at medium Gt_{mix} condition average floc size was 395.1± 44.8 µm and D_f was 2.6 before settling. While in SFW-2 at medium Gt_{mix} average floc size was 498.2±29.7 µm with D_f of 2.7 giving very compact and strong flocs that can easily settle down without causing any hindrance to subsequent process of drinking water treatment.

Recommendations

1) It is recommended that compact and large flocs can be used as an adsorbent for further removal of organic matter.
2) Effect of velocity gradient on removal of emerging pollutants is also very crucial to study
3) In this study flocs prepared on different velocity gradient can be further studied for their filterability

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