UTILIZATION OF AQUEOUS TWO PHASE SYSTEM FOR THE REMOVAL OF COLOUR FROM TEXTILE WASTEWATER

By

SAMUEL BILLY MAMZA

DEPARTMENT OF CHEMICAL ENGINEERING

AHMADU BELLO UNIVERSITY, ZARIA

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By

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DECLARATION

I declare that the work in this thesis entitled "Utilization of Aqueous Two Phase System for the Removal of Colour from Textile Wastewater" has been carried out by me in the Department of Chemical Engineering, Ahmadu Bello University, Zaria. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

MAMZA Samuel Billy _____ _____

Signature Date

CERTIFICATION

This thesis entitled "UTILIZATION OF AQUEOUS TWO PHASE SYSTEM FOR THE REMOVAL OF COLOUR FROM TEXTILE WASTEWATER" by Samuel Billy MAMZA meets the regulations governing the award of the degree of Master of Science in Chemical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Dr. S.M. Waziri Chairman, Supervisory Committee	_____ Signature	_____ Date
Dr. M.T. Isa Member, Supervisory Committee	_____ Signature	_____ Date
Dr. J.A. Muhammad Member, Supervisory Committee	_____ Signature	_____ Date
Dr. I.A. Mohammed-Dabo Head, Department of Chemical Engineering, A.B.U Zaria.	_____ Signature	_____ Date
Professor A. Z. Hassan Dean, School of Postgraduate Studies, A.B.U Zaria.	_____ Signature	_____ Date

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ABSTRACT

Colour removal from effluent textile wastewater will greatly improve the quality of water bodies, which is vital to environmental health and sustainability. This study is based on finding more efficient methods of treating the effluent of textile wastewater by removing colour as a contaminant. The effects of concentration of dye solution, tie line length and weight ratio on the effectiveness of aqueous two phase system were studied. Five different textile dye colours were simulated at concentrations of 500 mg/l and 250 mg/l, and the efficiency of decolourization using polyethylene glycol/ammonium sulphate (PEG/$(NH_4)_2SO_4$) and polyethylene glycol/sodium carbonate (PEG/Na_2CO_3), aqueous two phase systems (ATPS) as a separation technique was tested. The study showed that the best tie line length (TLL) of 52.51 % (w/w) and 55.50 % (w/w) for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS removed textile dye colours excellently within the range of 84.9 to 99.7 %. This operating condition was then used to remove colour from untreated effluent textile wastewater and result showed 99.1 % and 98.8 % of colours were removed using PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS respectively. Further analysis showed an improvement in pH, total dissolve solids, dissolved oxygen, Calcium, Sulphate, chemical oxygen demand and biological oxygen demand (BOD_5) of the treated water. All the parameters were found to meet National Environmental Standard and Regulations Enforcement Agency (NESREA, 2009) effluent limit discharge requirements.

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LIST OF ABBREVIATIONS

ATPS	Aqueous Two Phase System
TWW	Textile Wastewater
PEG	Polyethylene Glycol
$(NH_4)_2S0_4$	Ammonium Sulphate
Na_2CO_3	Sodium Carbonate
BOD_5	Biological Oxygen Demand
COD	Chemical Oxygen Demand
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
NESREA	National Environmental Standards and Regulations Enforcement Agency
SS	Suspended Solids
DO	Dissolved Oxygen
Conc.	Concentration (mg/l)
APHA	American Public Health Association
TLL	Tie-Line Length
STL	Slope of the Tie-Line
WR	Weight Ratio
AMTC	Africa Manufacturing Textile Company

CHAPTER ONE

INTRODUCTION

1.1 Preamble

Colour provides a vital enhancement to the entire world. Everyday materials used such as textile, paint, pharmaceutical, plastics, paper and foodstuffs are appealing if they are colourful. Colour can be described by the three properties: hue (the 'colour', for example blue or red), chroma (the intensity, brightness or dullness) and value (the amount or lightness or darkness). Colour in water and wastewater on the contrary is viewed as contaminants and unwanted properties (Szstarr, 2008).

Wastewater sources are categorized as industrial, domestic sewage, agricultural runoff and storm (urban) run-off. Sources of colour in industrial wastewater are metallic ions, suspensions of colloidal and oily substance, fats and lubricants (Eckenfelder, 1970). The colour of industrial wastewater is often a significant characteristic especially in the food, pharmaceutical, tanning, paper, rubber, plastics, cosmetics, leather and textile industries (Shiri *et al,*. 2012).

Textile industry use a lot of chemicals and dyes throughout the production process. Thus making the textile industry the most complicated one among manufacturing industries (Paul and Dhas, 2008). Two per cent of dyes produced are discharged directly in aqueous effluent and ten percent are subsequently lost during the textile coloration process (Robinson and Grand, 2001).

In textile wastewater (TWW), about 53 % of dyes identified are non-biodegradable (Al-Kdasi *et al.,* 2005), making conventional treatment to lose relevance in achieving desired results especially with more stringent standards required by environmental

protection agencies. Advanced treatment of colour removal such as chemical coagulation may be used as pre-treatment in order to enhance the biodegradability of wastewater during the conventional treatments (Rahbar et al., 2006).

As a result of these challenges, new methods of treating colour in industrial wastewater are being developed and applied. Amongst which are oxidation, adsorption, membrane technologies, ozonation, photo catalysis using bacterial cell, anaerobic digestions and aqueous two phase system (ATPS).

ATPS has been an attractive technique for recovery of biological materials over other methods. It constitutes gentle environmental condition containing high water content in both liquid phases up to 70 - 90 %, interfacial tension between the two phases is extremely low resulting in high mass transfer (Albertsson, 1986). This technique has stabilizing effects with many polymers, it is hoped that it will be beneficial in removing colour in effluent textile wastewater (TWW), considering the fact that it is straightforward and requires relatively simple equipment that are easy to operate. Also, conditions for separation on a large scale do not considerably change from small scale, thus it is easy to scale-up and very reliable (Ratanapongleka, 2010).

1.2 Problem Statement

Textile industries are facing serious and continuous challenge in meeting standard effluent discharge requirements, due to the molecular size of dyes and non–biodegradability nature of effluent produced from the conventional treatment methods. Although, these methods are cheaper but not efficient or reliable. Thus, there is a need to get more suitable methods in reducing these challenges to ensure the sustainability of the industry.

1.3 Aim and Objectives

The aim of this research is to remove colour from effluent textile wastewater.

The specific objectives are:

i. To prepare ATPS from (PEG)/$(NH_4)_2SO_4$ and PEG/Na_2CO_3.
ii. To generate phase diagram data which can be used for this and further research work.
iii. To obtain the best composition, which can adequately utilize ATPS in treating colour in textile wastewater.
iv. To study the effectiveness of ATPS on improving water quality characteristics – Colour, BOD_5, COD, TDS, DO, pH and heavy metals.

1.4 Scope of Research

The scope of this study is limited to:

i. Preparing ATPS from PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 and utilizing it to remove colour in effluent textile wastewater.
ii. Characterizing the quality of the untreated effluent textile wastewater and treated textile wastewater.
iii. Evaluating the effectiveness of ATPS as a textile wastewater treatment method.

1.5 Justification of Research

The following validates the quintessence of this research work

i. Coloured dyes and chemicals found in effluent textile wastewater which are mostly non-biodegradable pose serious environmental and health problems.
ii. Aqueous two phase system as a separation technique is straightforward and requires relatively simple equipment and relatively a cheap physical separation method.
iii. Aqueous two phase system involves only two unit operations, equilibration and separation processes, which are easy to operate and to scale-up.

CHAPTER TWO

LITREATURE REVIEW

2.1 Overview of Textile Wastewater

Textile wastewater (TWW) is characterized by high content of dyestuff, salts, high Chemical Oxygen Demand (COD) derived from additives, suspended solid (SS) and fluctuating pH. About 100,000 commercial dyes exist with annual production rate of 700,000 tonnes/year (McMillan et al, 2007) and a global textile market of US $600 Billion by 2014 (McMillan et al, 2007). The quantity of effluent TWW generated by a textile factory is estimated to be between 3800 – 7600 cubic metres per day (Dos et al, 2007), about 80 % of chemicals and 50 % of dyes are discharged in the effluent (Trovaslet *et al,* 2007). The effluents from textile industry are sometimes partially treated before being discharged into a larger water body (Punmia and Jain, 1998).

2.2 Characteristics of Textile Wastewater

Typical characteristics of textile effluent wastewater across textile industries in the world are presented in Table 2.1. The data show a large extent of variation from plant-to-plant and sample-to-sample (Al-Kdasi *et al.,* 2005).

Table 2.1: Composite textile industry wastewater characteristics

Parameters	Values
pH	7.0 – 9.0
Biochemical Oxygen Demand (mg/l)	80 – 6,000
Chemical Oxygen Demand (mg/l)	150 – 12,000
Total Suspended Solids (mg/l)	15 – 8,000
Total Dissolved Solids (mg/l)	2,900 – 3,100
Chloride (mg/l)	1,000 – 1,600
Total Kjeldahl Nitrogen (mg/l)	70 – 80
Colour (Pt-Co)	50 – 2,500

(Source:Al-kdasi *et al.* 2005)

2.2.1 Biological Oxygen Demand (BOD5)

The standard 5 - day BOD_5 test is the most commonly used method to estimate the total quantity of biodegradable organic material in TWW. The results of the 5 - day BOD_5 test are considered to be estimates of the amount of oxygen that would be consumed by microorganisms in the process of using the organic materials contained in a TWW for food, growth and energy. Some of the organic material will thus be converted to additional microorganisms. Some will be converted to carbon dioxide and some to water; oxygen is needed for all three purposes (Woodard, 2001).

2.2.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is the second method of estimating how much oxygen would be depleted from a body of receiving TWW as a result of bacterial action. COD test uses a strong chemical oxidizing agent, potassium dichromate or potassium permanganate, to chemically oxidize the organic material in the sample of wastewater under conditions of heat and strong acid. The COD test has the advantage of not being subject to interference from toxic materials as well as requiring only 2 or 3 hours for test completion, as opposed to 5 days for the BOD_5 test. It has the disadvantage of being completely artificial, but is nevertheless considered to yield a result that may be used as the basis on which to calculate a reasonably accurate and reproducible estimate of the oxygen-demanding properties of a wastewater. The COD test is often used in conjunction with the BOD_5 test to estimate the amount of non-biodegradable organic material in a wastewater. In the case of biodegradable organics, the COD is normally in the range of 1.3 – 1.5 times the BOD_5. When the result of a COD test is more than twice that of the BOD test, there is good reason to suspect that a significant portion of the organic material in the sample is not biodegradable by ordinary microorganisms (Woodard, 2001).

2.2.3 pH, acidity, and alkalinity

The term pH refers to the concentration of hydrogen ions in an aqueous solution. The normal pH range is between 0 to 14, this equals the negative logarithm of the hydrogen ion concentration in moles per litre. TWW that is highly acidic or alkaline is said to be highly buffered and will not readily change in pH value as a result of influences such as bacterial action or chemical reaction.

2.2.4 Dissolved Oxygen (DO)

Dissolved Oxygen (D.O) concentration is usually determined by either a wet chemistry method known as the azide modification of the Winkler method or by use of a probe and meter. The wet chemistry method is considered to be the standard for comparison, when the colour and other properties of the TWW do not preclude its use; however, the probe and meter method is the most commonly used because of its simplicity (Tchobanoglous *et al.*, 2004).

Oxygen is only sparingly soluble in water and its solubility decreases with increasing temperature. Increasing DO concentrations also decrease the solubility of oxygen. The saturation concentration of oxygen in de-ionized water at 1ºC and standard air pressure is 14.2 parts per million (ppm). Moreover, small differences in DO concentration in aerobic wastewater treatment systems, such as activated sludge, result in significant changes in the populations of different species of microorganisms (Al-Degs, 2000). These changes, in turn, change the settleability of the sludge, the clarity of the treated effluent and the overall performance of the treatment system.

2.2.5 Colour

Colour is measured using visual comparison to an arbitrary standard. The standard is normally made by dissolving potassium chloroplatinate (K_2PtCl_6) and cobalt chloride in

deionised water. The colour produced by 1 mg/l of potassium chloroplatinate is taken as one standard unit of colour. The cobalt chloride is used in very small amounts to tint the colour standard to match the test solution. The cobalt chloride does not affect the intensity of the colour of the standard (Allen, 1971).

"APHA" stands for American Public Health Association Colour Scale, the organization responsible for the original definition and implementation of this visual colour scale as a standard method for rating water quality. It is also called "Pt-Co" for Platinum-Cobalt, another name used for this same colour scale is "Hazen", named after Allen Hazen, the chemist who first defined the colour scale for the American Public Health Association. "APHA", "Pt-Co" and "Hazen" are three names for the same colour scale (Szstarr, 2008).

Dyes possess colour because they absorb light in the visible spectrum (400–700 nm), have at least one chromophore, a conjugated system, and exhibit resonance of electrons, which is a stabilizing force in organic compounds (Abrahart, 1977). When any one of these features is lacking from the molecular structure, the colour is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (colour helpers), examples of which are carboxylic acid, sulphuric acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility (Santhy and Selvapathy, 2006). All these chemical can affect the final colour and other parameters in an effluent TWW.

2.2.6 Total Dissolved Solids (TDS)

Substances can exist in aqueous solution in either the dissolved or the un-dissolved state. The residue that is left after evaporating a sample of water at 103^{o} C is referred to

as the TDS value of that sample. It is generally regarded as everything that was in the sample that was not water; however, any of the substances originally present, organic or inorganic that volatilized at 103^{o}C or less will not be in the residue (Allen, 1971).

2.2.7 Total Suspended Solids (TSS)

Solids that will not pass through a 0.45 micron filter are referred to as total suspended solids (TSS). The standard method for measuring TSS involves shaking the sample thoroughly before filtering, the TSS actually includes all undissolved solids as opposed to the dissolved solids that will not settle under the influence of gravity (Allen, 1971).

2.2.8 Settleable Solids

Settleable solids are undissolved solids that settle to the bottom of a container under the influence of gravity. The standard device for measuring settleable solids is the Imhoff cone. The standard test for settleable solids involves shaking a sample thoroughly, filling the 1-litre Imhoff cone to the full mark, and allowing the sample to settle for 1 hour under quiescent conditions. Settleable solids is reported as millilitres of settleable materials per litre of sample (ml/l). In order to obtain a value of the weight of settleable material, it would be necessary to remove the supernatant and to evaporate to dryness that volume of sample that contained the settleable solids. The result will include the dissolved solids contained in the liquid remaining with the settled solids. If this volume is small compared to the total (1-litre) sample, the error will be small (Tchobanoglous *et al.*, 2004).

2.2.9 Heavy metals

Heavy metals are those elements with larger atomic density than 5 g/cm^3 (Chunrong, 1999). Commonly said heavy metals are those metals in the periodic table with an atomic number greater than 20, excluding the alkali metals. This is due to the similarity

of their chemical properties and environmental behavior. Many of them are trace metals in the earth crust and most of them are toxic even in very low concentrations (Mahimaraja, 1996 and Chunrong, 1999). Heavy metals tend to accumulate in soil mainly by adsorption mechanisms (Aucejo *et al.*, 1996). Heavy metals are not only toxic for plants, they are also toxic for human beings. For human beings some heavy metals are essential for growth, such as zinc. They are all toxic if larger amounts are ingested or inhaled. The main issue with heavy metals are the bioaccumulation due to long residence times. The residence time of cadmium in the soil has a range of 75 – 380 years. Lead and zinc have residence times of 1000 – 3000 years. However, half-life for cadmium is 15 – 1100 years and 740 – 5900 years for lead. Even though the ranges are wide in different soil conditions it is clear that heavy metal pollution is a very long-term matter (Alloway, 1995).

Cadmium (Cd) is a natural element in the earth's crust. It is found as a mineral combined with other elements such as oxygen, chlorine or sulphur. All soils and rocks, including coal and mineral fertilizers, contain a very small amount of cadmium. Thus if a higher concentration is found, the soil is probably contaminated (Alloway, 1995). Cadmium when compared to other heavy metals, dissolved easy in nature. It is used in batteries, pigments, metal coatings and plastics. Cadmium has no essential biological function. It is not biodegradable, but can easily change form in the environment. Cadmium stays in the human body a very long time and the amounts could be built up from many years of exposure to low levels. Cadmium is highly toxic to plants and animals. Breathing high levels of cadmium severely damages the lungs and can cause death, especially after long-term exposure. Ingestion of cadmium can cause weak bones and kidney diseases. Animals given cadmium in food or water were found to have high blood pressure, iron - poor blood, liver disease and nerve or brain damage.

Chromium (Cr) is an element found in rocks, animals, plants and soil. In the environment it occurs in different forms that are pH dependent. The most common form is chromium (III), which is an essential nutrient helping the body to consume sugar, protein and fat. Chromium is used for chrome plating, colour, pigments, leather tanning and wood preserving. Chromium enters the air, water and soil mostly in the chromium (III) and chromium (VI) forms. Chromium is strongly attached to the soil, so only small amounts can dissolve into water and therefore it does not enter the groundwater in large amounts (Alloway, 1995).

Iron (Fe) is defined as an essential micronutrient due to involvement in the formation of chlorophyll. It is found in the earth's crust, often in combination with other chemical elements. Some iron compounds are considered to be soluble in the whole pH range, ferric and ferrous humates. The availability of iron is always increasing with decreasing pH (Sauchelli, 1969). Iron is an essential nutrient, which is involved in the oxygen transport inside human beings. Many enzymes throughout the body contain iron. The red blood cell contains hemoglobin, partly made from iron, which is a part and parcel of myoglobin, a special protein that helps the muscle tissue to store oxygen and also give muscles the red colour. The enzymes that are involved in energy production include iron. Proper functioning of the immune system relies, in part, on sufficient amounts of iron (Tchobanoglous *et al.*, 2004).

Lead (Pb) naturally occurs in small amounts in the earth's crust. Lead can be found in all parts of our environment. Lead itself does not break down, but lead compounds are changed by sunlight, air and water. Once lead reaches the soil, it usually sticks to soil particles. Movement of lead from soil into groundwater will depend on the type of lead compound and the characteristics of the soil. Due to low solubility it tends to

accumulate and influence the microbial activities and thereby reduce the soil productivity (Alloway, 1995).

Lead can have an effect on almost every organ and system in the body. The most sensitive system is the central nervous system, particularly for children. Lead could also cause problems with the kidneys. At high levels lead may, decrease reaction time, cause weakness in fingers, wrists or ankles and possibly affect the memory. Lead may also cause anemia and problems with the blood. It can also damage the male reproductive system. There is not enough evidence to clearly determine the carcinogenicity to people. Even low levels of exposure to lead can affect a child's mental and physical growth.

Zinc (Zn) is essential for maintaining good health. If zinc levels are too low it will cause loss of appetite, skin lesion, sexual immaturity, depression, and affect taste (Alloway, 1995). Zinc compounds are widely used in industry to make paint, rubber, dyes and wood preservatives. Depending on the type of soil, some zinc compounds can move into the groundwater and into lakes, streams and rivers. The solubility of zinc in water is highly dependent on the compounds, for example zinc phosphate is insoluble, while zinc nitrate is very soluble (Sauchelli, 1969).

2.3 Convectional Wastewater Effluent Treatment Methods

Generally, it is rather difficult to treat effluent TWW because the industry produces multi-component wastewater. The dye contained in the effluent can vary daily and even hourly. The hot and strongly coloured wastewater contains high chemical oxygen demand concentration and greatly fluctuating pH which can be difficult to be treated. Generally the treatment options can be divided into three main categories namely biological, chemical and physical methods. Considerable amount of research has been

undertaken on the treatment of effluent TWW to decrease the impacts on the environment (Al-Kdasi *et al,*. 2005).

2.3.1 Biological method

Biological treatment of industrial wastewater is a process whereby organic substances are used as food by bacteria and other microorganisms. Almost any organic substance can be used as food by one or more species of bacteria, fungi, ciliates, rotifers or other microorganism. In being so used, complex organic molecules are systematically broken down or disassembled, then reassembled as new cell protoplasm. Oxygen is required in either the dissolved molecular form or in the form of anions such as sulphate and nitrate. The end result is a decrease in the quantity of organic pollutants, and an increase in the quantity of microorganisms, carbon dioxide, water, and other by-products of microbial metabolism (Tchobanoglous *et al.*, 2004).

There are many types of biological treatment methods. These include trickling filters, activated sludge process, anaerobic process, and oxidation pond. To date the commonest treatment of effluent TWW has been based mainly on aerobic biological process, consisting mainly conventional and extended activated sludge system. The trickling filters simulate stream flow by spraying wastewater over a broken, medium such as stone or plastic. The medium serves as a base for biological growth, which attacks the organic matter of wastewater, and uses it as food. In activated sludge process, the wastewater flows into a tank after primary settling. The microorganism in activated sludge is suspended in the wastewater as aggregates. The sludge and wastewater is kept in suspension by compressed air, which also supplies the oxygen, necessary for biological activities. The aerated waste is continuously withdrawn and settled and a portion of the sludge is returned to the influent (Tchobanoglous *et al.,* 2004).

Biological methods are generally cheap and simple to apply and are currently used to remove organic matter and colour from dyeing and textile wastewater. Most of existing process includes an initial step of activated sludge treatment to remove the organic matters, followed by oxidation, membrane and activated carbon (Tchobanoglous *et al.,* 2004). Anaerobic and aerobic treatments have been used together or separately for the treatment of textile effluents. Hence aerobic treatment is not effective in colour removal from textile wastewater containing azo dyes. Conventional biological process are not effective for treating dyestuff wastewater because many commercial dyestuff are toxic to organisms and result in the problems of sludge bulking, rising sludge and pin flock. Because of low biodegradability of many textiles chemicals and dyes, biological treatment is not always effective for effluent TWW (Pala and Tokat, 2003).

2.3.2 Chemical method

Chemical method includes coagulation or flocculation and oxidation. The main advantage of the conventional coagulation and flocculation is removal of the waste stream due to the removal of dye molecules from the dye-bath effluent and not due to partial decomposition of dyes which can lead to an even more potentially harmful and toxic aromatic compound. Physical and chemical treatment techniques are effective for colour removal but use more energy and chemicals than biological processes. They also concentrate the pollution into solid or liquid side streams requiring additional treatment before disposal. The major disadvantage is the production of sludge. In coagulation process large amount of sludge is created which may become a pollutant itself and increase the treatment cost (Paul and Dhas, 2008).

Chemical oxidation uses strong oxidizing agents such as hydrogen peroxides, chlorine and others to force degradation of resistant organic pollutant. Chemical oxidation is the most commonly used method of decolourization by chemical owing to its simplicity and

the main oxidizing agent is hydrogen peroxide. Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenol, pesticides and aromatic hydrocarbon. One of the major advantage of ozonation, is that it does not increase the volume of wastewater and sludge. A major disadvantage of this process is its short-half-life typically being 20 minutes (Paul and Dhas, 2008).

Chemical methods of wastewater treatment take advantage of two types of properties:

(1) The chemical characteristics of the pollutants, regarding their tendency to react with or interact with the treatment chemicals and

(2) The chemical characteristics of the products of reaction between pollutants and treatment chemicals, regarding their solubilities, volatilities, or other property that relates to the inability of the product to remain in water solution or suspension.

In general, five chemical processes can be used to remove substances from wastewater:

1. Reaction to produce an insoluble solid.
2. Reaction to produce an insoluble gas.
3. Reduction of surface charge to produce coagulation of a colloidal suspension.
4. Reaction to produce a biologically degradable substance from a non-biodegradable substance.
5. Oxidation or reduction to produce a non-objectionable substance or a substance that can be removed more easily by one of the previous methods.

2.3.3 Physical method

Physical method includes membrane filtration such as filtration, reverse osmosis and adsorption. Membrane filtration is an effective mean of removing pollutant from

wastewater, however the initial investment cost is very huge and the periodic replacement of membrane is remarkably high. Adsorption is an effective method of lowering the concentration of dissolved dyes in the effluent resulting in colour removal. Although the laws and regulations that require industrial wastewater treatment are constantly changing, the fundamental principles on which treatment technologies are based do not change (Tchobanoglous *et al.*, 2004).

The fundamental idea is that once the mechanisms by which individual pollutants become incorporated into a waste stream can be identified, analyzed and described; then the most efficient methodology of removal or treatment, will be very clear. Some of the principles to be observed for physical treatment of TWW based on the results of its analysis are:

i. All metals are sparingly soluble in water.
ii. Iron in the divalent state is highly soluble in water, whereas iron in the trivalent state is not.
iii. Iron can be converted from the divalent state to the trivalent state by passing air through the aqueous solution containing the dissolved iron. (The oxygen in the air oxidizes the ferrous (divalent) ion to ferric (trivalent) ion.)
iv. Because substances such as cadmium, zinc, and lead are so sparingly soluble, they adsorb to the surface of almost any solid particle in an aqueous environment (Arslan and Isil, 2002).

2.4 Aqueous Two Phase System

The preparation of aqueous two-phase systems (ATPS) is quite straightforward. Normally, it involves the preparation of the stock solutions of all the phase components, which are then mixed in appropriate amounts (by weight), and then the emulsion is

allowed to separate into two phases under gravity or in a centrifuge. After complete phase separation is achieved, the phases can be sampled (Albertsson and Tjerneld, 1994).

2.4.1 Basis of two-phase formation

Phase separation in solutions containing polymer mixtures is a very common phenomenon; in fact, miscibility of the polymer mixtures is an exception (Albertsson, 1986). Hydrophilic polymer pairs are incompatible in aqueous solutions yielding two coexisting phases in equilibrium with each other, with each of the phases containing predominantly water and one of the polymer types. It is worth noting that the association of unlike polymer species into a polymer-rich phase coexisting with a polymer-poor phase, referred to as complex coacervation can also occur.

The phase separation in polymer mixtures is attributed to the high molecular weight of the polymers combined with interaction between the segments of the polymers (Albertsson, 1986). The phenomenon has been treated theoretically by applying theories on the thermodynamic properties of polymers in solution. The driving force for the demixing process in polymer–polymer–solvent systems is the enthalpy associated with the interactions of the components, which is opposed by the loss in entropy associated with the segregation of the components during phase separation (Flory, 1953). Water as the solvent is able to engage in a number of non-covalent interactions with the polymer, which makes the quantitative description of the phenomenon quite complex. Because the interactions increase with the size of the molecules, the phase separation in the present systems occurs at very low polymer concentrations because of their large size and corresponding small loss in entropy upon demixing (Walter et al., 1985; Baskir *et al.,* 1989; Abbot ,1990).

The phase behaviour of aqueous polymer solutions is also influenced by the presence of salts, the effect depending on both their type and concentration. Often, a sufficiently high concentration of salt in a single polymer–water system can induce phase separation to yield a salt-rich, polymer-poor bottom phase that coexists with salt-poor, polymer-rich top phase (Albertsson, 1986; Walter *et al.,* 1985; Abbot, 1990). The contribution of the anion is more important than that of the cation in determining the effectiveness of a particular salt. The multivalent anions are most effective in inducing phase separation with polyethylene glycol.

2.4.2 A tool for bio-separations

Both polymer–polymer and polymer–salt aqueous two-phase systems (ATPS) have advantages over conventional extraction using organic solvents. Since the bulk of both phases consists of water, ATPS forms a gentle environment for biomaterials (Albertsson, 1986). The interfacial tension is extremely low, between 0.0001 and 0.1 dyne/cm compared with 1–20 dyne/cm for water organic solvent systems, creating a high interfacial contact area of the dispersed phases and thus an efficient mass transfer. Furthermore, the polymers are known to have a stabilizing influence on the particle structures and the biological activities (Albertsson, 1958).

It is over 50 years since the potential of both polymer–polymer and polymer – salt systems was first realized by a Swedish biochemist, P. A. Albertsson, for separations of cells, cell particles, and proteins (Albertsson, 1986). Separation could be achieved by a batch procedure or by counter-current distribution. Since then, ATPS has become a powerful tool for separation of a range of biomaterials, including plant and animal cells, microorganisms, fungi and their spores, virus, chloroplasts, mitochondria, membrane vesicles, proteins, and nucleic acids.

The basis of separation in a two-phase system is the selective distribution of substances between the two phases. Generally, small molecules are more evenly distributed between the phases; the partitioning of macromolecules is extremely variable, whereas that of particles is relatively one-sided. This distribution is governed by a number of parameters relating to the properties of the phase system and the substance, as well as the interactions between the two (Albertsson, 1958). The multiplicity of factors contributing to partitioning also makes the system very powerful, in contrast to the other established separation techniques, like centrifugation, electrophoresis, and others, allowing the fractionation of molecular or particulate species differing very slightly from each other. Thus, separation by partition in ATPS may often be used to substitute these other separation forms.

ATPS are easy to use, involving two unit operations; equilibration and phase separation (Hustedt and Kroner, 1985). Equilibration is rapid, involving mixing of the components that constitute the phase system with the material subjected to partitioning, and dispersing the phases to obtain equilibrium of phase compositions and partition. This is followed by separation of the liquid phases. The phase separation under gravity is not as rapid as in water-organic solvent systems, varying between a few minutes and a few hours because of a rather low difference in the densities of the two phases (about 0.05 – 0.15 g/cm^3) (Hustedt and Kroner, 1985), their viscosities, and the time required by the small droplets, formed during mixing, into larger droplets (Walter *et al.,* 1985). Centrifugation at low speed is commonly used to hasten the process.

2.4.3 Economy of ATPS

Cost of chemicals is the dominant factor for large-scale ATPS Process recovery. Hence, the use of inexpensive phase components and their recycling has been considered essential. This has favoured the choice of PEG/salt systems for industrial use; these

systems also have the advantage that the phases have a lower viscosity, thus needing a shorter time for phase separation (Ananthapadmanabhan, 1987). Processing of the PEG phase prior to recycling increases the cost. Different procedures to clean up the PEG phase have been developed. These include deproteinization, desalting by ultrafiltration, and extraction of PEG from the phase with an organic solvent followed by evaporation.

Salts, like phosphates or sulphate, also need to be recycled; otherwise, they increase the load on waste-water treatment. Salt recycling has been shown to be possible. However, it has not proved more economical than processes without salt recycling. This has motivated the use of salts that do not create waste-water treatment problems, e.g., citrate, which is easily degraded (Walter *et al.,* 1985) and ammonium carbamate, which is volatile. Efforts have also been put into replacement of the fractionated polymer by less expensive ones, such as crude dextran, starches, maltodextrins, as the bottom-phase component, which greatly reduces the processing cost (Rogers *et al.* 1998).

2.5 Mechanism of Partitioning

The ATPS can be formed by combining aqueous solutions of two incompatible polymers or from a mixing solution of polymer and salt above critical concentration. Two liquid layers are obtained at equilibrium. After adding solution to the system, mixing and phases settling, the partitioning of target product should be one side whereas the undesirable particles on the other. A general characteristic of phase forming and molecules partitioning between the phases is shown in Figure 2.1.

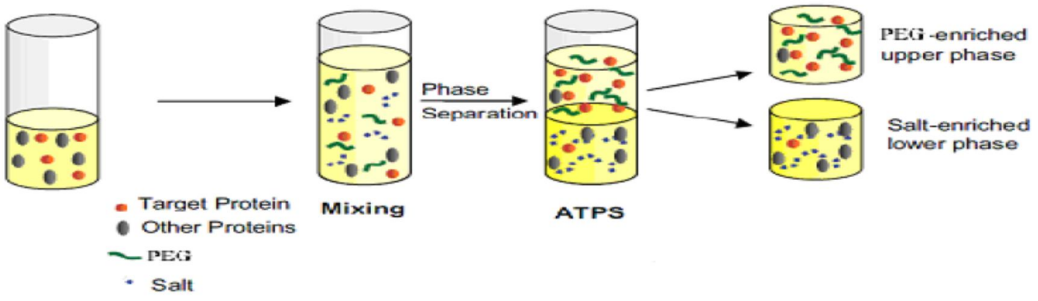


Figure 2.1: Schematic distribution of molecules in ATPS

The mechanisms that cause the uneven distribution of molecules are largely unknown. The partitioning behaviour of the molecule between the two phases is uncertain phenomena due to the involvement of many factors in the interactions between the molecules and phase-forming components such as hydrogen bond, charge interaction, van der Waals' force, hydrophobic interaction and steric effect (Albertsson 1986; Hachem et al, 1996). The net effect of these interactions is likely to be different in the two phases and therefore the molecules will partition into one phase where the energy is more favourable. The relationship between the partition coefficient (K) and ΔE at equilibrium can be expressed as:

—

Where ΔE (J) is the energy needed to move molecules from one side to the other, k is the Boltzmann constant and T (K) is the absolute temperature. ΔE depends on the size of the partitioned molecule.

The partition coefficient, K is also defined as the ratio of molecular concentration in the top phase (C_T) to that in the bottom phase (C_B) as shown in eq. (2.1). If the coefficient is higher than 1, the molecules prefer the top phase and if lower than 1 is in the bottom phase.

$$K = \frac{C_T}{C_B} \tag{2.2}$$

The partition coefficient has also been found empirically to depend on several factors, which act roughly independent. Therefore, the overall partition coefficient may be written as:

$$\ln K = \ln K_0 + \ln K_{el} + \ln K_{hfob} + \ln K_{biosp} + \ln K_{size} + \ln K_{conf} \tag{2.3}$$

where el, *hfob, biosp, size* and *conf* stand for electrochemical, hydrophobic, biospecific, size, and conformational contributions to the partitions coefficient respectively and ln K_0 includes other factors (Baskir et al, 1989). In addition to partition coefficient, other parameters (equations 2.4 to 2.7) (Ratanapongleka, 2010) are evaluated in order to understand the distribution behaviour of target molecules between the phases. Phase volume ratio (R_V) is defined as the ratio of volume in the top phase (V_T) to that in the bottom phase (V_B).

$$R_v = \frac{V_T}{V_B} \tag{2.4}$$

Yield recovery from top phase (R_T) and from bottom phase (R_B) are calculated in order to evaluate the purification ratio (PR) from aqueous two phase system, according to following equations:

$$R_T = \frac{100}{1 + \frac{1}{R_V K}} \tag{2.5}$$

$$R_B = \frac{100}{1 + R_V K} \tag{2.6}$$

$$PR = \frac{\mathrm{R_T}}{R_B} \tag{2.7}$$

2.5.1 Factors affecting molecular partitioning behaviour

The partitioning of molecules in ATPS depends on many variables such as type and concentration of polymers, the surface properties of particles and temperature. The role of these factors on partitioning behaviour are explained in the following subsections:

Polymer Molecular Weight

The molecular weight of phase polymers influences molecule partitioning both by altering the phase diagram and by changing the number of polymer-molecule interactions. In general, increasing the molecular weight of the phase polymers resulting in the distribution of molecule strongly towards the other phase as the repulsive interactions between the polymer and molecule become stronger. When the same molecules are added into phase system with different molecular weight of polymer, their partition coefficient decrease as molecular weight increase. The reason of this phenomenon is that an increase in molecular weight of polymer results in an increase in the chain length of the polymer and the exclusion effect, which lead to the reduction in the free volume. Thus, polymer acquires a more compact conformation with intra-molecular hydrophobic bonds and hindered the partition of molecule into the top phase (Mohamadi *et al*., 2007).

However, a very low molecular weight polymer is also unsuitable to be used in phase forming because the exclusion effect decreases with decreasing chain length and as a result the polymer can induce all the particles including undesired molecules to the polymer phase (Mohamadi et al., 2007). Therefore, the selection of the proper molecular weight of polymer is the key point in this technique. Furthermore, the differential partitioning of molecule may be influenced by the interfacial tension between the phases (Bamberger *et al*., 1984; Srinivas *et al.*, 2002). Decreasing the molecular weight of phase forming polymers also decreases interfacial tension (Wu *et al.*, 1996).

Polymer Concentration

In general, an increase in polymer concentrations relates to high density, refractive index and viscosity of the phase. Thus high concentration of polymer provides large difference in properties between the phases. In case of polymer-salt system, lower concentration of salt is required for ATPS preparation when using higher concentration of polymer. The role of molecular weight also concerns with concentration used in phase forming. The higher the molecular weight of the polymer, the lower the concentration required for phase separation. The viscosity of the phase is affected by the molecular weight of polymer. Since the viscosity of a polymer solution mainly depends on the concentration. High viscosity might impact further process. The viscosity of one phase might be decreased by employing a higher molecular weight of the polymer. The interfacial tension between the two phases of polymers system is very small in comparison to the interfacial tension between an aqueous phase and an organic solvent phase (Srinivas et al., 2002).

The interfacial tension is dependent on the polymer and salt composition. When the polymer concentration is increased, the composition of the phase system is removed from the critical point and the interfacial tension is increased (Walter and Johansson, 1994). As a result, the molecules will favour more to the top or bottom phase. For example Babu et al (2008) found that increasing the concentration of PEG 1500 from 12 to 18 % (w/w) resulted in increased partitioning of polyphenol oxidase to the bottom phase.

Molecular Surface Properties

The surface properties of molecule, such as surface net charge, molecular weight, shape, surface hydrophobic and the existence of specific binding site, affect the partitioning (Oliveira *et al.* 2002). The actual surface of molecule, which contacts the surrounding

solution, may be quite different from the overall material properties. The partitioning is related to the surface properties of the material. Different molecular weights of molecules also have an effect on partitioning. It is found that molecule with higher molecular weights are more influenced by changes in the molecular weight of polymers than those with small molecular weights.

Temperature

The effect of temperature is very different for each phase system relying on the type of polymer used. For example at high temperature, it is easy to form two phase with small concentration of PEG or salt whereas in case of PEG and dextran system, two phases will easily form at lower temperature (Walter and Johansson, 1994). An increase in temperature results in increased differences in the phase composition. It enhances the concentration of PEG and salt in the top and bottom phase respectively. Consequently, the number of water molecules available for solute solvation in the bottom phase decrease due to an increase in salt concentration. This also reduces the solubility of molecules in the phase. Furthermore, increasing temperature can destroy the bonds of molecule. As these bonds are weakened and broken, the molecule becomes more flexible structure. Water in two phase systems can interact and form new hydrogen bonds with the functional group of the molecules. The presence of water further weakens nearby hydrogen bonds by causing an increase in the effective dielectric constant near them. As the structure is broken, hydrophobic groups are exposed to the solution. As a consequent, losses in solubility of molecule are observed.

2.6 The Phase Diagram

The phase diagram delineates the potential working area for a particular two-phase system and is a "fingerprint" unique to that system under set conditions of, for example,

pH, temperature and salt concentration. Information that can be generated from such a diagram includes:

i. The concentration of phase-forming components necessary to form a system with two phases that is in equilibrium.
ii. The subsequent concentration of phase components in the top and bottom phases
iii. The ratio of phase volumes.

Present on the diagram is a binodal curve, which divides a region of component concentrations that will form two immiscible aqueous phases (above the curve) from those that will form one phase (at and below the curve). Coordinates for all "potential" systems will lie on a tie-line; the tie-line connects two nodes on the binodal, which represent the final concentration of phase components in the top and bottom phases. Moving along the tie-line coordinates denote systems with differing total compositions and volume ratios, but with the same final concentration of phase components in the top and bottom phases. Also present on the binodal is a critical point; just above this point the composition and volume of both phases are almost equal (as is partitioned material). A theoretical account of the phase diagram can be found in the work of Albertsson (1986).

2.6.1 The binodal

The construction of a binodal is such that a systematic choice of systems can be used for preliminary partitioning experiments, for instance systems are often chosen by extrapolating through the critical point. If, however, published phase diagrams are used, a few systems should be made up and the resultant bottom phase polymer/salt X (%

w/w) is plotted on the abscissa and top phase polymer Y (% w/w) is plotted on the ordinate. An illustration of the phase diagram is given in Figure 2.2.

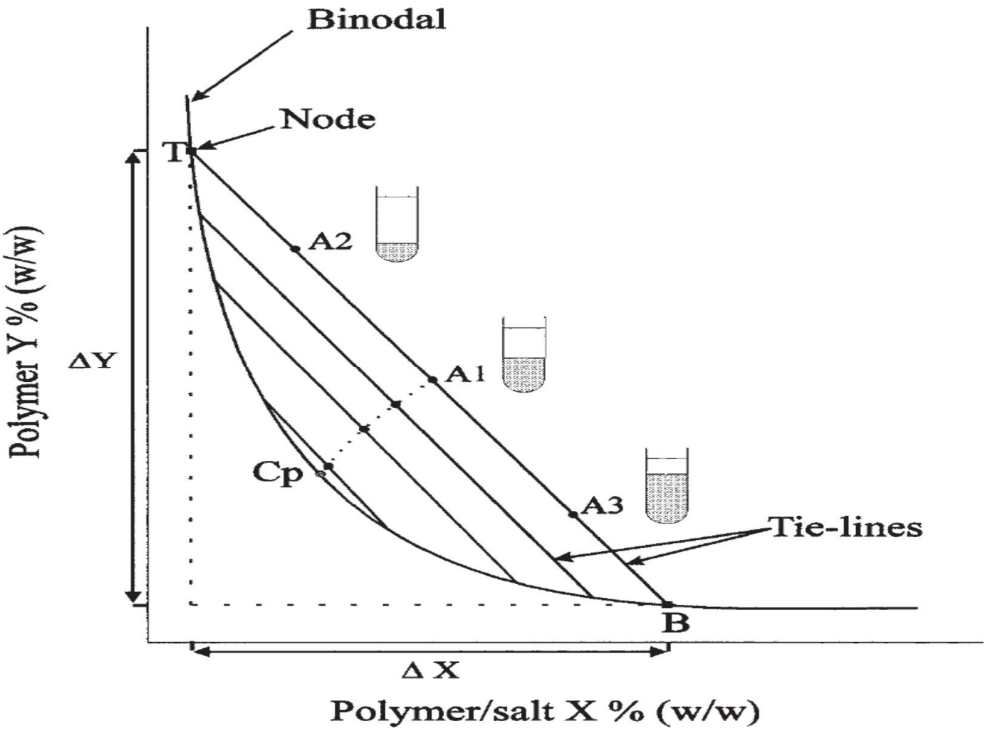


Figure 2.2: Illustration of the phase diagram

A1, A2, and A3 represent the total compositions of three systems lying on the same tie-line with different volume ratios. The final composition of the top and bottom phase is represented by nodes T and B, respectively. The ratio of the segments AB (top phase) and AT (bottom phase) can be approximated graphically by the volume ratio of the two phases. The critical point, Cp is determined by extrapolation through the midpoints of a number of tie-lines. The difference in concentration of component X and Y between the two phases is represented by ΔX *and* ΔY. Volume ratios and/or phase compositions should be compared to those predicted; thus, ensuring that similar experimental conditions have been achieved.

When phase components are mixed, only when immiscibility occurs does the resultant mixture become 'turbid'. This permits a 'visual' measurement of the binodal. Turbidometric titration is a relatively quick and commonly used method for determination of the binodal. A series of systems of known total composition and weight are prepared. Upon dilution with the appropriate solvent, the mixture will eventually turn 'clear' when one phase is formed. The resultant composition, at the point of transition, is calculated and lies on the binodal. The cloud-point method follows a similar principle.

At the cloud point, the mixture will become turbid and is indicative of two-phase formation. The composition, just prior to two-phase formation, is calculated and provides a point on the binodal. The mixture is then diluted to below the cloud point and the procedure is repeated. An alternative method is by determination of the nodes for a series of systems, thus, providing points on the binodal. The former methods are relatively inaccurate when using polymers that are polydisperse. Such polymers produce a gradual decrease/increase in turbidity rather than a sharp change, making the point of transition awkward to calculate.

2.6.2 Tie-line length

The tie-line length (TLL) has the same units as the component concentrations (% w/w) and is often used to express the effect of system composition on partitioned material. The ratio of segments AB and AT (see Figure 2.2) can be estimated graphically by using the weight ratio (WR).

$$\frac{V_t \rho_t}{V_b \rho_b} = \frac{AB}{AT} \tag{2.8}$$

Where V and ρ are the volume and density of the top (*t*) and bottom (*b*) phase.

A more precise method is by analysis of the top and bottom phase composition where the

$$TLL = (\Delta X^2 + \Delta Y^2)^{\frac{1}{2}} \quad (2.9)$$

where, X is the concentration of component 1

Y is the concentration of component 2 (Figure 2.2).

However, if the total composition and weight ratio are known, then analysis of one phase is sufficient by using,

$$\frac{V_t \rho_t}{V_b \rho_b} = \frac{X_b - X_0}{X_0 - X_t} \quad (2.10)$$

where, X_t is the concentration of component 1 in the top phase (*t*),

X_b is the concentration of component 1 in the bottom phase (*b*)

X_0 is the total concentration of component 1 in the initial system

(Equation 2.10) holds true for component 2 (Albertsson, 1986).

Tie-lines are commonly parallel and hence the slope of the tie-line (STL) can also be calculated, $STL = \Delta Y_1 / \Delta X_2$ thus, facilitating the construction of further tie-lines (Zaslavsky, 1995). Phase density can be determined using a pycnometer or by weighing a known volume of phase in a volumetric flask using an analytical balance. Analysis of phase composition is routinely carried out by using a combination of either optical rotation (for phase components containing an asymmetric center that can rotate a plane of polarized light), refractive index, dry weight, or conductivity measurements (Albertsson *et al*., 1994).

2.6.3 Critical composition

As tie-lines decrease in length, they ultimately approach a critical point on the binodal where the TLL = 0. At this point the composition and volume of the two phases theoretically become equal. The critical composition can be determined by trial and error where a one-phase system, just below the binodal, forms a two-phase system with approximately equal volumes of the two phases on addition of one component. A less tedious method is by extrapolation through the mid-point of a number of tie-lines near the binodal.

2.6.4 Operation point

Once a phase diagram is constructed, the point of operation is dependent on acquiring:

1. The desired conditions for partition of the target molecule(s) (Albertsson *et al.* 1990), cells or cell particles.
2. An extreme phase volume ratio (if a concentration step is required).

However, if systems are to be scaled-up and/or phases are to be recycled, then the working point should also take into account the position relative to the binodal. In such cases, small variations in phase composition are likely to occur and the precision that is achieved at bench-scale may not as easily be achieved at large scale. A system should therefore be 'robust' and the consequence of any changes on the physical and chemical characteristics of the system should be considered. Check points should include:

1. Sudden changes in composition may occur near the critical point.
2. A one phase system may form near the binodal.

This may be owing to an unaccounted dilution effect or a variation in concentration of component 1 or component 2. Therefore, systems will differ in stability and the result of an individual change, or a combination of changes, will give a corresponding deviation

in the tie-line length and, thus, in the composition and volume of the phases. The behaviour of the partitioned material may, as a result, differ from that which would have been obtained in the 'selected' system and the separation/purification is rendered ineffective.

2.6.5 Methods

By convention, the component predominantly in the bottom phase is plotted as the abscissa and the component predominantly in the top phase is plotted as the ordinate. The three methods in determining the binodal points as illustrated in Figure 2.3 are:

1. Turbidometric titration.
2. Cloud point method.
3. Node determination.

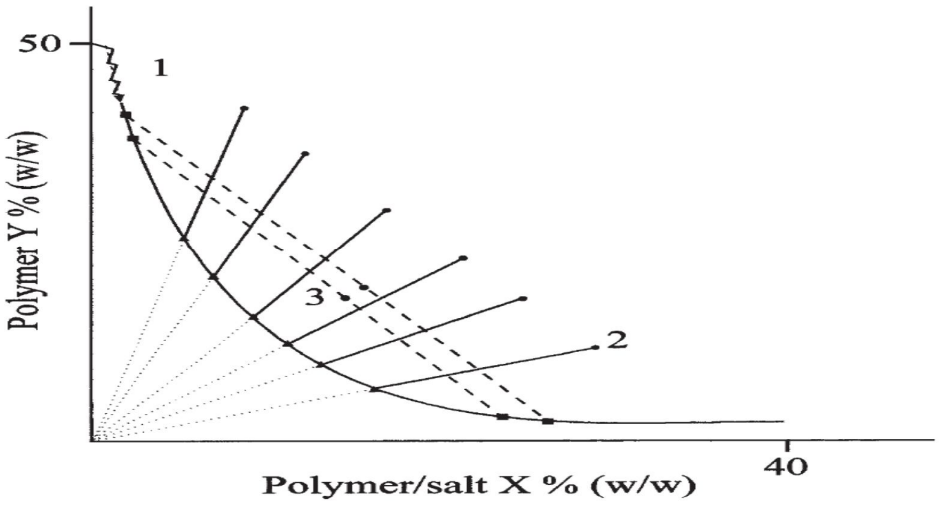


Figure 2.3: Graphical representation of three methods used to determine the binodal points

2.7 Related Works

Paul and Dhas (2008) treated TWW with the aim of removing COD and Colour using limestone (LS) and activated carbon (AC). Using particle size of LS and AC between (2.36 - 4.75 mm and 1.14 - 2.36 mm) respectively, in batch experiment the effective combined mixture ratio of LS:AC of 35:5 produced an optimal 92 % removal of COD and 80 % of colour removal. The batch reactor was easy to maintain but produce a lot of sludge which was another problem to contend with.

Al-Kdasi *et al.* (2005) also reviewed treating TWW using advanced oxidation processes. Ozone being a powerful oxidation agent was dissolved in textile wastewater using a convectional fine bubble contactor and by either direct oxidation as molecular ozone or by indirect reaction through the formation of secondary oxidant like hydroxyl radical. The ozone generator provided about 90 % transfer efficiency. Result showed about 80 % of colour was treated, improved odour removal was achieved and trace organic toxic synthetic organic compounds were eliminated.

Namboodri *et al.* (1994) revealed that ozone decolourize all dyes except non-soluble disperse and vat dyes. Arslan and Isil (2002) improving on earlier works, used a biological treatment method before ozonation of TWW and about 99 % of colour is removed when initial COD was 160 mg/l. Although the process is rapid, it is costly and forms by products.

Wijetunga *et al*. (2008) removed colour and COD from TWW using an upflow anaerobic sludge blanket reactor. Results obtained showed 95 % colour removal which was credited to biodegradation. However the anaerobic process has the advantage of producing biogas.

Pearce *et al.* (2003) reviewed the removal of colour from TWW using whole bacterial cells, the review demonstrates the great potential of treatment systems incorporating whole bacterial cells to metabolise the azo dyes, present in TWW. Under anaerobic conditions these systems can achieve total colour removal with short exposure times.

Rahbar *et al.* (2006) removed colour from industrial wastewater with a novel coagulant flocculant formulation which consisted of a pH adjuster, coagulant, coagulant aid and flocculant. A settling time of 2 hours was used. They concluded that the novel formulation removed colour content from wastewater efficiently, with a similar UV absorption close to distil water and colour removal was up 96 %.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The following are the list of materials used during the course of this work. The chemicals were of analytical grade.

3.1.1 Equipment

The equipment used for the experiment are listed in Table 3.1:

Table 3.1: List of Equipment

S/N	EQUIPMENT	AVAILABILITY	MANUFACTURER
1	6405 UV/Vis Spectrophotometer	Multi-User Lab, Chemistry Dept. ABU Zaria	JENWAY
2	General Laboratory Centrifuge (GLC-2)	Chem. Engg. Dept. ABU Zaria	SORVALE
3	Graphite tube atomizer AA240FS Atomic Absorption Spectrometer	Multi-User Lab, Chemistry Dept. ABU Zaria	VARIAN INC.
4	Conductivity meter	Chem. Engg. Dept. ABU Zaria	JENWAY
5	Refractometer	SHEDA Sci. and Tech. Complex, Abuja	ABBE
6	Weighing Balance	Chem. Engg. Dept. ABU Zaria	AEADAM
7	Distilled water machine A4000	Chem. Engr. Dept. ABU Zaria	A4000
8	pH meter 6307	Chem. Engg. Dept. ABU Zaria	JENCO
9	Desiccators	Chem. Engg. Dept. ABU Zaria	
10	Thermometer	Chem. Engg. Dept. ABU Zaria	BRANNAN

3.1.2 Reagents

The list of reagents used for this research work is shown in Table 3.2.

Table 3.2: List of Reagents.

S/N	Chemical	Specification and Manufacturer
1	Polyethylene glycol	4000 M.W, Hopkin & Williams, England
2	Sodium carbonate	105.99 M.W, Sigma – Aldrich, Canada
3	Ammonium sulphate	132.13 M.W, BDH Materials, May & Baker, Nigeria
4	Cibacron brilliant blue	Reactive dye, Ciba – Geigy, Switzerland
5	Erionyl red	Acid dye, Ciba – Geigy, Switzerland
6	Khaki brown	Vat dye, Unichem chemical Ltd., China
7	Cibacron navy blue	Reactive dye, Ciba – Geigy, Switzerland
8	Dispersal Yellow	Dispersal dye, Kirkley development, India
9	Sodium Oxalate	134.01 M.M., Sigma – Aldrich, Canada
10	Manganese Sulphate	169.02 M.M., Suvidhi industries, India
11	Sulfuric Acid	98.01 M.M., Sigma – Aldrich, Germany
12	Copper Sulphate	159.62 g/mol LabChem, U.S.A
13	Potassium permanganate	158.03 M.M., Servetel Industries, China
14	Zinc sulphate	161.47 M.M., Sigma – Aldrich, Switzerland
15	Barium chloride	208.23 M.M. Tarini Industries, China
16	Alkali Iodide	Ricca Chemical Company, U.S.A
17	Potassium hydroxide	56.10 M.M., Sigma – Aldrich, Canada

3.2 Methods

The method employed and steps followed for this research work are shown in Figure 3.1. PEG, ammonium sulphate, sodium carbonate and distilled water were used to form ATPS. The phase diagrams and operating points obtained was used to obtain treatment points for simulated dye solutions and textile wastewater effluent.

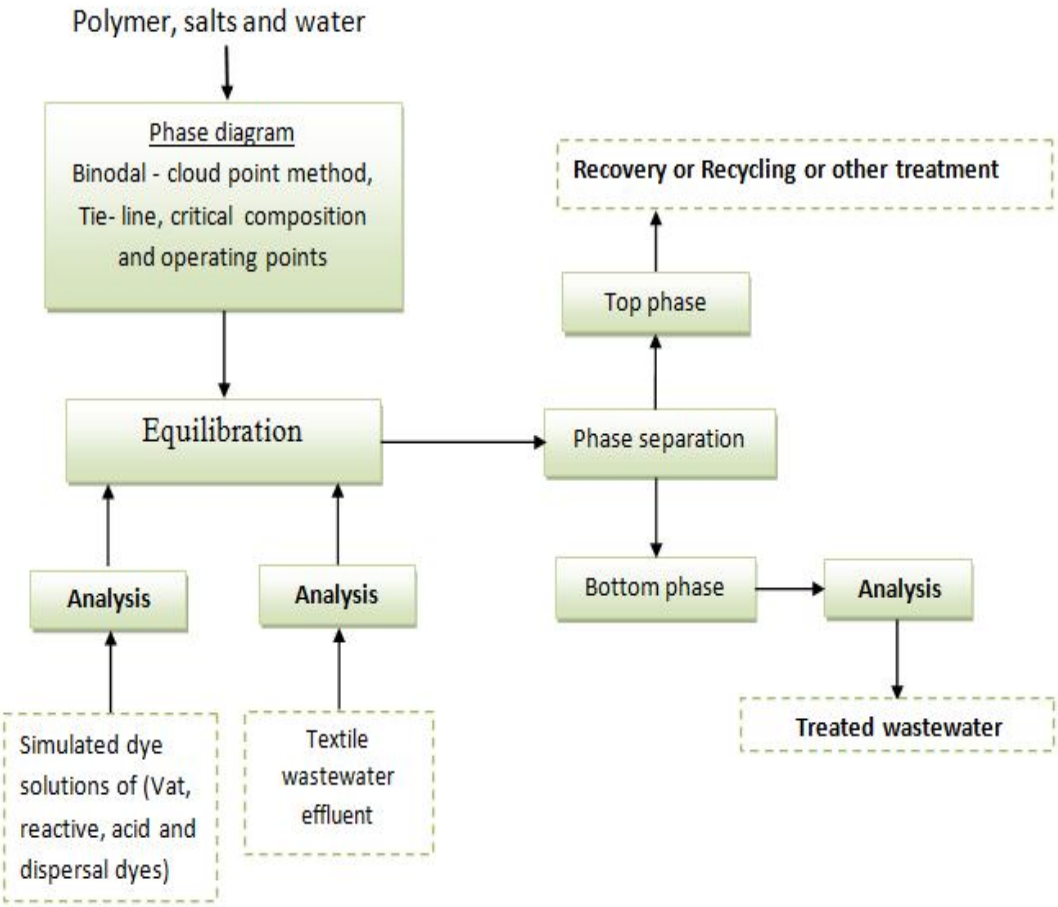


Figure 3.1: Summary of Experimental procedure.

3.2.1 Calibration of PEG stock and salt solutions

PEG Stock Solutions

Two different stocks solutions of PEG with $(NH_4)_2SO_4$ and PEG with Na_2CO_3 were prepared using different compositions by weight with distilled water as shown in Table 3.3. The refractive index of the samples was measured using an Abbe refractometer.

Table 3.3: PEG, salt ($(NH_4)_2SO_4$ and Na_2CO_3) and distilled water used in calibration

	Composition % (w/w)		
S/N	**Salt (g)**	**Water (g)**	**PEG (g)**
1	0.0	100.0	0.0
2	0.0	95.0	5.0
3	0.0	90.0	10.0
4	0.0	85.0	15.0
5	0.0	80.0	20.0
6	0.0	75.0	25.0
7	0.0	70.0	30.0
8	0.0	65.0	35.0
9	0.0	60.0	40.0
10	2.5	97.5	0.0
11	2.5	87.5	10.0
12	2.5	77.5	20.0
13	2.5	67.5	30.0
14	2.5	57.5	40.0
15	5.0	95.0	0.0
16	5.0	85.0	10.0
17	5.0	75.0	20.0
18	5.0	65.0	30.0
19	5.0	55.0	40.0

Calibration of Salts Solutions

The concentration of $(NH_4)_2SO_4$ and Na_2CO_3 solutions were determined by dissolving a known weight of salt in a known weight (volume) of distilled water and measuring the conductivity of the solution using a conductivity meter. Specifically, the density of the solution was measured by taking a known volume of solution (usually in millilitres and its corresponding weight, for three different sample volumes and the average taken), results obtained were tabulated.

3.2.2 Preparation of ATPS

Preparation of Stock Solutions

1. PEG stock of 50 % (w/w) was prepared by accurately weighing an equal weight of both polymer and distilled water into a conical flask which was covered. The solution was stirred for an hour using a magnetic stirrer until a clear solution was obtained. The flask was covered to avoid evaporation which can change the composition of the stock.
2. Ammonium sulphate stock of 35 % (w/w) concentration was prepared by accurately weighing 35 % by weight of ammonium sulphate from the total weight of stock solution intended to be produced. The balance 65 % by weight of distilled water was added in a conical flask which was covered and stirred for an hour with a magnetic stirrer until a clear salt solution was obtained. The flask was covered to avoid evaporation which can change the composition of the stock.
3. Sodium carbonate stock of 30 % (w/w) concentration was prepared by accurately weighing 60 g of sodium carbonate in a flask and dissolved with 140 g of distill water. The stock solution was stirred for an hour with a magnetic stirrer until a clear salt solution was obtained. A maximum of 200 g of stock

solutions were prepared and used for analysis and fresh ones were prepared when stock was exhausted.

Preparation of the Phase Diagram

The Cloud Point Method was used in preparing the ATPS diagram for the two phases.

a) PEG/$(NH_4)_2SO_4$ phase system

5.0 g of 50 % (w/w) PEG stock solution was poured into a 25-ml conical flask of a known weight on a weighing balance and a stock solution of 35 % (w/w) $(NH_4)_2SO_4$ was added drop-wise until the first sign of turbidity was observed (the cloud point). The mixture was mixed thoroughly, but gently to avoid spillage. When the cloudy solution failed to become colourless, meaning a two phase is formed, the weight of $(NH_4)_2SO_4$ stock added was calculated by taking the difference between the new weight from the previous weight. Thus forming the first point on the binodal. Distilled water of a known weight was added drop-wise into the solution and shaken carefully until it became colourless (the point below the binodal point) and the weight noted. Repeatedly, drop-wise stock solution of $(NH_4)_2SO_4$ was added until the second sign of turbidity was observed and noted. This procedure was repeated until many binodal points were obtained (conical flask got filled).

The complete experiment was repeated by starting with 5.0 g of 35 % (w/w) $(NH_4)_2SO_4$ stock solution which was poured into a 25 ml conical flask of a known weight on a weighing balance and 50 % (w/w) stock solution of PEG was added drop-wise until the first sign of turbidity was observed (the cloud point). The mixture was mixed thoroughly, but gently to avoid spillage. When the cloudy solution failed to become colourless, meaning a two phase is formed; the weight of PEG stock added was calculated by taking the difference between the new weight from the previous weight. Thus forming the first point on the binodal. Distilled water of a known weight was

added drop-wise into the solution and shaken carefully until it became colourless (the point below the binodal point) and the weight noted. Repeatedly, drop-wise stock solution of PEG was added until the second sign of turbidity was observed and noted. This procedure was done until many binodal points were obtained (conical flask got filled).

b) PEG/Na_2CO_3 phase system

5.0 g of 50 % (w/w) PEG stock solution was poured into a 25 ml conical flask of a known weight on a weighing balance and a stock solution of 30 % (w/w) Na_2CO_3 was added drop-wise until the first sign of turbidity was observed (the cloud point). The mixture was mixed thoroughly, but gently to avoid spillage. When the cloudy solution failed to become colourless, meaning a two phase is formed, the weight of Na_2CO_3 stock added was calculated by taking the difference between the new weight from the previous weight. Thus forming the first point on the binodal. Distilled water of known weight was added drop-wise into the solution and shaken carefully until it became colourless (the point below the binodal point) and the weight noted. Repeatedly, drop-wise stock solution of Na_2CO_3 was added until the second sign of turbidity was observed and noted. This procedure continued until many binodal points obtained (conical flask got filled).

The complete experiment was repeated by starting with 5.0 g of 30 % (w/w) Na_2CO_3 stock solution which was poured into a 25 ml conical flask of a known weight on a weighing balance and 50 % (w/w) stock solution of PEG was added drop-wise until the first sign of turbidity was observed (the cloud point). The mixture was mixed thoroughly, but gently to avoid spillage. When the cloudy solution failed to become colourless, meaning a two phase is formed; the weight of PEG stock added was calculated by taking the difference between the new weight from the previous weight.

Thus forming the first point on the binodal. Distilled water of a known weight was added drop-wise into the solution and shaken carefully until it became colourless (the point below the binodal point) and the weight noted. Repeatedly, drop-wise stock solution of PEG was added until the second sign of turbidity was observed and noted. This procedure was repeated until many binodal points were obtained (conical flask got filled).

3.2.3 Determination of tie-lines and operating points

To calculate the nodes and tie line length (TLL) for PEG/$(NH_4)_2SO_4$ starting with 50 % (w/w) of PEG and 35 % (w/w) $(NH_4)_2SO_4$ stock solutions. The following compositions by weight in Table 3.3 (Initial solutions) were added in a well graduated test tube of known internal diameter to form an ATPS (Prepared composition). The internal diameter, the refractive index, density and height of top phase and density, conductivity, height of bottom phases were recorded.

Table 3.3: Initial and final compositions used in forming PEG/$(NH_4)_2SO_4$ ATPS

S/No.	**Initial (starting) solutions (g)**			**Prepared composition forming ATPS**		
	50 % (w/w) PEG	35% (w/w) $(NH_4)_2SO_4$	Distill H_2O	PEG % (w/w)	$(NH_4)_2SO_4$ % (w/w)	H_2O % (w/w)
1	4.0001	4.7714	1.2286	20.00	16.70	63.30
2	3.0001	6.2143	0.7857	15.00	21.75	63.25
3	2.0001	6.9997	0.9002	10.00	24.85	65.15
4	0.9999	8.0001	0.6000	5.00	28.00	67.00

From the prepared phase systems, a known volume of both the top and bottom phases were extracted using a well graduated syringe and weighed.

The conductivity, density and refractive index of the top phase were obtained using a conductivity meter, calculation and refractometer respectively. The density of the

bottom phase was also calculated by taking 1 ml and diluted with 19 ml of distilled water before the conductivity of the salt solution was taken. This was done due to the high concentration of salt to avoid errors in determining the concentration. Appropriate calculations were done to determine the quantity of salt present, after reading the conductivity versus concentration calibration chart. The concentration of polymer in the top phase was obtained by comparing the refractive index to the equivalent concentration from the calibration graph.

Material balance calculation were done to obtain the composition of the top and bottom phase (providing the nodal positions). See Appendix A1 for detailed calculation.

The TLL and WR were calculated using equation 2.8 and 2.9 respectively.

Table 3.4: Initial and final compositions used in forming PEG/ Na_2CO_3 ATPS

S/No	**Initial (starting) composition (g)**			**Prepared composition forming ATPS**		
	50 % (w/w) PEG	30 % (w/w) Na_2CO_3	Distill H_2O	PEG % (w/w)	Na_2CO_3 % (w/w)	H_2O % (w/w)
1	4.0000	5.0000	1.0000	20.00	15.00	65.00
2	3.0001	5.6665	1.3334	15.00	17.00	68.00
3	2.0000	6.4160	1.5840	10.00	19.25	70.75
4	0.9999	7.1666	1.8333	5.00	21.50	73.50

To calculate the nodes and tie line length (TLL) for PEG/Na_2CO_3 starting with 50 % (w/w) of PEG and 30 % (w/w) Na_2CO_3 stock solutions. The following compositions by weight in Table 3.4 (Initial solutions) were added in a well graduated test tube of known internal diameter to form an ATPS (Prepared composition). The internal diameter, the height of both top and bottom phases were recorded. Material balance calculations were done to obtain the composition of the top and bottom phase (providing the nodal positions). See Appendix B1 for detailed calculation.

3.2.4 Preparation and calibration of simulated dye solutions

500 mg, 250 mg, 167 mg, 100 mg and 50 mg of each of textile dye colours (blue, red, brown, yellow and navy blue) were dissolved separately in 1000 ml of distilled water to produce 500 mg/l , 250 mg/l, 167 mg/l, 100 mg/l and 50 mg/l respectively simulated dye solutions.

Distill water was calibrated to zero absorbance using the UV/Vis spectrophotometer. Using distill water as a blank, the peak absorbance and wavelength for each of the 500 mg/l simulated dye colours was analysed using the UV/Vis spectrophotometer. Subsequently, the absorbance of the remaining simulated dye colours were obtained by setting the UV/Vis spectrophotometer to that colour particular wavelength. The absorbance recorded was then plotted against concentration, to produce the colour concentration calibration graph.

3.2.5 Treating simulated dye solutions with ATPS

250 mg/l and 500 mg/l of each of the colour dye solutions were used to prepare PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS at different (TLL) and different (WR). The absorbance of the treated bottom phases were obtained by running the samples in the UV/Vis spectrophometer at the particular colour wavelength and the corresponding colour concentration deduced from the colour concentration calibration graph.

3.2.6 Analysing the physical and chemical properties of textile wastewater

Textile wastewater effluent sample was collected from Africa Manufacturing Textile Company (AMTC), Kano. The sample was used to prepare ATPS of PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3, using TLL of 52.5 and 55.5 respectively. The following experiments were carried out to determine physical, chemical and biological properties of the textile wastewater effluent and treated samples.

Determination of Chemical Oxygen Demand (COD)

The COD was determined according to the method reported by Woodard (2001). 10 ml of the sample was taken in a 100 ml bottle, then 5 ml of concentrated H_2SO_4 was added and 1 g of copper sulphate ($CuSO_4$) also added. 3 ml of prepared 0.025 M $KMnO_4$ solution was added and the bottle was immersed in boiling water for 30 min while keeping the surface of the boiling water at the higher level than the surface of the sample. Then 3 ml of prepared 0.025 M sodium oxalate ($Na_2C_2O_4$) was added and immediately titrated with 0.025 M potassium permanganate ($KMnO_4$) until violet colour appeared. The procedure was repeated for the blank separately under same condition using 10 ml of distilled water instead of 10 ml of sample. COD is evaluated using equation (3.1).

$$COD(mg/l) = ml\ of\ sample \times 0.025 \times 8000 \times (A - B) \quad (3.1)$$

Where,

A = volume (ml) of $KMnO_4$ used for sample.

B = volume (ml) of $KMnO_4$ used for blank.

8000 = milliequivalent weight of oxygen × 1000 ml/l.

Determination of Biochemical Oxygen Demand (BOD)

The BOD_5 was determined using Winkler method as described by Woodard (2001). Two 200 ml bottles with lid were obtained and cleaned well. 25 ml sample was taken in each bottle and 75 ml of distilled water was added into each of the bottles. Both bottles were well closed. One bottle was kept in the incubator at (20-22)°C for 5 days. 10 ml of manganese sulphate solution and 2 ml of alkali-iodide solution were added to the other bottle well below the surface of the liquid using a syringe. The bottle was closed and mixed by inverting the bottle several times. When the precipitate settled leaving a clear supernatant above the precipitate, the bottle was shaken again slowly by inverting the

bottle, and when the setting has produced at least 50 ml supernatant, 8 ml of concentrated H_2SO_4 was added. The bottle was closed and mixed by gentle inversion until dissolution was completed. Then 100 ml of the sample was titrated with 0.05 M $Na_2S_2O_3$ solution until sample turned pale yellow. 2 ml of freshly prepared starch solution was added and titration was continued until a blue colour appeared.

The procedure was then repeated using 100 ml distilled water (blank). Then, repeated for the incubated sample after 5 days. The BOD_5 was calculated as follows:

(a) When dilution water is not seeded

$$BOD_5(mg/l) = \frac{(D_1 - D_2) \times 100}{\%\ dilution} \quad (3.2)$$

(b) When dilution is seeded

$$BOD_5\ (mg/l) = \frac{(D_1 - D_2) - (B_1 - B_2) \times 100}{\%\ dilution} \quad (3.3)$$

(c) When material is added to sample or to seed control

$$BOD_5(mg/l) = \frac{(D_1 - D_2) - (B'_1 \times B'_2) \times F \times 100}{\%\ dilution} \quad (3.4)$$

where, D1 = DO of sample immediately after preparation, mg/l

D2 = DO of sample after incubation period, mg/l

B1 = DO of blank (seeded dilution water) before incubation, mg/l

B2 = DO of blank (seeded dilution water) after incubation, mg/l

F = ration of seed in diluted sample to seed in seed control (Volume of seed in diluted sample / volume of seed in seed control)

B'1 = DO of seed control before incubation, mg/l

B'2 = DO of seed control after incubation, mg/l

Determination of Total Dissolved Solids (TDS)

Total dissolved solids were determined by evaporating the waste samples to dryness (Woodard, 2001). In this method 50 ml of sample were transferred to a weighed evaporating dish, and evaporated to dryness by heating for 1-2 hours at 180°C to a constant weight. Total dissolved solids were calculated as follows:

$$\text{TDS (mg/l)} = \text{mg residue x } 1000 / \text{ml of sample} \quad (3.5)$$

Determination of pH

The electrodes from the pH meter were rinsed with distilled water and dried with a soft tissue paper. It was standardized by immersing in a buffer solution removed and rinsed thoroughly with distilled water and dried. The electrode was immersed in distil water and the pH adjusted to 7.0. Subsequently, the electrode was removed and immersed into the TWW, the pH recorded from the pH meter. The electrode was removed and rinsed thoroughly and dipped into the distilled water giving a pH of 7.0, then cleaned and immersed to the next wastewater sample.

Determination of Dissolved Oxygen (DO)

200 ml of Samples were collected in a BOD_5 bottle using DO sampler. 1 ml MnSO4 was added followed by 1ml of alkali-iodide-azide reagent to another 200 ml sample collected in 300 ml sampler. The tip of the pipette was below the liquid level while adding these reagents and covered immediately. The samples were mixed well by inverting the bottle 2-3 times and the precipitate was allowed to settle leaving 150 ml clear supernatant. The precipitate was white when the sample was devoid of oxygen, and became increasingly brown with rising oxygen content. 1 ml concentrated H_2SO_4 was added and mixed well till precipitate goes into solution.

201 ml of this solution was taken into a conical flask and titrated against standard $Na_2S_2O_3$ solution using 2 ml of starch as an indicator. When 1ml of $MnSO_4$ followed by 1ml alkali-iodide-azide reagent was added to the samples above, 2 ml of original sample was lost. Therefore 201 ml was taken for titration which corresponded to 200 ml of original sample.

$$\frac{200 \times 300}{300 - 1} = 201\text{ml}$$

Calculation

$$1\text{ ml of } 0.025\text{ N } Na_2S_2O_3 = 0.2\text{ mg of } O_2$$

$$\text{DO}\left(\frac{\text{mg}}{\text{l}}\right) = (0.2 \times 1000) \times (0.025\text{N})\text{ ml of thiosulphate}/200 \qquad (3.6)$$

Determination of Total Solids

200 ml of the sample was taken in a dish ignited to constant weight (W1). The sample was evaporated to dryness at 103 - 105 °C for 24 hours cooled in a desiccator and weighed (W2). The dish was ignited for 15 minutes in a muffled furnace maintained at 550 ± 50 °C. The dish was cooled partially in air until most of heat has been dissipated, and then transferred to the desiccator for final cooling in a dry atmosphere and final weight recorded (W3). The concentration was calculated in percent by weight.

The total and the volatiles solids are expressed as:

$$\text{Volatile solids}\left(\frac{\text{mg}}{\text{l}}\right) = (W_2 - W_1) \times \frac{1000}{\text{ml}}\text{ of sample} \qquad (3.7)$$

$$\text{Total solids}\left(\frac{\text{mg}}{\text{l}}\right) = \frac{(W_2 - W_3)}{W_1} \times \frac{1000}{\text{ml}}\text{ of sample} \qquad (3.8)$$

Determination of Ammonia

To determine amount of ammonia present, 100 ml of sample was added to 1 ml of $ZnSO_4$ solution and an appropriate amount of NaOH solution to obtain the pH of 10.5. The supernatant was allowed to settle and filtered through a filter paper. An aliquot of the sample was taken and 3 drops of Rochelle salt solution was added and mixed well. 1 ml of Nessler reagent was added. The sample was added to solution to make up to 100 ml, mixed well and using a spectrophotometer at a wavelength of 410 nm the absorbance was taken, and quantity of ammonia was obtained from a standard graph.

Determination of Sulphate

50 ml of the sample was placed in a 250 ml Erlenmeyer flask and diluted to 100 ml with distil water. 20 ml of buffer solution was added and mixed well. The content was constantly stirred with a stirrer. 1 spatula $BaCl_2$ crystals was added upon stirring. The content was stirred for 1 minute afterwards. The suspension was poured into an absorption cell of photometer and the turbidity measured after 5 minute.

Buffer solution : dissolve 30 g of Magnesium chloride ($MgCl_2.6H_2O$), 5 g of Sodium acetate ($CH_3COONa.3H_2O$), 1 g of Potassium nitrate (KNO_3) and 20 ml of acetic acid (CH_3COOH (99%)) in 500ml distilled water and make up to 1000ml.

Calculation

$$SO_4\ (mg/l) = [mg\ (SO_4) \times 1000]/[ml\ of\ sample] \quad (3.9)$$

Determination of Calcium

50 ml of sample was poured into porcelain dish and drops of NaOH solution were added to raise the pH to 12.0. A pinch of murexide indicator was added to the mixture. The pink solution was titrated immediately with Ethylene Diamine Tetracetic Acid (EDTA) until the pink colour changed to purple. The volume of EDTA used (A_1) was noted,

similarly a blank reagent was ran and the volume of EDTA used as (B_1) was also noted. The volume of EDTA required by sample was calculated as:

$C_1 = A_1 + B_1$. The EDTA (0.1M) solution was standardized following the procedure of calcium hardness, using standard calcium solution.

Murexide indicator: A well mixed 200 mg of murexide with 100 g of solid NaCl.

Standard EDTA solution 0.01 M: Dissolve 3.723 g EDTA sodium salt and dilute to 100ml.

Standard Calcium solution = 1 mg of CaCO3/ml

UV-Visible Spectroscopic Analysis

Graphite tube atomizer AA240FS Atomic Absorption Spectrometer was used for determination of concentration of all the heavy metals - chromium, copper, iron, mercury, cadmium, lead and nickel as per the following procedure. The system prior to operation was switched on and warmed up for 30 minutes. Carefully cleaned quartz cuvettes were used throughout the analysis. One cuvette was filled with the reference compound and the other with the compound whose absorbance is to be determined at λ max (maximum wavelength). A calibration curve was made to get the relationship between concentration and absorbance of the compound. Calibration solutions were made from standard solutions of known concentration. Absorbance was plotted against known concentration of the calibration samples. These calibration curves were stored in the system itself and the concentration of the unknown sample were calculated directly from the absorbance.

CHAPTER FOUR

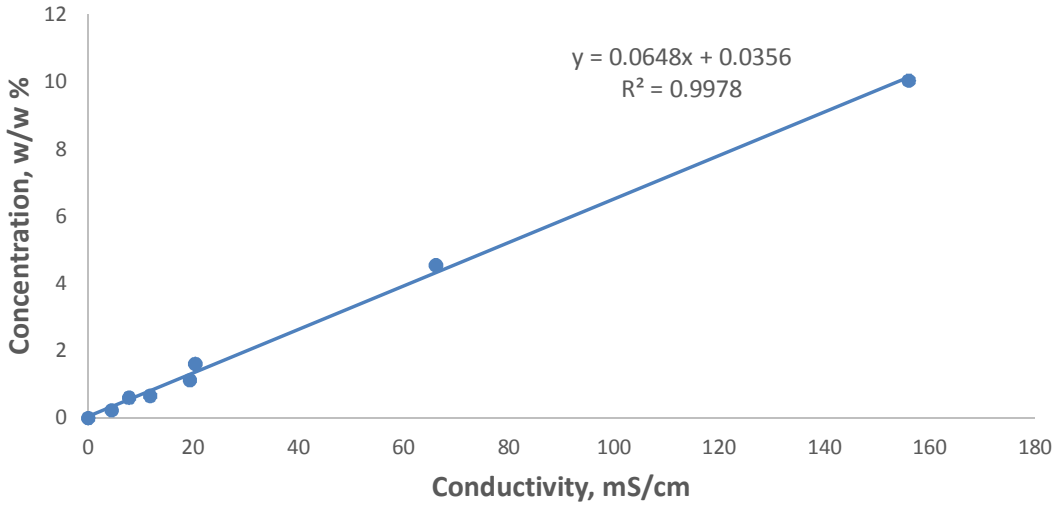
RESULTS AND DISCUSSION

4.1 Overview

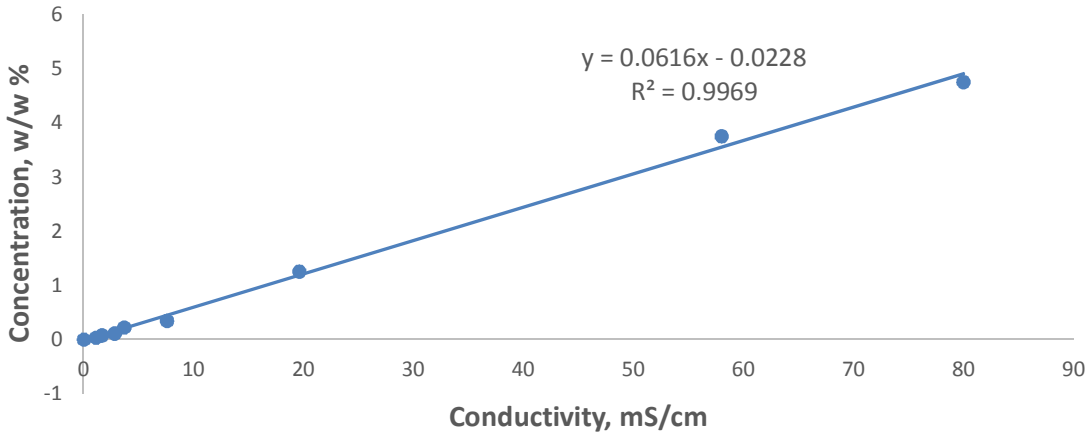
This chapter gives the results showing the calibration plots of salt solutions of $(NH_4)_2SO_4$ and Na_2CO_3. The refractive index calibrations of PEG at different concentrations were presented. Phase diagrams of PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS were formed using the cloud point method. Simulated dye solutions of 500 mg/l and 250mg/l were treated with PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS. The Physico-chemical characteristics of untreated effluent TWW and treated TWW using ATPS were also compared to NESREA, 2009 standards.

4.2 Calibration Plots

Figures 4.1 (a) and (b) shows the calibration plots for $(NH_4)_2SO_4$ and Na_2CO_3 salt solutions, prepared by dissolving different amount of salts to obtain different concentration in distill water. A very good linear relationship ($R^2 = 0.998$ and 0.997) respectively were obtained between the salt concentration and conductivity.



(a)

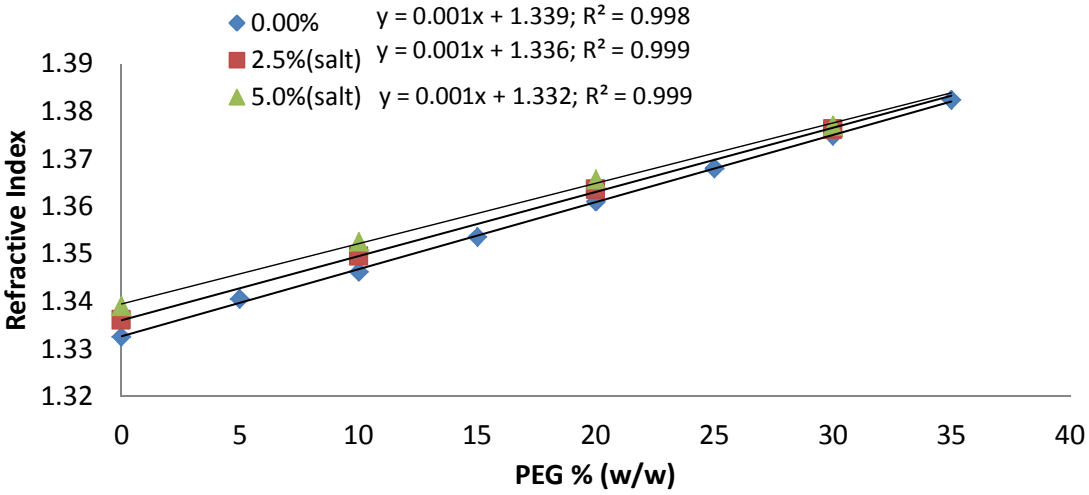


(b)

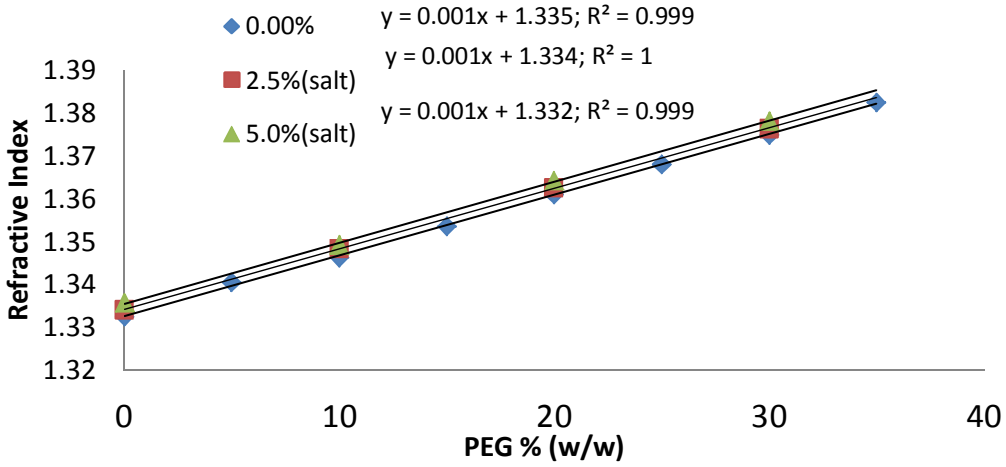
Figure 4.1: Calibration plots for salt solutions (a) $(NH_4)_2SO_4$ (b) Na_2CO_3

The refractive index calibration plot of PEG at different polymer concentrations in Figures 4.2 (a) and (b) showed that despite the additional increase of salt concentrations of 2.5 % and 5.0 %, a linear relationship was clearly observed with a refraction index increase of 0.004 and 0.007 for 2.5 % and 5.0 % ammonium sulphate concentration

increase. Whereas, increase in concentration by 2.5 % and 5.0 % of sodium trioxocarbonate increased refractive index by 0.003 and 0.004 respectively.



(a)



(b)

Figure 4.2: Refraction index calibration of PEG at 0%, 2.5% and 5% salt concentrations. (a) $(NH_4)_2SO_4$ (b) Na_2CO_3

4.3 Phase Diagrams

The bi-nodal points (Appendix C) obtained was represented graphically in Figures 4.3 and 4.4 using the cloud point method. The bi-nodal points similarly conformed to data points from similar works of Antov *et al*., (2004) and Kianmehr *et al.,* (2014) for PEG/$(NH_4)_2SO_4$ ATPS and Taboada *et al.,* (2001) for PEG/Na_2CO_3 ATPS respectively.

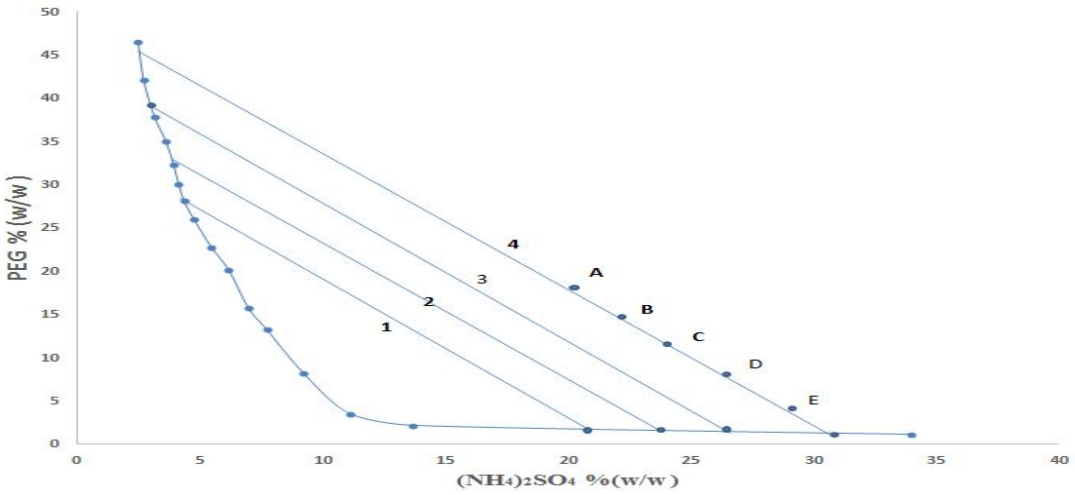


Figure 4.3: Phase diagram of PEG/$(NH_4)_2SO_4$ ATPS

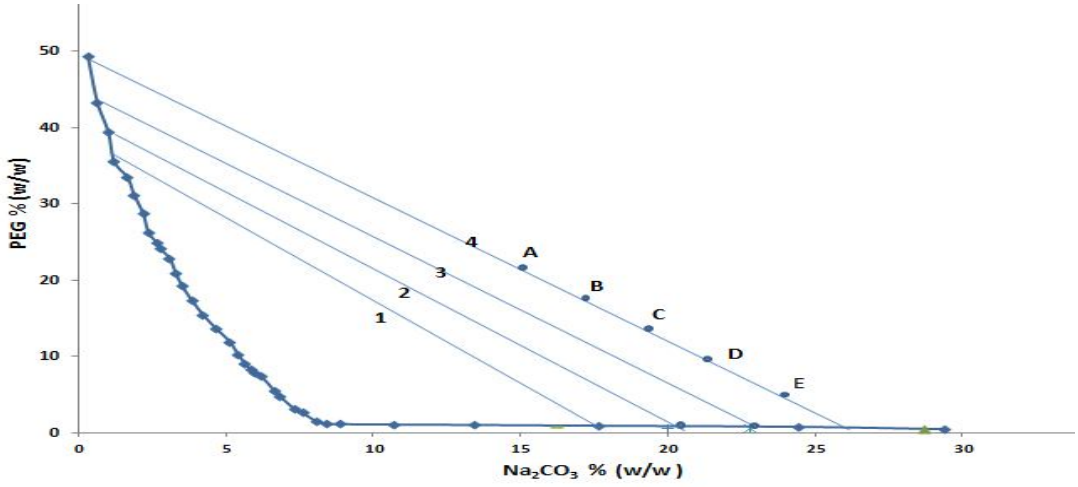


Figure 4.4: Phase diagram of PEG/Na_2CO_3 ATPS

Of most interest and advantage to note is that as low as 2 % (w/w) of PEG in PEG/$(NH_4)_2SO_4$ and 1.5 % (w/w) of PEG in PEG/Na_2CO_3 can be used to form an

ATPS. This quantity of PEG shows how much it can be utilized for treatment. Similarly, salts composition below 13.5 % (w/w) for $(NH_4)_2SO_4$ and 7.6 % (w/w) Na_2CO_3 are adequate for treatment. This is good for two reasons. First, salts are cheaper and readily available as compared to PEG and secondly, the two salts used in this work are biodegradable (Albertsson, 1986) and hence will not pose a threat if disposed into natural water together with the treated effluent.

Table 4.1 and Table 4.2 show the phase compositions of each tie lines, the densities of both top and bottom phases and the TLL % (w/w) which was represented in Figures 4.3 and 4.4.

Table 4.1: Tie lines for PEG (1) + water (2) + $(NH_4)_2SO_4$ (3) systems at 27^0C at various initial mass fraction w

Initial component			Top phase		Bottom phase		TLL % (w/w)
w_1	w_2	w_3	w_1	w_3	w_1	w_3	
0.2000	0.6330	0.1670	0.2834	0.0430	0.0201	0.2138	31.38
0.1500	0.6325	0.2175	0.3318	0.0417	0.0179	0.2391	37.08
0.1000	0.6515	0.2485	0.3756	0.0319	0.0151	0.2603	42.67
0.0500	0.6700	0.2800	0.4611	0.0313	0.0132	0.3055	52.51

Table 4.2: Tie lines for PEG (1) + water (2) + Na_2CO_3 (3) systems at 27^0C at various initial mass fraction w

Initial component			Top phase		Bottom phase		TLL % (w/w)
w_1	w_2	w_3	w_1	w_3	w_1	w_3	
0.2000	0.6500	0.1500	0.3681	0.0102	0.0083	0.1880	40.13
0.1500	0.6800	0.1700	0.3954	0.0089	0.0081	0.2095	43.62
0.1000	0.7075	0.1925	0.4391	0.0052	0.0079	0.2306	48.66
0.0500	0.7350	0.2150	0.4935	0.0025	0.0073	0.2612	55.50

4.4 Colour Absorbance

The dye calibration chart in Figure 4.5 was obtained after using the UV/Vis Spectrophotometer to measure colour concentration (absorbance of colour) of simulated dye solutions as was reported by Suding and Buccigross (1994) and Meric *et al*. (2004).

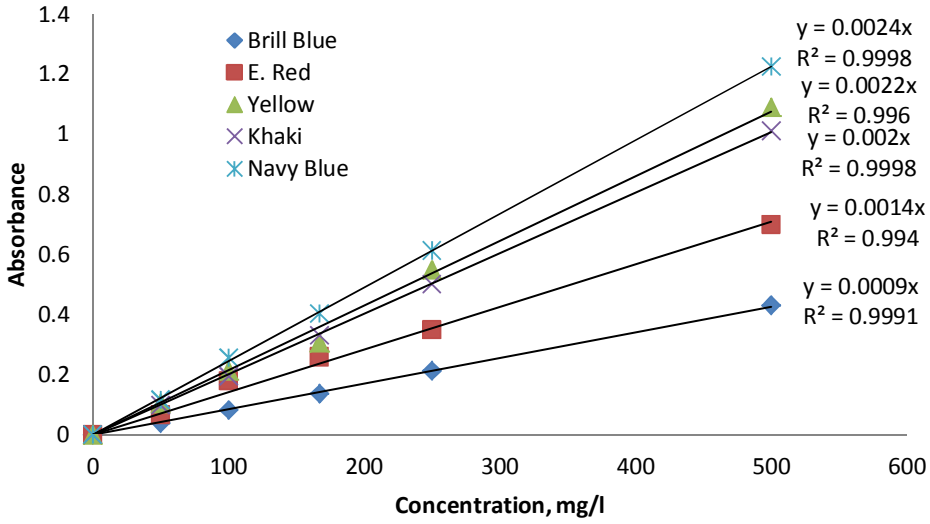
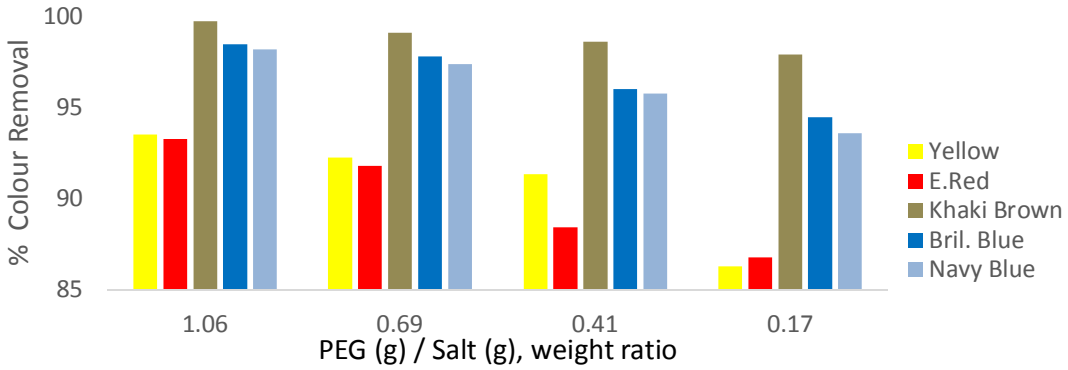


Figure 4.5: Dye calibration chart

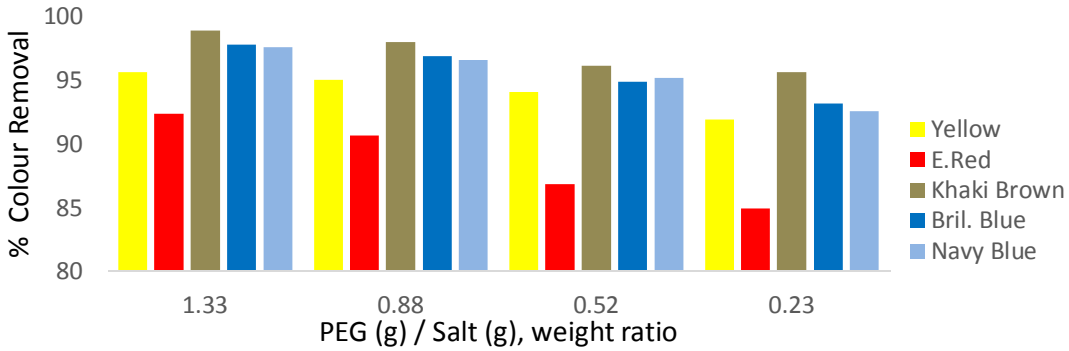
This linear relationship obtained was used to evaluate the concentration of colour removed in dye solution.

4.5 Effect of ATPS of Simulated Dye Solutions

The PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS prepared using 500 mg/l and 250 mg/l for five different colours of simulated dye solutions as aqueous medium are represented in Figure 4.6 (a) and (b) and Figure 4.7 (a) and (b) respectively.



(a)



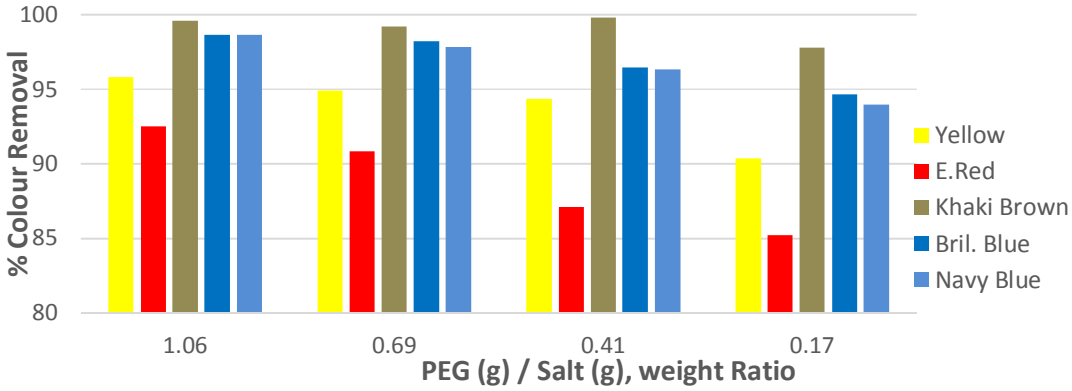
(b)

Figure 4.6: ATPS of initial colour concentration of 500mg/l (a) PEG/$(NH_4)_2SO_4$ and (b) PEG/Na_2CO_3

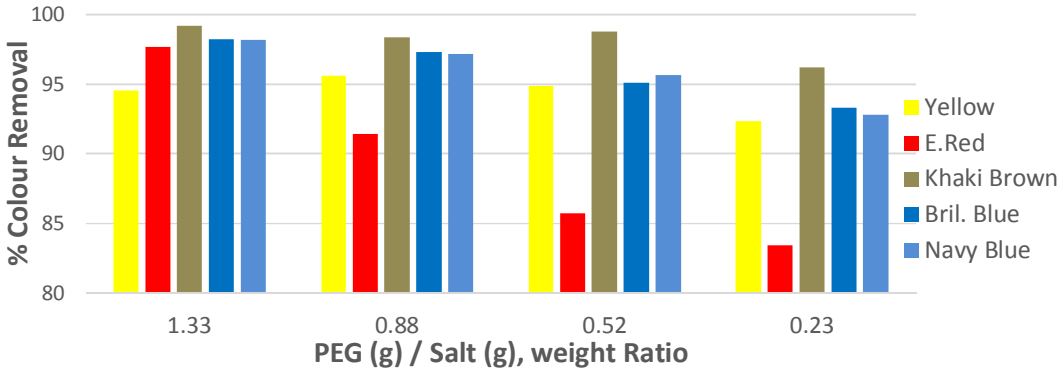
All the colours were separated to the top phase, leaving a clear bottom phase. The percentage colour removal in all the four Figures shows that an increase in WR resulted to an increase in the rate of colour removed. Figure 4.6 (a) and (b) depicts khaki brown (Vat dye) having the best removal of 99.7 % and 98.9 % in 500 mg/l for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 systems respectively, Similar trend was also observed in the 250 mg/l dye solutions in Figure 4.7 (a) and (b).

Brilliant blue and navy blue, which are both reactive dyes maintained a consistency in percentage removal within the range of 92.5 % to 98.7 % for the two systems. Dispersal

yellow dye solution was removed best at 95.8 % using a WR of 1.03 for PEG/$(NH_4)_2SO_4$ ATPS (Figure 4.6 (a)) when compared to the remaining figures.



(a)



(b)

Figure 4.7: ATPS of initial colour concentration of 250mg/l (a) PEG/$(NH_4)_2SO_4$ and (b) PEG/Na_2CO_3

Erionyl red gave the least colour removal amongst all the dye colours used for this work. The best result obtained was in PEG/Na_2CO_3 ATPS (Figure 4.6 (b)) , with a removal range of (84.9 - 92.3 %) across different WR. Generally, PEG/$(NH_4)_2SO_4$ removed colour better than PEG/Na_2CO_3.

4.6 WR and Amount of Treated Effluent

A relationship was established between the WR and the amount of treated effluent (treated volume as a percentage of the total volume of effluent) as shown in Figure 4.8. The weight ratio of phases shows the quantity of polymer used in relation to salt used for separation in each phase (Appendix D).

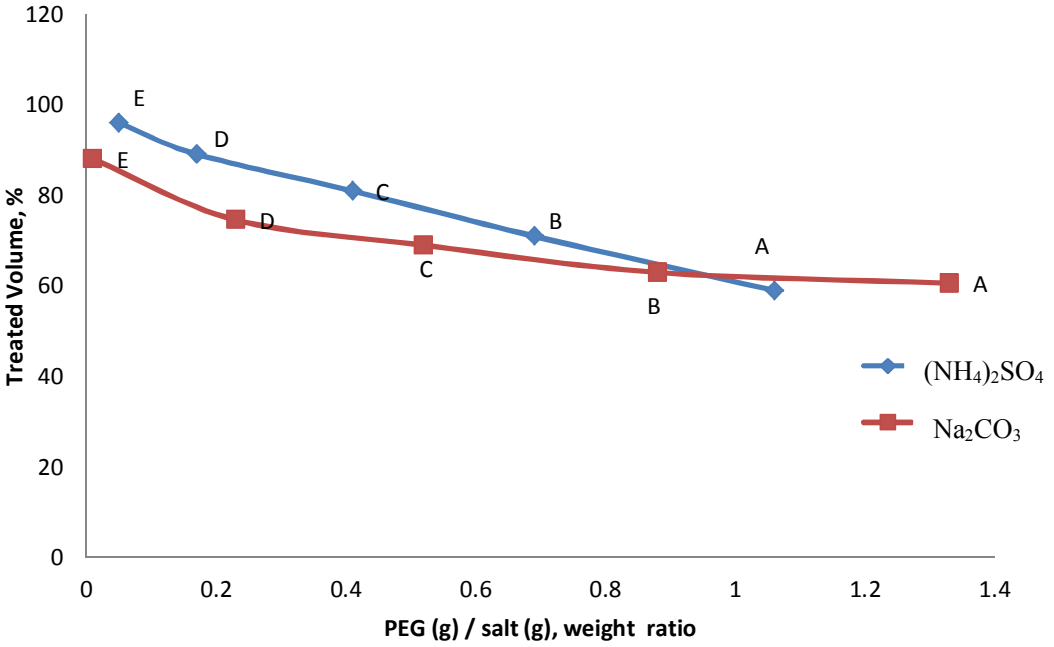


Figure 4.8: Volume of treated ATPS phases versus the weight ratio (WR) of polymer/salts used for $(NH_4)_2SO_4$ and Na_2CO_3.

From Figure 4.8, increasing the WR resulted in a gradual decrease in the phase volume ratio or percentage treated volume of the two systems. However, PEG/Na_2CO_3 ATPS had a lower percentage treated volume than PEG/$(NH_4)_2SO_4$ ATPS, and gradually became almost steady at point B and A. The volume of treated phase in PEG/$(NH_4)_2SO_4$ ATPS decreased steadily as the WR was increased from point E to A.

All points A to E, removed colour excellently, however point E in the two systems had the highest volume of treated phase. Therefore, point E was used for treating effluent TWW from African Textile Manufacturing Company, Kano, Nigeria.

4.7 Effect of TLL on Colour Treatment

Figure 4.9 shows the effect on colour treatment as the operation point is moved further away from the critical point (increase in TLL), a resultant increase in the percentage of colour removed was observed. 70.2 %, 79.8 %, 91.6 % and 99.1 % colour was removed using TLL of 31.4, 37.0, 42.7 and 52.5 % (w/w) respectively, for PEG/$(NH_4)_2SO_4$ ATPS. Similarly, 68.9 %, 76.5 %, 87.1 % and 98.8 % colour was removed using TLL of 40.1, 43.6, 48.7 and 55.5 % (w/w) respectively for PEG/Na_2CO_3 ATPS.

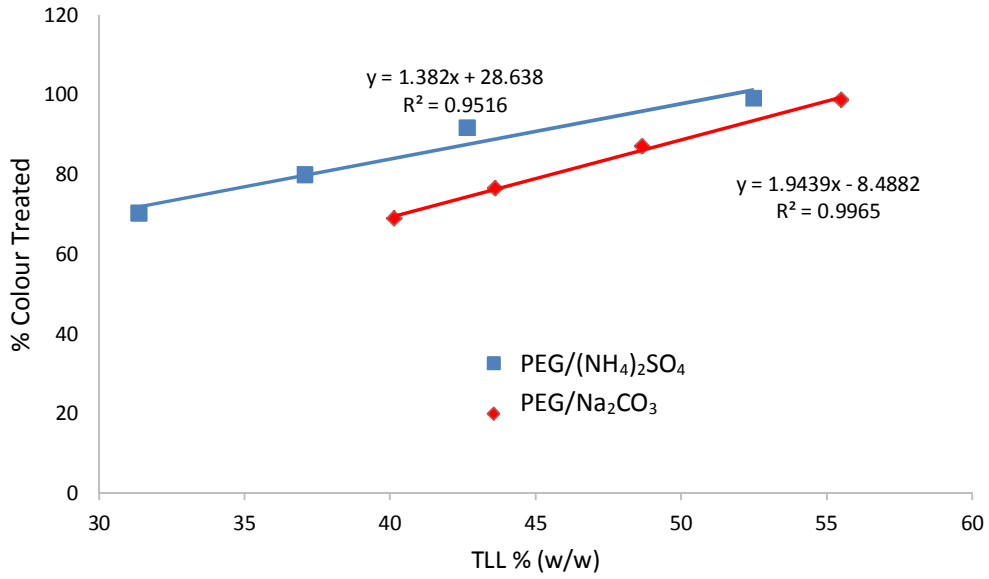


Figure 4.9: Effect of TLL on percentage colour removal in PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS of initial concentration of 250mg/l.

As a result of these, the TLL that provided the best treatment for the two systems were 52.5 % (w/w) and 55.5 % (w/w) for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS respectively and were used to treat the effluent TWW.

4.8 Physico-Chemical Characteristics of Untreated and Treated TWW

From Table 4.3, the pH of untreated effluent TWW which is alkaline and above NESREA (2009) range was greatly improved when treated using the two ATPS. The pH of the untreated effluent TWW can affect the rate of microbial growth by altering metabolic enzymes if not within the approval range. Abnormal or irregular pH can result in a significant decrease in the rate of removal of organic compounds, which will affect the biochemical oxygen demand (BOD_5).

Table 4.3: Physical-chemical characteristics of untreated and treated textile wastewater compared to NESREA, 2009 standards

S/N	Parameter	NESREA (2009)	Untreated	PEG/$(NH_4)_2SO_4$	PEG/Na_2CO_3
1	pH	6 – 9	10.90	8.90	8.20
2	TDS (mg/l)	2000	2905	450	440
3	DO (mg/l)	>0.05	0.08	0.06	0.05
4	Ammonia (mg/l)	0.2	ND	ND	ND
5	Calcium (mg/l)	200	89.00	59.00	61.00
6	Sulphate (mg/l)	300	147.00	99.00	87.00
7	Appearance	Clear	Brown	Clear	Clear
8	COD (mg/l)	80	167.40	42.00	39.00
9	BOD_5 (mg/l)	50	124.85	27.00	19.00

*ND=Not detected

The pH of the treated effluent was adjusted to be within NESREA (2009) acceptable range for the two ATPS studied.

Ammonia was not detected in the effluent TWW sample.

Total Dissolved Solids (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular suspended form. TDS is used as an indication of aesthetic characteristics of drinking

water and as an aggregate indicator of the presence of a broad array of chemical contaminants. NESREA standard for freshwater TDS < 1000 mg/l, results shows that ATPS as a treatment method has improved TDS from an initial effluent concentration level of 2905 mg/l (brackish water) to fresh water range for the two systems.

DO measures the amount of gaseous oxygen dissolved in water, treatment of effluent wastewater using ATPS reduced DO for the two treatment systems, the method still maintained DO content within NESREA (2009) approval range.

Initial calcium and sulphate levels in effluent TWW fell below NESREA (2009) standard and however ATPS still reduced their concentration in both systems. Therefore, ATPS can be used to treat effluent wastewater with high calcium and sulphate content.

The change in appearance of TWW of all the treated phase from brown to clear or colourless is a physical confirmation that ATPS strips off colour from untreated effluent TWW.

ATPS reduced the COD of PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS by 74.9 % and 76.7 % respectively, which was within NESREA (2009) effluent discharged limit range.

ATPS reduced the BOD_5 of PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS by 78.4 % and 84.8 % respectively, which was within NESREA (2009) effluent discharged limit range.

4.9 Heavy Metals

Heavy metals concentrations of effluent TWW and treated TWW using ATPS were compared to NESREA, 2009 standards in Table 4.4 to show the extent of treatment achieved by the ATPS.

Table 4.4: Heavy metals concentrations of untreated and treated textile wastewater compared to NESREA, 2009 standards

S/N	Parameter	NESREA, 2009	Untreated	PEG/$(NH_4)_2SO_4$	PEG/Na_2CO_3
1	Chromium (mg/l)	<0.1	ND	ND	ND
2	Copper (mg/l)	<0.5	1.09	0.569	0.408
3	Iron (mg/l)	20	0.600	0.550	0.400
4	Mercury (mg/l)	<0.05	ND	ND	ND
5	Cadmium (mg/l)	<0.1	0.274	0.021	0.013
6	Lead (mg/l)	<0.1	0.336	0.152	0.036
7	Nickel (mg/l)	<0.2	0.301	0.119	0.074

*ND=Not detected

Chromium was not detected in the untreated effluent TWW.

Copper was reduced by 47.8 % and 62.6 % for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 respectively. However, only PEG/Na_2CO_3 ATPS treated copper concentration to the minimum level required by NESREA (2009).

Iron concentration in the sample was inadequate and fell below the minimum permissible limit. Mercury was not detected in the untreated TWW sample.

Cadmium level was reduced by 92.3 % and 95.3 % for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS respectively, and levels were within NESREA (2009) permissible discharge range.

Lead was reduced by 54.8 % and 89.3 % for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS. However only the treatment performed by PEG/Na_2CO_3 was below the NESREA (2009) effluent discharge limit.

Nickel was reduced by 60.5 % and 75.4 % for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS. Both ATPS were able to reduce the concentration of nickel in the TWW to levels below NESREA (2009) recommendations.

4.10 Colour

The objective was to determine how efficient ATPS can be used as a means of treating colour from effluent TWW. Table 4.3 shows the colour concentrations of untreated effluent TWW and treated TWW compared to NESREA (2009) standards. The colour concentration was determined using Lavibond tintometer.

Table 4.5: Colour concentrations of effluent and treated textile wastewater compared to NESREA (2009) standards

Parameter	NESREA (Pt-Co)	Untreated (Pt-Co)	PEG/$(NH_4)_2SO_4$ (Pt-Co)	% Treated	PEG/Na_2CO_3 (Pt-Co)	% Treated
Colour	<10	585	5	99.1	7	98.8

Analyzing results from Table 4.3, PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 ATPS decolorized TWW by 99.1 % and 98.8 % respectively, which was better when compared to decolourization of simulated textile dye colours solutions. Shiri *et al*., (2012) using ATPS for determining brilliant blue in water and food samples also obtained a recovery between 96 - 99.9%.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results and discussion presented in the previous chapter, the following conclusions can be stated:

1. Aqueous two phase system were successfully prepared using (PEG)/$(NH_4)_2SO_4$ and PEG/Na_2CO_3.
2. Phase diagrams of (PEG)/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 were generated and successfully used to treat five different dyes with colour removal between 82 - 99.7 %.
3. The general trend for colour removal using the ATPS is: Khaki brown > Brilliant blue> Navy blue > Dispersal yellow> Erionyl red.
4. TLL of 52.5 and 55.5 for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3, respectively, provided the best treatment amongst the ones constructed for the two systems.
5. The best weight ratio obtained were 1.06 and 1.33 for PEG/$(NH_4)_2SO_4$ and PEG/Na_2CO_3 systems respectively.
6. Physico-chemical analysis of textile wastewater shows that PEG/Na_2CO_3 performed better in the treatment of BOD_5, COD and TDS than PEG/$(NH_4)_2SO_4$, but in the removal of colour the latter performed better.
7. PEG/Na_2CO_3 ATPS reduced heavy metals comparatively better than PEG/$(NH_4)_2SO_4$ ATPS while PEG/Na_2CO_3, 95.3 %, 89.3 % and 75.4 % of heavy metals were removed in Pb, Ni and Cd respectively.

5.2 Recommendations

Furtherance to the study of utilization of aqueous two phase system for the removal of colour from textile wastewater, the following recommendations have been made:

1. Locally sourced materials should be explored to substitute PEG to increase the viability of using ATPS as a treatment method of TWW.
2. Sodium chloride can be used as a salt forming phase. Hence, the possibility of using locally mined salts, which is in abundance, should be investigated.
3. An ATPS pilot plant for treatment of TWW should be developed.
4. The use of ATPS should be explored in separation processes which have not yielded good result by other form of separation methods..

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APPENDICES

Calculations of tie line length, weight ratio for PEG/$(NH_4)_2SO_4$

1. 3.0002g of 50% (w/w) of PEG solution was added to 3.3097g of 35% (w/w) of $(NH_4)_2SO_4$ solution and 3.1900g of distilled water. This formed an ATPS with the following volumes and densities of the top and bottom phases respectively.

   $V_t = 4.647cm^3, \rho_t = 1.0206g/cm^3, V_b = 4.871cm^3, \rho_b = 1.1237g/cm^3$

   1ml of V_b + 19ml of distillled water = 20ml of diluted bottom solution

   Conductivity of diluted bottom solution = $\frac{18.219mS}{cm}$ (Conductivity meter)

   = equivalent to $\frac{1.2012wt}{vol}\%$ from figure 4.1(a)

   $\Rightarrow \frac{1.2012g}{100ml} \times 20ml = 0.2402g$ Mass of salt in 1ml

   Mass of salt in 4.871ml , $M_s = 4.871 \times 0.2402 = 1.17g$

   Mass of bottom phase, $M_b = \rho_b V_b$, ρ_b is the density of the bottom phase

   $= 1.1237 \times 4.871$

   $= 5.4735\ g$

   weight % ratio of salt at bottom = $\frac{M_s}{M_b} = \frac{\text{Mass of salt in the bottom phase}}{\text{Mass of the bottom phase}}$

   $\frac{M_s}{M_b} = \frac{1.17}{5.4735} \times 100$

   $= 21.3755$

   $\approx 21.38\ \%\ (w/w)$

   volume of top, $V_t = 4.643cm^3$

   $\rho_t = 1.0206g/cm^3$

   Mass of top phase, $M_t = \rho_t V_t$

   $= 1.0206 \times 4.647$

   $= 4.7427g$

Salt balance = $1.334 - 1.17$

(Total weight of salt used to form ATPS = 1.334g, 35wt. % of 3.3097g $(NH_4)_2SO_4$ solution used in the ATPS formation) - (weight of salt in bottom phase)

= $0.1634g$

weight % ratio of salt at top phase

= $\frac{0.1634}{4.7427} \times 100$

= $3.44\% (w/w)$, graphically in figure 4.2 (a) is 4.3% (w/w)

Refractive index, μ top phase = 1.3673 = 28.34% (w/w) From figure 4.2(a)

Refractive index, μ bottom phase = 1.3421 = 2.01% (w/w)

These % (w/w) calculated forms the binodal points of TLL_1

TLL_1, binodals = (21.38, 2.01) and (4.4, 28.34)

Similarly, the same procedure was used to calculate the other binodal points of the remaining TLL. The values used for the calculations are tabulated in Table A1

Table A1: Parameters used to calculate TLL for PEG/$(NH_4)_2SO_4$

	PEG (g)	**$(NH_4)_2SO_4$ (g)**	**H_2O (g)**	**V_t (cm^3)**	**P_t (g/cm^3)**	**V_b (cm^3)**	**P_b (g/cm^3)**	**μ_b (mS/cm)**	**$\square_b$**	**$\square_t$**
TLL_1	3.0002	3.3097	3.1900	4.647	1.0206	4.871	1.1237	18.219	1.3421	1.3673
TLL_2	2.0012	1.5004	1.7107	4.786	1.269	5.157	1.1498	22.840	1.3414	1.3851
TLL_3	2.5003	1.6674	2.5003	4.906	1.0293	6.082	1.1750	27.497	1.3412	1.3971
TLL_4	3.0007	1.7242	3.2943	4.919	1.0427	7.078	1.2410	33.295	1.3407	1.4102

Table A2: Binodals for PEG /$(NH_4)_2SO_4$

	Abscissa, %(w/w)		**Ordinate, %(w/w)**	
	$(NH_4)_2SO_4$	**PEG**	**$(NH_4)_2SO_4$**	**PEG**
TLL_1	21.38	2.01	4.30	28.34
TLL_2	23.91	1.79	4.17	33.18
TLL_3	26.03	1.51	3.19	37.50
TLL_4	30.55	1.32	3.13	46.11

APPENDIX B

Calculations of tie line length, weight ratio for PEG /Na_2CO_3

Similarly, the same procedure was used to calculate the other binodal points. The values used are tabulated in Table B1

Table B1: Parameters used to calculate TLL for PEG/Na_2CO_3

	PEG (g)	Na_2CO_3 (g)	H_2O (g)	V_t (cm^3)	P_t (g/cm^3)	V_b (cm^3)	P_b (g/cm^3)	μ_b (mS/cm)	$\square_b$	$\square_t$
TLL_1	3.0002	3.8801	3.1198	3.17	1.0775	5.021	1.1965	18.795	1.3353	1.3718
TLL_2	4.0802	4.0802	1.9197	3.371	1.0896	5.911	1.2197	20.588	1.3353	1.3789
TLL_3	5.0002	4.5432	0.4547	3.705	1.1136	6.091	1.2577	27.095	1.3352	1.3850
TLL_4	6.0001	1.4401	2.5598	4.088	1.1729	6.287	1.2806	30.833	1.3348	1.3917

Table B2: Binodals for PEG/ Na_2CO_3

	Abscissa, %(w/w)		Ordinate, %(w/w)	
	Na_2CO_3	PEG	Na_2CO_3	PEG
TLL_1	18.80	0.83	1.02	36.81
TLL_2	20.95	0.81	0.89	39.54
TLL_3	23.06	0.79	0.52	43.91
TLL_4	26.12	0.73	0.25	49.35

APPENDIX C

Table C1: ATPS bi-nodals for PEG/ Na_2CO_3

PEG	**Na_2CO_3**	**PEG**	**Na_2CO_3**
0.5	29.4	10.3	5.4
0.8	24.41	17.39	3.83
0.95	17.62	19.21	3.51
1.04	13.42	20.92	3.29
1.1	10.72	22.9	3.08
1.14	8.89	24.09	2.76
1.18	8.42	24.87	2.66
1.5	8.07	26.26	2.36
2.63	7.6	28.73	2.18
3.15	7.32	31.2	1.87
4.8	6.82	33.46	1.65
5.56	6.63	35.58	1.19
7.37	6.2	39.48	0.99
7.84	5.95	43.35	0.62
8.3	5.83	49.39	0.3
9.04	5.65		
10.3	5.4		

Table C2: ATPS bi-nodals for PEG/ $(NH_4)_2SO_4$

PEG	$(NH_4)_2SO_4$
46.45	2.48
42.07	2.7
37.78	3.15
35	3.61
32.3	3.92
30.06	4.13
28.07	4.35
26	4.75
22.75	5.46
20.08	6.18
17.77	7.06
16.16	7.48
15.68	6.98
13.22	7.72
8.14	9.23
3.48	11.11
2.13	13.7
1.09	33.96

APPENDIX D

Table D1: Calculation of WR for PEG/$(NH_4)_2SO_4$ ATPS

Position	Volume of treated phase, %	Weight of PEG (WPEG), g	Weight of $(NH_4)_2SO_4$ (WSalt) g	WR = (WPEG)/(WSalt)
A	96.0	0.15	3.14	0.05
B	89.1	0.47	2.82	0.17
C	81.0	0.95	2.34	0.41
D	71.0	1.34	1.95	0.69
E	59	1.69	1.60	1.06

Table D2: Calculation of WR for PEG/Na_2CO_3 ATPS

Position	**Volume of treated phase, %**	**Weight of PEG (WPEG), g**	**Weight of Na_2CO_3 (WSalt) g**	**WR = (WPEG)/(WSalt)**
A	88.0	0.02	2.62	0.01
B	74.6	0.50	2.15	0.23
C	69.0	0.90	1.74	0.52
D	63.0	1.24	1.41	0.88
E	60.6	1.52	1.13	1.33

APPENDIX E

Table E1: Initial colour concentration, 500mg/*l* for PEG/$(NH_4)_2SO_4$

PEG/Salt % (w/w)	Yellow (mg/l)	Erionyl red (mg/l)	Khaki Brown (mg/l)	Brilliant Blue (mg/l)	Navy Blue (mg/l)
1.06	23.18	7.86	1.5	7.78	9.17
0.69	27.73	36.43	4.5	11.11	13.33
0.41	30.91	50.71	7.0	20.00	21.25
0.17	49.09	72.14	10.5	27.78	32.08
0.05	56.10	83.51	12.2	32.40	40.15

Table E2: Initial colour concentration, 500mg/*l* for PEG/Na_2CO_3

PEG/Salt % (w/w)	Yellow (mg/l)	Erionyl red (mg/l)	Khaki Brown (mg/l)	Brilliant Blue (mg/l)	Navy Blue (mg/l)
1.33	21.81	15.00	5.5	11.11	12.08
0.88	25.00	50.71	10.0	15.56	17.08
0.52	29.55	77.86	19.5	25.56	24.17
0.23	40.46	85.00	22.0	34.44	37.08
0.01	51.25	92.30	34.0	45.12	49.81

Table E3: Initial colour concentration, 250mg/*l* for PEG/$(NH_4)_2SO_4$

PEG/Salt % (w/w)	Yellow (mg/l)	Erionyl red (mg/l)	Khaki Brown (mg/l)	Brilliant Blue (mg/l)	Navy Blue (mg/l)
1.06	10.45	3.57	1.0	3.33	3.33
0.69	12.72	15.00	2.0	4.44	5.42
0.41	14.09	22.86	3.0	8.88	9.17
0.17	24.09	34.29	5.5	13.33	15.00
0.05	32.17	46.12	7.1	18.59	22.10

Table E4: Initial colour concentration, 250 mg/l for PEG/Na_2CO_3

PEG/Salt % (w/w)	Yellow (mg/l)	Erionyl red (mg/l)	Khaki Brown (mg/l)	Brilliant Blue (mg/l)	Navy Blue (mg/l)
1.06	8.64	5.71	2.0	4.44	4.58
0.69	10.9	21.42	4.0	6.67	7.08
0.41	12.73	35.71	8.0	12.22	10.83
0.17	19.09	41.43	9.5	16.67	17.92
0.05	24.18	53.22	11.0	23.57	25.02

Table E5: PEG/$(NH_4)_2SO_4$ % colour removal at initial concentration 500 mg/l

PEG/Salt % (w/w)	Yellow (mg/l)	% Redu.	Erionyl red (mg/l)	% Redu.	Khaki Brown (mg/l)	% Redu.	Brilliant Blue (mg/l)	% Redu.	Navy Blue (mg/l)	% Redu.
1.06	32.45	93.51	33.71	93.26	1.5	99.7	7.78	98.44	9.17	98.17
0.69	38.82	92.24	41.18	91.76	4.5	99.1	11.11	97.78	13.33	97.33
0.41	43.27	91.35	58.08	88.38	7.0	98.6	20.00	96.00	21.25	95.75
0.17	68.73	86.26	66.29	86.74	10.5	97.9	27.78	94.44	32.08	93.58

Table E6: PEG/Na_2CO_3 % colour removal at initial concentration 500 mg/l

PEG/Salt % (w/w)	Yellow (mg/l)	% Redu.	Erionyl red (mg/l)	% Redu.	Khaki Brown (mg/l)	% Redu.	Brilliant Blue (mg/l)	% Redu.	Navy Blue (mg/l)	% Redu.
1.33	21.81	95.64	38.34	92.33	5.5	98.9	11.11	97.78	12.08	97.58
0.88	25.00	95.00	46.84	90.63	10.0	98.0	15.56	96.89	17.08	96.58
0.52	29.55	94.09	66.03	86.80	19.5	96.1	25.56	94.89	24.17	95.17
0.23	40.46	91.91	75.50	84..9	22.0	95.6	34.44	93.11	37.08	92.58

Table E7: PEG/$(NH_4)_2SO_4$ % colour removal at initial concentration of 250 mg/l

PEG/Salt % (w/w)	Yellow	Erionyl red	Khaki Brown	Brilliant Blue	Navy Blue
			% Colour Removal		
1.06	95.82	92.50	99.60	98.66	98.66
0.69	94.91	90.85	99.20	98.22	97.83
0.41	94.36	87.10	99.80	96.44	96.33
0.17	90.36	85.20	97.80	94.66	94.00

Table E8: PEG/Na_2CO_3 % colour removal at initial concentration of 250 mg/l

PEG/Salt % (w/w)	Yellow	Erionyl red	Khaki Brown	Brilliant Blue	Navy Blue
			% Colour Removal		
1.33	94.54	97.71	99.20	98.22	98.17
0.88	95.64	91.43	98.40	97.33	97.17
0.52	94.90	85.71	98.80	95.11	95.66
0.23	92.36	83.43	96.2	93.33	92.83

APPENDIX F

DENSITY CALIBRATION

Table F1: $(NH_4)_2SO_4$ Top Phase

Top (w/w) %	Density, g/cm^3
1	1.0450
2	1.0340
4	1.0220
6	1.0100
8	1.0060

Table F2: $(NH_4)_2SO_4$ Bottom Phase

(w/w)%	Density, g/cm^3
10	1.0570
15	1.0880
20	1.1150
30	1.1720
35	1.2000
40	1.2280

Table F3: Na_2CO_3 Top Phase

(w/w)%	Density, g/cm^3
0.20	1.0756
0.34	1.0802
0.41	1.0851
0.67	1.0935
0.89	1.0976
1.20	1.1052

Table F4: Na_2CO_3 Bottom Phase

(w/w)%	Density, g/cm^3
13.06	1.2972
14.27	1.2482
16.90	1.2240
21.35	1.1761
23.65	1.1491
26.80	1.1289

APPENDIX G

EFFECT OF TLL ON COLOUR TREATMENT

Table G1: PEG/$(NH_4)_2SO_4$ ATPS

TLL	% Colour treated
31.38	70.21
37.08	79.80
42.67	91.60
52.51	99.10

Table G2: PEG/Na_2CO_3 ATPS

TLL	% Colour treated
40.13	68.92
43.62	76.51
48.66	87.10
55.50	98.80