

**Recovering Energy, Nutrient and Water from Wastewater
of Bulgur Plants**

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ABSTRACT

RECOVERING ENERGY, NUTRIENT AND WATER FROM WASTE WATER OF BULGUR PLANTS

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In this study, recovering energy, nutrient and water from wastewater of bulgur plants were investigated. Especially, the washing and cooking steps are important operations in bulgur processing due to the significant amount of water usage and disposal. At present, the wastewater from the washing and cooking operations is discharged without any recovering operation in the industry. Washing (20 °C) and cooking (97 °C) were made using 1 and 2 ratios of water to 1 ratio of wheat, respectively. The wastewater obtained from the washing and cooking was treated with filtration, centrifugation and column which contains sand, activated carbon and resin, and then finally treated with UV. Before and after the treatments, the properties of water (DO, BOD₅, color values, pH, turbidity, conductivity, total solid content, Brix and microorganism load only for the washing wastewater) were determined to find the effect of the treatments.

It was found that these treatments were significantly ($p < 0.05$) effective on the reduction of the BOD₅ values from 311.5 to 169.9 and from 429.5 to 93.7 mg/l, for the washing and cooking, respectively. For both wastewater, the treatments improved

the color values (L^* , a^* , b^* , YI). Total solid content, Brix, conductivity and turbidity decreased.

In addition to the recovering treatments, the wastewater of cooking was used in the next cooking operation by mixing with fresh water. It was found that the reuse of wastewater could be possible for the subsequent cooking operations. Also, the nutrients leached during the cooking lead to increase the BOD_5 value of the wastewater of cooking. At this point, the spray drying method was used to recover the nutrients. The spray dried product can be used in ready soup, baby foods recipes, because of containing 19 % protein, 10 % starch and 12 % ash.

According to the result, 73.4 and 49.5 % of wastewater can be obtained from the washing and cooking operations, respectively. Additionally, one bulgur plant, having 50 tons/day capacity, can save nearly \$ 70524 and 19080 tons of water, annually. The net profit after the evaluation of investment cost, processing cost, salvage value and service life of system was calculated as \$ 51524.

Keywords: wastewater, recovery, bulgur, cooking, washing, energy, water, nutrient

ÖZET

BULGUR FABRİKALARININ ATIK SULARINDAN ENERJİ, BESİN VE SU GERİ KAZANIMI

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Bu çalışmada bulgur fabrikalarının atık sularından enerji, besin ve suyun geri kazanımı araştırılmıştır. Bulgur üretiminde yüksek miktarda su kullanımı ve atılmasından dolayı, özellikle yıkama ve pişirme işlemleri önem arz etmektedir. Günümüzde, sanayide yıkama ve pişirme işleminden meydana çıkan atık su herhangi bir işleme konmadan atılmaktadır. Bu çalışmada, yıkama (20 °C) ve pişirme (97 °C) işlemi 1 oran buğday oranına sırasıyla 1 ve 2 oran su kullanıldı. Yıkama ve pişirmeden elde edilen atık suyu sırasıyla filtrasyon, santrifüj ve içersinde kum, aktif karbon ve reçine bulunan kolon ve en sonunda ultraviyole ışıktan geçirilmiştir. Bu işlemlerin etkilerini öğrenmek amacıyla, atık suyun özellikleri (çözünmüş oksijen, BOİ₅, renk değerleri, pH, bulanıklık, iletkenlik, toplam katı madde, Brix ve sadece yıkama suyunda mikrobiyal yük) işlemlerden önce ve sonra belirlendi.

İstatistiksel olarak, atık su işlemlerinin yıkama ve pişirme sularına ait BOİ₅ değerlerinde sırasıyla 311.5'ten 169.9'a ve 429.5'ten 93.7 mg/l olmak üzere önemli (p<0.05) etkileri olduğu belirlenmiştir. Her iki atık suda da renk değerleri olumlu

yönde deęişmiştir. Toplam katı madde, iletkenlik, Brix ve bulanıklık deęerleri düşmüştür.

Ayrıca uygulanan atık su deęerlerine ek olarak, pişirme işleminden elde edilen atık su bir sonraki pişirme işleminde temiz su ile karıştırılarak kullanılmıştır. Ve daha sonraki pişirme işlemlerinde de kullanılabilceęi anlaşılmıştır. Bununla beraber pişirme suyuna geçen besinler, pişirme suyundaki BOİ₅ deęerinin yükselmesine sebep olmaktadır. Bu noktada, bu besinleri geri kazanmak için püskürtmeli kurutma yöntemi kullanılmıştır. Püskürtmeli kurutma yöntemi ile elde edilen ürün %19 protein, %10 nişasta ve %12 kül oranı ile hazır çorba, bebek maması olarak ta kullanılabilir.

Elde edilen sonuçlara göre, yıkama ve pişirme işlemlerinden sırasıyla %73.4 ve %49.5 oranında su geri kazanılabilmektedir. Ayrıca, 50 ton/gün kapasiteli bir bulgur fabrikası, yıllık olarak \$ 70524 ve 19080 ton su geri kazanabilecektir. Yatırım maliyeti, işletme maliyeti, hurda deęeri ve servis ömrünün hesaplanmasının ardından net kar \$ 51524 olarak ortaya çıkmıştır.

Anahtar kelimeler: atık su, geri kazanım, bulgur, pişirme, yıkama, enerji, su, besin.

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ABBREVIATIONS

ρ_G	Density of water, (g/ml)
ρ_W	Density of wastewater, (g/ml)
A_D^{20}	conversion factor (specific rotation) of Ewer's method for starch (182.7 / (dm x g/ml))
AF-1	Treatments of the washing wastewater
AF-2	Treatments of the cooking wastewater
a_p	Polarization value
B_1	Dissolved oxygen of seed control before incubation, (mg/l)
B_2	Dissolved oxygen of seed control after 5 days incubation, (mg/l)
Back-1	Back cooking operation after the cooking operation
Back-2	Back cooking operation after the Back-1 cooking operation
BOD	Biochemical oxygen demand, (mg/l)
BOD₅	Biochemical oxygen demand in 5 days, (mg/l)
CFU	Colony forming unit
COD	Chemical oxygen demand, (mg/l)
C_p	Specific heat capacity, (j/kg K)
DO	Dissolved oxygen, (mg/l)
DO₁	DO of the diluted sample 15 minutes after preparation, (mg/l)
DO₂	DO of the diluted sample after 5 days incubation, (mg/l)
Ec	Electrical conductivity, (S/cm)
EU	The European Union
f	Fraction of seeded dilution water volume of sample in to volume of seeded dilution water in seed control
L_p	Length of polarization tube, (dm)
MPN	Most probable number method
P	Decimal fraction of sample used
PCA	Plate count agar
Rpm	Revolution per minute

RW	Recovered water
TSC	Total solid content, (%)
TSE	Turkish Standard
TSS	Total suspended solids
UV	Ultraviolet, (nm)
V_{TS}	Total volume of sample, (ml)
WABO	Wastewater after Back cooking operation
WAT	Water after treatments
WB1O	Wastewater of Back-1 operation
WB2O	Wastewater of Back-2 operation
WCO	Wastewater of the cooking operation
W_s	Weight of sample, (g)
WWO	Wastewater of the washing operation
YI	Yellowness index

CHAPTER I

INTRODUCTION

1.1. Definition of Bulgur

Bulgur is an excellent food source due to its low cost, storability (long shelf-life), ease of preparation, and high nutritional value, which resists mould contamination and attack by insects and mite (Bayram et al., 1996; Bayram, 2000).

One million ton of bulgur (\$ 800 million) is produced in Turkey by 500 plants. About twenty percent of bulgur production is exported. Out of Turkey, there is also important amount of bulgur production. In addition, 250,000–300,000 tonnes (15–20 bulgur plants) in the United States plus Canada, 60,000–80,000 tonnes (4–6 bulgur plants) in the EU and 100,000–120,000 tonnes (10–15 bulgur plants) in the Arabic countries are produced (Bayram et al., 2006).

Bulgur is coming into commercial prominence in the United States, as large amounts are being shipped overseas under government assistance programs, and its availability in domestic food channels is growing. Because, it is a whole grain food and popular in the health foods sector, and its hearty flavour lends itself to be included frequently in vegetarian meals (Bayram et al., 2004a).

Apart from being labour-intensive, the conversion of wheat into bulgur entails wastage of nutrients especially as only 84-86% of the wheat is normally recovered as bulgur (Williams et al., 1984). Bulgur is still second only to bread in importance in the diets of village and rural people. Although, both bread wheat and durum wheat cultivars are used in bulgur production, generally durum wheat is the preferred raw material. Homemade maize bulgur is a traditional food in the northern regions of Turkey. In earlier days, barley was also used in bulgur production especially when wheat was in short supply for economic reasons (Köksel et al., 1998).

Bulgur is a cleaned, cooked, dried, dehulled, milled and finally classified wheat product (generally produced from *Triticum durum*), which is grouped in semi-ready-to-eat (for pilaf etc.) or ready-to-eat (for köfte i.e. meatball, kısır like tabbouleh etc.) foods and its production and consumption around the world increased due to its having low cost, long shelf life, ease of preparation, high nutritional value and pre-cooked property. It is a whole grain food and popular in the health foods sector, and its hearty flavor lends itself to be included frequently in vegetarian meals (Bayram et al., 1996; Bayram, 2000; 2002; 2004a; 2004b; 2004c).

Its starch is almost completely gelatinized because the kernel is cooked. It is more stable than wheat in hot and humid environments. Biological differences between wheat and bulgur are that wheat has respiration activity and its enzymes are active in the kernel in contrast to bulgur (Bayram et al., 1996, Bayram, 2000). It is also stored for military and humans nutrition purposes in some countries because of its resistance to absorption of radiation (today, bulgur is one of the important wheat products in the U.S.A., and it is included in the special list of food rations in nuclear fallout shelters), prevents cancer and is consumable alone in diets. It is a critical food material for Turkish, Arabic, Mediterranean, and North African and East European peoples because of its economical and nutritional value.

The consumption of bulgur is also important to understand its economical and nutritional properties. It is approx. 2.5 and 2.0 times higher than that of pasta and rice in Turkey, respectively. The average annual consumption of bulgur is about 12 kg/person. This consumption is amazingly huge in the East and South Parts of Turkey (~25 kg/person) and in Syria, Iraq, Iran, Israel, Lebanon, Arabia i.e. Middle East countries (~30-35 kg/person) (Bayram, 2000, 2005a,b,c; Bayram et al., 1996; 2002; 2004a,b). The amount of bulgur for food-aid programs annually reached to 60,000-80000 tonnes and gradually increase each year, which is made by United Nation and WFP. The same amount of bulgur is additionally supplied from USA to the developing countries.

Bulgur is also important as a dietary fibre source, having 18.3 g dietary fibre per 100 g. Its dietary fibre content is 3.5, 6.8, 1.1, 1.8, 7.0, 15.3, 9.2, 2.3, 1.3 and 4.3 times higher than rice, wheat flour, barley, oat meal, spinach, tomato, turnip, whole wheat bread, soybean and pasta, respectively (Dreher, 2001). The detailed nutritional

properties of bulgur were given in literature (Bayram, 2000; 2005a, b, c; Bayram et al., 2003a, b).

Due to the significant trend to produce bulgur in developing and developed countries, some technological upgrades are required. Therefore, each step in the bulgur production system should be strictly controlled and adapted with new technologies.

1.2. Bulgur Production System

Cleaning operation in bulgur production system is similar to flour and semolina systems. Cleaning is made by using the aspirator installed sieving machine. This stage removes dust, soil and foreign materials. Cleaning step is finished with the washing. Then cooking is applied to wheat until 40-60% of water is absorbed by the kernel for complete gelatinization of starch. The gelatinized starch adheres to the nitrogenous compound and it is not disturbed. Cooking is generally made under atmospheric conditions using specially designed cooker. The cooked bulgur is dried under sun or in tower dryer until the moisture content decreases to 10-12%. Optionally, the second washing is made in general for sun dried products. After the drying operation, wheat bran is peeled using emery machine. During peeling, aleurone and endocarp layers should not be damaged. The peeled wheat is grinded with mill. The milled bulgur is classified with sieve into coarse, medium and fine sizes. The processed bulgur is packaged into bag or sack and then stored.

Energy, water and nutrients losses are significant in bulgur plants especially during the washing and cooking operations. Discharged waste water causes environmental problems and additional waste water treatment cost. The recovering discharged water will supply decreasing processing cost, low energy consumption, new by-products and new bulgur plant investments opportunity in arid regions i.e. hot climate Arabic countries (50 tones capacity having bulgur plant needs 100-120 tones of fresh water per day).

The washing and cooking steps are important in bulgur processing due to the significant amount of water usage and dispose. For example, in Turkey, 1,350,000 tones of cleaned wheat and 2,700,000 tones of water (2,025,000 tones for cooking, 2:3 (wheat: water) + 675,000 tones for washing, 2:1 (wheat: water)) are annually used to produce 1,000,000 tons of bulgur (yield 75%). After washing, 675,000 tones

of waste water are discharged. Also, in the cooking operation, unabsorbed water (remaining water, 25% of used water) is discharged (506,250 tones) at 95 °C. Total water discharge and economical loss are annually 1,181,250 tones and \$ 885,937 (\$0.75/ton), respectively. In addition to this water loss, \$10,824,168 is another loss due to the discharge of remaining 506,250 tones of hot cooking water from the cooking operation at 95 °C (\$0.5 /kg of fuel, 9200 kcal/kg of fuel, as 85% burning efficiency, initial temperature of water is 15 °C). As a result, \$11,578,858 is totally lost, annually from bulgur plants in Turkey.

In addition to the energy and water losses, the significant amount of nutrient loss (water-soluble nutrients i.e. vitamins, minerals, pigments, starch, proteins etc.) occurs from wheat during the cooking operation due to the leaching of components into the discharge water. The transfer of nutrients from wheat kernel to cooking water is well-known in bulgur production. Some of the remaining substances in the discharge water after the cooking operation are important for the nutritional properties of bulgur and environmental pollution. This discharge water might be re-used for the next cooking operation to recover energy and water. Also, it can be used to produce new-products using concentration or spray drying methods such as powders for baby foods or ready soups formulas etc.

1.3. Wastewater Treatment

Cereal plants use huge amounts of water. This water can easily be processed to reuse. At the same time, energy and nutrient can be recovered. In bulgur plants waste water may appear, at first sight, to be very attractive source of cheap and free substances for fermentation process.

1.3.1. Properties of Wastewater

Waste is classified as solid, liquid and gas. Wastewater is liquid waste. The physical, chemical and biological constituents found in wastewater.

1.3.1.1. Physical properties of wastewater

1.3.1.1.1. Color

The color of the wastewater is depending on the sources of the waste. The industrial and domestic wastewater's colors are different as their content changes. Fresh wastewater is usually a light brownish-gray color. Some industrial wastewaters may add color to domestic wastewater. In most cases, the gray, the dark gray and black color of the wastewater is due to the metallic sulfides, which form as the sulfide produced under anaerobic conditions reacts with the metals in the wastewater (Tchobanoglus et al., 2003).

1.3.1.1.2. Odor

Odors of wastewater is usually caused by decomposition of organic matter or by substances added to the wastewater. Fresh wastewater has a distinctive, somewhat disagreeable odor, which less objectionable than the odor of wastewater which has undergone anaerobic (devoid of oxygen) decomposition (Tchobanoglus et al., 2003).

1.3.1.1.3. Total solid content and brix

The most important physical characteristic of wastewater is its solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Wastewater contains a variety of solid materials varying from rags to colloidal materials. In the characterization of wastewater, coarse materials are usually removed before the sample is analyzed for solids. The brix of wastewater can be used to measure soluble solid content in the wastewater (Tchobanoglus et al., 2003).

1.3.1.1.4. Turbidity

Turbidity, a measure of the light-transmitting properties of water, is another test used to indicate the quality of waste discharges and natural waters with respect to colloidal

and residual suspended matter. Colloidal matter will scatter or absorb light and thus prevent its transmission (Tchobanoglous et al., 2003).

1.3.1.1.5. Absorption and transmittance

The absorbance of a solution is a measure of amount of light, of a specified wavelength, that is absorbed by the constituents in a solution. Absorbance is measured with a spectrophotometer using a specified wavelength. Percent transmittance is affected by all substances in wastewater that can absorb or scatter light (Tchobanoglous et al., 2003).

1.3.1.1.6. Temperature

The temperature of wastewater is commonly higher than that of the local water supply, because of the addition of warm water from households and industrial activities. The temperature of the wastewater is also depending on the location and the time of the year. The temperature of water is a very important parameter because of its effect on chemical reactions and reaction rates, aquatic life, and the suitability of the water for beneficial uses. It affects the oxygen solubility and the biological reactions as reactions increase the temperature of the wastewater (Tchobanoglous et al., 2003).

1.3.1.1.7. Conductivity

The electrical conductivity of water is a measure of the ability of a solution to conduct an electrical current. Because the electrical current is transported by ions in solution, the conductivity increases as the concentration of ions increase. At present, the EC of water is one of the important parameters used to determine the suitability of the water from irrigation (Tchobanoglous et al., 2003). In general, the measurement of conductivity is a rapid way of determining the ionic strength of a solution.

1.3.1.1.8. **Density and specific gravity**

Density is an important physical characteristic of wastewater because of the potential for the formation of the density currents in sedimentation tanks, chlorine contact tanks, and other treatment units. In some cases the specific gravity of the wastewater, s_w , is used in place of the density. The specific gravity is defined at Eq. 1.1:

$$s_w = \frac{\rho_w}{\rho_o} \quad (1.1)$$

Both the density and specific gravity of wastewater are temperature-dependent and vary with the concentration of total solids in the wastewater (Tchobanoglus et al., 2003).

1.3.1.2. **Chemical properties of Wastewater**

The chemical constituents of wastewater are typically classified as organic and inorganic.

1.3.1.2.3. **Organic compounds**

Organic constituents of interest in wastewater are classified as aggregate and individual. Aggregate organic constituents are comprised of a number of individual compounds that cannot be distinguished separately. Both aggregate and individual organic constituents are of great significance in the treatment, disposal, and reuse of wastewater. A number of organic compounds are found in wastewater, including humic substances, lignin, tannin, and various aromatic compounds. Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. The organic matter in wastewater typically consists of proteins (40 to 60 percent), carbohydrates (25 to 50 percent), and oils and fats (8 to 12 percent). Individual organic compounds are determined to assess the presence of priority pollutants and a number of new emerging compounds of concern. Priority pollutants (both inorganic and organic) have been and are continuing to be selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. As the techniques used to identify specific compounds continue to improve, a number of other organic

compounds have been detected in public water supplies and in treated wastewater effluents. Figure 1.1 shows the classification of the organic substances (Tchobanoglus et al., 2003).

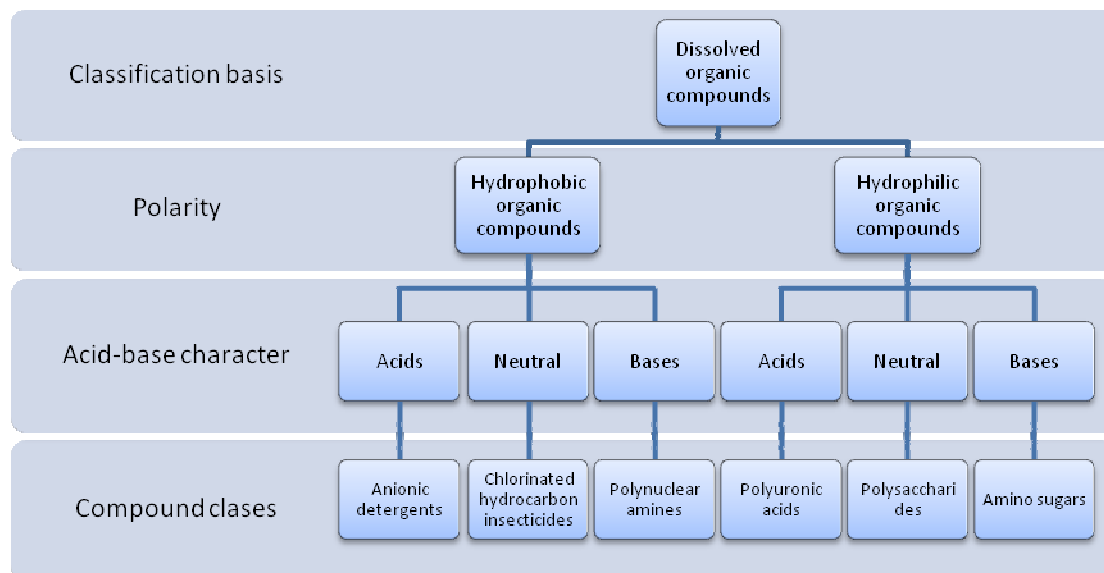


Figure 1.1. Procedure for the characterization of the organic fractions (Tchobanoglus et al., 2003)

1.3.1.2.4. Inorganic compounds

Inorganic chemical constituents of concern include nutrients, nonmetallic constituents, and metals. The source of inorganic constituents and metallic constituents in wastewater derive from the background levels in the water supply and from the additions resulting from domestic use, from the addition of highly mineralized water from private wells and groundwater, and from industrial use. Domestic and industrial water softeners also contribute significantly to the increase in mineral content and, in some areas, may represent the major source. Occasionally, water added from private wells and groundwater infiltration will (because of its high quality) serve to dilute the mineral concentration in the wastewater. Inorganic nonmetallic constituents considered in this section include pH, nitrogen, phosphorus, alkalinity, chlorides, sulfur, other inorganic constituents, and odors (Tchobanoglus et al., 2003).

1.3.1.2.4.1. pH

The hydrogen ion concentration is an important quality parameter of both natural waters and wastewaters. The concentration range suitable for the existence of most biological life is quite narrow and critical (typically 6 to 9). Wastewater with an extreme concentration of hydrogen ion is difficult to treat by biological means, and if the concentration is not altered before discharge, the wastewater effluent may alter the concentration in the natural waters. For treated effluents discharged to the environment the allowable pH range usually varies from 6.5 to 8.5. The hydrogen ion concentration in water is connected closely with the extent to which water molecules dissociate (Tchobanoglus et al., 2003).

1.3.1.2.4.2. Chlorides

Chloride is a constituent of concern in wastewater as it can impact the final reuse applications of treated wastewater. Chlorides in natural water result from the leaching of chloride-containing rocks and soils with which the water comes in contact and in coastal areas from salt water intrusion. In addition, agricultural, industrial, and domestic wastewaters discharged to surface water are a source of chlorides (Tchobanoglus et al., 2003).

1.3.1.2.4.3. Alkalinity

Alkalinity in wastewater results from the presence of the hydroxides [OH⁻], carbonates [CO₃²⁻], and bicarbonates [HCO₃⁻] of elements such as calcium, magnesium, sodium, potassium, and ammonia. Of these, calcium and magnesium bicarbonates are most common. Borates, silicates, phosphates, and similar compounds can also contribute to the alkalinity. The alkalinity in wastewater helps to resist changes in pH caused by the water supply, the groundwater, and the materials added during domestic use (Tchobanoglus et al., 2003).

1.3.1.2.4.4.Nitrogen

The elements nitrogen and phosphorus, essential to the growth of microorganisms, plants, and animals, are known as nutrients or biostimulants. Trace quantities of other elements, such as iron, are also needed for biological growth, but nitrogen is an essential building block in the synthesis of protein, nitrogen data will be required to evaluate the treatability of wastewater by biological process. Insufficient nitrogen can necessitate the addition of nitrogen to make the waste treatable (Tchobanoglus et al., 2003).

The principal sources of nitrogen compounds are:

1. The nitrogenous compounds of plant and animal origin,
2. Sodium nitrate,
3. Atmospheric nitrogen.

The chemistry of nitrogen is complex, because of the several oxidation states that nitrogen can assume and the fact that changes in the oxidation state can be brought about by living organisms. The most common and important forms of nitrogen in wastewater and their corresponding oxidation state in the water/soil environment are ammonia (NH_3 , -III), ammonium (NH_4^+ , -III), nitrogen gas (N_2 , 0), nitrite ion (NO_2^- , +III), and nitrate ion (NO_3^- , +V). The oxidation state of nitrogen in most organic compounds is -III (Tchobanoglus et al., 2003).

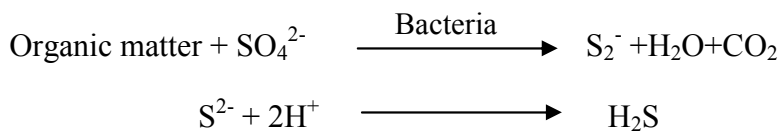
1.3.1.2.4.5.Phosphorus

Phosphorus is also essential to the growth of algae and other biological organisms. Because of noxious algal blooms that occur in surface waters, there is presently much interest in controlling the amount of phosphorus compounds that enter surface waters in domestic and industrial waste discharges and natural runoff. Municipal wastewaters, for example, may contain from 4 to 16 mg/L of phosphorus as P. The usual forms of phosphorus that are found in aqueous solutions include the orthophosphate, polyphosphate, and organic phosphate. The orthophosphates, for example, PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4 , are available for biological metabolism without further breakdown. The polyphosphates include those molecules with two or more phosphorus atoms, oxygen atoms, and, in some cases, hydrogen atoms

combined in a complex molecule. Polyphosphate undergo hydrolysis in aqueous solutions and revert to the orthophosphate forms; however, this hydrolysis is usually quite slow. The organically bound phosphorus is usually of minor importance in most domestic wastes, but, it can be an important constituent of industrial wastes and wastewater sludges (Tchobanoglus et al., 2003).

1.3.1.2.4.6.Sulfur

The sulfate ion occurs naturally in most water supplies and is present in wastewater as well. Sulfur is required in the synthesis of proteins and is released in their degradation. Sulfate is reduced biologically under anaerobic conditions to sulfide which, in turn, can combine with hydrogen to form hydrogen sulfide (H₂S). The following generalized reactions are typical (Tchobanoglus et al., 2003).



Hydrogen sulfide gas, which will diffuse into the headspace above the wastewater in sewers that are not flowing full, tends to collect at the crown of the pipe. The accumulated H₂S can then be oxidized biologically to sulfuric acid, which is corrosive to concrete sewer pipes (Tchobanoglus et al., 2003).

1.3.1.2.5. Gases

Gases commonly found in untreated wastewater include nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), hydrogen sulfide (H₂S), ammonia (NH₃), and methane (CH₄). The first three are common gases of the atmosphere and will be found in all waters exposed to air. The latter three are derived from the decomposition of the organic matter present in the wastewater and are of concern with respect to worker health and safety. Although not found in untreated wastewater, other gases with which the environmental engineer must be familiar include chlorine (Cl₂), and ozone (O₃) (for disinfection and odor control), and the oxides of sulfur and nitrogen (in combustion processes) (Tchobanoglus et al., 2003).

1.3.1.2.5.1.Dissolved oxygen

Dissolved oxygen is required from the respiration of aerobic microorganisms as well as all other aerobic life forms. However, oxygen is only slightly soluble in water. The actual quantity of oxygen (other gases too) that can be present in solution is governed by;

- Solubility of gases,
- The partial pressure of the gas in the atmosphere,
- Temperature,
- The concentration of the impurities in the water (e.g., salinity, suspended solids, etc.).

Because the rate of biochemical reactions that use oxygen increase with increasing temperature, dissolved oxygen levels tend to be more critical in summer months. The problem is compounded in summer months because streams flows are usually lower, and thus the total quantity of oxygen available is also lower. The presence of dissolved oxygen in wastewater is desirable because it prevents the formation of noxious odors (Tchobanoglus et al., 2003).

1.3.1.2.5.2.Hydrogen sulfide

Hydrogen sulfide is formed from the anaerobic decomposition of organic matter containing sulfur or from the reduction of mineral sulfites and sulfates. It is not formed in the presence of an abundant supply of oxygen. This gas is a colorless, inflammable compound having the characteristic odor of rotten eggs. Hydrogen sulfide is also toxic, and great care must be taken in its presence. The blackening of the wastewater and sludge usually results from the formation of hydrogen sulfide that has combined with the iron present to form ferrous sulfide (FeS) (Tchobanoglus et al., 2003).

1.3.1.2.5.3.Methane

The principle byproduct from the anaerobic decomposition of the organic matter in wastewater is methane gas. Methane is a colorless, odorless, combustible hydrocarbon of high fuel value. In treatment plants, methane is produced from the anaerobic treatment process used to stabilize wastewater sludges (Tchobanoglus et al., 2003).

1.3.1.3. Biological properties of wastewater

The biological characteristics of wastewater are of fundamental importance in the control of disease caused by pathogenic organisms of human origin, and because of the extensive and fundamental role played by bacteria and other microorganisms in the decomposition and stabilization of organic matter both in nature and in wastewater treatment plants. Organisms found in surface water and wastewater includes bacteria, fungi, algae, protozoa, plants and animal, and viruses. Bacteria, fungi, algae, protozoa, and viruses can only be observed microscopically (Tchobanoglus et al., 2003).

1.4. Important contaminated materials in wastewater

- Suspended solid materials,
- Bio-degradable materials,
- Pathogenic organisms,
- Nutrients for microorganisms,
- Pollutants,
- Hardly degradable organic compounds,
- Heavy metals,
- Dissolved organic materials.

1.5. Wastewater Treatment Processes

Water treatment systems have the objective of producing water suitable for a particular use (Schroeder, 1979). Many of the new treatment methods being developed are designed to deal with health and environmental concerns associated with findings of recent research (Tchobanoglus et al., 2003). A significant problem in wastewater treatment is deciding which process modification or new panacea should be used for a particular problem. Theoretical studies offer many advantages and

disadvantages also. The most important and difficult feature of this type research is the need to maintain a relationship with the real world. Selection of processes for treatment of a particular water or wastewater is based upon product-water requirements, influent-water characteristics, and, where alternatives are available, cost. In development of a treatment system consisting of a train of individual processes, the interaction of steps must be considered, and this is often a distinct economic factor (Schroeder, 1979).

1.5.1. Physical Processes

Operations used for the treatment of wastewater in which change is brought about by means of or through application of physical forces are known as physical unit operations.

1.5.1.1. Screening

The first unit operation generally encountered in wastewater-treatment plants is screening. A screen is a device with openings, generally of uniform size, that is used to retain solids found in the effluent wastewater to the treatment or in combined wastewater collection systems subject to overflows, especially forms stormwater. The principle role of screening is to remove coarse materials from the flow stream that could:

- Damage subsequent process equipment
- Reduce overall treatment process reliability and effectiveness
- Contaminate waterways.

Fine screens are sometimes used in a place of or following coarse screens where greater removals of solids are required to protect process equipment or eliminate materials that may inhibit the beneficial reuse of biosolids (Tchobanoglus et al., 2003).

1.5.1.2. Communication

As an alternative to coarse bar screens or fine screens, comminutors and macerators can be used to intercept coarse solids and grind or shred them in the screen channel.

High speed grinders are used in conjunction with mechanically cleaned screens to grind and shred screenings that are removed from wastewater. The solids are cut up into a smaller, more uniform size for return to the flow stream for subsequent removal by downstream treatment operations and processes. Communicators, macerators, and grinders can theoretically eliminate the messy and offensive task of screenings handling and disposal (Tchobanoglus et al., 2003).

1.5.1.3. Flotation

Flotation is a unit operation used to separate solid or liquid particles from a liquid phase. Separation is brought about by introducing fine gas (usually air) bubbles into the liquid phase. The bubbles attach to the particulate matter, and the buoyant force of the combined particles and gas bubbles is great enough to cause the particles to rise to the surface. Particles that have higher density than the liquid can thus be made to rise. The rising of particles with lower density than the liquid can also be facilitated (e.g. oil suspension in water) (Tchobanoglus et al., 2003).

1.5.1.4. Primary sedimentation

The objective of treatment by sedimentation is to remove readily settleable solids and floating material and thus reduce the suspended solids content. Primary sedimentation is used as a preliminary step in the further processing of the wastewater. Efficiency designed and operated primary sedimentation tanks should removed from 50 to 70 percent of the suspended solids and from 25 to 40 percent of BOD. The purpose of sedimentation is to remove a substantial portion of the organic solids that otherwise would be discharged directly to the receiving waters. Sedimentation tanks have also been used to provide detention periods sufficient for effective disinfection of such overflows (Tchobanoglus et al., 2003).

For separating liquids of density, thickening slurries, or removing solids, the centrifugation process is widely used in industry. The process is applicable to the dewatering of wastewater sludges and has been widely used in both United States and Europe (Tchobanoglus et al., 2003).

Sometimes gravity separation may be too slow because of the closeness of the densities of the particle and the fluid, or because of association forces holding the components together, as in emulsions (Geankoplis, 1994).

1.5.1.5. Flow equalization

Flow equalization is a method used to overcome the operational problems caused by flow rate variations, to improve the performance of the downstream processes, and to reduce the size and cost of downstream treatment facilities. Flow equalization simply is the damping of flow rate variations to achieve a constant or nearly constant flow rate and can be applied in a number of different situations, depending on the characteristics of the collection systems. The principal applications are for the equalization of dry-weather flows to reduce peak flows and loads, wet-weather flows in sanitary collection systems experiencing inflow and infiltration or combined stormwater and sanitary system flows (Tchobanoglus et al., 2003).

1.5.1.6. Mixing and flocculation

Mixing is an important unit operation in many phases of wastewater treatment including mixing of one substance completely with another, blending of miscible liquids, flocculation of wastewater particles, continuous mixing of liquid suspensions, and heat transfer. Most mixing operations in wastewater can be classified as continuous-rapid (less than 30 s) or continuous (Tchobanoglus et al., 2003).

The purpose of wastewater flocculation is to form aggregates or flocs from finely divided particles and from chemically destabilized particles. Flocculation is a transport step that brings about the collisions between the destabilized particles needed to form larger particles that can be removed readily by settling or filtration. Fluctuation typically follows rapid mixing where chemicals have been added to destabilize the particles. The destabilization of particles resulting from the addition of chemicals is defined as “coagulation” (Tchobanoglus et al., 2003).

1.5.1.7. Grit removal

Removal of grit from wastewater may be accomplished in grit chambers or by the centrifugal separation of solids. Grit chambers are designed to remove grit, consisting of sand, gravel, cinders or other heavy solid materials that have subsiding velocities or specific gravities substantially greater than those of the organic putrescible solids in wastewater. Grit chambers are most commonly located after the bar screens and before the primary sedimentation tanks. Primary sedimentation tanks function for the removal of the heavy organic solids (Tchobanoglus, 2003).

1.5.1.8. Aeration systems

There are several types of aeration systems for wastewater treatment. The systems used depend on the function to be performed, type and geometry of the reactor, and cost to install and operate the system.

1.5.1.8.1. Oxygen transfer

Oxygen transfer, the process by which oxygen is transferred from the gaseous to the liquid phase, is a vital part of a number of wastewater-treatment processes. The most common application of oxygen transfer is in the biological treatment of wastewater. Because of the low solubility of oxygen and the consequent low rate of oxygen transfer, sufficient oxygen to meet the requirements of aerobic waste treatment does not enter water through normal surface air-water interfaces (Tchobanoglus et al., 2003).

1.5.1.8.2. Volatilization and gas stripping

At some wastewater treatment facilities, volatile organic compounds (VOCs) such as trichloroethylene (TCE) and 1,2-dibromo-3-chloropropane (DBCP) have been detected in wastewater. The uncontrolled release of such as compounds that now occurs in wastewater collection systems and wastewater treatment plants is an area of concern. The mechanism governing the release of these compounds, the locations where the release of these compounds is most prevalent, and the methods of

controlling the discharges of these compounds to the atmosphere are very important (Tchobanoglous et al., 2003).

1.5.1.9. Gravity settling

The removal of suspended and colloidal materials from wastewater by gravity separation is one of the most widely used unit operations in wastewater treatments. The terms sedimentation and settling are used interchangeably. A sedimentation basin may also be referred to as a sedimentation tank, clarifier, settling basin, or settling tank. Accelerated gravity settling involves the removal of particles in suspension by gravity settling in an accelerated flow field (Tchobanoglous et al., 2003).

1.5.1.10. Filtration

The general problem of the separation of solid particles from liquids can be solved by using a wide variety of methods, depending on the type of solids, the proportion of solid to liquid in the mixture, viscosity of the solution, and other factors. In filtration a pressure difference is set up and causes the fluid to flow through small holes a screen or cloth which blocks the passage of the large solid particles, which, in turn, build up on the cloth as a porous cake. In filtration, suspended solid particles in a fluid of liquid or gas are physically or mechanically removed by using a porous medium that retains the particles as a separate phase or cake and passes the clear filtrate (Geankoplis, 1994).

1.5.2. Chemical processes

Those processes used for the treatment of wastewater in which change is brought about by means of or through chemical reactions are known as chemical unit processes. In the field of wastewater treatment, chemical unit processes usually are used in conjunction with the physical unit operations, and the biological unit processes, to meet specific treatment objectives (Tchobanoglous et al., 2003).

1.5.2.1. **Chemical coagulation**

Colloidal particles found in wastewater typically have a net negative surface charge. The size of colloids (about 0.01 to 0.000001 m) is such that the attractive body forces between particles are considerably less than the repelling forces of the electrical charge. Under these stable conditions, Brownian motion keeps the particles in suspension. Brownian motion is brought about by the constant thermal bombardment of the colloidal particles by the relatively small water molecules that surround them. Coagulation is the process of destabilizing colloidal particles so that particle growth can occur as a result of particle collisions. The theory of chemical coagulation reactions is very complex (Tchobanoglous et al., 2003).

Coagulant and flocculent are terms that will also be encountered in the literature on coagulation. In general a coagulant is the chemical that is added to destabilize the colloidal particles in wastewater so that floc formation can result. A flocculent is a chemical, typically organic, added to enhance the flocculation process. Typical coagulants and flocculants include natural and synthetic organic polymers, metal salts such as alum or ferric sulfate, and pre-hydrolyzed metal salts such as polyaluminum chloride (PACl) and polyiron (PICI). Flocculants, especially organic polymers, are also used to enhance the performance of granular medium filters and in dewatering of digested biosolids. In these applications, the flocculent chemicals are often identified as filter aids (Tchobanoglous et al., 2003).

1.5.2.2. **Chemical precipitation**

Chemical precipitation is used as a means of improving the performance of primary settling facilities, as a basic step in the independent physical-chemical treatment of wastewater, for the removal of phosphorus, and for the removal of heavy metals.

Over the years a number of different substances have been used as precipitants. The degree of clarification obtained depends on the quantity of chemicals used as the care with which the process is controlled. It is possible by chemical precipitation to obtain a clear effluent, substantially free from matter in suspension or in colloidal state. The most used chemicals for precipitations are:

- Alum; when alum is added to wastewater containing calcium and magnesium bicarbonate alkalinity, a precipitate of aluminum hydroxide will form,
- Lime; a sufficient quantity of lime must therefore be added to combine with all the free carbonic acid and with the carbonic acid of the bicarbonates (half-bound carbonic acid) to produce calcium carbonate,
- Ferrous sulfate and lime; in most cases, ferrous sulfate cannot be used alone as a precipitant because lime must be added at the same time to form a precipitate,
- Ferric chloride,
- Ferric chloride and lime,
- Ferric sulfate and lime.

The degree of clarification obtained when chemical when chemical are added to untreated wastewater depends on the quantity of chemicals used, mixing times, and the care with which the process is monitored and controlled. With chemical precipitation, it is possible to remove 80 to 90 percent of TSS including some colloidal particles, 50 to 80 percent of the BOD, and 80 to 90 percent of the bacteria (Tchobanoglous et al., 2003).

1.5.2.2.1. Chemical precipitation for phosphorus removal

The removal of phosphorus from wastewater involves the incorporation of phosphorus into TSS and the subsequent removal of those solids phosphorus can be incorporated into either biological solids or chemical precipitates. The chemical precipitation of phosphorus is brought about by addition of the salts of multivalent metal ions that form precipitates of sparingly soluble phosphates. The multivalent metal ions used most commonly are calcium [Ca (II)], aluminum [Al (III)], and iron [Fe (III)] (Tchobanoglous et al., 2003).

1.5.2.2.2. Chemical precipitation for removal of heavy metals and dissolved inorganic substances

Metals of interest include arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), selenium (Se), and zinc (Zn). Most of these metals can be

precipitated as hydroxides or sulfides. The technologies available for the removal of heavy metals from wastewater include chemical precipitation, carbon adsorption, ion exchange, and reverse osmosis. Of these technologies, chemical precipitation is most commonly employed for most of the metals. Common precipitants include hydroxide (OH) and sulfide (S²⁻). Carbonate has also been used in some special cases (Tchobanoglus et al., 2003).

1.5.2.3. **Chemical oxidation**

Chemical oxidation in wastewater treatment typically involves the use of oxidizing agents such as ozone (O₃), hydrogen peroxide (H₂O₂), permanganate (MnO₄), chloride dioxide (ClO₂), chlorine (Cl₂) or (HOCl), and oxygen (O₂), to bring about change in the chemical composition of a compound or a group of compounds. Chemical oxidation is especially effective for the elimination of odorous compounds (e.g., oxidation of sulfides and mercaptans) (Tchobanoglus et al., 2003).

1.5.2.4. **Neutralization and stabilization**

The removal of excess acidity or alkalinity by treatment with a chemical of the opposite composition is termed neutralization. In general, all treated wastewaters with excessively low or high pH will require neutralization before they can be dispersed to the environment. Alkaline wastes are less of a problem than acid wastes but nevertheless often require treatment. If acidic waste streams are not available or not adequate to neutralize alkaline wastes, sulfuric acid is commonly employed (Tchobanoglus, 2003).

Chemical stabilization is often required for highly treated wastewaters to control their aggressiveness with respect to corrosion. Wastewater effluent that is demineralized with reverse osmosis will generally require pH and calcium carbonate adjustment (stabilization) to prevent metallic corrosion, due to the contact of the demineralized water with metallic pipes and equipment (Tchobanoglus et al., 2003).

1.5.2.5. **Disinfection with chemicals**

Disinfection refers to partial destruction of disease-causing organisms. All the organisms are not destroyed during the process. Chemical agents that have been used as disinfection include chlorine and its compounds, bromine, iodine, ozone, phenol and phenolic compounds, alcohols, heavy metals and related compounds, dyes, soaps and synthetic detergents, quaternary ammonium compounds, hydrogen peroxide, paracetic acid, various alkalines, and various acids (Tchobanoglus et al., 2003).

1.5.2.5.1. **Disinfection with chlorine**

Chlorine is the one used most commonly throughout the world. The principal chlorine compounds used at wastewater treatment plants are chlorine (Cl_2), sodium hypochlorite (NaOCl), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], and chlorine dioxide (ClO_2). The disinfection efficiency of chlorine compounds in wastewater applications is depends on the importance of initial mixing, the chemical characteristics of the wastewater, the impact of particles found in wastewater, particles with coliform organisms and the characteristics of the microorganisms (Tchobanoglus et al., 2003).

1.5.2.5.2. **Disinfection with ozone**

Ozone is an unstable gas produced when oxygen molecules dissociate into atomic oxygen. Ozone can be produced by electrolysis, photochemical reaction, or radiochemical reaction by electrol discharge. Ozone is an extremely reactive oxidant, and it is generally believed that bacteria kill through ozonation occurs directly because of cell wall disintegration (cell lysis). Ozone is also a very effective viricide and is generally believed to be more effective than chlorine. Ozonation does not produce dissolved solids and is not affected by the ammonium ion or pH influent to the process. For these reasons, ozonation is considered as an alternative to either chlorination or hypo chlorination; especially where dechlorination may be required and high-purity oxygen facilities are available at the treatment plant (Tchobanoglus et al., 2003).

1.5.3. Advanced treatments

Advanced wastewater treatment is defined as the additional treatments needed to remove suspended, colloidal, and dissolved constituents remaining after convective secondary treatments processes. Dissolved constituents may range from relatively simple inorganic ions, such as calcium, potassium, sulfate, nitrate, and phosphate, to an ever-increasing number of highly complex synthetic organic compounds. In recent years, the effects of many of these substances on the environment have become understood more clearly (Tchobanoglous et al., 2003).

Increasing population and increasing water use has already created, in many locations, pollution problems which cannot be adequately solved by secondary treatment. It is inevitable that the number of these instances will increase in the future. It is also inevitable that the deliberate reuse of treated wastewaters will be required in order to meet the future water demands. Indirect water reuse is already commonly practiced, with some estimates indicating that 40 percent of the United States population is using water that has been used at least once before for domestic or industrial purposes. This indirect reuse will also increase in the future. All of these factors indicate that use of advanced wastewater treatments techniques will become increasingly common. The most common processes are reverse osmosis, advanced chemical oxidation, electrodialysis, distillation, carbon adsorption, distillation and UV radiation (Culp et al., 1977).

1.5.3.1. UV radiation

Ultraviolet light has been known to kill pathogens for a long time. A low pressure mercury bulb emits between 30 to 90 % of its energy at a wave length of 253.7 nm, right in the middle of the UV band. If water is exposed to enough light, pathogens will be killed. The problem is that some pathogens are hundreds of times less sensitive to UV light than others. The least sensitive pathogens to UV are protozoan cysts. The efficiency of water treatment is very dependent on the turbidity of the water. The more opaque the water is, the less light that will be transmitted through it (Cheremisinoff, 2002).

1.5.3.2. Adsorption

Adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbate is the substance that being removed from the liquid phase at the interface. The adsorbent is the solid, liquid, or gases phase onto which the adsorbate accumulates. The adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent, including toxicity reduction, have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon treatment of wastewater is usually thought of as a polishing process for water that has already received normal biological treatment. The carbon in this case is used to remove a portion of the remaining dissolved organic matter. Activated carbon is used most commonly in wastewater treatment applications (Tchobanoglus et al., 2003).

Carbon adsorption is used principally for the removal of refractory organic compounds, as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. The removal of taste and odor compounds from the wastewater is another important application, especially in reuse applications. Both powdered and granular activated carbon is used to appear to have a low adsorption affinity for low molecular weight polar organic species. There are several factors which affect adsorption by activated carbon, including: (Culp et.al., 1977)

- Characteristic of the activated carbon,
- Characteristic and concentration of the material to be adsorbed,
- Characteristics of the wastewater, such as pH and suspended solid content,
- Contacting system and its mode of operation.

1.5.3.3. Depth filtration

Filtration is the key process in the production of high quality effluents from wastewater. Efficient filtration can remove the particulate and colloidal matter not settleable after either biological or chemical flocculation or both, increase removal of suspended solids, turbidity, phosphorus, BOD, COD, heavy metals, asbestos,

bacteria, virus, and other substances, improve the efficiency and reduce the cost of disinfection through removal of suspended matter and other interfering substances, assure continuous plant operation and consistent effluent quality, increase overall plant reliability by overcoming common irregularities in biological and chemical treatment (Culp et.al., 1977).

Depth filtration involves the removal of particulate materials suspended in a liquid by passing the liquid through a filter bed comprised of a granular or compressible filter medium. Although depth filtration is one of the principal unit operations used in the treatment of potable water, the filtration of effluent from wastewater treatment processes is becoming more common. Depth filtration is now used to achieve supplemental removals of suspended solids (including particulate BOD) from wastewater effluents of biological and chemical treatment processes to reduce the mass discharge of solids and perhaps more importantly, as a conditioning step that will allow for the effective disinfection of the filtered effluent (Tchobanoglous et al., 2003).

1.5.3.4. **Membrane filtration**

Filtration involves the separation (removal) of particulate and colloidal matter from a liquid. In membrane filtration the range of particle sizes is extended to include dissolved constituents. The role of the membrane is to serve as a selective barrier that will allow the passage of certain constituents and will return other constituents found in the liquid (Cheryan, 1998). Table 1.1 shows the comparison of the membrane filtration types.

Table 1.1. The comparison of the membrane processes (Cheremisinoff, 2002)

Technology	Driving Force	Influencing Factors			
		Size	Diffusivity	Ionic Charge	Solubility
Microfiltration	Pressure	+++	-	-	-
Ultrafiltration	Pressure	+++	-	+	-
Nanofiltration	Pressure	+++	+	+	-
Reverse Osmosis	Pressure	+	+++	+	+++
Electrodialysis	Electrical	+	+	+++	-

1.5.3.4.1. Micro, ultra and nano filtration

Suspended materials and macromolecules can be separated from a waste stream using a membrane and pressure differential, called ultrafiltration. This method uses a lower pressure differential than reverse osmosis and doesn't rely on overcoming osmotic effects. It is useful for dilute solutions of large polymerized macromolecules where the separation is roughly proportional to the pore size in the membrane selected (Cheremisinoff, 2002).

In the case of microfiltration, a more porous membrane is used than in the other membrane separation technologies, thus yielding a relatively higher flux. It is mainly useful in removing turbid causing materials and can replace conventional granular filtration processes (Table 1.2). Microfiltration membranes might be used to achieve very low turbidity effluents with very little variance in treated water quality. Because bacteria and many other microorganisms are also removed, such membrane disinfection might avoid the need for chlorine and subsequent dechlorination. Metal salts of iron or aluminum may also be added to enhance membrane performance (Cheremisinoff, 2002).

The nanofiltration process softens water by removing calcium and magnesium ions. These so-called nanofilters are also effective in removing the precursors to disinfection by-products that result from such oxidants as chlorine (Cheremisinoff, 2002).

Table 1.2. Comparing membrane structure (Cheremisinoff, 2002)

Technology	Structure	Driving Force	Mechanism
Microfiltration	Symmetric microporous (0.02-10 m)	Pressure, 1 - 5 atm	Sieving
Ultrafiltration	Asymmetric microporous (1 - 20 nm)	Pressure, 2 - 10 atm	Sieving
Nanofiltration	Asymmetric microporous (0.01 - 5 nm)	Pressure, 5 - 50 atm	Sieving
Reverse Osmosis	Asymmetric with homogeneous skin and microporous support	Pressure, 10 - 100 atm	Solution diffusion
Electrodialysis	Electrostatically charged membranes (cation and anion)	Electrical potential	Electrostatic diffusion

1.5.3.4.2. **Electrodialysis**

The filtering membranes are sheet-like barriers made out of high-capacity, highly cross-linked ion exchange resins that allow passage of ions but not of water. Two types are used: cation membranes, which allow only cations to pass, and anion membranes, which allow only anions to pass (Sincero, 2003).

1.5.3.4.3. **Reverse osmosis**

When two solutions having different solute concentration are separated by a semipermeable membrane, a difference in chemical potential will exist across the membrane. Water will tend to diffuse through the membrane from the lower concentration (higher potential) side to the higher concentration (lower potential) side. In a system having a finite volume, flow continues until the pressure difference balances the chemical potential difference. This balancing difference is termed the

osmotic pressure and is function of the solute of the characteristics and concentration and temperature. If a pressure gradient opposite in direction and greater than the osmotic pressure is imposed across the membrane, flow from the more concentrated to the less concentration region will occur and is termed reverse osmosis. Worldwide, reverse osmosis is used primarily for desalination. In wastewater treatment, reverse osmosis is used for the removal of dissolved constituents from wastewater remaining after advanced treatment with depth filtration or microfiltration (Tchobanoglus et al., 2003).

1.5.3.5. **Ion exchange**

Ion exchange is the displacement of one ion by another. The displaced ion is originally a part of an insoluble material, and the displacing ion is originally in solution. At the completion of the process, the two ions are in reversed places: the displaced ion moves into solution and the displacing ion becomes a part of the insoluble material. Two types of ion exchange materials are used: the cation exchange material and the anion exchange material. The cation exchange material exchanges cations, while the anion exchange material exchanges anions (Sincero, 2003).

Originally, natural and synthetic aluminum silicates, called zeolites, were the only ones used as exchange materials. Presently, they have been largely replaced by synthetic resins. Synthetic resins are insoluble polymers to which are added, by certain chemical reactions, acidic and basic groups called functional groups. These groups are capable of performing reversible exchange reactions with ions in solution. The total number of these groups determines the exchange capacity of the exchange material, while the type of functional group determines ion selectivity (Sincero, 2003).

1.5.3.6. **Distillation**

Distillation is a unit operation in which the components of a liquid solution are separated by vaporization and condensation. Along with reverse osmosis, distillation can be used to control the buildup a salts in critical reuse applications (Tchobanoglus et al., 2003).

The principal distillation processes are boiling with submerged-tube heating surface, boiling with long-tube vertical evaporator, flash evaporation, forced circulation with vapor compression solar evaporation, rotating-surface evaporation, wiped-surface evaporation, vapor reheating process, direct heat transfer using an immiscible liquid, and condensing-vapor-heat transfer by vapor other than steam. Of these types of distillation processes, multistage flash evaporation, multiple effect evaporation, and the vapor-compression distillation appear most feasible for the reclamation of municipal wastewater (Tchobanoglous et al., 2003).

1.5.4. Removal of dissolved organic constituents

Many treatments can be used for the removal of dissolved organic constituents. Because of the complex nature of the dissolved organic constituents, the treatment methods must consider the specific characteristics of the wastewater and the nature of the constituents. Treatment processes used to remove some of the specific dissolved organic constituents include: carbon adsorption, reverse osmosis, chemical oxidation, advanced chemical oxidation, electrodialysis and distillation (Tchobanoglous et al., 2003).

1.5.5. Removal of dissolved inorganic constituents

A number of different unit operations and processes have been investigated in various advanced wastewater treatment applications. Although many of them have proved to be technically feasible, other factors, such as cost, operational requirements, and aesthetic considerations, have not been favorable in some cases. Nevertheless, it is important that environmental engineers be familiar with the more important operations and processes so that in any given situation they can consider all treatment possibilities. Removal of dissolved inorganic constituents is accomplished by chemical processes or membrane filtration. The principle unit operations and processes are: chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, electrodialysis and distillation (Tchobanoglous et al., 2003).

1.5.6. Removal of biological constituents

In addition to the constituents discussed above, the removal of biological constituents is also of interest. The unit operations and processes that is useful for the removal of biological constituents including bacteria, protozoan cysts and oocysts, and viruses. Because the effectiveness of the unit operations and processes is variable, disinfection of the treated effluent is required for most applications (Tchobanoglus et al., 2003). Table1.3 shows the processes that can be used during the removal of organic constituents.

Table 1.3. The processes that can be used during the removal of organic constituents (Tchobanoglus et al., 2003).

Residual constituents	Unit operation or process											
	Depth filtration	Surface filtration	Micro and ultra filtration	Reverse osmosis	Electro dialysis	Adsorption	Air stripping	Ion exchange	Advanced oxidation processes	Distillation	Chemical precipitation	Chemical oxidation
Inorganic and organic colloidal and suspended solids												
Suspended solid	x	x	x	x	x	x		x		x	x	
Colloidal solid	x	x	x	x	x	x		x		x	x	
Organic matter(particulate)				x	x					x		x
Dissolved organic matter												
Total organic carbon				x	x	x		x	x	x	x	x
Refractory organics				x	x	x			x	x		
Volatile organic compounds				x	x	x	x		x	x		
Dissolved inorganic matter												
Ammonia				x	x		x	x		x		
Nitrate				x	x			x		x		
Phosphorus				x	x					x	x	
Total dissolved solids				x	x			x		x		
Biological												
Bacteria			x	x	x					x		
Protozoan cysyts and oocysts	x		x	x	x	x		x		x	x	
Viruses				x	x					x		

1.6. Aims of This Study

Bulgur is a very important food material in Turkey. Bulgur has very important characteristics due to, its low cost, long shelf life, ease of preparation, high nutritional value and precooked properties.

The number of bulgur plants has increased to nearly 600 worldwide (about 500 in Turkey, 15-20 in the United States and Canada, 4-6 in EU, 10-15 in Arabic countries). Water discharge from the washing and cooking operations, in the bulgur production, is at high amount. Recently, water is very important because of the fewer amounts of rain and bad using of the water sources.

Besides wastewater, nutrients leaching into wastewater especially during the cooking operation, disposed into environment. This is a very big problem because, the amount of nutrient in wastewater leads to high value of BOD which increase the microbial load in river and lakes. Additionally, besides of the quantity of the nutrients, the quality is also high. There are no toxic materials in bulgur plants; wastewater has only the high quality nutrients such as protein, starch, vitamin and minerals etc.

The energy loss during the production of bulgur is another issue has to be discussed. Since, bulgur is cooked at 97 °C. Most of the times, the cooking wastewater is disposed into environment without any recovery operation. Heat recovered from the hot wastewater can also be used to pre-heat the inlet water of cooking operation.

The study is focused on the wastewater treatment to recover water, energy and nutrient. By this study, the results can be used to design industrial recovery systems.

CHAPTER II

MATERIALS AND METHODS

2.1. Materials

In this study, wheat was washed for 5 min and cooked for 30 min with distilled water.

2.1.1. Wheat

Wheat, *Triticum durum* cultivar, which has a moisture content of 9.13 % (w.b.), was obtained from a local Bulgur producer in Gaziantep.

2.1.2. Reagents

HCl (Merck, Germany) and Phosphore-Wolfram acid “Phosphotungstic acid, $2\text{H}_3\text{PO}_4 \cdot 24\text{WO}_3 \cdot n\text{H}_2\text{O}$ ” (Carlo Erba, Italy) were used to measure the amount of starch in the waste water samples and wheat.

2.2. Experimental Set-up

2.2.1. Water Recovery from Wheat Washing Operation

Wheat was washed in a beaker for 5 min at room temperature. Amount of water was the half of that of wheat. Then, the washing water was filtered with a cloth filter into another beaker and then measured. The experimental set-up is illustrated in Figure 2.1.

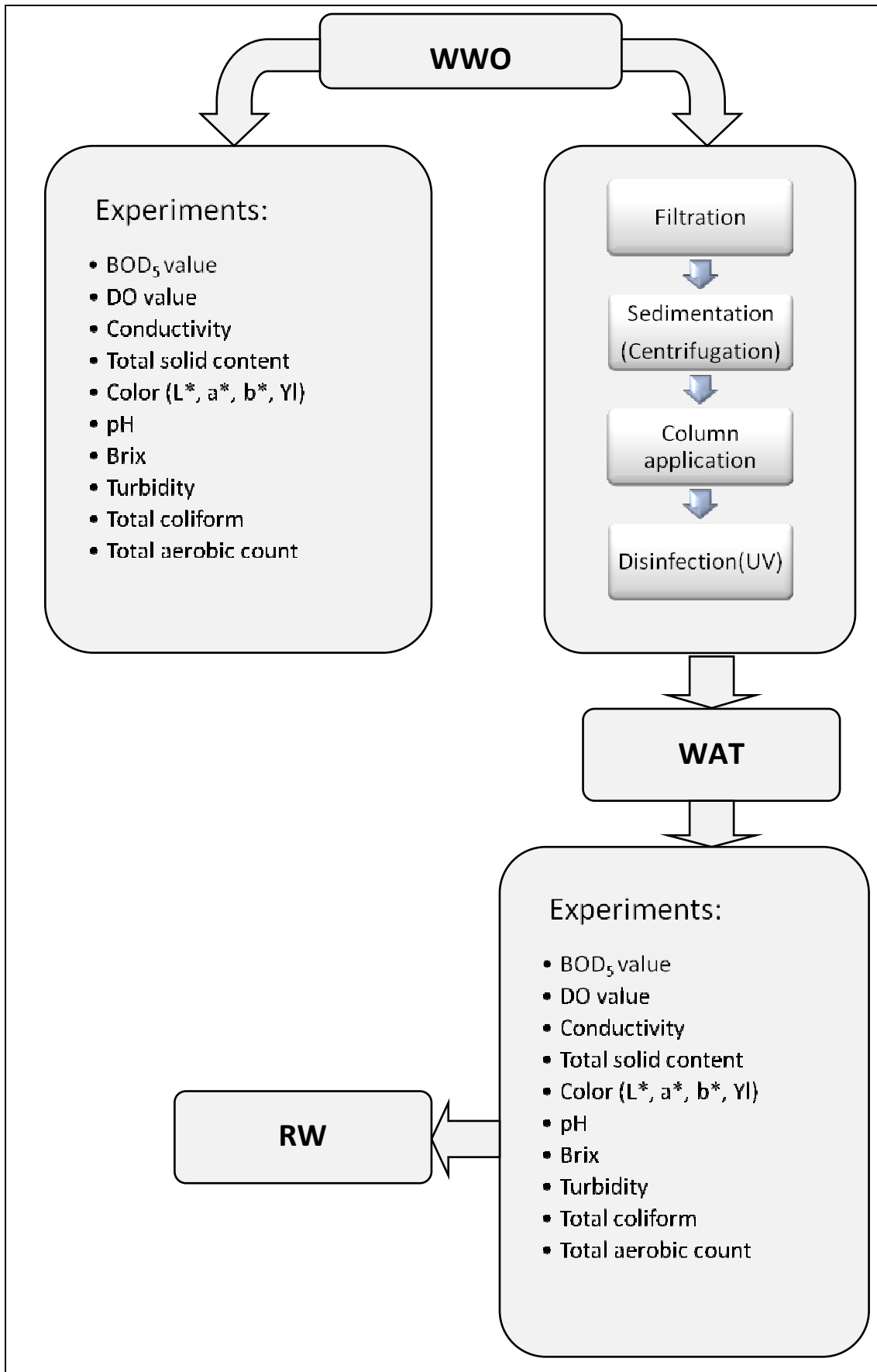


Figure 2.1. Experimental set-up for washing operation

2.2.2. Water recovery from wheat cooking operation

Firstly, water was boiled and then wheat was added to the boiling water. Wheat was cooked at 97 °C for 30 minutes with its double amount of water. After 30 minutes, the cooking water was filtered with a cloth. The cooking wastewater was kept at 4 °C in a refrigerator. The experimental set-up is illustrated in Figure 2.2.

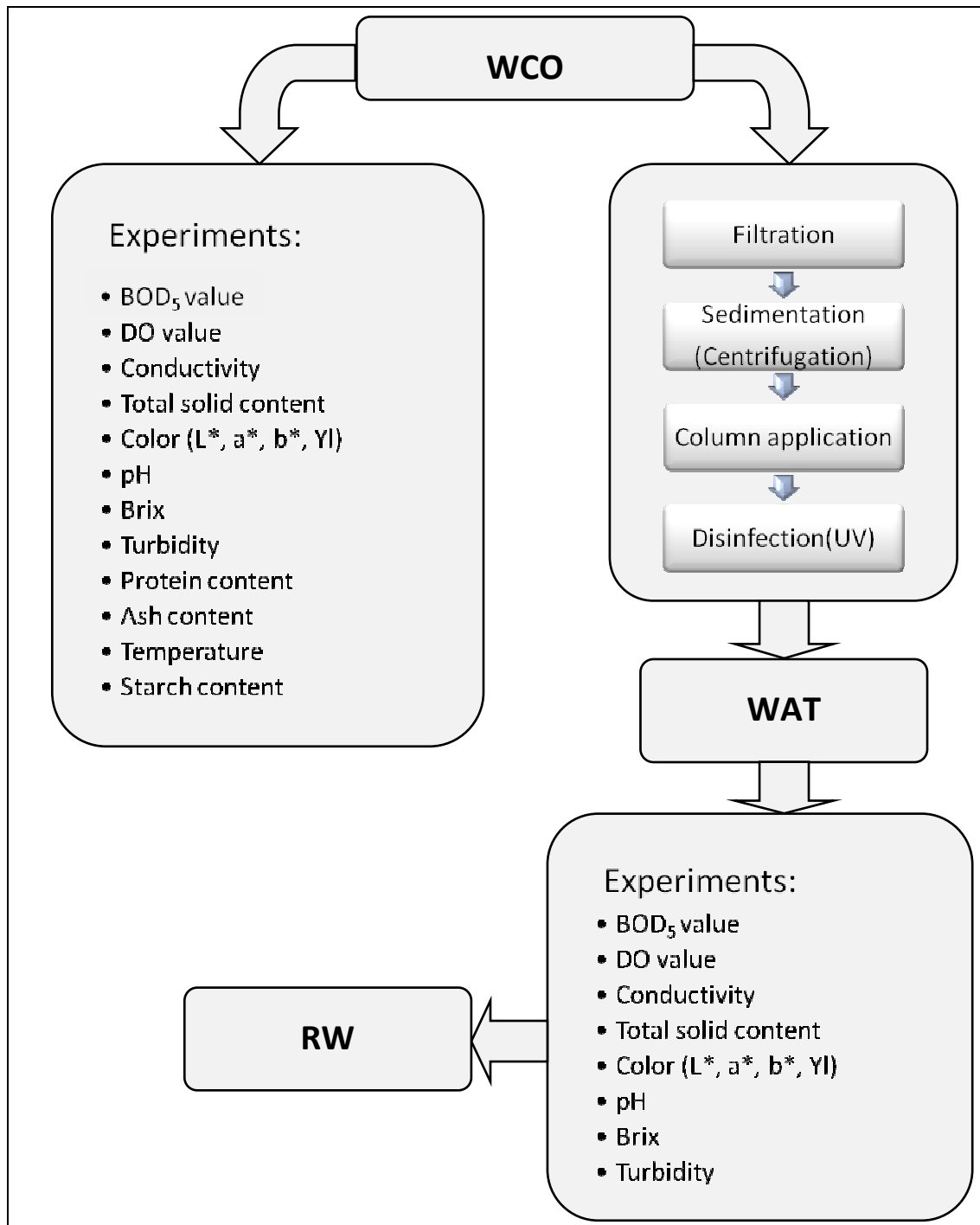


Figure 2.2. Experimental set-up for water recovery from cooking operation

2.2.3. Energy and nutrient recoveries from cooking operation

Energy recovery was calculated using hot wastewater obtained from the cooking operation. Nutrient recovery was made using a spray dryer Wastewater of cooking operation was applied to the spray dryer (Armfield, England) at 130 °C (Figure 2.3). The air flow rate and feed flow rate were 10-20 m/sec and 0.07 ml/sec, respectively.

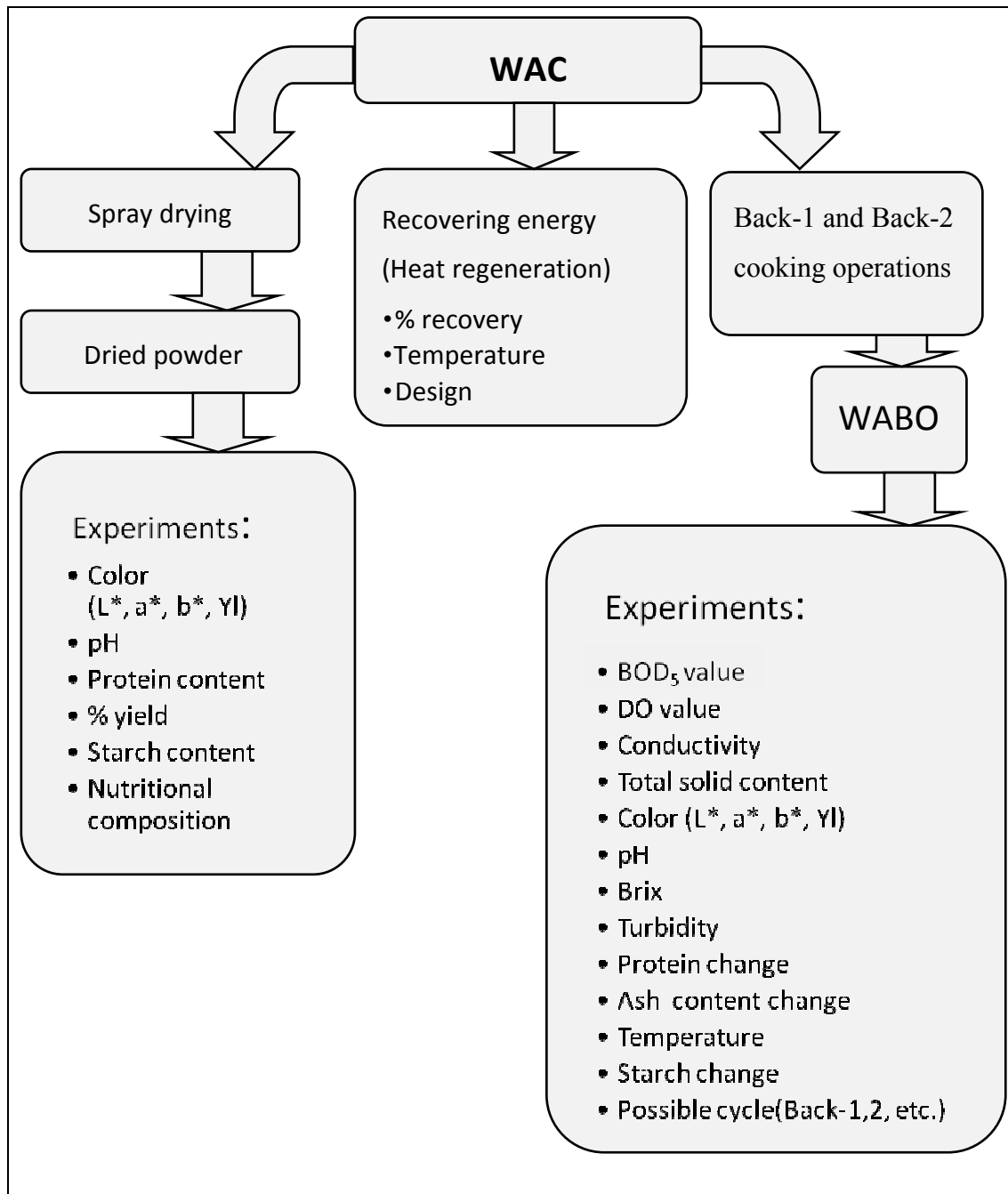


Figure 2.3. Experimental set-up for energy, nutrient and water recovery from cooking operation

Back-1 and Back-2 operations are also cooking operations. They were made after by after cooking to recover the wastewater. Back-1 cooking was made with 1 part of water from the previous cooking operation and 1 part of fresh water. The procedure of the Back-1 operation was same with cooking operation. Back-2 cooking was made with 1 part of wastewater of Back-1 cooking and 1 part of fresh water. The experimental operation is illustrated in Figure 2.4.

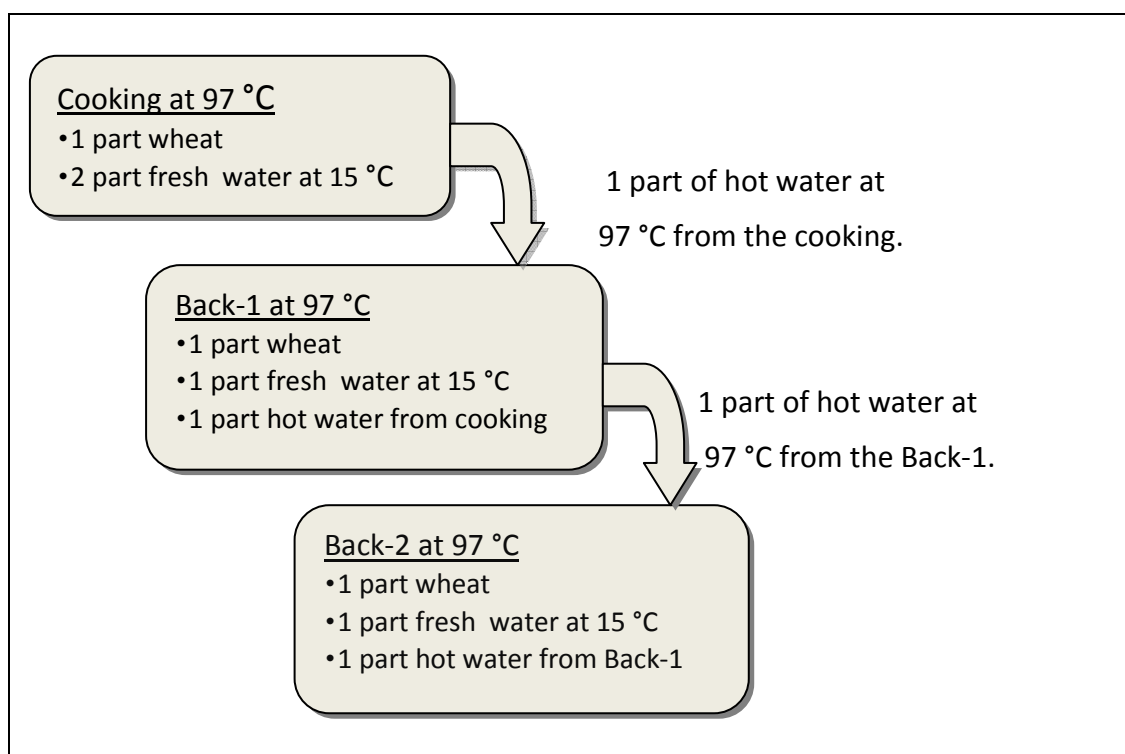


Figure 2.4. Back-1 and Back-2 cooking operations

3.2.4. Wastewater treatments (filtration, sedimentation, sand, activated carbon, resin, UV)

The overall treatments are illustrated in Figure 2.5. The washing and cooking water were filtered with coarse filter paper to separate the coarse particles from the waste water as shown in Figure 2.6. It was the first physical treatment for wastewater. The sedimentation was made in a centrifuge (Hettich, Roto Silenta III, Germany). The supernatant liquid was then quickly decanted from the tube without disturbing the precipitate. Sedimentation was the second physical treatments, which separated the fine particles from the wastewater by centrifugation.

Centrifugation was made at 8000 rpm for 20 minutes. Centrifugation was made for the separation of some insoluble fine particles. These particles were not separated with the coarse filtration and a driving force was applied to separate them using a centrifuge.

A column was prepared, which contained sand, activated carbon and resin. The column was wetted before using distilled water. The flow was slow, therefore the activated carbon column was left overnight. Sand was kept any other coarse or fine particle remaining after the filtration and centrifugation. Sand, at the same time, adjusts the flow rate for the activated carbon and resin to increase the efficiency of the treatments.

Activated carbon (Norit activated carbons, Norit, USA), (9 ml, Bulk density =12-30 lbs/ft³, black powder with no odor, insoluble in water) was used to filter some harmful chemicals and some color pigments from the waste water. The activated carbon column contained sand and resin as shown in Figures 2.6 and 2.7.

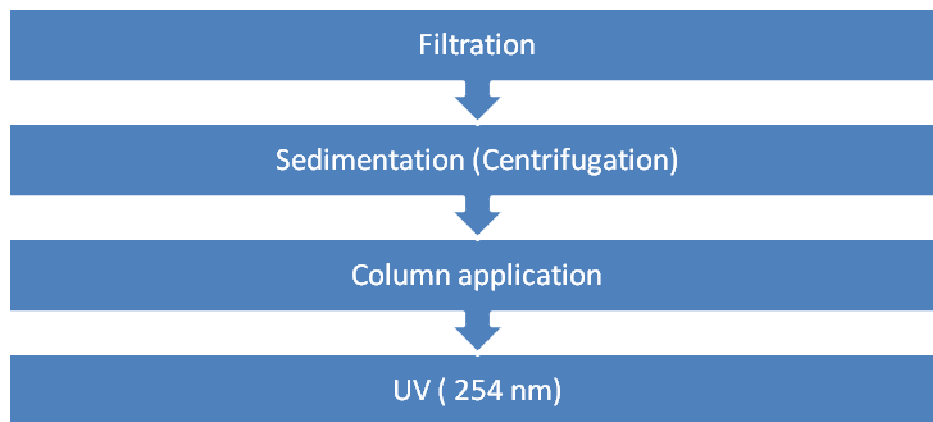


Figure 2.5. Experimental design of the treatment process



Figure 2.6. Activated carbon column

Sand (6ml, Particle Size Range= 2.2-2.6 mm) and resin (Lewatit S 1468, Bayer, Germany), (7ml, Crosslinked Polystyrene Divinylbenzene; Particle Size Range= +1.2 mm <5%, -0.3 mm <1%; Specific Gravity= 1.27; Physical Form and Appearance= Clear spherical beads) were used to filter and eliminate some rough materials and ionic compound in the wastewater, respectively. Last of all, the waste water was exposed to UV-C light of 30 W (Philips, TUV/30W, Holland) 254 nm for 2 hours. This part provided the elimination of some microbial activity.

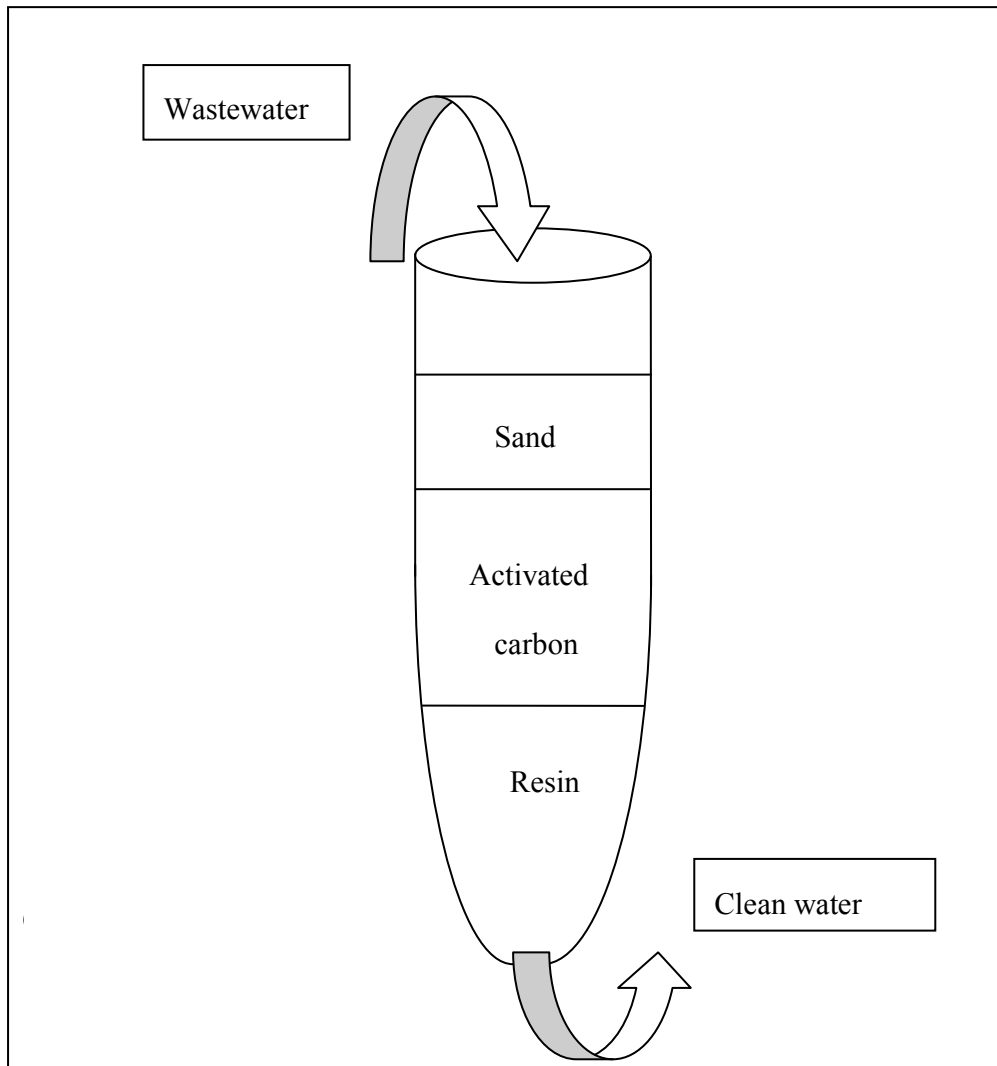


Figure 2.7. Column system for wastewater

3.3. Experiments

3.3.1. Measurements of DO, BOD₅ and Conductivity

DO and conductivity of wastewater were measured at 20 °C with a portable multi-meter (HQ40, Hach, USA). In the WWO and WAT seed was not added and Equation 2.1 was used. Due to low microbial load, WCO, WB10 and WB20 were seeded with an inoculum obtained from organic waste containing dirty river. Wastewater was diluted and aerated for BOD₅ test. Due to seeding, Equation 2.2 was used. To determine BOD₅ value of WWO, the samples were diluted to 1, 2 and 5 %. Then, it

was aerated with a pump and then DO was measured. The samples were stored under anaerobic condition (American Public Health Association, 1989).

$$\text{BOD}_5 \text{ (mg/l)} = \frac{\text{DO}_1 - \text{DO}_2}{P} \quad (2.1)$$

$$\text{BOD}_5 \text{ (mg/l)} = \frac{(\text{DO}_1 - \text{DO}_2) - (\text{R}_1 - \text{R}_2)t}{P} \quad (2.2)$$

3.3.2. Measurements of color

Color of the water samples were measured at D65 with Hunter Lab Colorimeter (Colorflex, USA). Before each of the color measurement, white standard tile was used to calibrate colorimeter (L= 93.01, a=-1.11, b=1.30).

In the Hunter scale, L* measures lightness and varies from 100 for perfect white to 0 black, approximately as the eye could evaluate it. The chromatically (a* and b* values) gives understable designation of color as follows; “a*” measures redness when positive, gray when zero and greenness when negative. “b*” measures yellowness when positive, gray when zero and blueness when negative. YI (yellowness index) visually; yellowness associated with scorching, soiling, and general product degradation by light chemical exposure, and processing. Yellowness indices are used chiefly to measure these types of degradation.

3.3.3. Measurements of pH, Brix, total solid content and turbidity

The pH, Brix and turbidity of wastewater obtained from the washing and cooking operations were measured at 20°C using a pH meter (Jenway-3010, UK), refractometer (PTR 46X, Index Instrument Ltd., England) and visible spectrophotometer (Pharmacia, LKB-Novaspec II, UK), respectively. The turbidity was measured at 500 nm (Bayram et al., 2003a).

The pH of wheat was measured using 20 g of ground wheat in 20 ml of water. The pH of spray dried product was measured using 1.5188 g of powder in 25 ml of water.

3.3.4. Determinations of protein content

Kjeldahl method was used to determine the protein contents of wastewater samples and wheat (AOAC, 1990).

3.3.5. Determinations of ash content

The ash contents of wheat and waste water were measured at 900 °C using AOAC method (AOAC, 1990).

3.3.6. Determinations of starch (Ewer's method)

Starch was hydrolyzed with HCl, and then the amount of starch was measured with a polarimeter (Polaar 3000, Optical Activity Ltd., England). Each of the samples was stored in the refrigerator. 1.25 g of sample were treated with 12.5 ml of 1% HCl in a 25 ml flask and shaken. The mixture was kept for 15 minutes in water bath at 95-100 °C. During heating period the mixture was shaken continuously. Then, 7.5 ml of distilled water was added and cooled to the room temperature. In order to obtain a precipitate of free nitrogenous matter, 2.5 ml of 4% phosphore- wolfram acid was poured into 2 dm of polarization tube and polarization value was determined by using the polarimeter. Percent starch was calculated using the following equation (Elgün et al., 1987).

$$\% \text{ Starch} = \frac{V_{TS} \times a_p}{A_D^{20} \times L_p \times W_s} \times 100$$

3.3.7. Measurements of total aerobic count and coliform

Aerobic plate count was made using Plate count agar (PCA, Merck, Darmstadt, Germany) with the aerobic spread plate count method as described in TSE (TS7703, 1989).

One milliliter of wastewater from the washing operation was serially diluted and 0.2 ml of this dilution was transferred into corresponding labeled plate and spreaded plate over the agar surface. Inoculated PCA plates were incubated at 37 °C for 1 day

to 2 days. In the range from 30 and 300 colonies on the agar plates were counted as shown in Figure 2.10. Average value was taken from the duplicate count.

Coliform count was made with the presumptive test Most Probable Number (MPN) method as described in TSE (TS7725, 1989). In this count Lauryl Sulfate Trypose Broth (LSTB, Merck, and Darmstadt, Germany) was used. One milliliter of waste water from washing operation was serially diluted and 0.2 ml of this dilution was transferred into corresponding labeled tube. Inoculated LSTB tubes were incubated at 37 °C for 2 days to 3 days. Formation of gas in Durham tubes and the color changes showed the positive presumptive test. The MPN method was used to calculate the number of coliform. Average value was taken from the duplicate count.

2.3.8. Determination of moisture content of wheat

The moisture content of wheat was measured at 105 °C using oven method (AOAC, 1994).

3.4. Statistical Operations

ANOVA was performed for predicted data to determine significant differences ($\alpha=0.05$). Duncan multiple range tests were carried out. The measurements were duplicated.

CHAPTER III

RESULT AND DISCUSSION

3.1. Properties of Raw Materials

Table 3.1 shows the properties of wheat used in the experiments. The water used in the experiments was distilled water (DO: 7.72 mg/l). The limits of drinking water according to TSE are given in Table 3.2.

Table 3.1. The properties of wheat used in the experiments

	Properties	Values
Color	L*	51.13
	a*	8.82
	b*	25.26
	YI	74.95
	Moisture content (% , w.b.)	9.13
	pH	6.44
	Protein (% , d.b.)	13.07
	Ash (% , d.b.)	1.76
	Starch (% , d.b.)	52.70

Table 3.2. The properties of drinking water according to TSE (TS266, 1997)

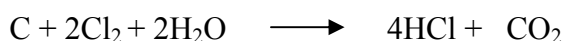
Properties	Suggested	Max
Temperature (°C)	12	25
pH	6.5-8.5	6.5-9.2
Turbidity	5	25
Conductivity (S/cm)	0.0004	0.002
Total coliform (number of mio's)	0	1
Total bacteria (number of mio's)	100	500

3.2. Wastewater Treatment for the Washing and Cooking Operations

The wastewater obtained from the washing and cooking operations was treated using different recovering techniques (coarse filtration with paper filter, centrifugation, sand filtration, activated carbon filtration, resin filtration and UV). It was observed that wastewater of cooking operation had more visible coagulant than the wastewater of washing operation due to the high amount of organic substances.

Coarse filtration was made to separate the big materials like rags, dust and dirty materials. After the separation of wheat, using cloth filter media, the wastewater of cooking operation was allowed to cool. Coarse filtration was taken overnight due to the lack of driving force.

Activated carbon adsorption for dechlorination provides complete removal of both combined and free residual chlorine. When activated carbon is used for, the following reaction occurs (Tchobanoglus et al., 2003):



The processes in Figure 3.1 show the characteristic functions for the treatments of the wastewater of washing and cooking operations. Activated carbon separates the colored substances such as vitamins, minerals and pigments.

The last part of the column was resin. Resin was prepared from the colloidal particles of resin wetted and swallowed. Resin was used to remove ions. It also decreases the Na^+ while shifting with the Ca^{2+} , lead to increase in the alkalinity of the water.

The last treatment was UV application. UV was applied using a UV lamp to inactivate bacteria by photochemically altering the DNA of the cells.

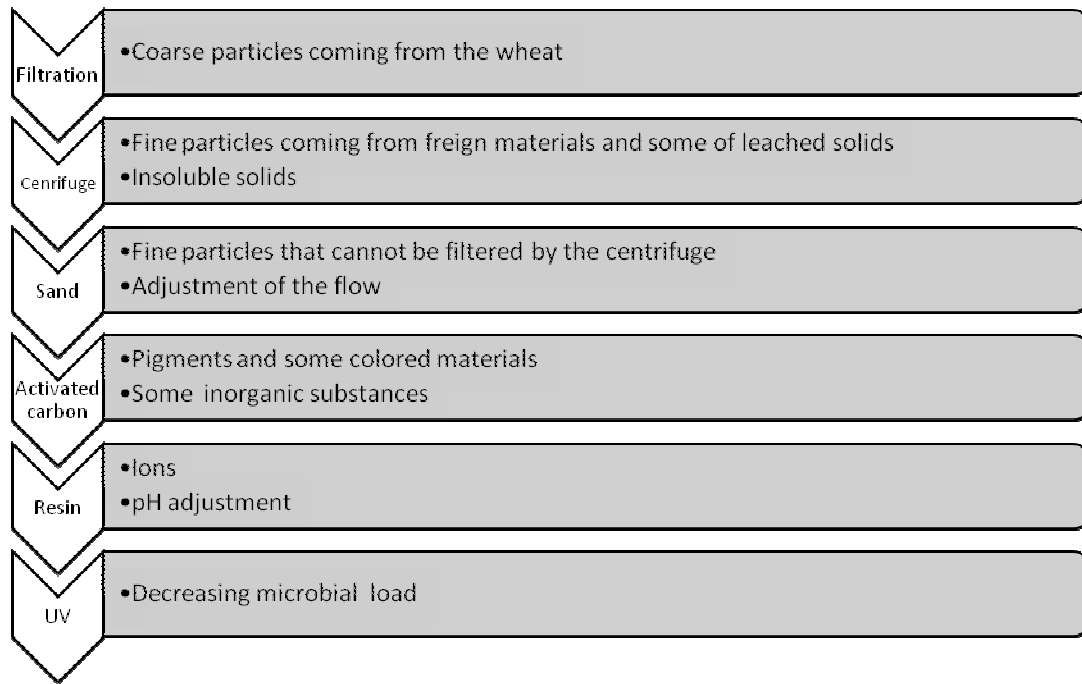


Figure 3.1. Characteristic functions of the treatment processes

3.3. Washing Operation

Wastewater was mostly including the foreign materials such as dust, soil, fiber etc. Materials leached to water from wheat were low, because there was neither heat nor any other processes.

DO and BOD₅ are used to obtain the information about the wastewater. The biodegradable organic content of the wastewater can be estimated using the BOD₅. The microorganisms use oxygen while degrading substances. The washing wastewater had high microbial load, therefore, there were no need to inoculate with seed culture to determine the BOD₅. As shown in Figure 3.2, the DO and BOD₅ decreased after Treatment-1 operation. The decrease in BOD₅ value showed that the inorganic and foreign matters, microbial load and the organic constituents decreased.

According to the literature, the value of DO in fresh water at 20 °C can be max as 9.2 mg/l (<http://www.engineeringtoolbox.com>). DO value of the distilled water used in the experiments was 7.72 mg/l and DO value of washing wastewater was measured as 6.92 mg/l. Since, the wastewater of washing operation is not pure as much as distilled water. The organic matters in the wastewater and the pH decrease the solubility of the oxygen. After treatments, the solubility of oxygen was very low

compared with the washing wastewater. According to the literature (<http://www.engineeringtoolbox.com>), the solubility of the oxygen decreases with increasing temperature and decreasing purity.

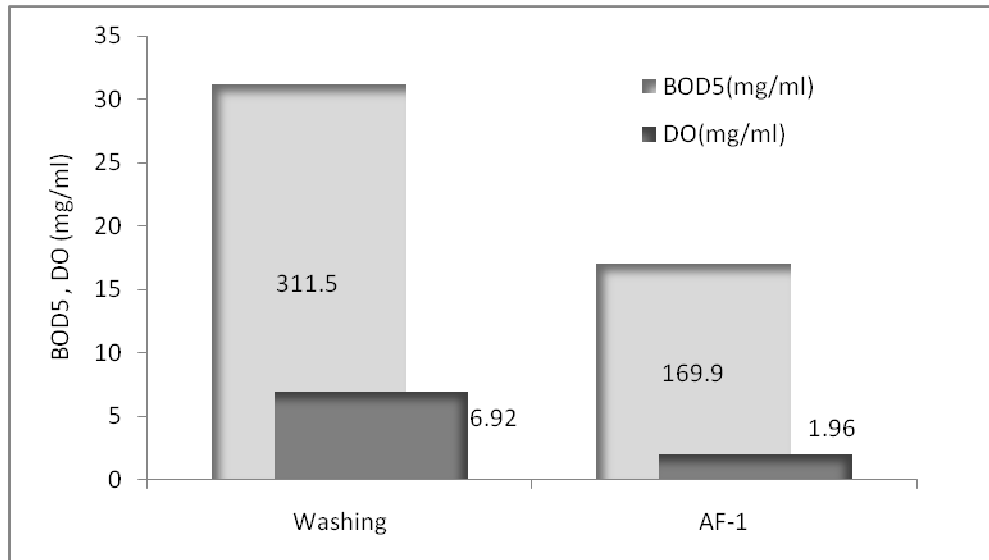


Figure 3.2. BOD₅ and DO changes during washing and wastewater treatments

The BOD₅ value of the washing water before the treatments was 311.5 mg/l. In the literature, it was found as 253.92 mg/l by Arslan (2005) for the Izmit Industrial and Domestic Wastewater Treatment Plant. In another result found by Yüceer, (2004) was for Seyhan river as 100 mg/l. According to our results, it was obvious that the washing wastewater had a high BOD₅ value and had to be treated before disposal. The treatments used in this study decreased the biodegradable substances in the wastewater (Figure 3.2). Especially coarse filtration, centrifugation and sand filtration decreased the biodegradable substances. The value of the BOD₅ of the treated wastewater is consistent with these statements. It was found that the treatment processes were significantly effective ($p < 0.05$) on BOD₅ and DO changes.

The color values of the washing water and treated water are shown in Figure 3.4. First of all, it was obvious that the clarity of the treated water should be higher than the treated water of the washing water, which means the higher L* values for the treated water. The treatment processes were significantly effective ($p < 0.05$) on the color changes. The Figure 3.3 shows the L* value increased from 43.87 to 62.67.

Many of the foreign substances in the washing wastewater provided the darkness of water. At the same time, the YI value inversely was affected from the treatment processes by decreasing to 25.58 from 46.29. The b^* value was parallel to YI value and decreased to 11.51 from 15.99. Coloring compounds, which leached into water, leads to dark color in the water (Bayram et al., 2004c). The treatments might reduce the coloring compound content in the water. Decreasing a^* value shows that the pigments, which lead to increase the redness, were reduced by the treatments.

In general, lower YI values indicate greater clarity (cleanness or clearness). The increase in YI value is opposite to decreasing the lightness (L^* value) and in parallel with the b value. Namely, a change of YI value is correlated with L^* and b^* values, which means that water losses its clarity and brightness. Additionally, losses of clarity and lightness could be correlated with the leaching of the soluble solids (pigments, organic materials etc.) and causes the darkness in water (Bayram et. al., 2004b).

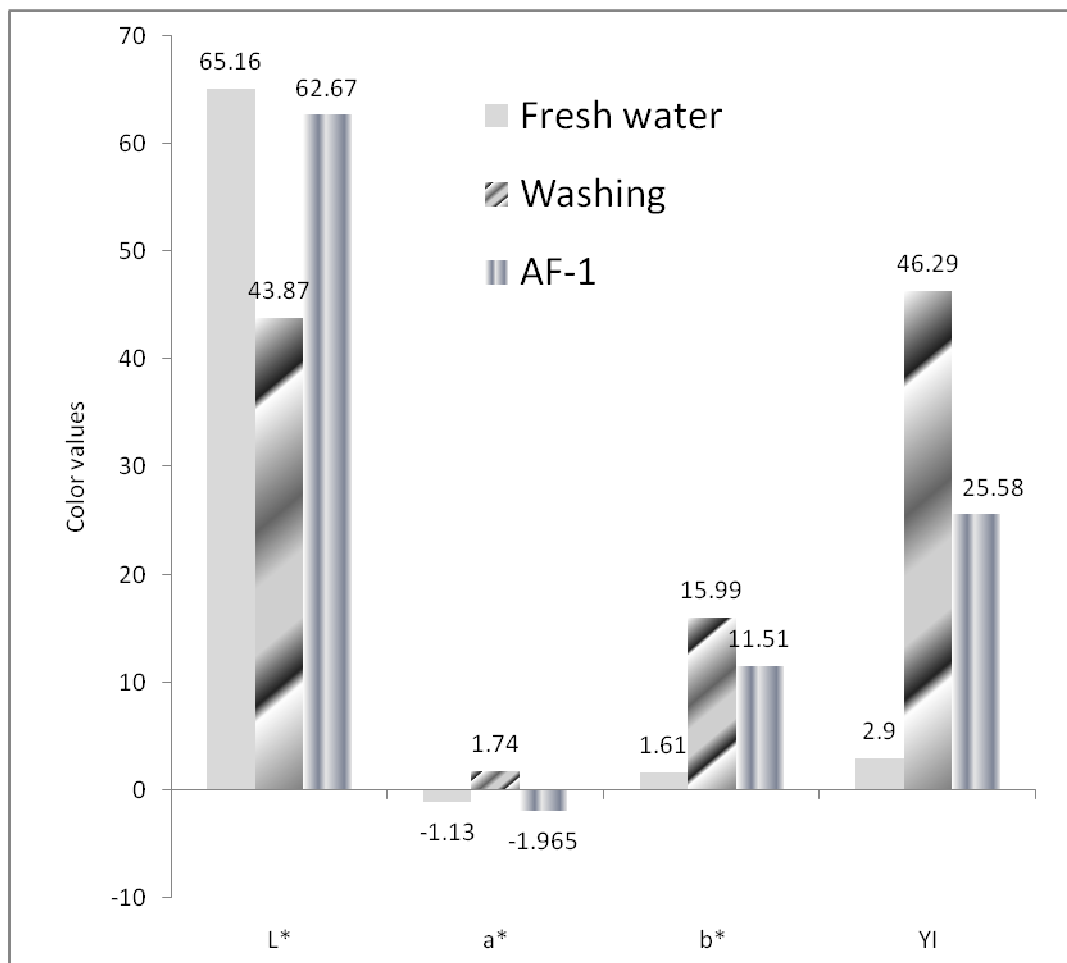


Figure 3.3. Color changes during washing and wastewater treatments

Figure 3.4 shows the pH changes of washing wastewater and treated water. The treatment processes were significantly effective ($p < 0.05$) on the pH changes. The decrease in pH of washing wastewater illustrated the leaching of some materials into washing water from the wheat. The increase in the pH of wastewater after the treatments most probably shows the elimination of that acidic matter formerly leached. The treatments provided an increase in alkalinity because of the ion exchange resin. Because, ion exchange resin gives two molecules of Na^+ for one molecule of Ca^{2+} .

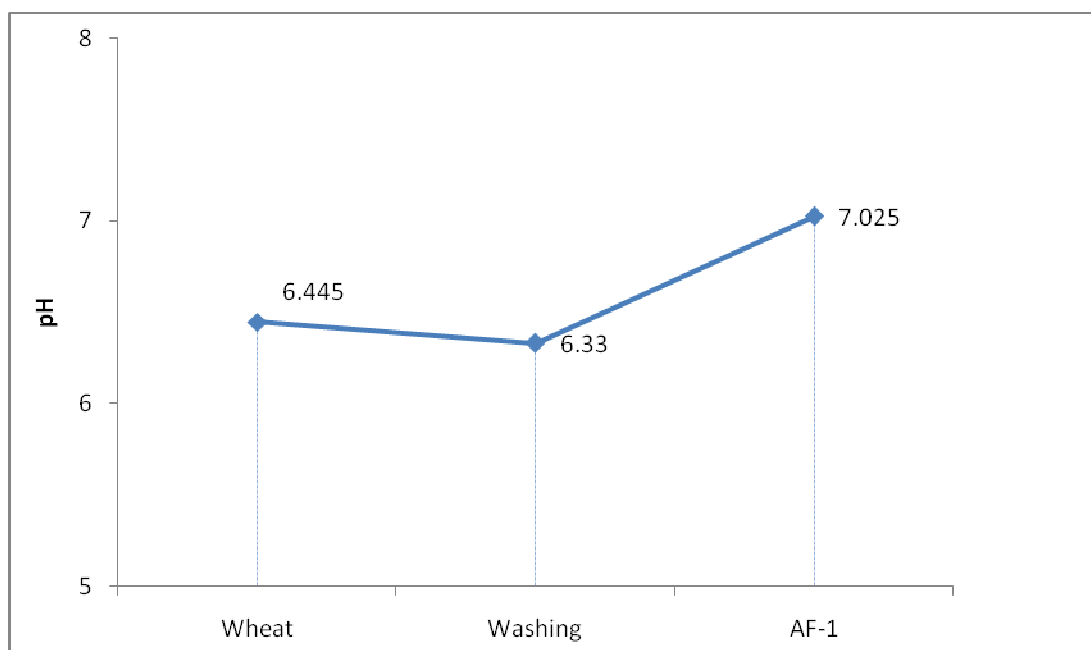


Figure 3.4. pH changes during washing and wastewater treatments

The Figure 3.5 shows the changes of Brix and TSC before and after the treatments. Brix is the soluble solid content of the solution. Total solid content is the whole solids in the solution; soluble and insoluble. Total solid content should be higher than Brix than the results are consisted with this statement. After treatments as expected, water had a lower value of Brix and TSC. The treatment processes reduced the amount of soluble and insoluble solids in the wastewater. Also, according to statistical analysis, the treatment processes were significantly effective ($p < 0.05$) on Brix and TSC changes. Especially, filtration, centrifugation and column materials formed bond with solid components found in the wastewater.

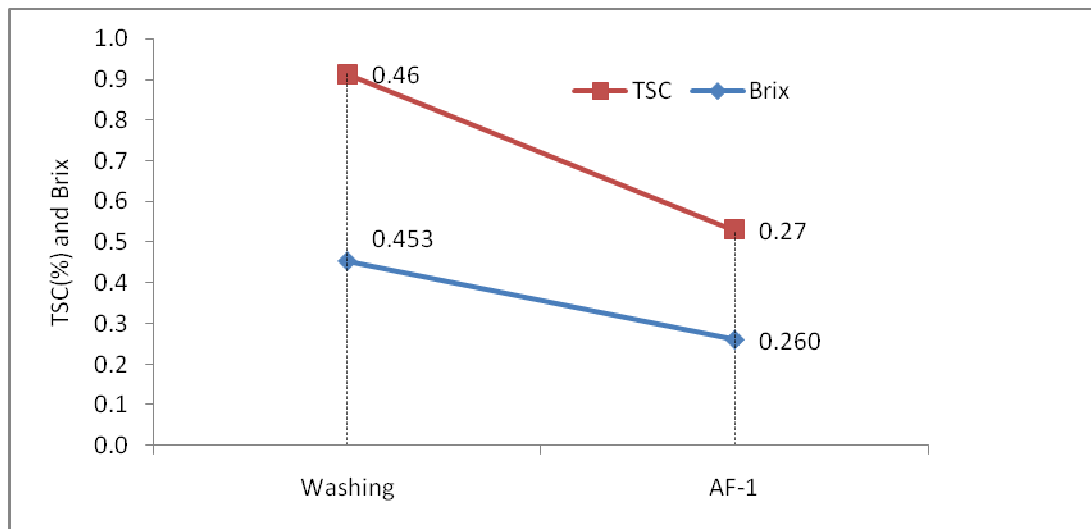


Figure 3.5. Brix and TSC changes during washing and wastewater treatments

The color changes were also corrected with the turbidity results. Turbidity decreased at very high level. After the treatments, the obtained result (0.168) was very good result comparing with the value of 0.97 as shown in the Figure 3.6. It was found that the treatment processes were significantly effective ($p < 0.05$) on conductivity and turbidity changes.

Conductivity is directly related with the ions in the solutions. Because of the resin process, it would be expected to decrease the conductivity as it was parallel to Brix, TSC and turbidity.

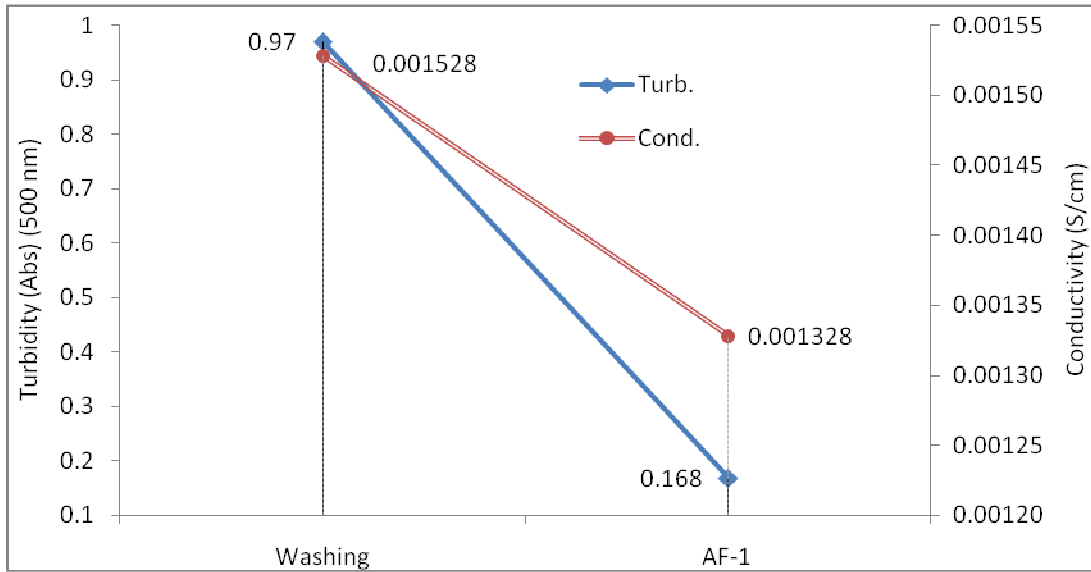


Figure 3.6. Conductivity and Turbidity changes during cooking and wastewater treatments

As shown in the Figure 3.7, total number of microorganism and coliform in the wastewater reduced significantly ($p < 0.05$) by the treatments especially by the UV radiation. This value is higher than the drinking water standard of TSE (TS266, 1997). However, the microbial load of wastewater can be decreased using long-time UV or disinfection chemicals.

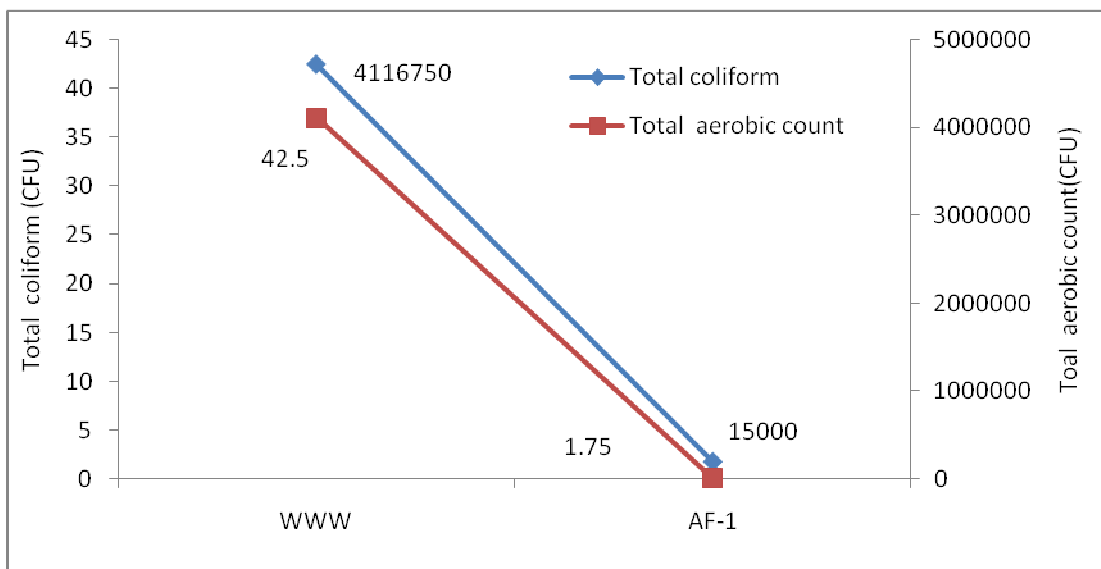


Figure 3.7. Microbial count for the washing and AF-1

3.4. Cooking operation

The wastewater obtained from the cooking operation was used for the treatment processes to investigate the possible recoveries and reuse for Back-1 and Back-2 cooking operations by mixing with fresh water. There was no treatment before Back-1 and Back-2 cooking operations. Back-1 and Back-2 were used to find possible cooking cycle using same remaining wastewater from previous cooking operation. In addition, the obtained water from the cooking was also used for spray drying to recover nutrients.

The one of the most important parameter to determine the quality of remaining water obtained from the cooking operations was BOD₅. During the cooking operations, starch gelatinized and its digestibility by microorganism changes. Additionally, the wastewater of Back cooking operations was coming from the former cooking operation, which means this cooking wastewater heated two times in Back-1 operation and three times with the Back-2 operation. Heat leads to decomposition of proteins and gelatinization of starch. Because of that, Back-1 operation had a higher BOD₅ value as shown in Figure 3.8.

Due to the cooking operation, microbial load of wastewater is very small. Therefore, the wastewaters were seeded with the inoculation media to measure BOD₅. It was found that, the treatment process and Back cooking operations were significantly effective ($p < 0.05$) on BOD₅ and DO.

As expected, DO values of the treated wastewater and Back operations wastewater were lower due to bubbling effect of the cooking operation. During the cooking, dissolved oxygen in water escapes from water.

During the cooking operation, organic compounds leached to wastewater. Therefore, BOD₅ values of cooking water were high. The treatments caused to decrease in BOD₅ value due to the separation of organic compounds at filtration, centrifugation, sand, activated carbon and resin filtrations.

In Figure 3.8, it should be noted that, BOD₅ values of Back-1 higher than BOD₅ value of the WCO. Due to excess organic solid contents, the difference between BOD₅ values of Back-1 and Back-2 can be explained using other parameters (pH, TSC etc.) in the next part of this study.

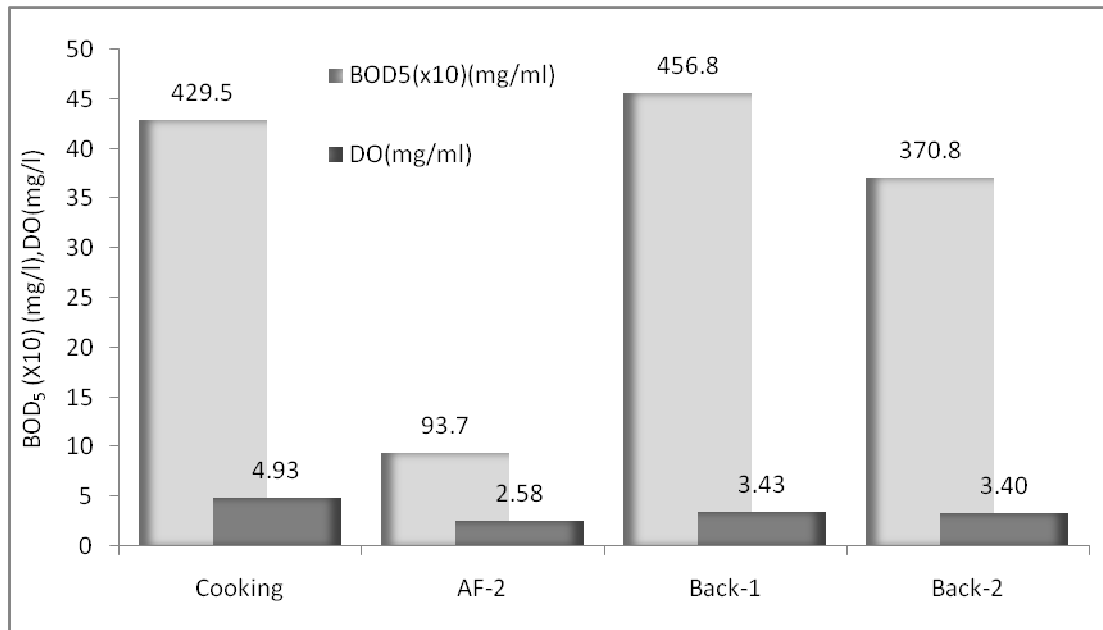


Figure 3.8. BOD₅ and DO changes during cooking and wastewater treatments

The color of the wastewater of the cooking operations changed because of the leached substances such as protein, inorganic substances and pigments into wastewater. The treatments, also changed the wastewater color, were significantly effective ($p < 0.05$) on L* and a* values. L* value increased during the treatments due to the removing some particles caused to darkening of wastewater. The increase in L*-value was correlated with the decrease in a*-value, which means that the treatments were very effective to clear wastewater by removing coloring compounds. YI value and b* value were parallel to each other and increased with the cooking and back operations (Figure 3.9).

The increase in YI-value was parallel to a* and b* values (or decrease in L*- value) during Back operations. This illustrated that; the heating during additional cooking caused the change in coloring materials (e.g. pigments) towards to darkness. It could be explained that each cooking during Back operations increased the content of leached compounds into wastewater and also increased the heat denaturation of pigments (e.g. browning). It is known that, during the thermal processing, the food materials may be exposed to temperatures which have an adverse effect on quality and which make these products susceptible to color deterioration (Bayram et al., 2004c).

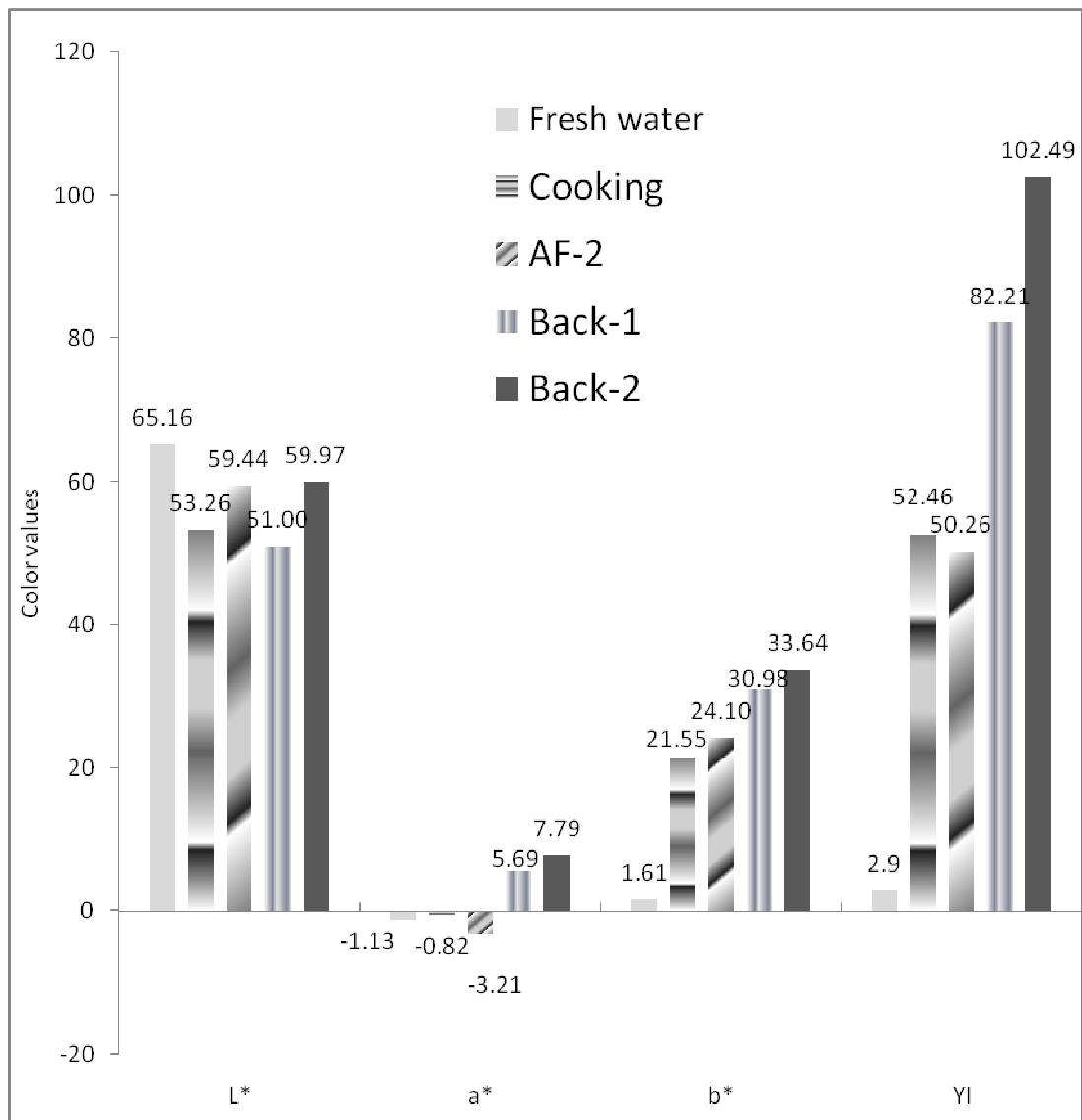


Figure 3.9. Color changes during cooking and wastewater treatments

It has been reported that many reactions can affect the color during the processing of the foods. Among them, the most common are pigment degradation, (especially carotenoids and chlorophyll), browning reactions (such as Maillard condensation of hexoses and amino components) and change of ingredient distribution and structure (swelling, salt or sugar distribution), recrystallization of some compounds (sugar, salt etc.), phenol polymerization and oxidation of ascorbic acid (Bayram et al, 2004c; Abers & Wrolstad, 1979; Kaya, 2002; Lee & Coates, 1999; Lozano & Ibarz, 1997; Maskan, 2001; Maskan, Kaya, & Maskan, 2002; Resnik & Chirife, 1979; Reynolds, 1965; Sherkat & Luh, 1976). Other factors affecting color include acidity, processing

temperature and time, cultivar and heavy metal contamination (Abers & Wrolstad, 1979; Garcia-Viguera et al., 1999; Skrede, 1985).

Cooking operation leads the leaching many of substances into wastewater. These substances decreased the pH of the wastewater. But the treatments eliminated these substances. So, pH of the wastewater increases after the treatments.

Back-1 and Back-2 operations were additional cooking operations. At each cooking, the leaching compound content increased, therefore pH of the wastewater decreased (Figure 3.10).

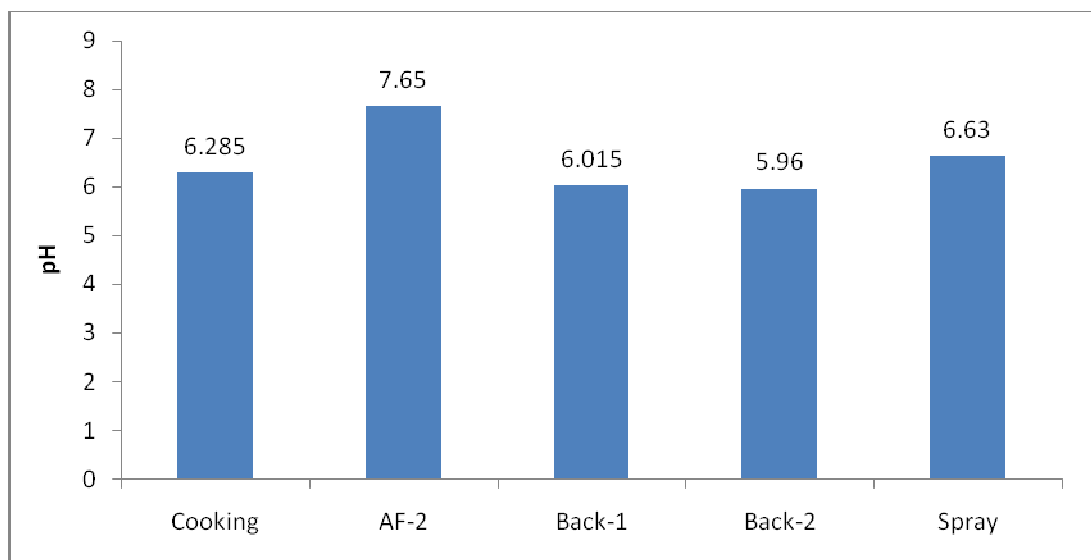


Figure 3.10. pH changes during cooking and wastewater treatments

The Figure 3.11 shows the changes of Brix and turbidity of the cooking, AF-2, Back-1, and Back-2 operations. All results shown were very consistent and nearly parallel with each other. The treatments decreased the amount of organic and inorganic substances in the wastewater of the cooking operation.

The results of pH and TSC explain the change of BOD₅ values of Back-1 and Back-2. As explained previously BOD₅ values of Back-2 was higher than Back-1. However, TSC value was opposite. In normal, both values should be parallel. However, pH value affected the results of BOD₅. The pH of Back-2 was higher than that of Back-1. Therefore, the low pH decreased the activity of microorganism used

in the BOD₅ measurement. Therefore, BOD₅ values decreased as parallel to pH in contrast to increase in TSC.

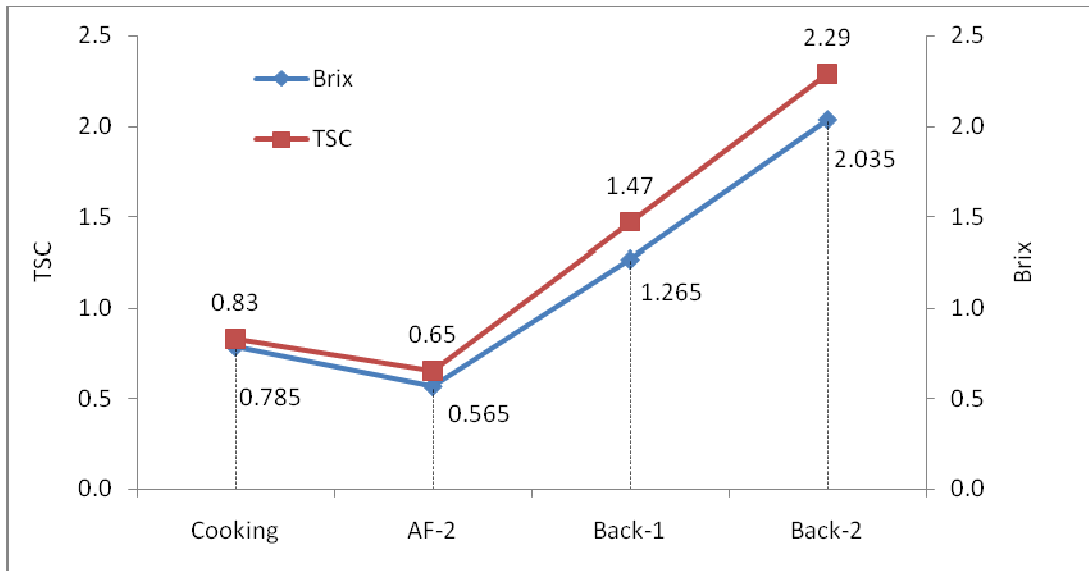


Figure 3.11. Brix and total solid content changes during cooking and wastewater treatments

Conductivity and turbidity values are given in Figure 3.12. Conductivity and turbidity increased during Back-1 and Back-2 operations. This increase correlated the change in the color values. For example, the increase in turbidity was parallel to the increase in YI, a* and b*. These changes illustrated that the leaching of organic and inorganic compounds increased during each cooking operations. And also, the treatments to remove these compounds were significantly effective ($p < 0.005$). Therefore, the treatments applied for the cooking operation can be used. It should be noted that the increase in turbidity for Back-1 and Back-2 was less important than the increase in conductivity. This showed that the leaching of inorganic compounds were more significant than organic compounds (Figure 3.12).

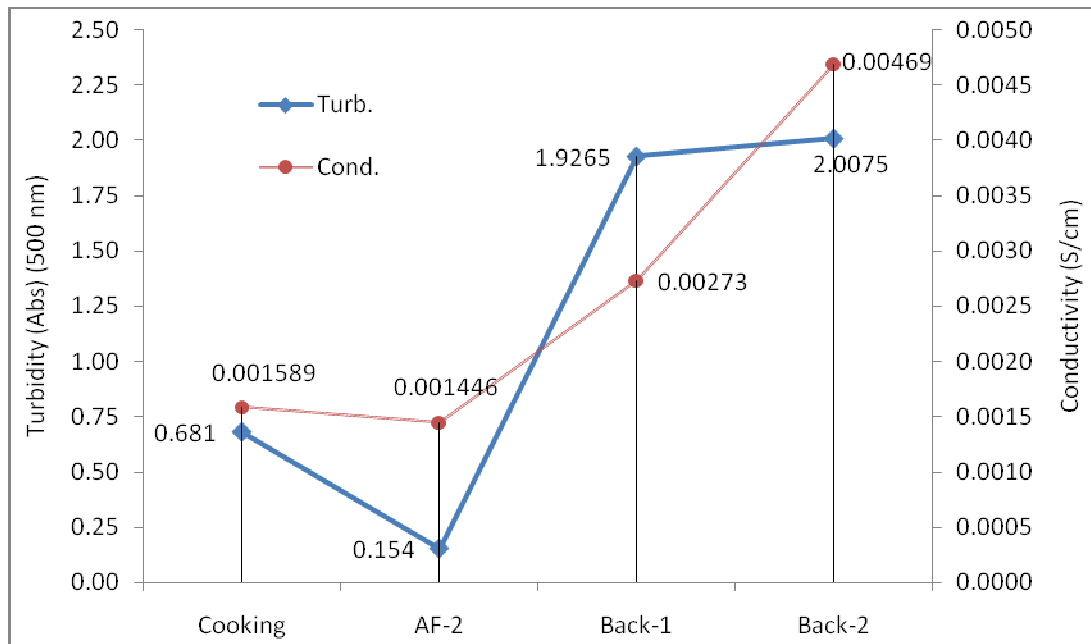


Figure 3.12. Conductivity and turbidity changes during cooking and wastewater treatments

3.5. Recoveries from the washing and cooking operations

Water, nutrient and energy were observed to be saved. The washing operation could only be manipulated to save the water. Also, after the cooking operation, water, energy and nutrient could be saved. All the treatments showed that, a bulgur plant can be designed to save water, nutrient and energy.

As stated, the washing operation was made with two part wheat and one part of water. Therefore, this means that wheat absorbs water as expected. For example, as shown in Figure 3.13, 200 g wheat was washed with 100 ml of water which means, 200 g wheat absorbed 27.2 ml water. 72.8 ml of water was recovered as a wastewater. The treatments were applied to the remained washing wastewater. After, filtration, sedimentation, activated carbon column consisting sand and resin parts and lastly the UV 254 nm application, it was decreased to 38 ml of water. 36.8 ml of water was lost during the treatment operations. During these operations, solid materials were removed; however, these solids absorbed water. Therefore, the removing solids and dirty materials, they caused loss of water due to absorption. At the same time all treatments were made at atmospheric conditions. So, evaporation of water should thought. According to this calculation, 38% of water can be recovered

from the washing operation. This water can be reused in the washing operation. The water recovery is also very important for environmental pollution based on BOD₅ values.

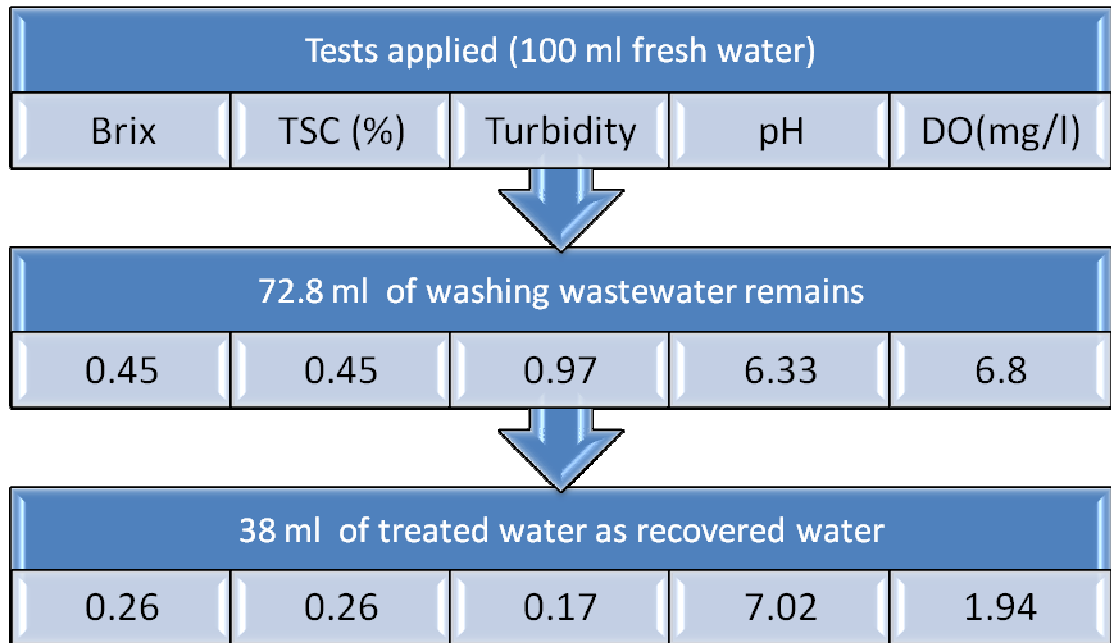


Figure 3.13. Example of 100 ml water+200 g wheat washing operation

In addition, the cooking operation was made with 2 part of water and 1 part of wheat. Wheat was added to boiled water and cooked for 30 minutes. The cooking operation was made at the atmosphere conditions which mean the water loss began during the boiling of water and cooking of wheat periods. Moisture content of wheat is generally increased up to 45 % from 10 % during the cooking. For example; 50 g of wheat can be cooked with 100 ml of water. Recovered water can be found as 50% of the initial water. In another word 50 ml of water was recovered after the cooking operation. Back-1 and Back-2 cooking operations can use this water. The amount of recovered water is given in Figure 3.14. When thinking the BOD₅ value and the amount of water in the cooking operations, it is significantly obvious to need to recover the water.

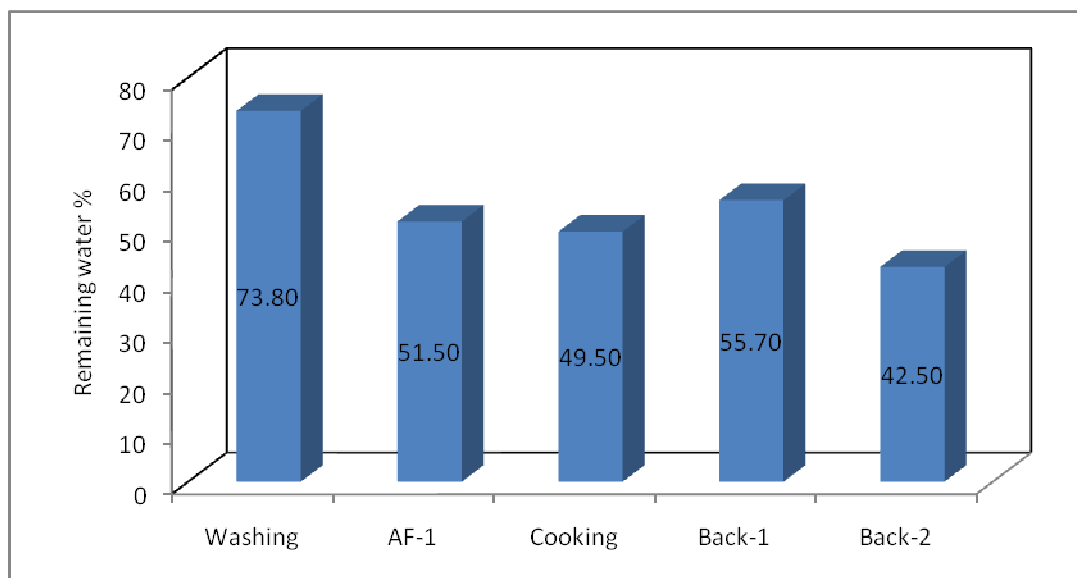


Figure 3.14. Remaining water as percent for all of the operations

Besides of the water and energy recoveries, the nutrients leached from wheat during the cooking operation can also be saved. The leaching of the nutrients (i. e. vitamins, minerals, pigments, starch, protein etc.) from wheat kernel to the cooking water is well known in bulgur production (Bayram et al., 2004a). The nutrients lead to increase in the BOD₅ value of the wastewater. At this point, the spray drying method was applied to recover the nutrients. Spray drier is an effective method to get dry matter as a powder. In the study, this powder was examined to its nutrient components based on protein, starch and ash contents. It was found that their contents in spray dried products were moderately high. The other properties of spray dried product were given in Figure 3.9 and 3.10 for color values and pH, respectively.

Figure 3.15 shows the changes of the protein content in the each part of the processes. The cooking operation had a very high amount of protein. Due to the cooking operation the leaching of the proteins into water increased and continued during subsequent Back-1 and Back-2 operations.

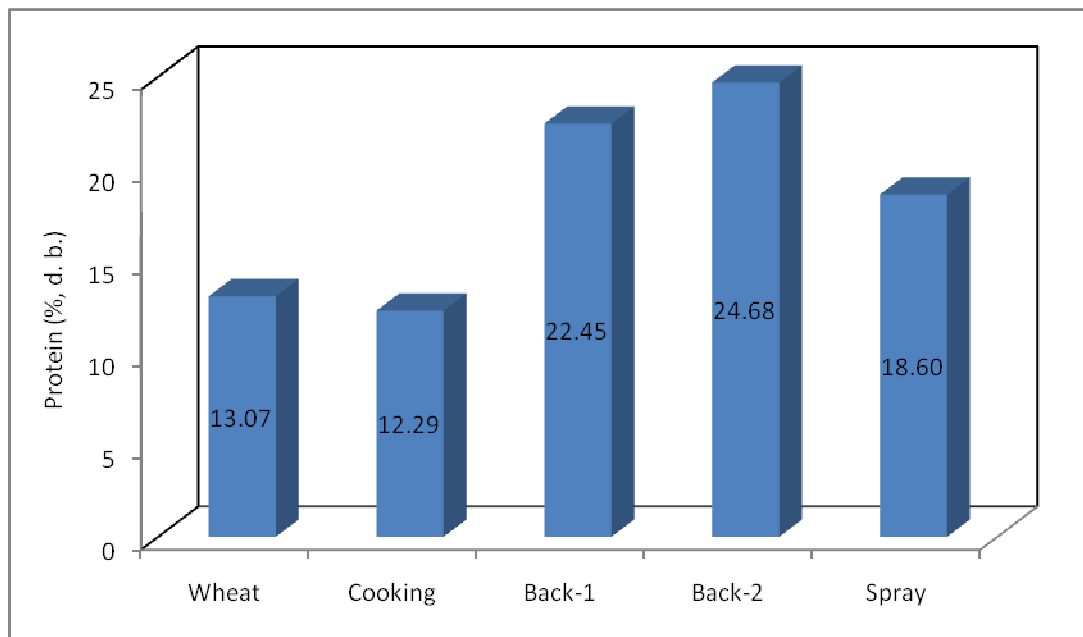


Figure 3.15. Changes in the protein contents

The ash content of the wastewater of cooking operation was maximum at Back-1 operations as expected (Figure 3.16). But, the ash content of Back-2 operation was smaller than Back-1. Ash content in cereal is related with bran content. The value measured in wastewater was also related with broken or suspended bran passed from wheat surface. The decrease in ash content of Back-2 might be explained by pH value. As stated, the pH of Back-2 was lower than the others. Therefore, the decrease in pH (i.e., more acidic) might caused the hardening of wheat texture. And also, this hardening might cause the decreasing the disruption of bran (Bayram, 2003).

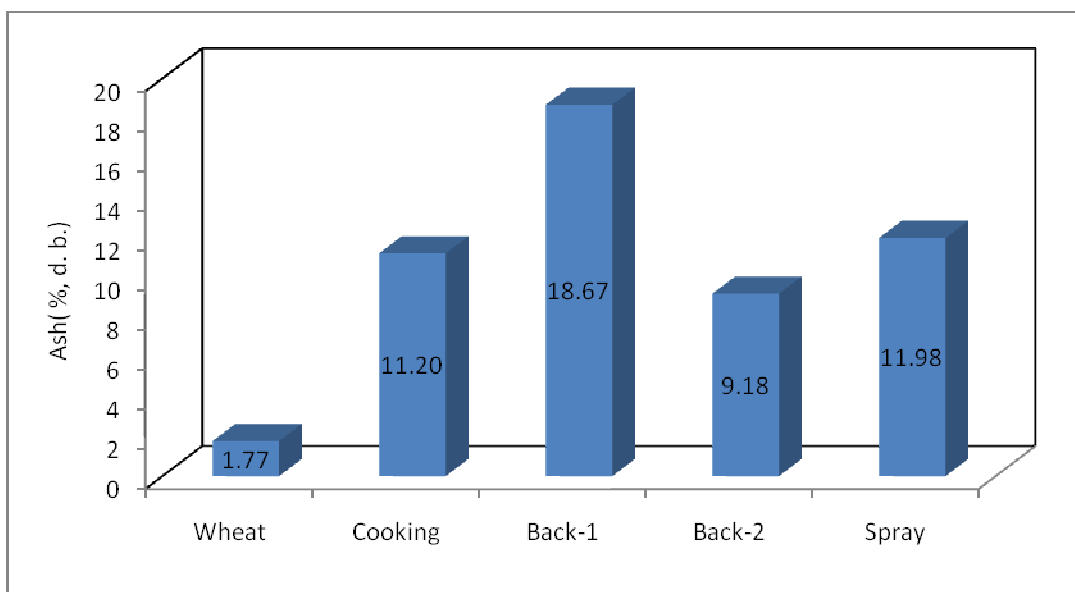


Figure 3.16. Changes in the ash contents

The starch contents are given in Figure 3.18. Being pre-cooked, bulgur does not need much cooking to make it edible i.e. all starch is completely gelatinized (Bayram et al., 2003a). Because of the gelatinization of the starch it was not possible to leach all starch in the wastewater. At each subsequent cooking, the diffusion of starch decreased. However, the leaching of protein (Figure 3.17) increased.

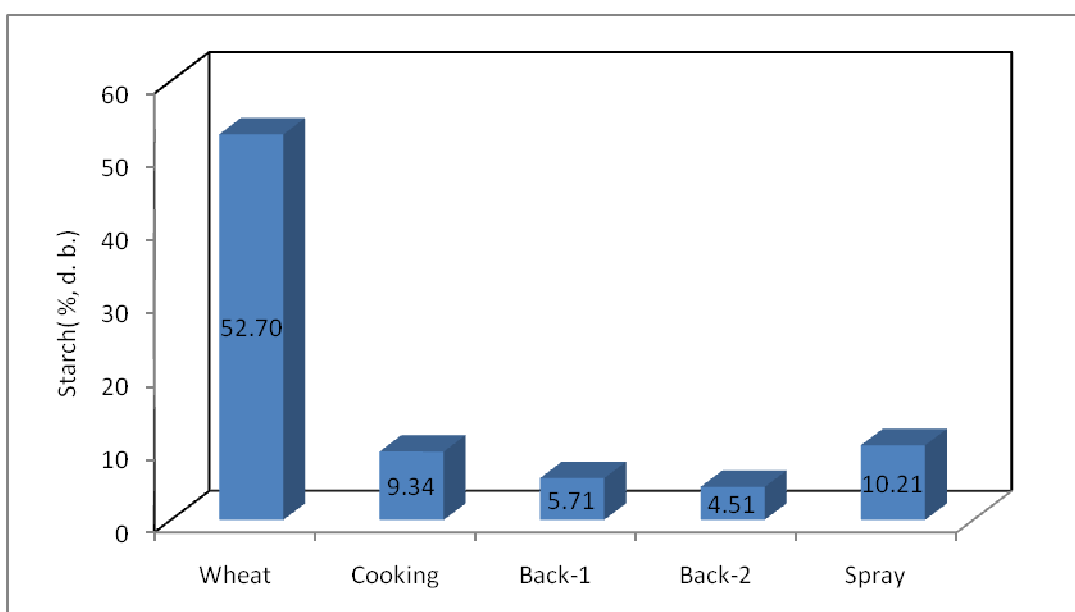


Figure 3.17. Changes in the starch contents

Energy and water recoveries from the wastewater of washing and cooking operations were calculated by the view of economy in Table 3.3. One bulgur plant, having 50 tons/day capacity, can save nearly 70.524 \$ and 19.080 tons of water annually. When the investment cost, processing cost, salvage value and service life of system were calculated, the annual net profit was obtained as \$ 51524. In Turkey, there is 1 million ton of bulgur production annually, the calculation of this amount, 3.9 million \$ and 1.06 million tons of water can be saved. In the view of the loss of water sources in our country and the global warming in the world, these results make sense. It is known that arid region in Turkey and the world increased each year with less rain fall, therefore the recovery of wastewater from food plants will be very important point today and in future.

Table 3.3. Energy and water recovery form the washing and cooking operations

In a plant in 1 day		In this project in one day	
50	tons of wheat requires	50	tons of wheat requires
25	tons of water for washing	25	tons of water for washing (38% save)
75	tons of water for cooking	75	tons of water for cooking (50% save)
ENERGY CALCULATION		ENERGY CALCULATION	
15	Water temperature in °C	50	Water temperature in °C, from the PHE (37.5 tons of water coming from the previous cooking operation at 97 °C and 37.5 tons of fresh water at 15°C) 90% eff.
97	Cooking temperature °C	97	Cooking temperature °C
75000	Mass(kg)	75000	Mass(kg)
4187	cp(j/kg/K)	4187	cp(j/kg/K)
82	Temperature difference (K)	47	Temperature difference (K)
6.160.299	Q=m cp T(kcal)	3.530.903	Q=m cp T(kcal)
\$334.80	(9200 kcal needs 0.5 \$ of fuel) 85% eff.	\$191.90	(9200 kcal needs 0.5 \$ of fuel) 85% eff.
WATER LOSS CALCULATION		WATER LOSS CALCULATION	
37.5	tons from cooking	0	tons from cooking
25	tons from washing	9.5	tons from washing
62.5	tons total	9.5	tons total
\$62.5	money(1 ton water=1 \$)	\$9.5	money(1 ton water=1 \$)
TOTAL MONEY CALCULATION IN A DAY		TOTAL MONEY CALCULATION IN A DAY	
\$334.8	For heating the water	\$191.9	For heating the water
\$62.5	Due to the water loss	\$9.5	Due to the water loss
\$397.3	Total	\$201.4	Total
so;			
In a year(360 days working), a bulgur plant can save		70524	\$.
		19080	tons water.
1.000.000 tons of bulgur produced in Turkey , can be saved		3918000	\$.
		1060000	tons water.
For a bulgur plant			
Equipment investment cost	= \$ 75000		
Processing cost, annually	= \$12000		
Service life	=10 years		
Salvage value	= \$5000		
Annual cost of system	=[(75000-5000)/10 + 1200]=19000		
Net profit, annually	= \$70524-\$19000= \$51524		

CHAPTER IV

CONCLUSION

Wheat was washed and cooked to obtain the wastewater. Wastewater treatments were treated to recover water. The energy, nutrient and water saving were recovered. Wastewater from the washing operation had not much nutrient and energy, it was only used as the source of the water by recovering. . Materials leached to water from wheat were low, because there was neither heat nor any other processes. The cooking operation was the main sources of the energy and nutrients. Especially, Back cooking operations with the use of cooking water for the subsequent cooking operation was very rich in nutrients. The energy was obtained after the cooking operation, because, the cooking operation was made at 97 °C. In general, this hot water is discharged in the industry.

Wastewater of a bulgur plant is disposed to the environment. Wastewater of the bulgur plant has a very high value of BOD₅ (438 mg/l), which means high amount of nutrients that can be easily consumed by the microorganisms and can cause environment diseases. It decreases the amount of the dissolved oxygen in the river of lake. Therefore, decreasing DO in the water affects the life of the plants and the animals. At the same time, microorganisms using DO in the water, sometimes increases the toxicity of the water.

Water loss from the washing operation can be prevented for the reuse in the subsequent washing operation. The treatments must be used applied in the bulgur plants. 38% of the wastewater can easily recovered by the AF-1.

Cooking operation is made at a high temperature and this energy should be reused for the heating the fresh water (e. g. regeneration). Hot water, disposing through environment, directly kills the living organisms in the river and lakes. Wastewater of

cooking operation has high amount of nutrient that can be recovered by spray drying. These nutrients are easily used for ready soup, baby foods etc., because of containing 19 % protein, 10 % starch and 12 % ash.

Moreover, the result of the washing operation will be related with flour and semolina milling industries. In all sectors, the washing operation is same, based on washing technology, water quantity and raw material.

Further studies should be focused on the loss of water in the drying section of the bulgur plants. Because, a plant, that using 50 tons of wheat, loose 37.5 tons of water from the drying by evaporation of water. This water can be condensed and reuse in the production.

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APPENDICES

A. Properties of Wheat

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
Color-L*	51.09	51.17	51.13	0.057
Color-a*	8.63	9.02	8.825	0.276
Color-b*	25.46	25.06	25.26	0.283
Color-YI	74.90	75.00	74.95	0.071
pH	6.45	6.44	6.445	0.007
Protein (% d.b.)	13.09	13.05	13.07	0.026
Ash (% d.b.)	1.75	1.78	1.765	0.021
Starch (% d.b.)	52.7	52.7	52.7	0.000

B. Data of Washing Operation

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	329.5	293.5	311.5	25.456
OD(mg/L)	6.82	7.02	6.92	0.141
Conductivity(S/ml)	0.001528	0.0015	0.001514	0.000
TSC (% , g/ml)	0.46	0.45	0.455	0.007
Color-L*	43.97	43.77	43.87	0.141
Color-a*	1.76	1.73	1.745	0.021
Color-b*	16.02	15.96	15.99	0.042
Color-YI	46.40	46.18	46.29	0.156
pH	6.32	6.34	6.33	0.014
Brix	0.46	0.45	0.455	0.007
Total coliform (Number of mio's)	43	42	42.5	0.707
Total aerobic count (Number of mio's)	4116750	4116750	4116750	0.000
Turbidity (500 nm)	0.97	0.96	0.965	0.007
Remaining water %	72.8	74	73.4	0.849

C. Data of AF-1

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	143.8	196	169.9	36.911
OD(mg/L)	1.94	1.98	1.96	0.028
Conductivity(S/ml)	0.001328	0.0013	0.001314	0.000
TSC (% , g/ml)	0.27	0.26	0.265	0.007
Color-L*	62.70	62.65	62.675	0.035
Color-a*	-1.97	-1.96	-1.965	0.007
Color-b*	11.55	11.47	11.51	0.057
Color-YI	25.62	25.65	25.635	0.021
pH	7.03	7.02	7.025	0.007
Brix	0.26	0.26	0.26	0.000
Total coliform (Number of mio's)	1.5	2	1.75	0.354
Total aerobic count (Number of mio's)	15000	15000	15000	0.000
Turbidity (500 nm)	0.168	0.17	0.169	0.001
Remaining water %	51	52	51.5	0.707

D. Data of Cooking Operation

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	428	431	429.5	2.121
OD(mg/L)	5.42	4.45	4.935	0.686
Conductivity(S/ml)	0.001589	0.0015	0.001545	0.000
TSC (% , g/ml)	0.83	0.83	0.83	0.000
Color-L*	53.04	53.48	53.26	0.311
Color-a*	-0.73	-0.91	-0.82	0.127
Color-b*	22.32	20.78	21.55	1.089
Color-YI	54.53	50.40	52.465	2.920
pH	6.28	6.29	6.285	0.007
Brix	0.78	0.79	0.785	0.007
Turbidity (500 nm)	0.682	0.68	0.681	0.001
Remaining water %	50	49	49.5	0.707
Protein (% , d.b.)	12.29	12.29	12.29	0.000
Ash (% , d.b.)	11.5660	10.8430	11.2045	0.511
Starch (% , d.b.)	8.1930	10.4820	9.3375	1.619

E. Data of AF-2

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	145.4	42	93.7	73.115
OD(mg/L)	2.58	2.59	2.585	0.007
Conductivity(S/ml)	0.001446	0.0014	0.001423	0.000
TSC (% , g/ml)	0.64	0.66	0.65	0.014
Color-L*	59.21	59.68	59.445	0.332
Color-a*	-3.07	-3.36	-3.215	0.205
Color-b*	26.26	21.95	24.105	3.048
Color-YI	54.47	46.06	50.265	5.947
pH	7.65	7.65	7.65	0.000
Brix	0.57	0.56	0.565	0.007
Turbidity (500 nm)	0.15	0.158	0.154	0.006

F. Data of Back-1 Operation

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	458.6	455	456.8	2.546
OD(mg/L)	3.44	3.51	3.475	0.049
Conductivity(S/ml)	0.00273	0.002	0.002365	0.001
TSC (% , g/ml)	1.47	1.47	1.47	0.000
Color-L*	52.84	49.17	51.005	2.595
Color-a*	6.42	4.96	5.69	1.032
Color-b*	29.40	32.56	30.98	2.234
Color-YI	92.52	71.90	82.21	14.581
pH	6.01	6.02	6.015	0.007
Brix	1.26	1.27	1.265	0.007
Turbidity (500 nm)	1.923	1.93	1.926	0.005
Remaining water %	56.4	55	55.7	0.990
Protein (% , d.b.)	21.7690	23.1290	22.45	0.962
Ash (% , d.b.)	19.5240	17.8230	18.6735	1.203
Starch (% , d.b.)	4.7620	6.6670	5.7145	1.347

G. Data of Back-2 Operation

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
BOD(mg/L)	371	372.6	370.8	1.131
OD(mg/L)	3.43	3.38	3.405	0.035
Conductivity(S/ml)	0.00469	0.004	0.004345	0.000
TSC (% , g/ml)	2.33	2.25	2.29	0.057
Color-L*	60.82	59.12	59.97	1.202
Color-a*	9.11	6.48	7.795	1.860
Color-b*	30.06	37.23	33.645	5.070
Color-YI	103.19	101.79	102.49	0.990
pH	5.96	5.96	5.96	0.000
Brix	2.04	2.03	2.035	0.007
Turbidity (500 nm)	2.007	2.008	2007.5	0.707
Remaining water %	42	43	42.5	0.707
Protein (% , d.b.)	25.3330	24.0340	24.68	0.919
Ash (% , d.b.)	8.8410	9.5110	9.176	0.474
Starch (% , d.b.)	4.0440	4.9790	4.5115	0.661

H. Data of Spray Dryer

PROPERTIES	RUN 1	RUN 2	AVERAGE	STANDARD DEVIATION
TSC (% g/ml)	92.2	93	92.60	0.566
Color-L*	78.16	77.31	77.74	0.601
Color-a*	1.32	1.40	1.36	0.057
Color-b*	21.56	21.75	21.66	0.134
Color-YI	42.92	43.66	43.29	0.523
pH	6.63	6.62	6.63	0.007
Protein (% d.b.)	18.90	18.30	18.60	0.424
Ash (% d.b.)	12.311	11.646	11.978	0.470
Starch (% d.b.)	10.210	10.200	10.205	0.007