THE ROLE OF CATION AND ANION EXCHANGE RESIN FOR THE REMOVAL OF COD, COLOUR, AND NH_3-N FROM COFFEE PROCESSING WASTEWATER

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by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
AP	Adequate precision
APHA	American public health Association
APS	Activated sludge process
ASBR	Anaerobic sequencing batch reactor
BET	Brunauer-Emmett-Teller
BOD	Biochemical oxygen demand
CCD	Central composite design
CEC	Cation exchange capacity
COD	Chemical oxygen demand
CPW	Coffee processing wastewater
DO	Dissolve oxygen
DOE	Design of experiment
EBCT	Empty bed contact time
EC	Electrochemical oxidation
FO	Fenton oxidation
FTIR	Fourier transform infrared
HRT	Hydraulic retention time
MBR	Membrane bioreactor
MF	Microfiltration
MTZ	Mass transfer zone
NF	Nanofiltration
NH_3-N	Ammoniacal nitrogen

OH•	Hydroxyl radicals
pH	Hydrogen ions
PRESS	Predicted Residual Sum of Squares
R_2	Coefficient of determination
Adj	Adjusted Coefficient of determination
RL	Dimensionless equilibrium parameter
RO	Reverse osmosis
RSM	Response surface methodology
SEM	Scanning electron microscopes
SS	Suspended solids
Tb	Breakthrough time
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
XRD	X-ray Diffraction

PERANAN RESIN PENUKARAN KATION DAN ANION DALAM PENYINGKIRAN COD, WARNA, DAN NH_3-N DARI SISA AIR KOPI

ABSTRAK

Kopi adalah komoditi kedua yang paling banyak diperdagangkan selepas petroleum. Penanaman dan pengeluaran kopi telah meningkat secara global. Namun, pemprosesan kopi dari biji kopi untuk diminum memerlukan sejumlah besar air bersih, dan menghasilkan isipadu besar air sisa yang tercemar. Analisis sifat fizikokimia air sisa kopi menunjukkan bahawa air sisa tersebut. Air sisa pemprosesan kopi berwarna coklat gelap kerana mengandungi beberapa zarah organik koloid tidak terurai dan terurai . Oleh itu, ia mendorong rawatan air sisa pemprosesan kopi sebelum dibuang ke aliran air terdekat. Selama tahun-tahun kebelakangan ini, pelbagai teknologi telah dilaksanakan untuk merawat air sisa kopi untuk mengurangkan had pelepasan standard yang ditetapkan oleh badan-badan alam sekitar. Dalam kajian ini, pengaruh resin pertukaran kation dan anion ditentukan untuk penyingkiran COD, warna dan NH_3-N daripada air sisa kopi. Eksperimen dilakukan dengan pH yang berbeza-beza, dosis resin, masa reaksi, kelajuan gegaran dan suhu. Kinetika, termodinamik dan pemodelan permukaan digunakan untuk menentukan perilaku pertukaran ion pada penyingkiran COD, warna dan NH_3-N dari air sisa kopi. Metodologi permukaan tindak balas (RSM) digunakan untuk mengoptimumkan keadaan eksperimen pertukaran ion pada penghapusan maksimum COD, warna dan NH_3-N dari air sisa kopi. Selain itu, penyingkiran COD, warna dan NH_3-N dari air sisa kopi menggunakan kation dan resin pertukaran anion dilakukan dengan menggunakan sistem tiang aliran. Akhirnya, penjanaan semula resin pertukaran kation dan anion juga dilakukan. Keputusan kajian menujukkan bahawa pada dos kation optimum 37.55g, masa hubungan 126.28 minit, kelajuan gegaran 220 rpm pH 4 dan suhu 300^0C; 27.75, 27.47, dan 69.28%

penyingkiran COD, warna dan NH_3 -N dicapai masing-masing. Selanjutnya, pada dos anion optimum 50g, masa hubungan 210 minit, kelajuan gegaran 210.73 rpm pH 7 dan suhu 300C, penyingkiran 75.36, 59.54, dan 33.12% COD, warna dan NH_3-N dicapai. Keputusan kajian ini menunjukkan bahawa kation yang diikuti oleh anion memberikan penyingkiran yang lebih baik; iaitu sehingga 94.43% COD, 69.77% warna, dan 95.69% NH_3-¬N dicapai untuk memenuhi standard B DOE Malaysia. Dari permukaan pemodelan, nilai pekali korelasi menunjukkan bahawa penjerapan berlaku di tapak homogen tertentu untuk memenuhi model isoterm Langmuir. Dari kajian kinetik dan termodinamik, hasilnya menunjukkan bahawa penjerapan mengikuti kinetik urutan ke-2 pseudo yang menunjukkan proses pengawalan kadar adalah lebih jerapan kimia dan jerapan fizikal. Nilai negatif ΔH menunjukkan penjerapan bahan pencemar ke resin adalah eksotermik, ΔS positif menunjukkan bahawa rawak organisasi dalam antara muka larutan pepejal. Dari eksperimen regenerasi, kedua-dua resin menunjukkan kapasiti regenerasi yang luar biasa setelah 5 kali penggunaan semula. Hasil kajian 'tarus-kelas-atas' menunjukkan penyingkiran yang lebih tinggi pada kadar 10ml / m berbanding 20 dan 30ml / m. Kajian mekanisme juga bersetuju dengan kajian mekanisme kumpulan. Hasil kajian ini menunjukkan bahawa sisa COD, warna, dan pematuhan NH_3-N dengan had pelepasan Standard B yang ditetapkan oleh DOE, Malaysia. Oleh itu, resin pertukaran ion berpotensi untuk menggunakan air sisa kopi pada penyingkiran zarah organik yang tidak biodegradasi dan terampai dari air sisa kopi sehingga selamat keluar ke aliran air.

THE ROLE OF CATION AND ANION EXCHANGE RESIN FOR THE REMOVAL OF COD, COLOUR, AND NH_3-N FROM COFFEE PROCESSING WASTEWATER

ABSTRACT

Coffee is the second most traded commodity after petroleum. The cultivation and production of coffee have expanded globally. However, the processing of coffee from coffee bean to drink requires a large quantity of clean water and results in a considerable volume of contaminated wastewater. The physicochemical properties analyses of coffee wastewater reveal that the coffee processing wastewater is dark brown because it contains several non-biodegradable and suspended colloidal organic particles. Therefore, it urges to treat the coffee processing wastewater before discharge into the nearest watercourse. Over the years, various technologies have been implemented to treat the coffee wastewater to mitigate standard discharge limits set by Environmental agencies. In the present study, the influence of cation and anion exchange resins was determined to remove COD, colour, and NH_3-N from coffee wastewater. The experiments were conducted with varying pH, resin doses, reaction time, shaking speed and temperature. Kinetics, thermodynamics and surface modelling were employed to determine the ion-exchange resin behaviour in removing COD, colour and NH_3-N from coffee wastewater. Response surface methodology (RSM) was utilized to optimize the ion exchanges experimental conditions on maximum removal of COD, colour and NH_3-N from coffee wastewater. Besides, the removal of COD, colour and NH_3-N from coffee wastewater using cation and anion exchange resins was conducted using an up-flow column system. Finally, the regeneration of cation and anion exchange resins were also carried out. The result showed that at optimum cation dosage of 35 g, a contact time of 126.28 minutes, shaking speed of 220 rpm, pH of 4 and temperature of 30 ^{0}C, removal of 27.75 % COD, 27.47% colour and 69.28 % NH_{3}-N was achieved. Similarly, at optimum anion dosage of 50 g, a contact time of 210 minutes, shaking speed of 210.73 rpm, pH of 7 and temperature of 30 ^{0}C, removal of 75.4 %, 59.5 %, and 33.1 % of COD, Color and NH_{3}-N were achieved respectively. Results from series studies show that the cation followed by anion series gave a better removal of up to 94.43 % of COD, 69.77 % of colour, and 95.69 % of NH_{3}-N was attained, thereby meeting the Malaysian DOE standard B. From the surface modelling, correlation coefficient values show that adsorption occurred at specific homogeneous sites satisfying the Langmuir isotherm model. From the kinetics and thermodynamics studies, the results suggest that adsorptions follow pseudo-second-order kinetics, indicating the rate-controlling process to be more chemisorption than physisorption. Negative values of ΔH for COD, colour, and NH_{3}-N adsorption, indicate adsorption of pollutants onto resins was exothermic, ΔS were positive, indicating the randomness of organization in the solid-solution interface. From the regeneration experiment, both resins indicated outstanding regeneration capacity after 5-time re-use. From the upscale-column-study results, higher removal at 10 ml/m was observed compared to 20 and 30 ml/m. The present study's findings reveal that the residual COD, colour, and NH_{3}-N complied with Standard B discharge limits set by DOE, Malaysia. Thus, cation and anion ion exchange resins have the potential to remove COD, colour, and NH_{3}-N from coffee wastewater.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Wastewater is any water that has been affected by human activity (Tilley et al., 2008). Wastewater is simply a mixture of clean water, chemicals (organics and inorganics), and heavy metals. There are generally four significant wastewater sources, factories/industries, households, commercial businesses/offices, and farmlands/horticulture (World Health Organization WHO, 2018). Wastewater is composed of organic materials, heavy metals, suspended/dissolve solids, depending on the source.

In an aquatic environment, the accumulation of organic compounds can have a direct effect on oxygen reduction, which inhibits both micro and macro-organisms' growth. On land, depletion of soil nutrients, thereby causing stunted growth in plants and general imbalance (Bhatt & Rani, 2013). Other environmental impacts of wastewater include eutrophication, aerosols, and odour, which results in the spread of disease-causing organisms and nuisance.

The Global trend in population growth demands viable ways of achieving good environmental management practice using sustainable technologies (Lalevic et al., 2012). Growing concerns about environmental issues underlie the increasing need for policies and strategies to mitigate these problems (Figueroa et al., 2016). Besides, motivation for sustainable wastewater management is driven by factors such as disposal limits in sensitive water bodies, legislation, economic consideration regarding the cost of clean water, protection from water-related risk, industry image (as a form of corporate social responsibility of industry), moral reasons.

The coffee processing industry is an agro-based industry that contributes immensely to the ambient environment's pollution. (Woldesenbet et al., 2014). Coffee originated from east Africa in Ethiopia and subsequently spread to Egypt, Yemen, Italy, and Europe. The coffee plant belongs to the family *Rubiaceae*, genus *Coffea.* Its seeds are called coffee beans and are processed into drinks (Enden & Calvert, 2014). coffee production and processing have continuously gained a place worldwide, including countries like Malaysia and many parts of Asia. It is mainly produced in the tropics and consumed in the temperate region (Alemayehu et al., 2020). After petroleum, coffee is the second-largest most traded commodity globally. Three species of coffee dominates the international market; thus, Arabica (C*offea arabica*), Robusta (*Coffea canephora*), and Coffea *liberica* 2% (Enden & Calvert, 2014).

In Malaysia, two varieties are grown, particularly as a cash crop; Coffee Liberia 90% and Robusta10% (Wahab, 2016). Malaysia's coffee export market includes Thailand, Singapore, the Philippines, the United States of America, and Hong Kong. The amount of Coffee exported by Malaysia has an annual growth rate of 7.6% (Wahab, 2016). The Malaysian national agricultural policy (NAP3 1998-2010) noted that coffee production has a very high chance of fostering Malaysia's development.

The coffee processing is done either by the wet or dry method. As the name implies, wet processing uses water for its operations and produces a high volume of polluted effluent, which are traditionally discharged quickly into the immediate river or stream (Novita et al., 2019). Therefore treatment of the coffee effluent before discharge is of utmost priority (Dadi et al., 2018).

Although biological treatment is an environmentally friendly method of treating coffee wastewater, it is insufficient because the wastewater contains recalcitrant substances, and the biological process alone does not efficiently degrade them. Consequently, the integration of physicochemical and biological methods is adopted instead of the single treatment for effective treatment (Alemayehu et al., 2020).

Ion exchange technology has been successfully used as pretreatment in wastewater management in the removal of heavy metals and other recalcitrant substances such as phenol, organic and inorganic matter (Caetano et al., 2009; Cavaco et al., 2007; Víctor-Ortega et al., 2014). Ion exchange is the reallocation of the ion between two stages of diffusion. Ion exchange resins are solid, insoluble polymer materials that can replace charged ions from an aqueous solution with counter ions (Kremer, 1954). The capacity to exchange ions depends on the ion exchange resin material (Fu & Wang, 2011; Lucy, 2003). Ion exchange resins comprise acidic and basic functional groups and can interchange counter ions surrounding them within an aqueous solution (SenGupta, 2017). Ion exchange is an adsorption phenomenon where the mechanism is electrostatic. Electrostatic forces adsorb ions to charged functional groups of the ion exchange resin, and the adsorbed ion interchanges the ions on the resin's surface on a 1:1 charge basis (SenGupta, 2017). The resins are made up of an organic polymer substrate backbone; they are usually white or yellowish and are available in small beats (1-2 mm). The resin material has a high surface area because they are generally porous (Kunin, 1966).

1.2 Problem Statement

The constituent of coffee processing wastewater includes many toxic chemicals, including polyphenols, tannins, and caffeine. The existence of sugars, protein, and minerals makes it a suitable substrate for organic pollution. The coffee bean component undergoes structural changes leading to the formation of melanoidins during the roasting process, which are high molecular weight nitrogenous and brown-coloured compounds (Coelho et al., 2014; Moreira et al., 2017). The coffee Melanoidins consist of ligand groups, such as polysaccharides, tannins, and their combinations. Consequently, the discharge of coloured effluent results in its opacity, the depletion of oxygen level in water essential for biological break down of organic matter (biological oxygen demand), creating an anaerobic condition that is detrimental to aquatic habitat. High chemical oxygen demand and eutrophication result from a high nitrogen concentration (Said et al., 2020; Takashina et al., 2018).

Conventional biological treatment processes have not been successful in degrading these macromolecules (Teresa et al., 2007). Therefore, a range of physicochemical processes has reportedly been harnessed. However, the acidic nature of coffee wastewater and the cost implication have served as a serious drawback to many physicochemical processes. Additionally, the coffee processing wastewater properties themselves affect the efficacy of the treatment quality.

The efficiency of individual as well as the interactive effect of multiple operating parameters is a significant concern in wastewater treatment setup. Spent media management is an essential drawback in an adsorption experiment. Batch performance cannot sometimes represent the ideal result of a system because of the small volume of wastewater used, high consumption of sample dissipation of experiment, and not showing interaction between variables are also factors that impede treatment.

In this study, removal of COD, colour and NH_3-N from coffee wastewater using cation and anion ion exchange resin was achieved for the first time using central composite design of response surface method to optimize the experimental conditions.

1.3 Knowledge Gaps

Coffee wastewater has unique chemistry in comparison to traditional wastewater due to the presence of phenolic compound concentration. To effectively degrade these recalcitrant substances, various works on physicochemical methods were reported. These include adsorption, ionizing radiation, electrochemical oxidation, and, lately, chemical coagulation/flocculation coupled with advanced oxidation processes. There is no previous research investigating COD, colour, and NH_3-H, removal from coffee processing wastewater using the ion-exchange resin. Critical gaps in the literature include adsorption rate of COD, colour, and NH_3-H onto ion exchange resin, optimization of process parameters using RSM, removal efficiency as a function of resin dose, equilibrium capacity, and equilibrium sorption model.

As opposed to other physicochemical processes, the choice of this process is that the ion exchange resin has a stable structure. Its chemical composition is a determining factor in the degradation of organic compounds. It has minimal energy consumption. Additionally, it can tolerate different feed flow rates, it is simple to operate, and a wide variety of resins are readily available from many manufacturers. The process is also not affected by pH; it does not generate sludge, and ion exchange resins are easily regenerated and reused using very cheap regenerant.

Besides the choice of treatment technique, experimental design is also an essential task. Therefore, for developing, improving, and optimizing processes; interpreting the relationships between responses and factor effect in coffee wastewater treatment, a multivariate approach, Response Surface Methodology (RSM), was used in this study. Knowledge on the regeneration of spent media after adsorption of COD, colour, and NH_3-N from coffee processing wastewater has also been reported for the first time in the literature.

1.4 Objectives of Research

1. To assess the removal efficiency of COD, colour, and NH_3-N from coffee processing wastewater using a strong acid cation and a strong base anion exchanger resins.
2. To evaluate isotherm, kinetics, and thermodynamics properties analyses on the COD, colour, and NH_3-N removal from coffee processing wastewater using cation and anion ion exchangers
3. To optimize the experimental condition of cation and anion exchange resins to remove COD, colour, and NH_3-N from coffee processing wastewater using Response Surface Methodology.
4. To assess the regeneration and reuse capability of the cation and anion exchange resins on COD, colour, and NH_3-N removal from coffee processing wastewater.
5. To appraise the removal efficiency of COD, colour, and NH_3-N from coffee processing wastewater using cation and anion exchange resins in an up-flow continuous column.

1.5 Scope and Limitation

The study focused on the treatment of coffee wastewater generated by Syarikat Hang Tuah Sdn. Bhd located at Seberang Perai, Pulau Pinang, Malaysia, using the ion-exchange process. The study will use strong acid cation and strong base anion exchange resin with the styrene-divinylbenzene copolymer framework to remove COD, colour, and ammoniacal nitrogen, through batch and column conditions.

1.6 The Layout of the Thesis

Five chapters were used in this report to cover all the intended information. Chapter 1; introduces the subject matter and its importance. It further explains the problem statements, objectives as well as gaps in the literature. Chapter 2; describes the economic importance of the coffee processing industry, its manufacturing process, the wastewater physicochemical characteristics, and its threat to man and the environment. It further discusses the ion exchange resin, its characteristics, applications, regeneration, and behaviour in a column system. Chapter 3; elaborated the materials and methods used in this study. Chapter 4; discusses all the research findings. These include the characterization of raw coffee processing wastewater (CPW) and the properties of the resin.

Furthermore, the experiment's results on the effectiveness of the pre-treatment of the resin have been discussed, the significance of COD, colour, and NH_3-N removals from raw coffee processing wastewater in batch and column experiments using cation and anion exchange resin both separately and in the sequence were examined and discussed. The batch experiments for evaluating the effect of process variables, i.e., media dosage, shaking speed, contact time, pH, and temperature, are discussed. The treatment optimization results based on the central composite design (CCD) of RSM for treatment using cation and anion exchange resin were also presented and discussed. Surface modelling results using Langmuir and Freundlich and BET isotherms were plotted and discussed. The rate of adsorption, as defined by the adsorption kinetics (pseudo-first-order, pseudo-second-order, intra-particle diffusion) and thermodynamics, were discussed. The spend media regeneration results of the resins were also discussed in this chapter. Finally, from the findings, conclusions were arrived at in chapter 5, and further study recommendations were also given.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is a significant raw material in numerous industrial operations; the quantity of water used depends on the industry and the processing technique. The constituent of industrial wastewater can either be organic and inorganic effluent with various toxicity levels depending on the industrial activity. Inorganic wastewater (e.g., coal and steel industries) is characterized by a large proportion of suspended matter, dissolved metals and gases, oils, chemicals, and salts. While organic wastewater (e.g., from the coffee processing industry) is characterized by a high concentration of BOD, COD, extracts from natural and synthetic solvents, nutrients, odour, colour, high or low pH (Shi, 2011).

2.2 Coffee Processing Industry

Coffee first originated from Ethiopia, spreading across to Egypt, Yemen, Italy, and Europe. Today, Brazil is the largest producer and exporter globally (Louzada et al., 2016). Coffee has incessantly grown to be the highest consumed beverage and is now the second-largest most traded commodity globally (Enden & Calvert, 2014). It is generally produced in the tropics and consumed in the temperate region. Coffee is a plant that belongs to the family *Rubiaceae*, genus *Coffea*. Its seeds can be processed into drinks and are called coffee beans. Even though the coffee plant lifespan may be up to 100 years, it is most productive between 5–25 years and can grow from 5-25 m tall. Out of over 60 species of the coffee genus, three dominate the international market; Arabica (*Coffea arabica*) with about 70%, it has the highest quality in terms of taste and aroma, Robusta (*Coffea canephora*) 28%, it has the highest caffeine content, and Liberian Coffee (C*offea liberica*) 2%, (Wahab, 2016).

In Malaysia, coffee is grown as a cash crop, and the market for export include Thailand, Singapore, the Philippines, the United States of America, and Hong Kong. The amount of coffee exported by Malaysia has an annual growth rate of 7.6% (Wahab, 2016). According to the Malaysian national agricultural policy (NAP3 1998-2010), coffee production has a very high chance of fostering Malaysia's development.

2.3 The Anatomy of a Coffee Berry

The coffee berry outer skin is called the exocarp; underneath it lies the pulp (mesocarp) layer, followed by a slimy layer called the pectin layer (Tori Gay, 2018). The bean is covered in an endocarp generally referred to as the parchment; inside the bean is another thin layer referred to as the silver skin (epidermis), as demonstrated in Figure 2.1.

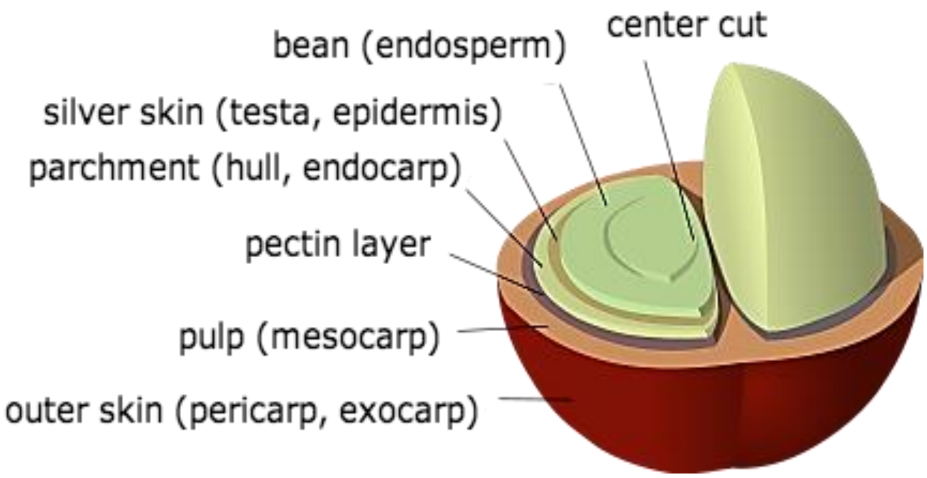

Figure 2.1: The Anatomy of Coffee Berry

2.4 The Chemistry of Coffee

The coffee bean comprises many components: caffeine, proteins, carbohydrate, lipids, tannin, minerals, polyphenol, and sugars (Oestreich-Janzen, 2010). Several amino acids derivatives such as glutamic acid, alanine, asparagine, arginine, phenylalanine, cysteine, glycine, isoleucine, histidine, leucine, lysine, methionine, threonine, proline, serine, tyrosine, and valine are also present in the coffee bean (Zuhair Mohd Zain, 2017). A fascinating chemical compound found in the coffee plant is polyphenol. It is a compound having numerous hydroxyl groups bonded to the aromatic rings, as shown in Figure 2.2.

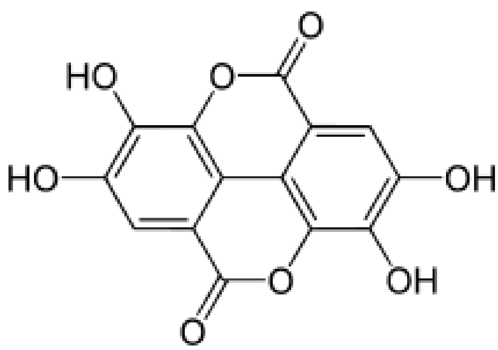

Figure 2.2: Chemical structure of coffee polyphenol

The polyphenol family contains about 8000 phenolic structures (Farah & Donangelo, 2006). They are the primary cause of taste and colour in the coffee plant. Flavonoid and Phenolic acid are the main polyphenol classes, while the less common ones are lignans and stilbenes. Caffeic acid is the most apparent phenolic acid; it is an ester, while the most abundant caffeoyl ester in coffee is the chlorogenic acid. Chlorogenic Acid (CGA) is a water-soluble ester of one or two quinic Acid and caffeic Acid (Figure 2.3).

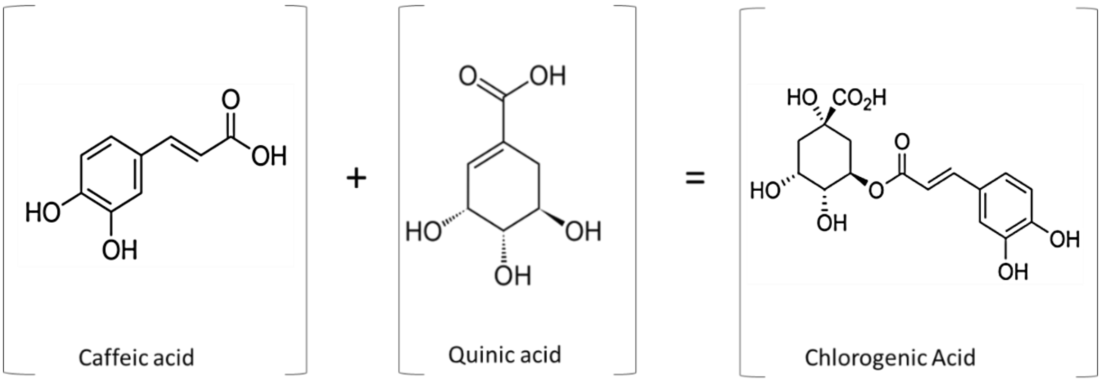

Figure 2.3: Chemical structure of quinic acid, caffeic acid and chlorogenic acid

A final class of compounds called melanoidins are formed as by-products of the roasting of coffee beans. They are formed during a chemical reaction between proteins and sugars responsible for flavouring in the roasting of coffee; the reaction is known as the Maillard reaction. The chemical structures of melanoidins are generally unknown because of their complexity. The literature reported that roasted coffee bean structure might contain more than 30% of melanoidins (Moreira et al., 2017; Rufián-Henares & Pastoriza, 2015), yet there is still little information about this class of compounds. Until now, three main proposals for the structure of melanoidins that have been put forward are; First, it is made of low molecular weight coloured substances that crosslink with free amino groups in proteins leading to high molecular weight coloured structures (Coelho et al., 2014). Second, it was suggested that melanoidins are recurring unit macromolecular complexes made up of polycondensed furan-like and pyrrole-like complexes (Moreira et al., 2012). Third, the melanoidin skeleton is made primarily from polymerised sugar degradation products and connected by amino compounds formed in the early stages of the Maillard reaction (Rufián-Henares & Pastoriza, 2015).

2.5 Coffee Processing

The coffee bean's quality begins to degrade a few hours after harvesting from the farm; therefore, processing begins immediately after harvesting. Thus, coffee processing industries should be situated near the coffee farm (Tori-Gay, 2018). Generally, the coffee processing method consists of dry and wet methods. Each processing stage produces a waste that is either solid or liquid, as illustrated in Figure 2.4. Moreover, the sturdiness of the processing decides the quality of the end product (von Enden et al., 2002).

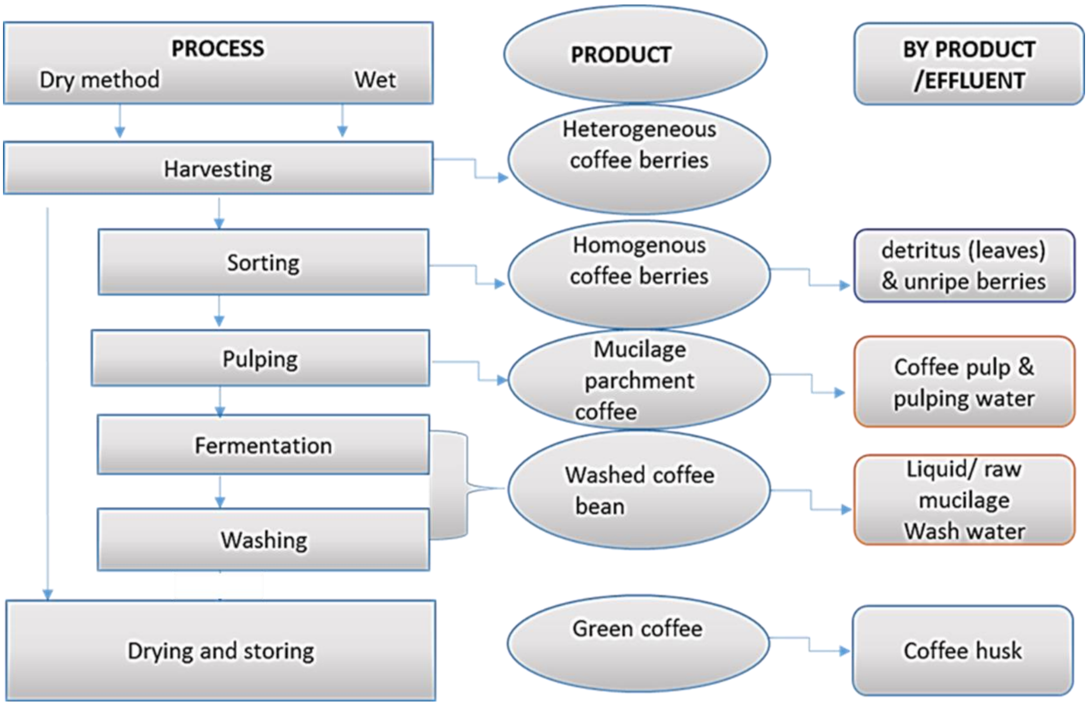

Figure 2.4: Schematic diagram of coffee processing

2.5.1 The Dry Coffee Processing Method

After harvest, coffee berries are left under the sun until the moisture content reaches a minimum of 10% (von Enden & Calvert 2010). It is followed by the removal of the outer skin and parchment mechanically. Although The dry method is the simplest method with minimum wastewater, limitations include; it requires a large space for the sun drying, rainstorms can efficiently inhibit it, it takes a long time to finish the process (e.g., 7-11 days), and does not usually produce good quality coffee as compared to the wet method (Rattan et al., 2015).

2.5.2 The Wet Coffee Processing Method

This method entails different processing stages and requires high technical expertise to ensure production from coffee berries to good quality dried green coffee beans (Garde et al., 2017). After harvesting, the processing is preceded by sorting, whereby coffee berries are first sorted out with a float test; whereby the berries are immersed in water, the poorly developed, degraded, or diseased floats on the water and is removed, other detritus such as twigs or leaves that may have been collected are also removed at this stage. Depulping follows this, and it involves removing the outer layer of the coffee seed (exocarp, mesocarp), leaving a slimy coating of mucilage around the bean. This process generates a high level of organic matter, making it difficult to degrade the coffee berries' mucilage layer (Rattan et al., 2015). Next is the mucilage (composed of sugars, proteins, and pectin, which gives it its gel-like feature). At this stage, the mucilage is subjected to microorganisms with the sole aim of decomposing the layer, after which the coffee bean is again washed. The temperature of the ambient environment determines fermentation time. According to Katzeff (2001), the most straightforward test for complete fermentation is by pushing one’s hand into the pile of coffee beans when it makes a hole, and then it is completely fermented. After the fermentation is completed, Washing follows next. It involves immersing the bean in clean water, stirring, and rinsing; the process continues until it is devoid of any trace of mucilage. This is because having any residue of mucilage could affect the quality of the green coffee bean. After the beans have been freed of all pulpy residue, it is subjected to drying either by solar energy or mechanical dryers until the moisture content is reduced to 10-12% according to the reading of digital grain moisture meter (Kebede et al., 2010). The dryness of the coffee is essential because it increases the quality, thus, increasing the value. It also inhibits the growth of fungi on the seed.

The second phase of the processing (Figure 2.5) involves sorting out the green beans for roasting. Several additives are used during the roasting process, which gives it the aroma and enhances the product's quality, such as margarine, sugar, are introduced, thus giving it its dark brown colour. It is followed by grinding, drying, and packing for the market (Alemayehu et al., 2020). The machines and equipment used for the roasting and grinding of the coffee needed to be washed and dried every day after use. The process requires a large volume of water, consequently generating a large volume of coffee processing wastewater.

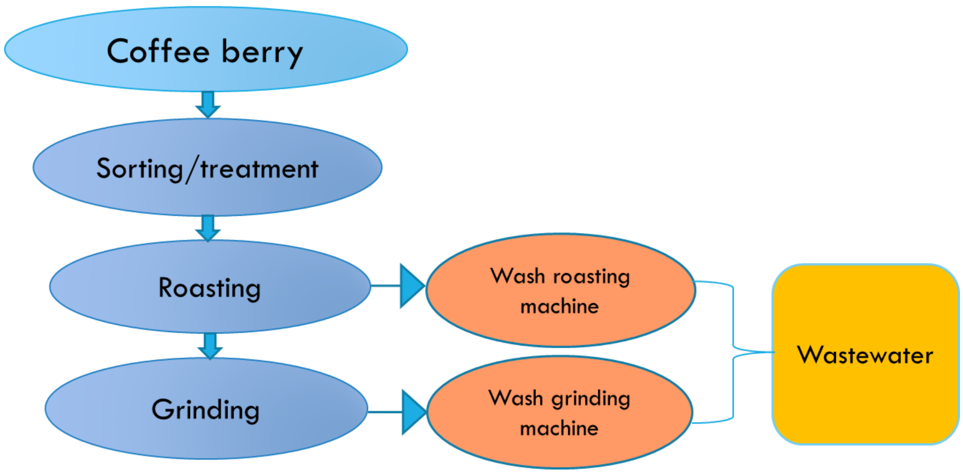

Figure 2.5: Schematic diagram of the second phase of coffee processing

2.6 Physicochemical Characteristics and Effects of Coffee Processing Wastewater

The physicochemical properties of coffee processing wastewater, as shown in Table 2.1, is characterized by a very high concentration of Chemical Oxygen Demand

(COD), Biological Oxygen Demand (BOD), acidity, odour, and colour, as has been highlighted in the literature (Chagas et al., 2015; Novita et al., 2019; Padmapriya et al., 2013; Woldesenbet et al., 2014).

Furthermore, the main environmental effect of organic pollution in water is the decrease or insufficiency of oxygen. The presence of toxic chemicals like tannins, phenolics, and alkaloids inhibits the biological degradation of organic materials in water bodies where the effluent has been discharged. Microbial processes beak down the organic substances released into water bodies slowly, using up the water's oxygen. As oxygen demand begins to exceed supply, a decrease in oxygen content gradually create an anaerobic condition (Rattan et al., 2015), this phenomenon results in an insufficient amount of oxygen needed to break down organic waste in an aqueous environment, and also insufficiency of required oxygen to combine with chemicals for other functions in the water body. The anaerobic conditions created in wastewater are responsible for the odour and are fatal to aquatic inhabitants. Bacterial that seep into potable water sources can also cause a direct health impact on humans (Kebede et al., 2010; Woldesenbet et al., 2014). Colour is a significant factor for aquatic life in the manufacture of food from sun rays. The photosynthetic activity decreases due to the dark-brown colour of CPW. Consequently, it will affect other parameters like temperature, and DO (Ahmad et al., 2015).

Table 2.1: Characteristics of Coffee Wastewater

Parameter	1^{st} stage	2^{nd} stage	Standard*	WHO
pH	3.92-4.99	3.5 - 4.2	5.5-9.0	6.8-8.5
Residual conductivity (µS/cm)	382-390	221- 354	-	$1X10^{-3}$
Temperature (^{0}C)	20-25	30.0 - 34.0	40	20
Colour (pt.co)	-	2512 - 5342	200	300
BOD_5 (mg/L)	10000-20000	1136 - 3200	50	100
COD (mg/L)	20000-50000	2309 - 7328	200	300
Total dissolve solids (mg/L)	4500	124.67-197.67	50	200
NH_3-N (mg/L)	168-212	125- 175	20	50

**Standard refers to standard B of Environmental quality regulation 2009 under the laws of Malaysia Environmental Quality Act (MEQA)1974*

2.7 Coffee Processing Wastewater Treatment

The most common and toxicologically threatening method of managing coffee processing wastewater (CPW) is direct discharge into the ambient environment. Other notable methods include collecting the raw CPW in a sump tank and treating it with alum or talc (Rattan et al., 2015). There are two treatment methods for coffee processing wastewater; the biological treatment method and the Physico-chemical treatment method.

2.7.1 Biological Treatment

The biological treatment technique uses natural material (unicellular or multicellular) for water and wastewater treatment (Sanabria et al., 2012). One of the objectives of biological treatment is to remove BOD and nutrients from wastewater. However, the method is not sufficient to remove colour or other organic components in the coffee wastewater. Besides, the processes require an extended period (e.g., a few months) to degrade organic materials. Biological treatment includes but is not restricted to aerobic/anaerobic treatment, membrane filtration, spray irrigation, activated sludge, immobilization, enzyme treatment, the use of bioreactors, and phytoremediation. This section gives an overview of the biological treatment methods that have been used to treat the CPW in recent years.

2.7.1.1. Phytoremediation

Phytoremediation is the direct and natural use of plants to absorb pollutants (organic and inorganic) through roots and eventually transmitted them to the plant's upper part (Rezania et al., 2016). The potential of phytoremediation for coffee processing wastewater (CPW) treatment have been well documented in the literature (Rauf et al., 2001). The efficiency of the technology on CPW is highly dependent on the growth rate of the target plant, its tolerant level to pollutants, and the species of plants. These have to be considered before the design of the system. According to Rezania et al (2016), more than one phytoremediation technique should be adopted for successful pollutant removal. Therefore, a two-stage plant system was studied in sequence to observe the treatment viability of CPW. Two plants (*Phragmites karka and Eichhornia crassipes*), each with a different medium was used. The result shows that 74% of Suspended Solids, 79% of colour, and 95% of COD concentration was successfully removed after seven days (Said et al., 2020).

2.7.1.2. Bioreactors

The use of various bioreactors for coffee processing wastewater treatment has been established in the literature (dos Santos et al., 2007; Selvamurugan et al., 2010; Selvamurugan et al., 2010). However, there have been many conflicting outcomes ranging from the difference between lab-scale experiments and the full-scale experiments to differences due to geographical location, the difference in concentration of CPW (Dinsdale et al., 1997). A study carried out in Mexico using a laboratory-scale Expanded Granular Scale Sludge Bed (EGSB) bioreactor with the optimum hydraulic retention time of the operation as 7-9 days removed 94-98% of COD concentration at a neutral pH from coffee processing wastewater (Cruz-Salomón et al., 2017). In another study, anaerobic reactors' performance filled with crush stones, polyurethane foam, and blast furnace cinders was assessed for COD removal in coffee processing wastewater. The reactor filled with foam performed better than the other two after 30-50 days due to its porosity; as a result, a better collection of biomass was noted within 26 hrs (Fia, Matos, Borges, Fia, & Cecon, 2012).

Other work looked at the energy generation potential of CPW while removing the COD concentration (Beyene et al., 2014; Chen et al., 2018; Chen et al., 2019). Results suggested that at optimum performance, 82.4% of COD was converted to methane at HRT of 10 days using an anaerobic membrane bioreactor in a thermophilic condition (Chen et al., 2019), on the other hand, with the HRT of 40-50 days, anaerobic digesters were used to treat CPW removing up to 90% of organic load and total solids generating considerable among of energy in the process (Beyene et al., 2014). Fundamentally, the more HRT, the higher the process's treatment efficiency (Asha & Kumar, 2016).

2.7.1.3. Expanded Granular Sludge Bed (EGSB) bioreactor;

Several anaerobic processes have been developed to treat CPW. The flow pattern, kinetics, toxicity inhibition, startup, optimization, and operation characteristics have been studied. The hydraulic retention time (HRT) is one of the most critical factors for controlling this kind of anaerobic bioreactor because it affects some aspects such as the hydrogen transfer, the anaerobic digestion processes and can produce the cell washing phenomenon (Cruz-Salomón et al., 2017).

It has been found that this type of bioreactor is an excellent system for treating high organic load wastewater, but it does not remove the nutrients (N and P). One of the limitations of the anaerobic degradation of coffee processing wastewater is its high content of fermentable organic matter. Organic matter compounds cause fast acidification of the wastewater that results in increased production of VFA (Chen et al., 2018; Lim & Aris, 2014; Qu, 2011).

2.7.1.4. Application of natural coagulant

Coagulation has been used over the years to remove impurities (majorly suspended particles). Although inorganic coagulants such as ferric chloride have proven effective, their drawbacks have prompted natural coagulants such as chitosan and plant-based coagulant to be improved by researchers. The significant advantages of natural coagulants include their cost-effectiveness, environmental friendliness, low sludge generation, non-toxic nature, and high biodegradability (Ang & Mohammad, 2020). Moringa seed is one of the prominent natural coagulants used in place of alum as a quick method of cleaning turbid and polluted water (Mahmood et al., 2010). Its efficiency as a suitable coagulant and anti-microbial species is due to its vast array of protein content (Kansal & Kumari, 2014). Furthermore, coagulant dosage is the primary independent factor in treatment (Saritha et al., 2019).

The performance of moringa seeds as natural coagulants for the treatment of CPW are well documented (Novita et al., 2019; Padmapriya et al., 2015). The major drawback is the time it takes to treat the pollutant, which is relatively long (Padmapriya et al., 2015). Recently this drawback was mitigated when the different particle size of moringa seed was studied in a jar test for the treatment of coffee wastewater, and 60 mesh was the most efficient resulting in the removal of above 60% of pollutants in few hours (Novita et al., 2019). In another study, Moringa seed doses varied from 0-4 g/L to assess its performance in removing COD, TSS, and total nitrogen in coffee processing wastewater (CPW). Results show excellent performance on the studied response. However, the method is not efficient in removing the dissolved organic content of CPW (Garde, Buchberger, Wendell, & Kupferle, 2017).

2.7.1.5 Biosorption

Adsorption by agricultural by-products has, in recent times, gained more attention than adsorption by activated carbon because the technology is economically and environmentally benign. Agricultural waste's capability as adsorbents was used to eliminate pollutants in industrial wastewater (Brinza et al., 2020; Corral-Bobadilla et al., 2020).

In the quest for removing the high concentration of the COD from coffee processing wastewater, Ramya et al (2015), utilized various agricultural waste, namely, banana stem powder (BSP), sorghum stem powder (SSP), and casuarina fruit powder (CFP) as low-cost adsorbent. With pH at a neutral level, the result shows that the adsorbents have a promising role in reducing COD with BSP up to 80%, SSP 92.7%, and CFP 99.2%.

2.7.2 Physicochemical Treatment

Physicochemical treatment methods for industrial wastewater have been preferred recently as compared to biological treatment because of its ability to break complex compounds in wastewater in a relatively short period (e.g., few hours) in a controlled environment; nascent treatment methods that have been studied and reported are highlighted in this section.

2.7.2.1. *Zero-Valent Iron (ZVI) Treatment*

Zero-valent iron (ZVI) particulates are non-toxic, abundant, and inexpensive materials. It has been used to remove organic and inorganic pollutants in different wastewater (Fu et al., 2014; Liu et al., 2013; Tomizawa et al., 2016). Its mechanism of pollution removal is reductive degradation, oxidative degradation, adsorption, and precipitation. Despite its successes, spent ZVI particulates are not easily regenerated, making the process not economically viable as materials need to be replaced after each treatment (Tomizawa et al., 2016).

2.7.2.2. *Photo Fenton method*

Recently, advanced oxidation processes (AOP) treatment of coffee effluent has been brought into the limelight, such as photo-catalysis with H_2O_2 and Fe^{2+}, with ZnO (P. Xu, Xu, & Zheng, 2019). This method uses the catalytic reaction between ferrous ions in solution and hydrogen peroxide producing hydroxyl (a species with high oxidation potential), the critical reagent in breaking down recalcitrant compound-related lignin (Hubbe et al., 2016). H_2O_2 of various doses was used to decolourize coffee effluent, and UV light enhanced the intensity. 93% of coffee effluent colour was removed in 250 min (Tokumura et al., 2008). In another study, a combined biological and chemical treatment using the anaerobic Up-flow Anaerobic Sludge Blanket (UASB) reactor and photo-Fenton to achieve 95% BOD removal at the optimal molar concentration of H_2O_2 as 2.5×10^{-1} Mol L^{-1} and that of F^{2+} 6.3×10^{-2} Mol L^{-1} (Kondo et al, 2010) . Although the Photo-Fenton reaction is very significant for decolourization, the additional supply of hydrogen peroxide consumed during the photo- Fenton process is needed, and the pH at around 3.0 after treatment is a disadvantage.

2.7.2.3 Ultraviolet Radiation (UV) Catalysis (with Ozone)

Ozonation has been advocated to be a better option as compared to photo Fenton being a more potent oxidant of many organic compounds (Satori & Kawase, 2014), even though a significant shortcoming of ozonation is its low mineralization, which is usually opposed by UV or hydrogen peroxide (Hubbe et al., 2016). Works of literature have established that UV alone is a less effective treatment method except combined with other AOP as shown in reducing large among organic compound loading, such as colour and turbidity (Takashina et al., 2018; Tokumura, Ohta, Znad, & Kawase, 2006).

2.7.2.4. *Electrooxidation*

When voltages and other factors in an electrode are optimized for in-situ generation, oxidizing and reactive species are called electro-oxidation (Hubbe et al., 2016). In this method, electrolysis produces different oxidative radicals (e.g., hydroxyl, chlorine) as organic compounds directly degrade on the electrode.

Studies on Electro-oxidation to treat coffee processing wastewater are well documented (Ibarra-Taquez et al., 2017). Another study by Cardenas (2009) compared a dimensionally stable anode composed of titanium with a ruthenium film, cobalt oxide, and iridium to reduce the level of pollutant after pretreatment with coagulation/chemical flocculation. After biological pretreatment, COD and colour removal showed that stealing anode effectively removed COD in the coffee wastewater (Bejankiwar et al., 2003).

2.7.2.5 *Coagulation and Flocculation (Electrochemical Coagulation)*

The settling down of solid particles in an effluent resulting from gravity can be enhanced by electrochemical coagulation. The electrochemical coagulation method efficiently removes colour, COD, and SS in coffee wastewater (Fu & Wang, 2011; Raghu & Ahmed Basha, 2007; Sahana et al., 2018). Chemical coagulation and flocculation are efficient, easy to handle, and cheap methods of coffee wastewater treatment. It does not require pre-treatment (Novita et al., 2012). The literature reviewed showed that although colour removal was effective, COD reduction was not as anticipated due to the organic matter's complex binding nature in coffee wastewater (Novita et al., 2012). Removal of suspended solids and oxygen demand occurs when high charged cation agents such as aluminium sulfate (coagulant is used to neutralize negatively charged wastewater solid, followed by high mass polyelectrolyte such as acrylamide (flocculants) (Hubbe, 2016).

The electrochemical method consists of two conductive metal plates (anode and cathode) connected to an external power source where oxidation corrodes the anode material, and the cathode is subjected to passivation (Sahana et al., 2018). Concerning other traditional methods of coffee processing wastewater treatment, electroplating has more advantages, including a high ability to remove contaminants that are generally difficult to remove, cost-effectiveness, environmental compatibility, energy efficiency, safety (Sahana et al., 2018; Mahesh 2006). Drawbacks have been seen in decreasing treatment efficacy through the cathode's passivation as the current flows through it. It also requires a higher rate of energy supply relatively. Furthermore, the presence of tannins is causing a short circuit in the coagulation and the flocculation process (Novita et al., 2012). Table 2.2 summarizes methods used in treating coffee