INVESTIGATION OF SURFACE TREATMENT AND DENSITY SEPARATION FOR SELECTIVE RECYCLING OF PLASTICS

Adilbek Baigabelov

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INVESTIGATION OF SURFACE TREATMENT AND DENSITY SEPARATION FOR SELECTIVE RECYCLING OF PLASTICS

by

Adilbek Baigabelov

A thesis submitted in partial fulfillment of the requirements for the degree of

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Abstract

Froth flotation has been a useful method for flotation separation of plastics. Teeter bed concentration may also be potentially employed to accomplish gravity-based separation of plastics from a mixture. This work investigates selective separation of six different types of plastics using a novel method by combining advanced gravity concentration and froth flotation techniques. Surface active reagents were used during flotation studies for modification of surface properties of certain plastics in order to enhance selectivity. Elutriation technology in a teeter bed separator was successfully employed to achieve gravity-based concentration of certain plastics. The novel flowsheet was shown to recover plastics of each individual type with reasonably high efficiency and selectivity.

Keywords: plastics separation, flotation, gravity separation, recycling
Dedication

I would like to dedicate this work to my family and thank them for filling my life with purpose.  
Ğylymnyń tamyry ashshy, jemisi tätti
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1. Introduction

Plastics have become an inherent part of modern people’s life. Start of large-scale plastics production can be identified as one of the main industrial achievements of the 20th century, which allowed cheaper and faster production of many materials and equipment, thus, greatly raising the standard of living. Mass production of plastics, however, brought certain problems and concerns with it, most important of which is plastic pollution that is considered to be one of the greatest ecological threats today and urgently requires immediate actions (Villarrubia-Gomez et al., 2018). Geyer et al. (2017) in their work outline 3 possible fates for plastic materials: recycling, which, however, usually just delays final disposal; incineration, which must be closely controlled and regulated to reduce negative effects on ecology and health from emissions; and disposal in the landfills. Since start of mass production of plastic in 1950s, approximately 8.3 billion tons of plastic have been produced, out of which only 9% has been recycled, 12% has been incinerated, and the remaining 79% still remains in the world in the form of plastic waste (Bullock, 2018). In 2015, approximately 55% of the total produced plastics was discarded to the landfills, 25.5% was incinerated and 19.5% was recycled, thereby showing a positive trend in increasing recycling rates (Ritchie & Roser, 2018). Plastics production grew dramatically from 1.5 million metric tons in 1950 to 348 million metric tons in 2017 (Garside, 2019) with the world’s total consumption of plastics having an average growth rate of 5-6% (Wang et al., 2015). According to Jambeck et al. (2015) as cited in Villarrubia et al. (2018), during 2010 an estimate of up to 12.7 million tons of “mismanaged land-based plastic waste entered the oceans”. In their study on Our World in Data, Ritchie and Roser (2018) report about the so-called Great Pacific Garbage Patch (GPGP), which has an estimate area of 1.6 million square km and is comprised of 1.8 trillion plastic pieces. Plastic particles released in the water possess danger to a number of
marine species and negatively affects health of people living along rivers and coastlines. Science for Environment Policy (2011) lists the following as the main dangers associated with plastic waste being present in the oceans: wildlife entanglement and ingestion of plastic, alteration of habitats and the transport of alien species and negative impact on health caused by chemical additives in the plastics, including bisphenol A, phthalates and flame retardants. In their work, Geyer et al. (2017) made a forecast that, by 2050, 34000 million metric tons of primary plastic waste will be generated, out of which 9000 million metric tons will have been recycled, 12000 million metric tons incinerated, and 12000 million metric tons discarded. Such concerning forecast highlights further accumulation of plastic waste in the environment at rates greatly exceeding rates at which this waste can naturally degrade. In order to improve current plastic pollution situation in the world and prevent it from worsen, a change in the way that plastic waste is treated must be made and better methods of plastic recycling must be found. Developing an efficient plastic separation technique can greatly contribute to a better plastic pollution state. Numerous research results show that separation of plastics by froth flotation can be efficiently used in the industry.

A number of comprehensive review papers on the subject separation of plastics by flotation have been published over the years including works by Shent et al. (1999); Fraunholcz (2004); Dodbiba and Tujita (2004); Wang et al. (2015) with the latest to date being a review by Wang et al. (2019). According to these review papers, flotation is the most promising method for plastic separation compared to other methods, such as automatic sorting, gravity separation and electrostatic separation, which all have a number of limitations (Shent et al., 1999) and surface treatment is the most efficient pretreatment method for selective flotation of plastics (Wang et al., 2019).
Numerous papers have been published describing the effects of various surface treatment reagents. Dodbiba et al. (2002) studied the use of polyvinyl alcohol (PVA) and dodecylamine acetate (DAA) in flotation of PET, PE and PP, managing to make PET’s surface hydrophilic, while PE and PP retained hydrophobic properties.

Wang et al. (2014) achieved separation of ABS from PC by flotation with ammonia pretreatment. ABS remained insensitive to ammonia treatment, while PC was successfully depressed. The paper also reported effect of changes in conditioning time, temperature, flotation time, frother concentration, and particle size.

According to Marques and Tenorio (2000), calcium lignin sulfonate can be used to successfully separate PVC from PET by depressing PET after a 60-minute conditioning time.

Le Guern et al. (1999) studied the effect of cations present in the tap water during the flotation tests using sodium and ammonium lignosulphonate for the separation of PVC from PET. An assumption was made that Ca cation serves as a “bridge” between the lignosulphonate and the plastics in the electrostatic interaction.

The research of Singh (1998) showed effective use of sodium lignin sulfonate and sorbitan monolaurate as a depressant for PVC and POM respectively.

Pongstabodee et al. (2008) combined three stages of sink-float method with further treatment with calcium lignosulfonate for a mixture of 6 different plastics, including HDPE, PP, PET, PVC, PS and ABS. In the first sink-float stage, the plastics were separated into 2 groups: low-density HDPE and PP and high-density PET, PVC, PS and ABS. Ethyl alcohol was then used to separate HDPE from PP and calcium chloride aqueous solution was used to separate a PVC-PET mixture from a PS-ABS mixture. Calcium lignosulfonate was then successfully used to separate PVC from PET by depressing PET and PS from ABS by depressing ABS.
Burat et al. (2009) studied separation of PET from PVC by treatment with alkaline NaOH solution for virgin plastics and with diethylene glycol dibenzoate and epoxidized linseed oil for post-consumer polymers. Addition of diethylene glycol dibenzoate and epoxidized linseed oil as plasticizers was aiming to reactivate the contaminated surface of the polymers. Olgac Kangal (2010) later published a work on separation of PET from HDPE acquired from used drinking water bottles using NaOH, Triton XL-100N and diethyl glycol dibenzoate treatment.

Shen, Forssberg and Pugh (2001) published a paper on selective flotation separation of seven different plastics including PS, ABS, PET, PVC, POM, PC and PMMA with the use of methylcellulose as wetting agent. Results showed that treatment with methylcellulose allows to divide given plastics into 3 groups: POM and PVC which are depressed at low dosage of methylcellulose; PET, PMMA and PC which are not fully depressed by methylcellulose; and ABS and PS which are not affected by addition of methylcellulose. The authors state that the depression effect is caused by adsorption of methylcellulose on plastics surface by means of van der Waals forces. The possibility of further separation of plastics within the acquired groups was not studied in this work.

A number of articles were published showing the effect of tannic acid as the wetting agent in flotation separation of plastics. Pita and Castilho (2017) studied the role of size, shape and density of plastics on the flotation kinetics along with tannic acid treatment. Six different types of plastics including PS, PMMA, and two different types of PVC and PET from different manufacturers were conditioned with tannic acid resulting in successful depression of all plastics with an exception for PS, which showed better floatability. Censori et al. (2016) performed a test on flotation separation of PS from ABS applying alkaline NaOH pretreatment combined with
further tannic acid treatment. Results showed depression of ABS with PS retaining its floatability.

Other methods, besides surface modification, have also been studied over the years. Gamma flotation is a method of adjusting the liquid-surface tension in such a manner that it falls in between the values of two plastics; thus allowing their separation (Shen et al., 2002). In their work, Shen et al. (2002) studied the floatability of seven different plastics: POM, PVC, PMMA, PET, PC, ABS and PS in the presence of different concentrations of surfactant 15-S-7. Results showed that PVC and POM are depressed at lower concentrations of the surfactant compared to PS and ABS with other plastics having intermediate floatability. However, gamma flotation’s lack of flexibility, due to the fact that proposed surfactants can not only reduce surface tension but also selectively adsorb onto plastics surface, is considered a significant limitation and new studies on gamma flotation have not been published recently (Wang et al., 2019).

Boiling treatment is another method proposed for flotation separation of plastics. It implies conditioning of plastics in boiling water for some time, followed by flotation testing. Mechanism of boiling treatment implies molecular rearrangement of plastics surface under elevated temperatures, making hydrophilic groups expose to water (Wang et al., 2014). In their work Wang et al. (2014) show significant drop in floatability of ABS after 60 minutes of boiling treatment, while PS kept its hydrophobic properties.

Flame treatment of plastics followed by flotation test was performed by Pascoe and O’Connell (2003). PET and PVC sheets were passed under the burner at a distance of 9 mm and then floated in the flotation cell. Flame treatment introduces hydrophilic oxygen-containing groups on the surface of plastics. Elevation of PVC temperature above its melting point allowed
to reintroduce hydrophobic groups on its surface, while PET remained hydrophilic. Flotation tests displayed depression of PET and flotation of PVC.

The application of surface treatment for selective flotation has certain applied issues associated with them. This will not be an issue for a binary mixture. However, for multicomponent systems, once treated with certain chemicals to suppress one from the rest, the surface-active reagent must be removed from the other plastics before further surface treatment can be employed. In view of this, it was decided to employ surface treatment at the end stages when binary mixtures are obtained from the starting mixture. Thus, this research is aimed at designing and developing a novel, affordable and easily implementable method for separation of six different plastics from a mixture by a combination of gravity separation and surface treatment. Such combination of methods has not been studied before thereby bringing an aspect of novelty to the research. It may be noted that gravity separation does not contaminate the original surface of the plastics.
2. Theoretical Perspective

2.1. Mechanism of Flotation

Froth flotation is a method of separation of materials based on their hydrophobicity. It has conventionally been used in the mineral processing industry as a method of separation of various minerals. Conventional flotation process requires a specifically designed flotation cell or column, a material crushed and ground to a fine size, frothing agent that contributes to the formation of froth, and certain reagents that depress or collect certain materials specifically. The flotation cell is filled with water, to which the material is introduced along with air, being pumped at constant speed through the impeller. Basic principle of froth flotation process can be found in an article by Michaud (2013) and is illustrated in Figure 1. Airflow creates air bubbles in the cell, which rise to the surface to form a layer of froth. Hydrophobic particles will tend to attach to the bubbles and be carried to the surface as a “concentrate,” whereas, hydrophilic particles will remain in the cell as “tailings.” Hydrophobicity is described in the Compendium of Chemical Terminology (McNaught & Wilkinson, 1997) as “tendency of hydrocarbons to form intermolecular aggregates in an aqueous medium, and analogous intramolecular interactions.” In hydrophobic-water interactions “apolar groups tend to cluster together in a polar liquid, like water, to minimize the surface between groups of different polarity” (Chandler, 2005). Hydrophobicity of the material can be characterized by the measure of contact angle of the said material. Common contact angle measurements are shown in Figure 2 for liquid droplets. Contact angle is measured as an angle between the surface of the material and the curvature of the drop of water contacting the surface of the material. High contact angle indicates poor wettability and high hydrophobicity of the material.
Figure 1. The froth flotation cell

Figure 2. Typical contact angle measurements of liquid droplets (KRÜSS GmbH, n.d.)
2.2. Mechanism of Crossflow Separation

Crossflow separation process was used in this work to separate plastics exploiting the difference in their densities. Crossflow separation is conventionally used in mineral processing industry for sizing and classification; density separation and concentration; and washing and neutralization of minerals (ERIEZ, n.d.). The main principle of separation in the Crossflow Separator is based on fluidization, hindered settling and elutriation (Hansen-Carlson & Das, 2019). General structure of the Crossflow Separator can be seen in Figure 3. Feed slurry or, in the case of this work, a feed mixture is introduced from the top of the separator in such a way that feed water does not cause any disturbance in the main teeter chamber; particles then settle against the rising teeter water that is introduced at a certain flowrate from the teeter tube generating an autogenous artificial heavy medium (Das & Sarkar, 2018). The denser and coarser particles penetrate the fluidized suspension and settle at the bottom, from where they are collected through the underflow valve, while the lighter and finer particles are carried with the teeter water flow upwards and overflow to the overflow outlet (Hansen-Carlson & Das, 2019).
A particle settling in a fluid experiences upward buoyancy and drag forces and a downward gravity force. This concept is illustrated in Figure 4.
The equation of motion for settling particle, according to Newton’s Second Law, appears as follows:

\[ m \frac{dV}{dt} = mg - m'g - D \]  \hspace{1cm} (1)

where, \( m \) is the mass of a particle, \( V \) is the particle velocity, \( t \) is time, \( g \) is acceleration of gravity, \( m' \) is the displaced fluid mass, and \( D \) is the drag force. The mass of the particle is given by the following equation:

\[ m = \frac{\pi}{6} d^3 \rho_s \]  \hspace{1cm} (2)

Where, \( d \) is the diameter of the particle and \( \rho_s \) is the density of the particle.

Whereas, displaced fluid mass is given by the following equation:

\[ m' = \frac{\pi}{6} d^3 \rho_f \]  \hspace{1cm} (3)

Where, \( \rho_f \) is the density of the fluid.

At terminal settling velocity, acceleration is equal to zero, therefore:

\[ \frac{dV}{dt} = 0 \]  \hspace{1cm} (4)

Considering that acceleration is equal to zero, drag force can be expressed as:

\[ D = mg - m'g \]  \hspace{1cm} (5)

By substitution of \( m \) and \( m' \) from the Equations (2) and (3), respectively, Equation (5) can be expressed as follows:

\[ D = \left(\frac{\pi}{6}\right) g d^3 (\rho_s - \rho_f) \]  \hspace{1cm} (6)

If it is assumed that the drag force is due to viscous resistance, which is the effect of surface friction between a particle and a liquid when the particle moves through the liquid, then Equation (6) can be expressed as following equation:
\[ D = 3\pi d\mu V_t \]  

(7)

Where, \( \mu \) is the fluid viscosity and \( V_t \) is the terminal settling velocity.

Equation (7) shows the expression of the drag force according to Stoke’s Law. However, Stoke’s Law is only applicable to ultra-fine particles settling in the fluid, for which creeping flow conditions are satisfied. The drag force in such cases is purely due to viscous resistance. In the case of this work, the size of the plastic particles settling in the Crossflow Separator is much larger (2.38 mm). Creeping flow conditions are not satisfied for the settling of such large particles. Therefore, the drag force acting on the plastic particles will no longer be governed by viscosity, but by the turbulent resistance. Accordingly, the drag force applicable for this investigation is given as follows:

\[ D = 0.055\pi d^2 V_t^2 \rho_f \]  

(8)

Expression of \( D \) in Equation (6) through equation (8) produces following:

\[ 0.055\pi d^2 V_t^2 \rho_f = \left(\frac{\pi}{6}\right)gd^3(\rho_s - \rho_f) \]  

(9)

Thus, the terminal settling velocity in Equation (9) can then be expressed as follows:

\[ V_t = \sqrt{\frac{3gd(\rho_s - \rho_f)}{\rho_f}} \]  

(10)

Equation (10) is commonly referred to as the Newtonian Drag Law equation.

### 2.3. Chemical Structure and Properties of Plastics

Four out of six plastics acquired for this research were identified as vinyl polymers, meaning that they have a similar structure, all based on the vinyl monomer (see Figure 5). PVC, PMMA, PS and PE can be considered vinyl polymers as they are structured by substitution of hydrogen atoms to a specific functional group in the vinyl monomer \( \text{CH}_2\text{-CH-} \) (Modern Plastics Magazine, 1994). The other two plastics PC and ABS have a more complex structure.
2.3.1. Poly Vinyl Chloride

Poly vinyl chloride (PVC) is a plastic that is most commonly referred to as “vinyl polymer” in industry. It is the third most widely produced plastic in the world after polyethylene and polypropylene (Allsopp & Vianello, 2000) representing 12% of the total produced plastics (Geyer et al., 2017). Main structural characteristic of PVC is a substitution of one hydrogen atom to a chlorine atom as shown in Figure 6 (a). PVC is considered to be the most versatile plastic due to its blending capability with plasticizers, stabilizers and other additives (Modern Plastics Magazine, 1994). PVC has the highest density out of the tested plastics of 1.4 g/cm³. PVC
microstructure can be mainly described as atactic stereochemistry, which implies that the orientation of the chloride centers is random, as shown in Figure 7. PVC has some degree of syndiotacticticity, meaning that the substituent chlorine atoms have alternate positions along the chain, giving PVC a few percent of crystallinity; however, the whole molecule is mostly amorphous (Clark, 2015). Industrially, PVC is mainly produced by suspension method (around 90%), which is a batch method where, vinyl chloride droplets are suspended in water by vigorous agitation, followed by heating the resin under vacuum to get rid of excessive monomers and running through the centrifuge to remove water (Modern Plastics Magazine, 1994). Produced PVC plastic is widely used in a variety of markets, primary being construction. PVC is used in pipes, sidings, wires, cables, bottles, food wraps, boxes and lids manufacturing.

![Chemical structure of atactic PVC](image)

**Figure 7. Chemical structure of atactic PVC (Clark, 2015)**

### 2.3.2. High Density Polyethylene

Polyethylene is the simplest vinyl polymer as it is composed of a series of basic vinyl monomers without any substituents as shown in Figure 6 (b). PE is the world’s most massively produced plastic with its total production is equal to 36% of the total production of all plastics (Geyer et al., 2017). PE is primarily used in the manufacturing of plastic bags, drinking bottles, geomembranes, etc. There is a variety of types of PE that differ in the number of monomers in the chain and structure of the chains, including Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), Very Low Density Polyethylene (VLDPE), High Density Polyethylene (HDPE) and High Molecular Weight-High-Density Polyethylene (HMW-HDPE). In this research, High Density Polyethylene (HDPE) was used. The main structural difference
between HDPE and LDPE is in the orientation of the monomers in the chain. HDPE is a linear polymer, meaning that monomers in its molecule are connected in a single linear chain, whereas the chain in the LDPE molecule branches out at various location within the molecule reducing the material’s crystallinity and lowering its density. Difference in chemical structure of HDPE and LDPE can be seen in Figure 8. HDPE possesses a number of characteristics that make it a valuable material in manufacturing, such as high resistance to most household and industrial chemicals, resistance to moisture, impact resistance and good electrical properties (Modern Plastics Magazine, 1994). HDPE is most commonly produced by a slurry process or gas phase process. HDPE is one of the most recyclable plastics as it can be reprocessed without major degradation of properties. It is typically made today by mixing of 25% recycled material with virgin HDPE for use in non-food contact containers (Modern Plastics Magazine, 1994).

![Figure 8. Comparison of chemical structure of HDPE and LDPE (ScienceStruck, n.d.)](image)

### 2.3.3. Polystyrene

PS is another amorphous atactic vinyl polymer, which is formed by substitution of one hydrogen atom to a phenyl group as illustrated in Figure 6 (c). Phenyl group is a derivative of benzene with a general formula C₆H₅ and is thus a cyclic group of six carbon atoms. In this “circle,” every other carbon atom is connected to the next by a double bond; however, each
carbon atom has one hydrogen atom attached by a single bond. Polystyrene material is available in different forms, depending on the properties of the plastic: general purpose PS, impact PS and expandable PS. For this work a general-purpose PS was used, which is generally comprised of 2000-3000 styrene units (Modern Plastics Magazine, 1994). Production of PS represents less than 10% of total production of plastics (Geyer et al., 2017). PS is used in a variety of applications including packaging (containers, lids and bottles), disposable medical ware, toys, tumblers, cutlery, tape reels, storm windows, consumer electronics, egg cartons, meat and poultry packaging trays, labels for bottles, and expanded PS cushioning materials (Modern Plastics Magazine, 1994). PS is manufactured by continuous mass-process, which includes passing of styrene through a reaction train until optimal conversion is reached, followed by stripping of the unreacted components and pelletizing.

2.3.4. Poly Methyl Methacrylate

PMMA is a type of acrylic plastic made by free radical vinyl polymerization of methyl methacrylate initiated by a peroxide or azo catalyst. PMMA can be produced by bulk, suspension, emulsion and solution processes (Modern Plastics Magazine, 1994). The general structure of PMMA is shown in Figure 6 (d). It is commonly referred to as “acrylic glass.” PMMA is most commonly used to produce windows, automobile taillights, signs, safety glazing, aircraft canopies, side markers, light pipes, pillar posts, instrument covers, and nameplates due to its weatherability, chemical resistance, toughness and light transmission properties (Modern Plastics Magazine, 1994).

2.3.5. Polycarbonate

PC is an amorphous thermoplastic, which contains carbonate group (-O-(C=O)-O-), and is produced by the reaction of bisphenol A with carbonyl chloride (COCl₂) under basic
conditions in the presence of an aqueous or organic phase (Modern Plastics Magazine, 1994). The general structure of PC can be seen in Figure 6 (e). PC found its use in manufacturing of bottles, electronic components, glazing, sound walls, compact discs, DVDs, Blu-ray discs, bumpers, body panels, wheel covers, traffic light housings, signal lenses, windows, safety glasses, tableware, and food storage containers due to its exceptional toughness, clarity, dimensional stability, ignition resistance and electrical properties. One major limitation of PC is a limited, long-term hydrolytic stability at elevated temperatures (Modern Plastics Magazine, 1994). A few particular negative ecological impacts associated with the disposal of PC have been identified. Bisphenol A can be leached from PC waste at elevated temperatures between 70 and 80°C and high humidity or even at environmental temperature and normal pH as the material grows older. Bisphenol A is considered to be potentially hazardous material as a known endocrine disruptor that is not decomposable under anaerobic conditions in the landfills (Morin et al., 2015). Thermal degradation of PC can also lead to release of hazardous pollutants into the environment, most dangerous of which are phenol derivatives and bisphenol A. Phenol derivatives are identified as volatile organic compounds that contribute to ground-level ozone formation and formation of photo-chemical smog and can also accumulate in aquatic organisms (Scottish Environment Protection Agency, n.d.).

2.3.6. Acrylonitrile Butadiene Styrene

ABS is a non-vinyl engineering thermoplastic, which is composed of three monomers: acrylonitrile, butadiene and styrene as shown in Figure 6 (f). It is produced by emulsion, continuous mass or suspension process. Each monomer component of ABS provides particular properties for plastic: acrylonitrile provides chemical resistance and heat stability, butadiene provides toughness and impact strength, and styrene increases materials rigidity and
processability (Modern Plastics Magazine, 1994). ABS found its application in transportation industry for the manufacturing of various interior automobile components, such as knobs, light bezels, instrument panels, etc. It is also used to produce a variety of kitchen appliances, power tools, vacuum sweepers, sewing machines, medical devices, furniture, cosmetics packaging, shower stalls and hair dryers. Lego bricks are typically made from ABS (May, 2009). Recently, ultrafine ABS has begun being used in 3D printing industry as a filament (3D Printing Industry, n.d.). It has been identified that, at higher temperatures of above 400 °C, ABS tends to decompose into its constituents: butadiene, acrylonitrile and styrene, out of which butadiene is proven to be carcinogenic to humans and acrylonitrile is a suspected carcinogenic (Unwin et al., 2013).

2.4. Chemical Structure and Properties of Reagents

2.4.1. Tannic Acid

A solution of 10% w/v tannic acid was used in this project as a depressant to alter the surface of particular plastics to hydrophilic due to its strong oxidizing properties. Tannic acid was chosen due to its availability, inexpensiveness and low toxicity if handled properly. Tannic acid is a polyphenol derivative of tannin and, is considered to be a weak acid with an acid dissociation constant of around 6. Tannic acid’s chemical structure can be seen in Figure 9. It is a large molecule, comprised of a large number of phenol groups. The general chemical formula of tannic acid can be written as $C_{76}H_{52}O_{46}$, but its composition tends to vary greatly. Tannic acid is conventionally produced from nutgalls formed on the twigs of some particular species of oak trees, such as Quercus infectoria Olivier and other related species. Other sources of tannic acid include seedpods of Tara in South America and nutgalls from certain Rhus species growing in China (Khan & Abourashed, 2009). Commercial tannic acid is composed of glycosides of
phenolic acid, a molecule in which sugar is attached to some of the acid functional group by a glycosidic covalent bond (Khan & Abourashed, 2009). Tannic acid is used in medical, pharmaceutical and cosmetic products; in food industry for clarification of alcoholic beverages and as a flavor ingredient; in traditional Chinese medicine; and in tanning hides as well as the manufacture of inks (Khan & Abourashed, 2009).

![General structure of tannic acid](image)

**Figure 9. General structure of tannic acid**

**2.4.2. Mechanism of Adsorption of Tannic Acid on the Plastics Surface**

Stuckrad (1997) studied the reaction of wetting agent/plastic interaction and concluded that there are four possible mechanisms: (a) mainly physical interaction represented by van der Waals forces and hydrogen bonds, formed between the plastic and the reagent due to the presence of non-polar carbon hydrogen in the lateral groups of the polymer chains of the plastics; (b) dipole-dipole van der Waals interaction and Lewis acid-base interactions between the polar lateral groups containing oxygen, nitrogen, chlorine and other atoms in plastics and the dipoles of wetting agent molecules; (c) chemical bonds between the plastics and the wetting agents, which, however, are unlikely to form due to chemical inertness and low surface energy of
plastics; and (d) electrostatic interactions, which are also rare because of the absence of the required amount of free charge carriers. Fraunholcz and Dalmijn (2007) contributed to the study of adsorption mechanisms and concluded that physisorption is the primary mechanism of adsorption of wetting agents onto plastics surface. They also suggested that hydrogen bonding might play a role in the adsorption mechanism; but, it requires certain specific orientation of hydrogen-acceptor and hydrogen-donor.

### 2.4.3. Potassium Permanganate

Potassium permanganate (KMnO₄) crystals were used in this work as an oxidizer to selectively depress certain particles in the mixture. Chemical structure of potassium permanganate is shown in Figure 10. Potassium permanganate molecule is comprised of a permanganate ion and a potassium ion. It is commonly characterized as a very strong oxidizer. Potassium permanganate possesses such strong oxidizing properties due to the highest oxidation state (+7) of manganese in it, hence the permanganate ion is charged negatively.

![Chemical structure of potassium permanganate](image)

**Figure 10. Chemical structure of potassium permanganate**

### 2.5. Spectroscopy

#### 2.5.1. Raman Spectroscopy

Raman spectroscopy was used in this work for identification of plastics and tracking of changes in the structure of plastics associated with surface treatment. Raman spectroscopy is a method of spectroscopy that employs natural ability of various materials to absorb and scatter monochromatic light. This method is “able to reveal the molecular composition of a sample at the micrometer scale in a nondestructive way” (Vandenabeele, 2010). Raman dispersion changes
the wavelength of incident light due to interaction of a photon with a vibrating quants of a dispersion molecule (Vasiliev, 2018). Each atom in the analyzed molecule produces a characteristic peak of a certain position and intensity, which can be identified using the database (Do Nascimento, 2018). Raman spectroscopy has a different origin and produces different spectra than the infrared (IR) spectroscopy because it is sensitive to symmetric vibrations and infrared is sensitive to asymmetric vibrations.

### 2.5.2. Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy (FTIR) is a method of spectroscopy “based on the vibrations of atoms in a molecule or in a mineral” (Bergaya & Lagaly, 2013). FTIR was used in this work complementary with Raman spectroscopy for identification of plastics and reagents used. FTIR analyzes the amount of light that the material absorbs at certain wavelengths. Factors that influence the absorption rate include overall symmetry of the unit cell and the symmetry of each individual atom within the cell (Bergaya & Lagaly, 2013). Both FTIR and Raman can be used simultaneously to complement each other. However, each method differs from the other in fundamental ways and these differences are listed in Table I.

| Table I: Differences between Raman spectroscopy and FTIR (Exline, 2013) |
|-----------------|-----------------|
| **Raman**       | **FTIR**        |
| Depends on a change in a polarizability of a molecule. | Depends on a change in the dipole moment. |
| Measures relative frequencies at which a sample scatters radiation. | Measures absolute frequencies at which a sample absorbs radiation. |
| Sensitive to hetero-nuclear functional group vibrations and polar bonds, especially OH stretching in water. | Sensitive to homo-nuclear molecular bonds. |
| Requires little to no sample preparation. | Has constraints on sample thickness, uniformity and dilution to avoid saturation. |
| May be affected by fluorescence. | Not affected by fluorescence. |

Raman and FTIR spectroscopy were used in this work to identify the adsorbed surfactant layer on the plastic surface by tracking the changes in the peaks comparing the treated surface
spectra with original spectra. These changes can provide information on the mechanism of changing the hydrophobic properties of the plastics.

2.6. Image Analysis

An online image color summarizer software developed by Martin Krzywinski from Genome Sciences Centre (2019) was used in this work to analyze the test results and determine the amount of particular types of plastics present in the sample. The idea behind the use of the color summarizer was to count the percentage of pixels of a certain color (pixel value), thereby allowing the mass-percentage of each plastic to be determined. The software reports the average, media, minimum and maximum of each component of various color models HSV, RGB, LCH and Lab (Krzywinski, 2019).
3. Strategy Formulation

This research focuses on multi-stage separation process of a mixture of six different plastics, namely PVC, PMMA, PC, PS, ABS and PE, by combining gravity separation methods with flotation separation by surface treatment. It aims to develop an inexpensive, easily implementable, environmentally friendly process for separation of plastics that is scalable to the industrial volumes. Tannic acid and potassium permanganate (KMnO₄) used in this work as wetting agents are proven to be non-toxic and cheap materials that do not possess any significant potential harm to environment and can be disposed safely. The research does not employ any sophisticated or expensive equipment to run a successful separation and is simply based on the strategy to develop a simple and efficient processing scheme for the separation of the plastic mixture and employ surface treatment towards the end of the process steps as needed. The proposed process can be installed directly at recycling plants without any significant difficulties. Additional costs associated with heating reagents or flotation cell are also eliminated by performing tests at room temperature. A mixture of six chosen plastics covers a significant majority of the plastics that are produced in the manufacturing industry and that are present in various plastic waste groups. Successful separation of each type of plastic from the mixture allows further recycling of each plastic type according to its characteristics.

Initially, the project was aiming to employ only surface treatment as the main mechanism for separation of the plastics. A scoping test was conducted with the PMMA particles in the absence of any surfactants to identify the optimal particle size for the tests. Scoping tests were followed by individual flotation tests for each plastic with and without the surface modifiers. Flotation kinetics obtained during the individual tests were used as the reference and compared with the results of further tests. Some degree of success was achieved with certain surface
modifying reagents, such as tannic acid and potassium permanganate. However, the results of further scoping tests using other reagents including Polyvinyl Alcohol (PVA) and sodium ligninsulfonate and initial attempts in the separation of binary mixtures of some plastics at lower concentration of tannic acid were found to be unsuccessful. Also, while trying to reuse the plastics, it was observed that removal of the surface layer of reagent was not simple and fast. In many instances, after prolonged removal of this layer, the plastic did not behave as the virgin plastic in flotation. Therefore, at this point, a revision of the overall strategy for separation of individual plastics from the plastic mixture was contemplated. Other properties of the plastics, that can be exploited to separate each plastic from the mixture, were looked at.

Notable differences in the densities of the plastics were identified and taken as a cornerstone for designing the flowsheet. Process development at this point began to aim to combine surface treatment with gravity separation to achieve successful separation of plastics. Flowsheet was designed in such way that the lightest HDPE was separated from the other plastics by a simple sink-flow process as HDPE, having a density of 0.98 g/cm³, would naturally float in water and other plastics with densities higher than water would sink. The heaviest of the plastics was targeted next. In the next stage PVC, having a density of 1.4 g/cm³, was separated from the mixture in the first round of the gravity separation test using the Crossflow Separator operating at a higher teeter water flow rate. The remaining mixture of four plastics was then separated into two groups of two plastics each at a lower teeter water flow rate in the Crossflow Separator. The first group was collected from the overflow of the Crossflow Separator and consisted of lighter PS and ABS that had similar densities of approximately 1.05 g/cm³. The second group included PC and PMMA, both having a density of 1.2 g/cm³ and was collected from the underflow of the Crossflow Separator. Each group then worked as a simple binary
mixture making it easier to separate the plastics within it by surface treatment without having to worry about removal of surface layer of reagent. Tannic acid and potassium permanganate were chosen based on the successful plastics separation results during the scoping tests in this work as well as some references found in literature (Wang et al., 2017; Pita and Castilho, 2017).

Another area of concern was quantification of the mass yield and recovery data. In view of this, the chosen colors of the plastics were all different, while each sheet had the same thickness. Due to a large number of particles in the resulting mixtures for each test (gravity separation and flotation), manual picking and calculation of a weight fraction of each plastic was out of question and an easier way needed to be found. Initially, grain analyzing software and other programs were tried out, but had to be abandoned as the results were unsatisfactory due to software’s operational inability to calculate the number of different color clusters. At this point the Image Color Summarizer software (Krzywinski, 2019) calculating the number of pixels of certain colors was used successfully. The differences in the color of the plastics were thus exploited successfully to achieve the objective.
4. Methodology

4.1. Materials and Equipment

Six types of plastics including PVC, ABS, PC, HDPE, PS and PMMA were purchased from TAP Plastics in the form of sheets of the following dimensions: 3 mm thick, 304.8 mm wide and 304.8 mm long. Each plastic had its own unique color for easy identification of product mixtures following each test. Colors of the plastics are presented in the Table II below.

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>Grey</td>
</tr>
<tr>
<td>PMMA</td>
<td>Red</td>
</tr>
<tr>
<td>PC</td>
<td>Clear (transparent)</td>
</tr>
<tr>
<td>PS</td>
<td>White (opaque)</td>
</tr>
<tr>
<td>ABS</td>
<td>Black</td>
</tr>
<tr>
<td>HDPE</td>
<td>Light grey</td>
</tr>
</tbody>
</table>

Densities of each plastic were obtained from the manufacturer and are presented in Table III. The density values supplied by the manufacturer were also verified using pycnometry. Pycnometry uses Archimedes’ Principle to estimate the density of an object. It can be seen in Table III, that the densities of all plastics, except for HDPE, are greater than the density of water.

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>1.40</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.20</td>
</tr>
<tr>
<td>PC</td>
<td>1.20</td>
</tr>
<tr>
<td>PS</td>
<td>1.05</td>
</tr>
<tr>
<td>ABS</td>
<td>1.06</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Chemicals including 10% aqueous solution of tannic acid, 87-89% hydrolyzed polyvinyl alcohol and sodium ligninsulfonate were purchased from Fisher Scientific. Potassium permanganate crystals were obtained from the Montana Tech chemical storage. Methyl isobutyl carbinol (MIBC) was used as a frother in the flotation experiments, which was also obtained from the Montana Tech chemical storage.
Hosokawa Polymer Systems plastic shredder (model number SS67) was used for size reduction of plastic particles, and it is shown in Figure 11 (a).

A Wemco laboratory flotation cell with 2.1 L capacity was used for flotation tests as shown in Figure 11 (b). A laboratory scale Crossflow Separator was used for gravity separation and is presented in Figure 11 (c).

Renishaw inVia Raman Microscope system was used for spectroscopy analysis. Rame-Hart contact angle goniometer, which is shown in Figure 12, and Rame-Hart DROPimage Software were used for contact angle measurements.
4.2. Procedure

The work started with the preparation of material for the experimentation. All six plastic sheets were cut with a metal shear into smaller pieces for easier feeding to the plastic shredder, which was then used to shred the plastics into finer sizes. The final desired size of -8 mesh (2.38 mm) fractions was obtained by screening. Each plastic was shredded separately in order to avoid cross contamination.

4.2.1. First Scoping Test

Essentially the appropriate particle size for flotation was identified through this test. At the beginning of the work a scoping test was designed and conducted, which served the purpose of determining the appropriate test conditions and particle size for future tests. PMMA particles were chosen as the material in this test due to its distinct red color and the fact that naturally brittle PMMA is shredded more readily in the shredder compared to other plastics. Plastic particles adding up to the total mass of 78 g were shredded and fed into the flotation cell. The
test conditions were the following: 1900 ml of water and 0.5 ml of MIBC (frother) with 3 minutes conditioning time. The test was conducted for a total of 30 minutes, which was divided into small time fractions for collecting cumulative samples. Floated particles for each time fraction were dried and weighed separately to obtain flotation kinetics data. After weighing was complete, all samples were combined and passed through a stack of sieves in the Ro-Tap RX-29 Test Sieve Shaker for size distribution analysis. The stack of sieves consisted of following screens: Tyler Mesh numbers 3, 4, 6, 8, 14, 24, 50 and 100. Results of this test and the decisions made based on them are presented and discussed in the Results and Discussion chapter.

4.2.2. Second Scoping Test

The second scoping test was conducted in order to identify an appropriate frother, its dosage and the effect of changing test conditions. This test used reground PMMA particles from the previous scoping test. The total of 76.4 g of material was fed into the flotation cell and conditioned with 1 ml of glycol-based frother for 3 minutes. Water volume in the cell was changed compared to previous scoping test from 1900 ml to 2100 ml. Rotor agitation rate was also changed from 900 rpm to 1300 rpm. The duration of the test was 30 minutes, which was divided into small time fractions to obtain a clear understanding of the overall process. Results of the test and observations are presented and discussed in the Results and Discussion chapter.

4.2.3. Natural Floatability Tests

For the next set of tests all plastics were shredded and floated in the flotation cell without the addition of any surfactants in order to obtain natural flotation kinetics of each plastic type. Considering the fact that all plastics are naturally hydrophobic, they were expected to float readily. This was actually observed during experimentation. However, it was also observed that kinetics and final extent of flotation for different plastics were different. These tests were
conducted separately for each plastic and employed 60 g of material, 1900 ml of water in the cell, 900 rpm of rotor agitation, and 0.5 ml of MIBC for each test. Plastic particles were conditioned with frother (MIBC) for 5 minutes in the flotation cell prior to the start of the test. Each test was performed for 30 minutes maximum and the total flotation time was divided into small time fractions in order to obtain a complete overview of the flotation kinetics. Results of these tests are shown and discussed in the Results and Discussion chapter as well.

4.2.4. Initial Tests for Surface Treatment with Tannic Acid

Tannic acid was initially chosen as a surfactant for rendering the surfaces of plastics hydrophilic and suppress their floatability. Tests were performed separately for each type of plastic under the following conditions: 1900 ml of water in the cell, 900 rpm of rotor agitation, 0.5 ml of MIBC, and $3.0 \times 10^{-4}$ mol/l of 10% w/v aqueous solution of tannic acid. Plastic particles in the amount of 60 g were added in the cell and conditioned with tannic acid for 5 minutes first and then with MIBC for additional 3 minutes. Each test was performed for a total of 30 minutes, which was divided into smaller time fractions for better comparability with the non-treated plastics tests results. Relatively high concentration of tannic acid was chosen for these tests in order to show the hydrophilicity inducing properties of this reagent. Kinetic data for these tests are also presented and discussed in the Results and Discussion chapter.

4.2.5. Surface Treatment with PVA and Sodium Ligninsulfonate

PVA and sodium ligninsulfonate were attempted to be used as surface modifiers as well in order to selectively render the surfaces of certain plastics hydrophilic. However, test results were considered unsatisfactory and a decision was made to focus on tannic acid treatment. Main disadvantages of PVA and sodium ligninsulfonate included a chemical reaction between PVA and some plastic particles resulting in the damaging of the particles surfaces. Also, the
conditioning time required with sodium ligninsulfonate was too long (1 hour) compared to tannic acid. Therefore, further studies with these surfactants were discontinued.

4.2.6. Studies with Lower Concentration of Tannic Acid

Next experimental campaign was undertaken in studying the flotation behavior at lower concentration of tannic acid for more selective depression of plastic particles. A separate test was conducted for each plastic type under the same conditions as in previous tests with tannic acid. However, two exceptions were made: (1) the dosage of tannic acid was lowered from $3.0 \times 10^{-4}$ mol/l to $6.0 \times 10^{-5}$ mol/l, and (2) the total test duration was shortened to more realistic 15 minutes. Results showed that the plastic surfaces are highly susceptible to tannic acid concentration and significant selectivity in their flotation can be obtained by differential adsorption of tannic acid on these surfaces at lower concentration of tannic acid. Kinetic data for these tests are also presented and discussed in the Results and Discussion chapter.

4.2.7. Gravity Separation Using Crossflow Separator

A mixture of PVC, PMMA, PC, PS and ABS of a total mass of 50 g consisting of 10 g of each plastic was prepared and fed in the Crossflow Separator from the feeding chamber by continuously stirring and washing out the particles from the chamber using a small flow rate of water. The Crossflow Separator was fed with a regulated flow of water from the regular tap water outlet through a flowmeter as shown in Figure 13. Additional water flow was provided from the submersible pump that was pumping water from a separate reservoir as shown in Figure 14. Additional water flow was required to provide higher overall teeter water flow into the separator. Water from the reservoir was recirculating back through the overflow outlet in the separator. A fine mesh screen was placed on top of the reservoir to catch plastic particles travelling with the overflow water. The pump was powered by a portable power generator, which
is shown in Figure 14 and the flow rate could be adjusted by changing the power setting of the generator. Teeter water flow from the tap water outlet to the separator was controlled by adjusting the valve of the flowmeter at the bottom of the separator, which can be seen in Figure 13. The separation test was conducted in two stages. The first stage was performed at higher water flowrate of 4320 l/h, out of which 200 l/h were coming from the tap water outlet and the remaining 4120 l/h were generated by the pump. The first stage was aimed at separating the heaviest plastic, PVC, from the rest. Particles of PVC were obtained in the underflow and a mixture of PS, ABS, PMMA and PC in the overflow. The mixture of the four plastics in the overflow constituted the feed for the second stage. In the second stage the total water flowrate was reduced to 2755 l/h, out of which 78 l/h were coming from the tap water outlet and the rest 2677 l/h were generated by the pump. This stage was performed in order to separate the mixture of these four plastics into two groups of two plastics each. The heavier PMMA and PC settled in the underflow and the lighter PS and ABS reported to the overflow. In both stages, the principle of elutriation was exploited to effect the separation. The volumetric flow rates used in each stage were estimated from terminal velocity considerations as explained in the Results and Discussion chapter. The separation details are presented in the Results and Discussion chapter along with the quantitative results of these tests.
Figure 13. Water connections in the Crossflow Separator
Figure 14. Gravity separation test setup
4.2.8. Surface Treatment with Tannic Acid for Separation of PS and ABS

The binary mixture consisting of PS and ABS particles was obtained during the second stage of gravity separation in the overflow discharge of the Crossflow Separator. Plastic particles in this product were combined in the flotation cell and conditioned for 5 minutes with $4.6 \times 10^{-5}$ mol/l of 10% aqueous solution of tannic acid. After conditioning with tannic acid was complete, 0.5 ml of MIBC (frother) was added to the cell and conditioned for 3 more minutes. The volume of water in the cell was 1900 ml and the rotor agitation level was set at 900 rpm. The test was carried out for 10 minutes. Due to differential adsorption of tannic acid, the PS floated and the ABS remained in the pulp as tailings. Products of the flotation test were dried and run through the image analysis software for quantification. The quantitative results are presented and discussed in the Results and Discussion chapter.

4.2.9. Surface Treatment with Potassium Permanganate for Separation of PMMA and PC

The plastics mixture obtained at the underflow discharge of the Crossflow Separator in the second stage consisted of PMMA and PC particles. The flotation test employed potassium permanganate as a surface modifier to separate PMMA and PC in the mixture. These plastic particles were mixed in the flotation cell filled with 1900 ml of water. About 0.05 g of potassium permanganate crystals were dropped into the cell and the plastics were conditioned for 10 minutes. Once conditioning with potassium permanganate was completed, the plastics were conditioned for 3 more minutes with MIBC (frother) in the cell. The test was performed at 900 rpm rotor agitation and was carried out for 10 minutes. Due to differential oxidation of surfaces by potassium permanganate, PC particles floated, while PMMA particles remained in the pulp as tailings. Products of the test were dried and run through the image analysis software. The quantitative data are also presented and discussed in the Results and Discussion chapter.
### 4.2.10. Contact Angle Measurements

Contact angle measurements were performed for each plastic before any surface modifying treatment. Contact angles of ABS, PS, PMMA and PC were measured after surface treatment to study changes in contact angle values caused by surface modification. Rectangular pieces of 100mm x 100mm were cut from the sheet of each plastic for this test. The sample was placed on a special panel, which is located between the high-resolution digital Rame-Hart camera and the source of light with adjustable magnitude. A drop of water was then placed on the surface of a sample with a pipette. The live image from the camera was then adjusted to reach the desired contrast between the surface of a sample and boundaries of a water drop. DROPimage software was then used to calculate the angle between the sample surface and the surface of a water drop. Contact angles were measured 10 times for each plastic and the average value was calculated for each plastic type. Results of the contact angle measurements are presented and discussed in Results and Discussion chapter.

### 4.2.11. Image Analysis and Quantification

All products from the crossflow separation and flotation tests were subjected to solid-liquid separation using a fine mesh screen. Plastic particles were then left to naturally dry overnight prior to any image analysis tests. Natural drying was preferred over faster drying in the oven due to the fact that higher temperatures in the oven may damage the surfaces of the plastics or further oxidize it, leading to discoloration. Dried plastic particles were spread on a green plastic sheet in order to provide a uniformly colored background that will be contrasting with the plastic particles, thus making it suitable for image analysis. Plastic particles on the green plastic sheet were then photographed using the iPhone X high-resolution digital camera. Obtained photographs were then run through the photo editor software (PIXLR, n.d.). Editing was
performed in order to increase the contrast and create distinct differences between the variously colored plastics and the background in the picture, thus making it suitable to analyze the picture with the color summarizer software (Krzywinski, 2019). Figure 15 demonstrates the contrast between the edited image and the original. Color summarizer used the following presets: html. output format, color clusters statistics, 5 color clusters, space delimiter and very high precision (200 pixels). Quantitative data obtained through image analysis are presented and discussed in the Results and Discussion chapter.

![Figure 15. Example of the image before and after editing](image-url)
5. Results and Discussion

5.1. Contact Angle Measurements

5.1.1. Contact Angle Measurements of Untreated Plastics Surfaces

As can be seen in Table IV, all relevant plastic types show relatively strong hydrophobic properties as indicated by the large contact angles. Contact angle measurements were taken 10 times in 3 separate tests for each plastic. Based on these results the standard deviation was calculated for each plastic and is shown in Table IV. Based on the contact angle measurement results, plastics used in this work can be placed in following order from least to most hydrophobic: PC→ABS→PS→PVC→PMMA→HDPE. Hydrophobicity of plastics depends on a number of variables, such as crystallinity of a plastic, electrochemical properties, chemical composition, degree of polymerization, surface structure, etc. These properties can be somewhat affected during prerequisite steps, such as washing, crushing and surface treatment (Wang et al., 2015).

<table>
<thead>
<tr>
<th>Plastic Type</th>
<th>Contact Angle (°)</th>
<th>Standard deviation (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>78.35</td>
<td>±1.28</td>
</tr>
<tr>
<td>ABS</td>
<td>80.15</td>
<td>±1.29</td>
</tr>
<tr>
<td>PS</td>
<td>81.01</td>
<td>±1.14</td>
</tr>
<tr>
<td>PVC</td>
<td>88.18</td>
<td>±1.20</td>
</tr>
<tr>
<td>PMMA</td>
<td>90.57</td>
<td>±1.41</td>
</tr>
<tr>
<td>HDPE</td>
<td>91.03</td>
<td>±1.72</td>
</tr>
</tbody>
</table>

5.1.2. Contact Angle Measurements after Surface Treatment

Table V demonstrates the changes in contact angle for four plastics that were actually used in flotation tests with surface treatment. PS and ABS were conditioned with tannic acid and PMMA and PC were conditioned with potassium permanganate. As can be seen in Table V, contact angle value for PS is practically unaffected by tannic acid treatment; whereas, contact angle reading for ABS drops significantly from 80.15° to 58.71° leading to its low floatability
(low hydrophobicity). PMMA treated with potassium permanganate becomes more hydrophilic, as the contact angle value of PMMA decreases from $90.57^\circ$ to $64.77^\circ$, while PC remains relatively hydrophobic and its contact angle value does not change much. These results prove that, under the conditions employed in the flotation experiments, tannic acid and potassium permanganate selectively adsorb on the surface of one plastic, primarily avoiding the other, thus, making the separation possible.

<table>
<thead>
<tr>
<th>Plastic Type</th>
<th>Contact Angle Before Treatment (*)</th>
<th>Contact Angle After Treatment (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>81.01</td>
<td>77.85</td>
</tr>
<tr>
<td>ABS</td>
<td>80.15</td>
<td>58.71</td>
</tr>
<tr>
<td>PMMA</td>
<td>90.57</td>
<td>64.77</td>
</tr>
<tr>
<td>PC</td>
<td>78.35</td>
<td>77.13</td>
</tr>
</tbody>
</table>

5.2. Initial Understanding of the Flotation System

5.2.1. First Scoping Test

The described scoping flotation test was chronologically the first test performed in this research. It used shredded PMMA particles of various sizes so no sizing had been done prior to the test. The test was aiming to establish the scope and particle size for future experimentation. As can be seen in Table VI, almost full recovery of the feed material was achieved after 30 minutes of the test, as 97% of the particles were collected in the concentrate by that time. The resulting flotation kinetics is shown in Figure 16. The kinetic data demonstrate overall high floatability of the PMMA particles, which is justified by the naturally hydrophobic surface of the plastic having a large contact angle. However, such recovery figures were determined to be unsatisfactory per industrial standards as the optimal duration of flotation is usually 10-15 minutes. As seen in Table VI, in 15 minutes of the test, only 63% of the PMMA particles had floated. One of the reasons for such behavior is too large a size of the particles. Larger particles
having greater masses would require more air bubbles to be attached on their surfaces to be lifted, thus requiring more residence time for the bubbles. A size distribution analysis was performed on the particles collected in the float fraction. The results of this analysis are shown in Table VII. As shown in Table VII, approximately 36% of PMMA particles collected during the test were over Number 8 mesh size, which corresponds to 2.36 mm. This 36% of the total mass of collected particles is equal to 27 g, which is the same mass that remained in the flotation cell after 15 minutes before being collected in the next 15 minutes. Accordingly, it was concluded that 2.36 mm is the optimal maximum size of a single plastic particle for realistic flotation. Thus, the number 8 mesh sieve was used in all following tests for sizing of the plastic particles.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Weight (Grams)</th>
<th>Recovery (%)</th>
<th>Cum. Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>2.4</td>
<td>3.1</td>
<td>4.7</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3.9</td>
<td>8.6</td>
</tr>
<tr>
<td>6</td>
<td>6.1</td>
<td>8.0</td>
<td>16.6</td>
</tr>
<tr>
<td>8</td>
<td>11.2</td>
<td>14.7</td>
<td>31.3</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>9.2</td>
<td>40.4</td>
</tr>
<tr>
<td>15</td>
<td>17.2</td>
<td>22.5</td>
<td>63.0</td>
</tr>
<tr>
<td>20</td>
<td>17.6</td>
<td>23.0</td>
<td>86.0</td>
</tr>
<tr>
<td>30</td>
<td>8.4</td>
<td>11.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Tailings</td>
<td>2.3</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>Total</td>
<td>76.4</td>
<td>100</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 16. Flotation kinetics for scoping test with PMMA particles

Table VII: Size distribution analysis results

<table>
<thead>
<tr>
<th>Mesh Number</th>
<th>Mesh Size (mm)</th>
<th>Fraction Mass (g)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 3</td>
<td>&gt; 6.68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3 &gt; x &gt; 4</td>
<td>6.68 &gt; x &gt; 4.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 &gt; x &gt; 6</td>
<td>4.75 &gt; x &gt; 3.33</td>
<td>4.7</td>
<td>6.4</td>
</tr>
<tr>
<td>6 &gt; x &gt; 8</td>
<td>3.33 &gt; x &gt; 2.36</td>
<td>22.3</td>
<td>30.2</td>
</tr>
<tr>
<td>8 &gt; x &gt; 14</td>
<td>2.36 &gt; x &gt; 1.4</td>
<td>39</td>
<td>52.8</td>
</tr>
<tr>
<td>14 &gt; x &gt; 24</td>
<td>1.4 &gt; x &gt; 0.701</td>
<td>6.6</td>
<td>8.9</td>
</tr>
<tr>
<td>24 &gt; x &gt; 50</td>
<td>0.701 &gt; x &gt; 0.297</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>50 &gt; x &gt; 100</td>
<td>0.297 &gt; x &gt; 0.15</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>&lt; 100</td>
<td>&lt; 0.15</td>
<td>&lt; 0.1 N/A</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>N/A</strong></td>
<td>73.9</td>
<td>100.00</td>
</tr>
</tbody>
</table>

5.2.2. Second Scoping Test

Oversized PMMA particles from the previous scoping test were reground until the desired size (< 2.36 mm) was achieved. Reground plastic particles were then combined with the rest of the particles from the previous scoping test. Another scoping test was performed using this feed material. This test was intended to study the applicability of frother type and other flotation conditions, such as rotor agitation level, frother dosage, volume of water in the cell, etc.
Table IX shows the comparison of the test conditions used in the first and second scoping tests, respectively. A glycol-based frother was chosen for this scoping test. As shown in Table VIII, only 40% of the total plastic particles were collected after 15 minutes of the test. In addition to that, complete recovery was not achieved even after 30 minutes of the test. According to these results, the test was concluded to be unsuccessful. The glycol-based frother was not used in any following tests and MIBC was chosen as the default frother for all future tests. Based on the results of this test, water volume in the cell and rotor agitation rate were set to 1900 ml and 900 rpm, respectively, for all future experimentation.

Table VIII: Second scoping test flotation results

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Weight (Grams)</th>
<th>Recovery (%)</th>
<th>Cum. Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>3.7</td>
<td>4.8</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>4.6</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>4.4</td>
<td>5.8</td>
<td>15.2</td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
<td>3.0</td>
<td>18.2</td>
</tr>
<tr>
<td>8</td>
<td>9.9</td>
<td>13.0</td>
<td>31.2</td>
</tr>
<tr>
<td>10</td>
<td>2.2</td>
<td>2.9</td>
<td>34.0</td>
</tr>
<tr>
<td>15</td>
<td>4.7</td>
<td>6.2</td>
<td>40.2</td>
</tr>
<tr>
<td>20</td>
<td>5.3</td>
<td>6.9</td>
<td>47.1</td>
</tr>
<tr>
<td>30</td>
<td>31.2</td>
<td>40.8</td>
<td>88.0</td>
</tr>
<tr>
<td>Tailings</td>
<td>9.2</td>
<td>12.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Total</td>
<td>76.4</td>
<td>100.0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table IX: Comparison of test conditions of first and second scoping tests

<table>
<thead>
<tr>
<th>Frother Type</th>
<th>Frother amount (ml)</th>
<th>Water Volume (ml)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBC</td>
<td>0.5</td>
<td>1900</td>
<td>900</td>
</tr>
<tr>
<td>Glycol-based Frother</td>
<td>1</td>
<td>2100</td>
<td>1200</td>
</tr>
</tbody>
</table>
5.3. **Studies on Natural Floatability**

A number of flotation experiments were conducted producing kinetic data for each plastic type under identified conditions. Flotation kinetics represented natural tendency of plastics to float without any surface modification.

### 5.3.1. PVC Flotation

As can be seen in Figure 17, PVC shows high natural hydrophobicity and, consequently, high floatability. The graph shows that 90% recovery is achieved after 15 minutes of the test. Maximum recovery reached after 30 minutes of the test was 94%. Only 6% of the feed material contributed to the tailings.

![Figure 17. PVC flotation kinetics](chart)

### 5.3.2. PMMA Flotation

Figure 18 shows the flotation kinetics for PMMA flotation test. PMMA shows very high level of natural floatability. Almost complete recovery of 99.8% was achieved within 15 minutes of the test. Due to such high recovery, the test was stopped after 15 minutes as conducting it for full 30 minutes was unnecessary. More than half of the total feed material floated in the first
minute of the test, emphasizing high natural floatability of PMMA. These flotation test results show a much greater floatability, compared to the scoping tests results, proving that the chosen test conditions and the maximum particle size are, in fact, optimal.

5.3.3. PC Flotation

As can be seen in Figure 19, PC shows slightly lower natural floatability compared to that of PMMA and PVC. Only 82% of the total feed mass floated in 15 minutes of the test. Total recovery of 90% was achieved after 30 minutes of the test. Lower floatability can be associated with lower natural hydrophobicity of PC compared to PMMA and PVC. This observation is supported by the contact angle measurements data.
5.3.4. PS Flotation

Figure 20 shows the flotation kinetics for PS flotation test. PS demonstrates flotation kinetics similar to that of PC, reaching only 83% recovery after 15 minutes of the test and 92% recovery after 30 minutes of the test.
5.3.5. HDPE Flotation

As can be seen in Figure 21, HDPE shows extremely high floatability, reaching 93% recovery within the first minute of the test. The test was finished in 10 minutes after 99.8% recovery had been achieved. Such high floatability is explained by high natural hydrophobicity of HDPE, which is evident from contact angle measurements data. In addition to that, density of HDPE is 0.98 g/cm³, making it lighter than water, this factor also contributes to easy flotation of this type of plastic.

5.3.6. ABS Flotation

As can be seen in Figure 22, ABS shows relatively high floatability, reaching 84.7% recovery after 10 minutes of the test. Total recovery after 30 minutes of the test was 87%.
5.4. Initial Studies for Surface Treatment with Tannic Acid

This series of tests was conducted at high concentration of tannic acid of $3.0 \times 10^{-4}$ mol/l. These tests were aimed at estimating the effect of tannic acid treatment on flotation kinetics of plastics. The high dosage of tannic acid resulted in severe depression of the plastic particles.

5.4.1. PVC Flotation

Figure 23 shows the flotation kinetics for PVC particles after they were treated with $3.0 \times 10^{-4}$ mol/l of aqueous solution of tannic acid. The graph clearly represents a significant decrease in the PVC particles’ floatability after tannic acid treatment. Only 2.5% of the total feed mass had floated after 10 minutes of the test. Maximum recovery that was achieved by the 30-minute mark of the test was 26.5%. The results show a 67% decrease in recovery of PVC particles in 30-minute test (see Figure 17).
5.4.2. PMMA Flotation

As can be seen in Figure 24, PMMA particles are greatly depressed by treatment with tannic acid at this high concentration. PMMA particles remained generally depressed for the first half of the test. Recovery reached only 7.6% after 15 minutes of the test. However, the flotation kinetics changed at this point and PMMA particles started floating after 15 minutes. This resulted in 56.8% recovery reached after 30 minutes of the test. Such increase in floatability can be explained by the fact that tannic acid does not form strong bond with PMMA surface upon adsorption, which breaks with time as more water is added to maintain the froth height, resulting in desorption of tannic acid molecule. Total recovery after 15 minutes of the test decreased by 92% after treatment with tannic acid, compared to flotation test results for untreated PMMA (see Figure 18).
5.4.3. PC Flotation

Figure 25 shows that PC particles are extremely sensitive to treatment with tannic acid. Only 1% of the total feed mass was collected after first 15 minutes of the test. The total recovery reached after 30 minutes of the test was only 2.9%. The decrease in total recovery after 30 minutes of the test was 87%, compared to natural floatability test results shown in Figure 19.
5.4.4. PS Flotation

As can be seen in Figure 26, PS particles remain completely depressed for the first 10 minutes of the test, reaching only 0.7% recovery. The recovery then proceeded to gradually increase for next 10 minutes before reaching 2% at 20-minute mark. This is followed by a rise in floatability, which resulted in about 18% recovery after 30 minutes of the test. Such flotation kinetics are similar to the ones of PMMA, discussed previously. The increase in floatability after some time within the test can be also associated with a weaker bonding between tannic acid molecule and the surface of a plastic particle. Total recovery after 30 minutes of the test decreased by 73% after treatment with tannic acid compared to its absence in Figure 20.

![Recovery - Time Chart for PS with Tannic Acid Flotation](image)

*Figure 26. PS flotation kinetics at higher concentration of tannic acid*

5.4.5. HDPE Flotation

As can be seen in Figure 27, HDPE particles retain gradual increase in floatability for the whole duration of the test. However, overall the particles remain depressed, as only 2.8% recovery was reached after 10 minutes of the test, whereas in the original flotation test practically full recovery of 99.8% was achieved after the same time period (see Figure 21). Total recovery reached after 30 minutes of the test was equal to 9%. 
5.4.6. ABS Flotation

As shown in Figure 28, ABS remains generally depressed for the entire duration of the test. Recovery achieved after 15 minutes of the test was 3%, compared to 84.7% for the previous test without tannic acid treatment (see Figure 22). Total recovery after 30 minutes was 10%, which is 77% less than the recovery for the previous test.
A conclusion can be made based on all of these results: that the concentration of tannic acid of $3.0 \times 10^{-4}$ mol/l renders the surfaces of all six plastics hydrophilic, resulting in low recovery levels and almost complete depression of most of the plastic particles. It was concluded that such a high dosage of tannic acid would not be appropriate to induce selectivity and separation of individual plastics; however, all that is now needed is to examine the effect of concentration.

5.5. **Studies with Lower Concentration of Tannic Acid**

For the next series of tests, concentration of tannic acid was lowered, compared to previous tests, from $3.0 \times 10^{-4}$ mol/l to $6.0 \times 10^{-5}$ mol/l. The concept behind it was that at lower concentration, tannic acid may not form as strong bonds with certain plastics as with the others, inducing some selectivity. This difference could then be exploited for selective separation of plastics from the mixture.

5.5.1. **PVC Flotation**

Figure 29 shows that at this concentration of tannic acid PVC particles remain generally depressed. However, some increase in floatability is observed, as 14% of the total feed mass of particles floated after 10 minutes of test compared to 2.5% in the previous test.
5.5.2. PMMA Flotation

As can be seen in Figure 30, PMMA particles were still depressed at this tannic acid concentration. Total recovery achieved after 10 minutes of the test was equal to 18.8%, compared to 2.7% recovery achieved after the same time period with higher tannic acid concentration.
5.5.3. PC Flotation

Figure 31 shows flotation kinetics of PC particles at lower concentration of tannic acid. It can be observed that at these conditions, PC demonstrates moderate floatability with 45% recovery achieved after 10 minutes of the experiment. Overall, the flotation kinetics curve appears to follow the original flotation kinetics curve for virgin PC with approximately 20% lower recovery for each time fraction. This suggests that the concentration of $6.0 \times 10^{-5}$ mol/l of tannic acid is a transitional concentration that is not high enough to completely depress the PC and not low enough to not affect natural floatability of PC particles.

![PC at Lower Concentration of Tannic Acid](image)

**Figure 31.** PC flotation kinetics at lower concentration of tannic acid

5.5.4. PS Flotation

As can be seen in Figure 32, PS is unaffected by tannic acid at this concentration. Total recovery of 97% was achieved after 10 minutes of the test as oppose to 0.7% during the previous test with high tannic acid concentration. These results demonstrate that PS is less sensitive to treatment with tannic acid at low concentration than the previously discussed plastic types and, potentially, can be separated from them under these conditions.
5.5.5. HDPE Flotation

Flotation kinetics presented in Figure 33 demonstrate that HDPE particles retain their hydrophobic properties after treatment with tannic acid at this concentration. The concentration of tannic acid at this level was not enough to depress the HDPE particles, as 98% recovery was achieved after 10 minutes of the test, compared to 2.8% during the previous test with high tannic acid concentration.
5.5.6. ABS Flotation

According to Figure 34, ABS particles are almost completely depressed even at this low concentration of tannic acid. Total recovery after 10 minutes of the test was 3.5%

![ABS at Lower Concentration of Tannic Acid](image)

Figure 34. ABS flotation kinetics at lower concentration of tannic acid

The results of this series of tests clearly show the differences in the response of certain plastics to treatment with tannic acid at this low concentration compared to others. This fact suggests the possibility of selective separation of certain plastics at lower concentration of tannic acid. For convenience of further experimentation, it was decided that plastics would be divided into binary mixtures by gravity separation using the Crossflow Separator, following which the surface treatment would be imparted for selective separation in the final stages.

5.6. Studies on Gravity Separation

Prior to gravity separation tests using the Crossflow Separator, the HDPE particles were completely removed from the feed mixture by sink-float separation in water exploiting the fact that HDPE was the only plastic with a density lighter than that of water. The mixture of six
plastics was taken in a large beaker, filled with water. All plastics sank to the bottom of the beaker, while HDPE remained on top of the water level. The HDPE particles were decanted off.

**5.6.1. Terminal Settling Velocity Estimation**

The gravity separation method used in this work employed the principle of elutriation to selectively separate plastics. Use of elutriation implies that the plastic particles, settling in the Crossflow Separator, are opposed by an upward flow of water. The particles will be carried with the water flow (overflow) and will rise to the surface if the velocity of rising water is greater than the terminal settling velocity of a particle. If the velocity of rising water is lower than the terminal settling velocity of a particle, then the particle will settle at the bottom of the Crossflow Separator as underflow. Terminal settling velocity is a maximum velocity that an object can reach as it is settling through a fluid. Terminal settling velocity value is different for each plastic as it depends on the density of the material and the size of the particle.

In order to determine the exact flow rate, required at each stage of the gravity separation test to achieve desired separation, terminal settling velocity of each plastic type was calculated according equation (10). Viscosity and density of the medium were assumed to be those of water at 25°C as the amount of feed material was not enough to alter those properties. Gravitational acceleration was taken as 9.81 m/s². Average diameter of the plastic particles was assumed to be 2 mm. Terminal settling velocities of each type of plastic used in this test were estimated from Equation (10) and are presented in Table X.

<table>
<thead>
<tr>
<th>Plastic Type</th>
<th>Density (g/cm³)</th>
<th>Terminal Settling Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>1.400</td>
<td>0.153</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.200</td>
<td>0.108</td>
</tr>
<tr>
<td>PC</td>
<td>1.200</td>
<td>0.108</td>
</tr>
<tr>
<td>ABS</td>
<td>1.060</td>
<td>0.059</td>
</tr>
<tr>
<td>PS</td>
<td>1.050</td>
<td>0.054</td>
</tr>
</tbody>
</table>
As can be seen in Table X, the plastics in this test can be separated into 3 groups: PVC, PMMA+PC and ABS+PS. This can be achieved if the teeter water is pumped into the Crossflow Separator at such flow rate that the upward velocity is in the values between 0.153 m/s and 0.108 m/s for the first stage and between 0.108 m/s and 0.059 m/s for the second stage. In order to do that, the flow rate into the Crossflow Separator was adjusted to reach the upward velocity of 0.117 m/s for the first stage (4320 l/h) and 0.075 m/s for the second stage (2755 l/h). This was achieved by adjusting the voltage generated by the power generator to arrive at the desired flowrate of the pump. Required flow rate for each stage was calculated according to the volumetric flow rate equation presented in equation (11).

\[ Q = V \times A \]  

(11)

where, Q is the volumetric flow rate, V is the fluid velocity and A is the cross sectional area. Cross sectional area of the Crossflow Separator was measured to be 1.025 x 10^{-2} m^2.

5.6.2. Quantification of Results through Image Analysis

Image color analyzer was used for calculation of grade and recovery of each plastic in the products of each stage of gravity separation.

5.6.2.1. First Stage Underflow

Figure 35 depicts the underflow product obtained at the first stage of the gravity separation. It may be recalled that in the first stage PVC particles were made to report to the underflow while other plastic particles were recovered in the overflow. The image was modified in order to generate a well-developed contrast between the differently colored plastic particles. A distinct difference in color is observed between dark blue PVC particles and red PMMA particles that were misplaced to the underflow. No other plastic particles were misplaced to the underflow. According to the image analysis software results, total area percentage of the image, covered by
dark blue (PVC) pixels is 21.02% and the total area percentage of the image covered by red (PMMA) pixels is 2.36%. Total feed mixture mass was 50 g, which was composed of 10 g of each plastic type. As stated earlier, this stage of gravity separation was aiming to separate PVC from the rest of the plastic types. Based on that, particles that contribute to the stage 1 overflow were considered tailings and particles that are collected as the underflow was considered concentrate.

Therefore, total area percentage of the image covered by both colors is:

\[
Total \ area \ % \ (PVC) + Total \ area \ % \ (PMMA) = 21.02\% + 2.36\% = 23.38\%
\]

Proportion of the total covered area covered by PVC is:

\[
\frac{Total \ area \ % \ (PVC)}{Total \ covered \ area \ %} \times 100\% = \frac{21.02\%}{23.38\%} \times 100\% = 89.91\%
\]

Proportion of the total covered area covered by PMMA is:

\[
\frac{Total \ area \ % \ (PMMA)}{Total \ covered \ area \ %} \times 100\% = \frac{2.36\%}{23.38\%} \times 100\% = 10.09\%
\]

It can be assumed that the area percentage is equal to volume percentage as all plastic particles are originally produced from the sheets of the same thickness. According to that, the relationship between area percentage and volume can be expressed as follows:

100% covered area \(\equiv\) 100 cm\(^3\)

89.91% area covered by PVC \(\equiv\) 89.91 cm\(^3\)

10.09% area covered by PMMA \(\equiv\) 10.09 cm\(^3\)

Therefore, theoretical mass of each plastic type particles in a total volume of 100 cm\(^3\) can be calculated as follows:

\[
Mass \ (PVC) = Volume \ (PVC) \times Density \ (PVC) = 89.91 \ cm^3 \times 1.4 \ \frac{g}{cm^3} = 125.87 \ g
\]

\[
Mass \ (PMMA) = Volume \ (PMMA) \times Density \ (PMMA) = 10.09 \ cm^3 \times 1.2 \ \frac{g}{cm^3} = 12.11 \ g
\]
Total theoretical mass of each plastic type particles in 100 cm$^3$ is:

$$Mass\ (PVC) + Mass\ (PMMA) = 125.87 + 12.11 = 137.98\ g$$

Mass percentage of PVC particles in total theoretical mass is:

$$\frac{Mass\ (PVC)}{Total\ mass} \times 100\% = \frac{125.87\ g}{137.98\ g} \times 100\% = 91.22\%$$

Mass percentage of PMMA particles in total theoretical mass is:

$$\frac{Mass\ (PMMA)}{Total\ mass} \times 100\% = \frac{12.11\ g}{137.98\ g} \times 100\% = 8.78\%$$

The sample was weighed, and the total mass of the stage 1 underflow product mixture was found to be 9.5 g. According to the mass percentages calculated earlier, mass of each plastic in the mixture was calculated as follows:

$$Mass\ of\ PVC\ in\ concentrate = 9.5\ g \times 0.9122 = 8.67\ g$$

$$Mass\ of\ PMMA\ in\ concentrate = 9.5\ g \times 0.0878 = 0.83\ g$$

Therefore,

$$Mass\ of\ PVC\ in\ tailings = 10\ g - 8.67\ g = 1.33\ g$$

$$Mass\ of\ PMMA\ in\ tailings = 10\ g - 0.83\ g = 9.17\ g$$

$$Total\ mass\ of\ tailings = 50\ g - 9.5\ g = 40.5\ g$$

$$Grade\ of\ PVC\ in\ tailings = \frac{1.33}{40.5} \times 100\% = 3.28\%$$

$$Grade\ of\ PMMA\ in\ tailings = \frac{9.17}{40.5} \times 100\% = 22.64\%$$

$$Total\ mass\ of\ feed = 50\ g$$

$$Grade\ of\ PVC\ in\ feed = \frac{10\ g}{50\ g} \times 100\% = 20\%$$

$$Grade\ of\ PMMA\ in\ feed = \frac{10\ g}{50\ g} \times 100\% = 20\%$$
Mass yield to tailings = \( \frac{\text{Mass of tailings}}{\text{Mass of feed}} = \frac{40.5}{50} \times 100\% = 81\% \)

Mass yield to concentrate = 100\% - 81\% = 19\%

Total mass of concentrate = 9.5 g

Grade of PVC in concentrate = \( \frac{8.67 \, g}{9.5 \, g} \times 100\% = 91.26\% \)

Grade of PMMA in concentrate = 100\% - 91.26\% = 8.74\%

Recovery of PVC in concentrate

= mass yield to concentrate × \( \frac{\text{grade of PVC in concentrate}}{\text{grade of PVC in feed}} \)

= 19\% \times \frac{91.26\%}{20\%} = 86.7\%

Recovery of PMMA in concentrate

= mass yield to concentrate × \( \frac{\text{grade of PMMA in concentrate}}{\text{grade of PMMA in feed}} \)

= 19\% \times \frac{8.74\%}{20\%} = 8.3\%

Clearly, these calculations show that a significant amount of PVC was successfully separated from other plastics and collected during the first stage of gravity separation with 91.26\% grade and 86.7\% recovery in a single run. Multiple runs to clean the underflow product would lead to further enrichment in grade albeit at a slightly lower yield. This calculations procedure was used to calculate grade and recovery in all further tests and will be further referred to as The Standard Calculations Procedure.
5.6.2.2. Second Stage Overflow

Figure 36 illustrates the edited image of the second stage of gravity separation overflow product mixture. This stage of gravity separation was aiming to separate remaining four plastics into 2 groups of 2 plastics each. Due to the lower density, PS and ABS particles were supposed to report to overflow while PC and PMMA particles were to constitute the underflow. As can be seen in Figure 36, second stage overflow mostly consists of ABS and PS particles, which are shown on the image as black-colored and white-colored particles respectively. A few blue PMMA particles can also be seen, which are considered misplacement. According to the image
color analyzer results, 15.14% of the image is occupied by PS particles, 12.91% of the image is occupied by ABS and 0.53% of the image is covered by PMMA particles. Total feed mass on this stage was 40.5 g and the total mass of the overflow product was 19 g. According to the Standard Calculations Procedure, results of the test were obtained and are presented in Table XI:

<table>
<thead>
<tr>
<th>Mass of PS in the overflow (g)</th>
<th>Mass of ABS in the overflow (g)</th>
<th>Mass of PMMA in the overflow (g)</th>
<th>Grade of PS in the overflow (%)</th>
<th>Grade of ABS in the overflow (%)</th>
<th>Grade of PMMA in the overflow (%)</th>
<th>Recovery of PS in the overflow (%)</th>
<th>Recovery of ABS in the overflow (%)</th>
<th>Recovery of PMMA in the overflow (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>8.60</td>
<td>0.40</td>
<td>52.61</td>
<td>45.29</td>
<td>2.10</td>
<td>100.00</td>
<td>86.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

As can be seen, complete recovery of PS was achieved at this stage. High recovery of ABS was also achieved. The recovery value could be affected by human error during the test as some ABS particles might have been lost during feeding. Small amount of PMMA particles recovered during this stage can be considered entrainment.
5.6.2.3. Second Stage Underflow

As can be seen in Figure 37, the second stage of gravity separation underflow product mixture mostly consists of purple PMMA particles and white PC particles. A small number of black ABS particles is also present, which, however, could not be identified by the image color analyzer due to its insufficient sensitivity. ABS content in this product mixture was ignored due to its insignificantly low quantity. According to the image color analyzer results, 6.7% of the image is covered by PC particles and 6.4% of the image is occupied by PMMA particles. Total feed mass on this stage was 40.5 g. Total mass of the underflow product was 17.7 g. According to the Standard Calculations Procedure, the following results were obtained as presented in Table XII.
High recovery rates of PC and PMMA were achieved at this stage of the test. Human error could potentially be present, resulting in the loss of insignificant amount of particles during feeding and other stages of the test, resulting in somewhat lower recovery values.

According to the results, obtained from the image color analyzer, the gravity separation technique was observed to be very efficient as high grade and recovery values were obtained by
single run in each stage of operation. Significantly high selectivity in each stage was also evident as the misplacement was indeed low.

5.7. **Separation by Flotation with Surface Treatment**

The binary mixtures, obtained as the underflow and overflow products during the second stage of the gravity separation test, were separately used as the feed material for different flotation tests. Each test was employing different surface treatment method and was aiming to separate the individual plastics within each binary mixture.

5.7.1. **PC-PMMA Separation by Surface Treatment with Potassium Permanganate**

PC and PMMA particles were treated with 0.05 g of potassium permanganate crystals. Concentration of potassium permanganate was enough to selectively adsorb on the surface of PMMA particles, avoiding adsorption on the surface of PC particles. Figure 38 shows the edited image of the concentrate, collected after 10 minutes, of the test. It can be seen that the majority of particles in the image are black, which represents PC, and only a few red PMMA particles are present. According to The Standard Calculations Procedure following results were obtained that are presented in Table XIII.

<table>
<thead>
<tr>
<th>Mass of PC in the concentrate (g)</th>
<th>Mass of PMMA in the concentrate (g)</th>
<th>Grade of PC in the concentrate (%)</th>
<th>Grade of PMMA in the concentrate (%)</th>
<th>Recovery of PC in the concentrate (%)</th>
<th>Recovery of PMMA in the concentrate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.73</td>
<td>0.87</td>
<td>90.94</td>
<td>9.06</td>
<td>87.30</td>
<td>8.70</td>
</tr>
</tbody>
</table>

It can be seen in Table XIII that a successful separation was achieved after treatment with potassium permanganate, as 87.3% of the PC particles was recovered after 10 minutes of the test, as opposed to 8.7% of the PMMA particles.
5.7.2. PS-ABS Separation by Surface Treatment with Tannic Acid

PS and ABS particles were treated with $4.6 \times 10^{-5}$ mol/l of aqueous solution of tannic acid. Figure 39 shows the edited image of the PS-ABS flotation test tailings. According to The Standard Calculations Procedure, the following results were obtained and are presented in Table XIV.

<table>
<thead>
<tr>
<th>Mass of PS in the concentrate (g)</th>
<th>Mass of ABS in the concentrate (g)</th>
<th>Grade of PS in the concentrate (%)</th>
<th>Grade of ABS in the concentrate (%)</th>
<th>Recovery of PS in the concentrate (%)</th>
<th>Recovery of ABS in the concentrate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.02</td>
<td>0.58</td>
<td>92.37</td>
<td>7.63</td>
<td>70.20</td>
<td>5.80</td>
</tr>
</tbody>
</table>
The results show high grade of 92.37\% and relatively high recovery of 70.2\% of PS in the concentrate after 10 minutes of the test.

Figure 39. Image analysis of the PS-ABS flotation test tailings

5.8. Spectroscopy

5.8.1. Studies with Raman Spectroscopy

5.8.1.1. Original Plastics Spectroscopy

Figure 40 shows the spectroscopy results for virgin HDPE, PC, PMMA, PS and PVC sheets. Raman spectroscopy was performed in order to identify the characteristic peaks for each plastic type and compare the differences in their structure. It can be seen that all five plastics share the same common peak at the region between 2800 and 3000 cm\(^{-1}\). Peaks at this area are associated with C-H vibrations, which correlates with the chemical structures of all five plastics.
5.8.1.1.1. **HDPE Spectrum**

HDPE spectrum is presented in Figure 40 as the black graph. Due to very simple chemical structure of HDPE molecule, there are not as many peaks can be observed as in the other spectra. Two weak peaks at 1060 cm\(^{-1}\) and 1127 cm\(^{-1}\) are identified as C-C vibrations. A series of peaks at the region from 1300 cm\(^{-1}\) to 1500 cm\(^{-1}\) are associated with CH\(_2\) bending.

5.8.1.1.2. **PC Spectrum**

Raman spectrum of PC is presented as the blue line in Figure 40. Chemical structure of PC is much more complex than that of HDPE as it includes phenyl groups and oxygen atoms. A medium peak at 700 cm\(^{-1}\) can be associated with C-C vibrations. Multiple peaks at approximately 890, 1178 and 1235 cm\(^{-1}\) can be identified as C-O-C vibrations. A series of peaks at 636, 829, 1006 and 1603 cm\(^{-1}\) are identified as aromatic ring chain vibrations. A weak peak at approximately 1770 cm\(^{-1}\) can be associated with C=O vibrations.

5.8.1.1.3. **PMMA Spectrum**

PMMA spectrum is represented in Figure 40 by the green line. A medium peak at approximately 810 cm\(^{-1}\) is associated with C-O-C vibrations. A weak peak at approximately 1710 cm\(^{-1}\) can be identified as C=O vibrations. Another weak peak at approximately 990 cm\(^{-1}\) can be associated with C-C vibrations.

5.8.1.1.4. **PS Spectrum**

PS spectrum in Figure 40 is represented by the purple line. A weak peak at 800 cm\(^{-1}\) can be identified as C-C vibrations. A strong peak at 1000 cm\(^{-1}\) is associated with expanding/contracting or “breathing” of the aromatic carbon ring. A medium peak at 1600 cm\(^{-1}\) is identified as C=C vibrations.
5.8.1.1.5.  PVC Spectrum

Raman spectrum of PVC is represented by the red line in Figure 40. Two medium peaks at 635 cm\(^{-1}\) and 695 cm\(^{-1}\) represent stretching vibrations of C-Cl bonds. A weak peak at 1190 cm\(^{-1}\) can be assigned to C-C vibrations.

![Figure 40. Raman spectra of virgin plastic samples](image)

5.8.1.2.  Spectroscopy after Surface Treatment

Tests were conducted to perform Raman spectroscopy of the surface treatment reagent, tannic acid, used in this work, and Raman spectroscopy of a plastic particle treated with tannic acid. The purpose of these tests was to identify the characteristic peaks of tannic acid and gather evidence of the presence of this reagent after treatment of certain plastics.

5.8.1.2.1.  Tannic Acid Molecule

Figure 41 shows spectrum of the surfactant tannic acid molecule. A series of weak peaks from approximately 800 cm\(^{-1}\) to 1200 cm\(^{-1}\) can be associated with C-O-C vibrations. A medium
peak at 1450 cm\(^{-1}\) can be assigned to CH\(_n\) groups deformations. A medium peak at 1700 cm\(^{-1}\) can be identified as C=C vibrations. A weak peak at approximately 1800 cm\(^{-1}\) may be representing C=O vibrations. Medium peaks at approximately 2880 cm\(^{-1}\) and 3060 cm\(^{-1}\) are identified as C-H vibrations. The strongest peak at 1603 cm\(^{-1}\) is associated with aromatic ring vibrations and can be considered a characteristic peak of tannic acid as its molecule is comprised of a large number of phenyl groups.

![Raman spectrum of tannic acid molecule](image)

**Figure 41. Tannic acid molecule spectrum**

### 5.8.1.2.2. PC Treated with Tannic Acid

Untreated PC spectrum is shown in Figure 42 as the red line. Spectrum of PC after treatment with 6.0 x 10\(^{-5}\) mol/l of tannic acid is represented by the black line in Figure 42. There are several changes in the treated spectrum that can be observed. Due to the structural characteristics of tannic acid, which is comprised of a large number of phenyl groups, strengthening of the related peaks is observed after treatment. Multiple peaks at 636, 829, 1006 and 1603 cm\(^{-1}\) in the PC spectrum are associated with aromatic ring chain vibrations. It can be seen in Figure 42 that all these peaks are more pronounced in the treated PC spectrum, compared
to the original spectrum. This confirms the adsorption of tannic acid on the surface of the PC particle affecting its hydrophobicity.

![Graph showing comparison of spectra of treated and untreated PC](image)

**Figure 42. Comparison of spectra of treated and untreated PC**

### 5.8.2. FTIR Spectroscopy

Figure 43 shows the FTIR spectrum of the virgin ABS. There are several highly pronounced peaks visible, which represent certain elements of the ABS chemical structure. The two medium peaks at approximately 2850 cm\(^{-1}\) and 2950 cm\(^{-1}\) are attributed to C-H stretching. A weak peak at approximately 2230 cm\(^{-1}\) is identified as C≡N stretching, which is related to the acrylonitrile component of ABS. A medium peak at approximately 1450 cm\(^{-1}\) is related to C-H bending. A medium peak observed at 980 cm\(^{-1}\) is identified as C=C bending. A strong peak at approximately 750 cm\(^{-1}\) is related to monosubstituted C-H bending. A strong peak at 690 cm\(^{-1}\) can be associated with the presence of benzene derivative.

As can be seen in Figure 44, the major peaks remained present after treatment with tannic acid. However, a series of very small and frequent peaks or “the noise” appears at the space from
1550 cm\(^{-1}\) to 1700 cm\(^{-1}\). This noise is commonly associated with the presence of phenyl groups, which form the molecule of tannic acid. Thus, the presence of a tannic acid coating was identified at the surface of the ABS particle after treatment with 4.6 \(\times 10^5\) of aqueous solution of tannic acid.

![FTIR spectrum of virgin ABS](image)

**Figure 43. FTIR spectrum of virgin ABS**
5.9. Final Flowsheet

The mixture of six different plastics was successfully separated into individual plastic fractions with a sequential series of processing steps. The steps involved sink-float gravity separation, gravity separation using the Crossflow Separator employing elutriation and, finally, flotation after surface treatment. The sequence of operation and the treatment are summarized in a flowsheet as shown in Figure 45. The yield grade and recovery data for all stages of operation are also shown in the flowsheet along with the main product for easy comprehension. The flowsheet shown in this figure actually summarizes the entire research in a concise manner.
Figure 45. Final flowsheet
6. Future Work

Future experiments planned for this project include:

- Optimization of the unit operations in the flowsheet;
- Multiple runs (cleaning and recleaning) of products from both gravity and flotation experiments to further reduce misplacement and improve the product grades;
- Investigation of different surface treatment reagents for alternatives;
- Broadening of the plastics variety present in the feed and consequent modification of the process; and
- Application potential of flotation column instead of the mechanical flotation cell.
7. Conclusions

A novel method for selective separation of a mixture of plastics was developed in this work. This method involves combination of elutriation-based, multi-stage gravity separation and froth flotation with surface treatment. Each of the six plastics considered in this work was successfully separated at a certain stage of the process. The lightest among them, HDPE, was separated from the others in the first stage of gravity separation by simple sink-flow process in water. This test exploited the fact that HDPE is the only plastic, which is lighter than water. The heaviest plastic, PVC, was successfully separated during the first stage of gravity separation. The remaining four plastics were then separated in two groups of two plastics each in the second stage of crossflow separation. The first group consisted of the lighter plastics, ABS and PS, which were successfully separated from each other after surface treatment with tannic acid, followed by froth flotation. Plastics within the second group, which contained the heavier PC and PMMA particles, were also successfully separated in froth flotation after being surface-treated with potassium permanganate. Analytical work performed in this research includes contact angle measurements, FTIR and Raman spectroscopy and image analysis to quantify the results and explain the experimental observations.

The quantification of the results indicated that separation efficiency in each unit operation was quite high as the misplacement of plastics in the wrong stream was very low. The developed flowsheet is simple and easily implementable. It does not involve expensive equipment and chemicals. The work is likely to contribute significantly in the recycling of plastics.
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SIGNATURE PAGE

This is to certify that the thesis prepared by Adilbek Baigabelov entitled “INVESTIGATION OF SURFACE TREATMENT FOR SELECTIVE SEPARATION OF PLASTICS” has been examined and approved for acceptance by the Department of Metallurgical and Materials Engineering, Montana Technological University, on this 26th day of November, 2019.

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