ADSORPTION OF RESIDUAL OIL FROM WATER USING WASTE TIRE POWDER

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ABSTRACT

The aim of this special project is to study the possibility of residual oil adsorption in synthetic oil-water mixture varying in adsorption time, tire powder a dosage and the initial concentration of oil in the mixture. Then, the quality of adsorbent was improved by pretreatment tire powder with acid solution (0.1M H_2SO_4), base solution (0.1M NaOH) and hexane. Then, the experiments in various pH oil solution were performed by preparing the oil-water mixture in pH3 and pH9 compare to pH7. The result of these experiments exhibited the best condition which is 90 minutes adsorption time and 5%v/v of initial oil concentration with 11.65% and 73.02% oil removal respectively. Studying the effect of tire powder dosage on oil removal, the best condition is 1%wt tire powder dosage with ratio of oil removal to tire powder dosage is 11.65. However, there is another method for improving the efficiency of oil removal that was the adsorption experiment with three different pretreated tire powder. Thus, a suitable condition was developed as 90 minutes adsorption time and 1wt% tire powder dosage and 20%v/v of oil concentration with 0.1M H_2SO_4, 0.1M NaOH and hexane-pretreated tire powder. The results of experiment were indicated that tire powder with 0.1M H_2SO_4 pretreatment had the best sorption capacity in synthetic oil-water mixture which was 22.92%. Next, the adsorption experiment with pretreated tire powder in various pH of oil solution was performed. pH of oil solution adjustment was done to study the effect of removing the residue oil using pretreated tire powder and it was exhibited that H_2SO_4 pretreated tire powder had a good removal of residue oil at solution condition of pH3 and pH9. Finally, determination of Iodine Number was done to determine the porosity or total surface area of non-pretreated and three different pretreated tire powder. The results indicated that acid (0.1M H_2SO_4) pretreated tire powder had the best Iodine Number which was 281.12.

หัวข้อโครงงานพิเศษ การศึกษาการดูดซับน้ำมันในน้ำโดยใช้ผงยางรถยนต์บด
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บทคัดย่อ

จากการศึกษา ค้นคว้าและวิจัยเกี่ยวกับการดูดซับน้ำมันด้วยผงยางที่ผ่านการบดละเอียด ในการทดลองนี้ ได้ทำการทดลองโดยเตรียมน้ำมันพืชผสมกับน้ำกลั่น ซึ่งทำการทดลองเพื่อหาสภาวะที่ดีที่สุดที่ผงยางบดมีความสามารถในการดูดมากที่สุด ซึ่งผลการทดลองแสดงให้เห็นว่าที่ช่วงเวลา 90 นาทีของการดูดซับ ใช้สัดส่วนของผงยางประมาณ 1 เปอร์เซ็นเทียบโดยน้ำหนักยาง และใช้ 20 เปอร์เซ็นเทียบโดยปริมาตรของปริมาณความเข้มข้นของน้ำมันที่ผสมอยู่ในน้ำ เมื่อได้สภาวะที่เหมาะสมที่สุดในการดูดซับน้ำมันแล้ว ขั้นตอนต่อไปเป็นการเพิ่มประสิทธิภาพของการดูดซับด้วยการปรับปรุงคุณภาพผงยางโดยการแช่ผงยางบดในสารละลายกรด (กรดซัลฟิวริก), ด่าง (โซเดียมไฮดรอกไซด์) และสารละลายอินทรีย์ (เฮกเซน) จากนั้นนำผลการทดลองที่ได้มาวิเคราะห์ พบว่าผงยางที่ผ่านการปรับปรุงคุณภาพด้วยกรดและสารละลายอินทรีย์ มีความสามารถในการดูดได้ดีที่สุดประมาณ 22.92% และ 21.6% ตามลำดับ จากนั้นได้ศึกษาความน่าจะเป็นของการดูดซับที่ดียิ่งขึ้นด้วยการเตรียมสารละลายในสภาวะที่เป็นกรดและด่าง ซึ่งในการทดลองส่วนนี้ได้เตรียมน้ำกลั่นให้มีค่าความเป็นกรดที่ pH3 ด้วยกรดซัลฟิวริก และเตรียมให้มีค่าความเป็นด่างที่ pH9 ด้วยโซเดียมไฮดรอกไซด์ และนำไปทำการทดลองอีกครั้งด้วยผงยางที่ปรับปรุงคุณภาพด้วยกรด และสารละลายอินทรีย์ ซึ่งได้ผลที่ดีมากในการทดลองก่อนหน้า ผลการทดลองของส่วนที่ใช้กับผงยางที่ปรับปรุงคุณภาพด้วยกรดปริมาณการดูดซับด้วย pH9 ในน้ำมันสังเคราะห์เป็นไปได้ดีที่สุด และผลการทดลองที่ทดลองกับผงยางที่ปรับปรุงคุณภาพด้วยสารละลายอินทรีย์ ปริมาณการดูดซับด้วย pH3 ในน้ำมันสังเคราะห์เป็นไปได้ดีที่สุด เพื่อยืนยันผลการทดลองในความสามารถของการดูดซับจึงได้ทำการทำลองหาค่าการดูดซับไอโอดีน ซึ่งค่าการดูดซับไอโอดีนของผงยางที่ปรับปรุงคุณภาพด้วยกรดมีค่ามากที่สุดคือ 281.12

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CHAPTER 1

INTRODUCTION

1.1 Motivation

According to rubber manufactures association, about 299 million tires were generate in the united states in 2005; where 52% of the scrap tires were converted into tire – derived fuel, 16% were used by the civil engineering applications, 12% were recycled by the ground rubber application 14% were land disposed, 2% were exported, and 4% of other application [1]. Waste tires are virtually non-degradable and take up landfill spaces. If not properly disposed, waste tires may accumulate water, and subsequently can cause the spread of mosquito-borne diseases. Offer tire fires occur and cause serious air, water and soil pollutions [2,3]. This makes waste tire disposal and management a prime issue for environment discussion.

Waste tires can also be recycled as a roadway pavement material, refuse derived fuel, or reproduced as tires. It seems that discarded tire are or useful in many recycling alternatives. Tire are primarily composed of rubber (40-45%) vulcanized with sulfur (1.5-2.5%), steel, and carbon black (27-33%). The carbon black used to strength then the rubber, is similar to activated carbon, a good sorbent to remove dissolved organic substances from waste water [4,5]. Moreover, tire rubber is a flexible and hydrophoblic (oil-philic), making it a good candidate as an oil sorbent for the recovery of spilled oil.

Oil spill is one of substance that causes water pollution. Fuel oil or vegetable oil are significant in daily life, especially in industry, however our everyday life is usually related in transportation and cooking, finally oil spill from these activities will become waste water. Some methods for treatment of oil spill in waste water such as physical separations based on gravity, making floating adsorption and extraction by solvents, chemical oxidation treatment or burning and biological treatment using microorganisms that have the ability to disintegrate oil spills [6].

The main objective of this research is to remove the residual oil from waste water using waste tire powder as the adsorbent. The effect of process variables, such as adsorbent dosage, amount of residual oil, and adsorption time, on removal of residual oil was studied in order to know the significantly variables using factorial design experiment. Moreover, the pre-treatment of tire powder before removed residual oil and type of oil were also studied. The adsorption equilibrium data were obtained to discover which isotherm model provided the best fit for this adsorption process.

1.2 Objective

1.2.1 To study the possibility of the use of tire powder as oil sorbent for removal residual oil from waste water.

1.2.2 To investigate the effect of oil type, amount of oil, adsorption time and method of tire pre-treatment on oil removal.

1.2.3 To improve the removal efficiency of oil removal by tire powder as adsorbent in various pH oil solutions.

1.3 Scope of study

1.3.1 Determination of significant parameters that effected on oil removal are as follows:

- Types of oil are vegetable oil.
- Volume ratios of oil to water are 5%, 10%, 20% and 30%.
- Dosages of tire powder are 0.5%, 1%, 2% and 3%.
- Adsorption time 30, 60, 90, 120, 180 and 240 minutes.
- Pretreatment of tire powder are acid treatment with H_2SO_4, Hexane treatment, and basic treatment with NaOH.

1.3.2 The studies about the characterization of tire powder are as follows:

- Surface texture of tire powder was measured by scanning electron microscope (SEM)
- Iodine number was determined.

1.4 Expected result

1.4.1 To know the parameters which are affected on residual oil removal by using tire powder as adsorbent.

1.4.2 To get the optimum conditions for residual oil removal by using tire powder as adsorbent.

1.4.3 To find the alternative adsorbent which is a tire powder for reduction of waste oil in the environment.

CHAPTER 2

THEORY

2.1 Adsorption [7]

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, shown as Figure 2.1, while desorption is the reverse process.

In simple terms, adsorption is "the collection of a substance onto the surface of adsorbent solids". It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated carbon, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

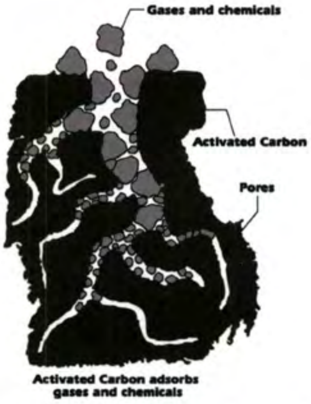


Figure 2.1 Adsorption of gases and chemicals on adsorbent.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption or chemisorption.

2.1.1 Physisorption [8]

Physisorption also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. The weak bonding of physisorption is due to the induced dipole moment of a nonpolar adsorbate interacting with its own image charge in the polarizable solid, shown as Figure 2.2.

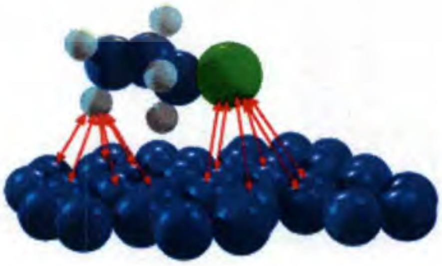


Figure 2.2 Interaction of adsorbate and adsorbent by physisorption

The fundamental interacting force of physisorption is caused by Van der Waals force. Even though the interaction energy is very weak (~10–100 meV), physisorption plays an important role in nature. For instance, the van der Waals attraction between surfaces and foot-hairs of geckos provides the remarkable ability to climb up vertical walls. In the point of view of molecular physics, the attractive force originates from the charge fluctuations between two correlated bonding molecules or atoms, in other words, the mutually induced dipole moments.

The features which are useful in recognizing physisorption including; the phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive; evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal; the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption; the energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive; the elementary step in physical adsorption from a gas phase does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes; in physical adsorption, equilibrium is established between the adsorbate and the fluid phase.

In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable; under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface.

2.1.2 Chemisorption [9]

Chemisorption is a classification of adsorption characterized by a strong interaction between an adsorbate and a substrate surface, as opposed to physisorption which is characterized by a weak Van der Waals force. A distinction between the two can be difficult and it is conventionally accepted that it is around 0.5 eV of binding energy per atom or molecule. The types of strong interactions include chemical bonds of the ionic or covalent variety, depending on the species involved.

It is characterized by : high temperatures, Type of interaction: strong; covalent bond between adsorbate and surface, high enthalpy: -50 kJ/mol $>\Delta H>$ -800 kJ/mol, adsorption takes place only in a monolayer, high activation energy, increase in electron density in the adsorbent-adsorbate interface, reversible only at high temperature. Due to specificity, the nature of chemisorption can greatly differ from system to system, depending on the chemical identity and the surface structure.

The features which are useful in recognizing chemisorption include: the phenomenon is characterized by chemical specificity; changes in the electronic state may be detectable by suitable physical means; the chemical nature of the adsorptive may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible; the energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large; the elementary step in chemisorption often involves an activation energy; where the activation energy for adsorption is large (*activated adsorption*), true equilibrium may be achieved slowly or in practice not at all.

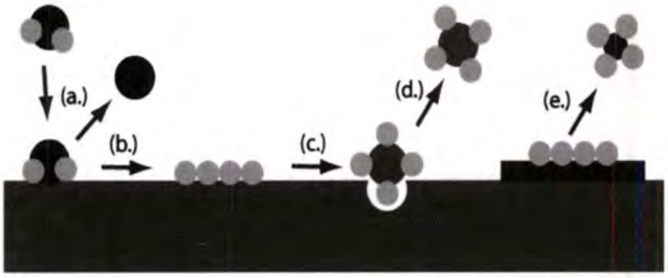


Figure 2.3 The chemisorption steps

The main way in which most chemists utilize the effect of chemisorption is in catalyzed reactions. The process of chemisorption is actually pivotal to the role of heterogeneous catalysis where the catalyst is in a solid phase—particularly transition metal catalysts. In many cases the chemical reagents will both bind to the catalytic surface. The chemical bonds then form and draw electrons away from the chemisorption bonds. The molecule then desorbs and is free to leave the surface. The comparison between physisorption and chemisorptions are shown as Table 2.1.

Table 2.1 The comparison between physisorption and chemisorption

Physical Adsorption	**Chemical Adsorption**
Occurs in any solid/fluid or solid/gas system.	Characterized by chemical specificity.
Perturbation of the electronic states of adsorbent and adsorbate is minimal.	Changes in the electronic states may be detectable by suitable physical means.
Binding energy 10-100 meV.	Bonding with energy of 1-10 eV.
The elementary step from gas phase does not involve an activation energy.	The elementary step from gas phase involve an activation energy.
Gas phase molecules can form multilayer adsorption.	Gas phase molecules can adsorbed on the surface by valence bonds and form monolayer adsorption.

2.2 Tire [10]

The tire is an assembly of numerous components that are built up on a drum and then cured in a press under heat and pressure. Heat facilitates a polymerization reaction that crosslinks rubber monomers to create long elastic molecules. These polymers create the elastic quality that permits the tire to be compressed in the area where the tire contacts the road surface and spring back to its original shape under high-frequency cycles. Typical components used in tire assembly are listed below. Showed in Figure 2.5 and listed below.

(a) Inner liner

The inner liner is an extruded halobutyl rubber sheet compounded with additives that result in low air permeability. The inner liner assures that the tire will hold high-pressure air inside, without the air gradually diffusing through the rubber structure.

(b) Cushion gum

Many higher-performing tires include an extruded component between the belt package and the tread to isolate the tread from mechanical wear from the steel belts.

(c) Body ply

The body ply is a calendered sheet consisting of one layer of rubber, one layer of reinforcing fabric, and a second layer of rubber. The earliest textile used was cotton; later materials include rayon, nylon, polyester and Kevlar. Passenger tires typically have one or two body plies. Body plies give the tire structure strength. Truck tires, off-road tires, and aircraft tires have progressively more plies. The fabric cords are highly flexible but relatively inelastic.

(d) Sidewall

Sidewalls are non-reinforced extruded profiles with additives to give the sides of the tire good abrasion resistance and environmental resistance. Additives used in sidewall compounds include antioxidants and antiozonants. Sidewall extrusions are nonsymmetrical and provide a thick rubber area to enable molding of raised letters and sidewall ornamentation.

Figure 2.4 Typical components used in tire assembly

(e) Beads

Beads are bands of high tensile-strength steel wire encased in a rubber compound. Bead wire is coated with special alloys of bronze or brass. Coatings protect the steel from corrosion. Copper in the alloy and sulfur in the rubber cross-link to produce copper sulfide, which improves bonding of the bead to the rubber. Beads are inflexible and inelastic, and provide the mechanical strength to fit the tire to the wheel. Bead rubber includes additives to maximize strength and toughness.

(f) Apex

The apex is a triangular extruded profile that mates against the bead. The apex provides a cushion between the rigid bead and the flexible inner liner and body ply assembly. Alternatively called "filler" (as in the diagram above).

(g) Belt package

Belts are calendered sheets consisting of a layer of rubber, a layer of closely-spaced steel cords, and a second layer of rubber. The steel cords are oriented radially in radial tire construction, and at opposing angles in bias tire construction. Belts give the tire strength and dent resistance while allowing it to remain flexible. Passenger tires are usually made with two or three belts.

(h) Tread

The tread is a thick extruded profile that surrounds the tire carcass. Tread compounds include additives to impart wear resistance and traction in addition to environmental resistance. Tread compound development is an exercise in compromise, as hard compounds have long wear characteristics but poor traction whereas soft compounds have good traction but poor wear characteristics.

(i) Other components

Tire construction methods vary somewhat in the number and type of components, as well as the compound formulations for each component, according to the tire use and price point. Tire makers continuously introduce new materials and construction methods in order to achieve higher performance at lower cost.

Materials used for tire production are listed below

- Natural rubber, or polyisoprene is the basic elastomer used in tire making.
- Styrene-butadiene co-polymer (SBR) is a synthetic rubber which is often substituted in part for natural rubber based on the comparative cost.
- Polybutadiene is used in combination with other rubbers because of its low heat-buildup properties.

- Halobutyl rubber is used for the tubeless inner liner compounds, because of its low air permeability. The halogen atoms provide a bond with the carcass compounds which are mainly natural rubber. Bromobutyl is superior to chlorobutyl, but is more expensive.
- Carbon Black, forms a high percentage of the rubber compound. This gives reinforcement and abrasion resistance.
- Silica, used together with carbon black in high performance tires, as a low heat build up reinforcement.
- Sulphur crosslinks the rubber molecules in the vulcanization process.
- Accelerators are complex organic compounds that speed up the vulcanization.

Materials used for tire production are listed below (continue)

- Activators assist the vulcanization. The main one is zinc oxide.
- Antioxidants and antiozonants prevent sidewall cracking due to the action of sunlight and ozone.

2.3 Adsorbent [11]

Adsorbent is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the adsorbate. Freshly prepared adsorbent has a clean surface. Adsorbent is a magnificent material for adsorption, its black color persists and adds a grey tinge if even trace amounts are left after treatment; however filter materials with fine pores remove carbon quite well.

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites. They present enormous surface areas per unit weight.
- Carbon-based compounds are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix.

Adsorbent is a highly porous, amorphous solid consisting of microcrystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. One of its main drawbacks is that it is combustible.

Surface Area and Porosity Determinations by Physisorption is a practical guide for industry or academics to the measurement of surface area and pore size using the tool of physical adsorption. The pore space is the internal volume of the carbon granule. The pore space consists of all the cracks and crevices created when the coal is crushed and glued back together, and the volume between the graphite plates. The distance between the graphite plates determines whether the space is an adsorption pore or a transport pore.

The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product.

2.3.1 Porous Structures of adsorbent

(a) Microporous Structure [12]

Micropore dimensions ranging from 3.5 to 20 Angstroms are important to researchers and to manufacturers using materials such as carbons, zeolites, silicas and aluminas in their processes. For analysis of pores in this range, the ability to reach and measure very low pressures is required. Factors such as temperature stability, vacuum capability and transducer sensitivity are crucial in micropore analysis and these factors are precisely what Micromeritics instrumentation provided. Micromeritics has pioneered instruments designed to collect data in the low pressure regions required to gain meaningful information about the microporosity of samples.

(b) Mesoporous structure [13]

Mesoporous materials are those with pores in the range 20-500Å in diameter. They have huge surface areas, providing a vast number of sites where sorption processes can occur. These materials have numerous applications in catalysis, separation and many other fields. The synthesis of these materials is of considerable interest and is constantly being developed to introduce different properties.

(c) Macroporous structure [14]

A macroporous material is a material containing pores with diameters greater than 50 nm. Porous materials are classified into several kinds by their size.

2.4 Vegetable Fats and Oils [15]

Vegetable fats and oils are lipid materials derived from plants. Physically, oils are liquid at room temperature, and fats are solid. Chemically, both fats and oils are composed of triglycerides, as contrasted with waxes which lack glycerin in their structure. Although many different parts of plants may yield oil, in commercial practice, oil is extracted primarily from seeds.

The melting temperature distinction between oils and fats is imprecise, since definitions of room temperature vary, and typically natural oils have a *melting range* instead of a single melting point.

Vegetable fats and oils may be edible or inedible. Examples of inedible vegetable fats and oils include processed linseed oil, tung oil, and castor oil used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial purposes. Although thought of as esters of glycerin and a various blend of fatty acids, fats and oils also typically contain free fatty acids, monoglycerides, and diglycerides.

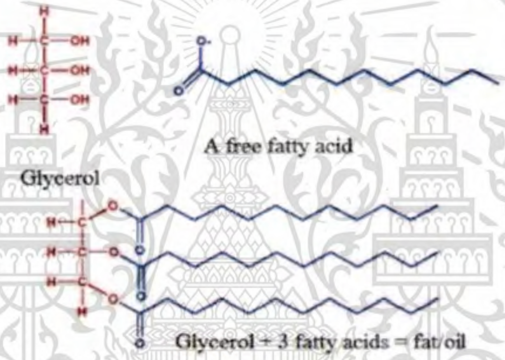


Figure 2.6 Composition and structure of fat and oil

The "modern" way of processing vegetable oil is by chemical extraction, using solvent extracts, which produces higher yields and is quicker and less expensive. The most common solvent is petroleum-derived hexane. This technique is used for most of the "newer" industrial oils such as soybean and corn oils. Another way is physical extraction, which does not use solvent extracts. It is made the "traditional" way using several different types of mechanical extraction. This method is typically used to produce the more traditional oils.

2.5 Hydrophobic and Hydrophilic

2.5.1 Hydrophobic [16]

In chemistry, hydrophobicity (from the combining form of water in Attic Greek hydro- and for fear phobos) refers to the physical property of a molecule (known as a hydrophobe) that is repelled from a mass of water. Hydrophobic molecules tend to be non-polar and thus prefer other neutral molecules and non-polar solvents. Hydrophobic molecules in water often cluster together forming micelles. Water on hydrophobic surfaces will exhibit a high contact angle. Examples of hydrophobic molecules include the alkanes, oils, fats, and greasy substances in general. Hydrophobic materials are used for oil removal from water, the management of oil spills, and chemical separation processes to remove non-polar from polar compounds. Hydrophobic is often used interchangeably with lipophilic, "fat loving." However, the two terms are not synonymous. While hydrophobic substances are usually lipophilic, there are exceptions such as the silicones and fluorocarbons.

2.5.2 Hydrophilic [17]

A hydrophilic molecule or portion of a molecule is one that is typically charge-polarized and capable of hydrogen bonding, enabling it to dissolve more readily in water than in oil or other hydrophobic solvents. A hydrophilic is made up of alcohol and fatty acyl chains. Hydrophilic and hydrophobic molecules are also known as polar molecules and nonpolar molecules, respectively. Some hydrophilic substances do not dissolve. This type of mixture is called a colloid. Soap, which is amphipathic, has a hydrophilic head and a hydrophobic tail, allowing it to dissolve in both waters and oils.

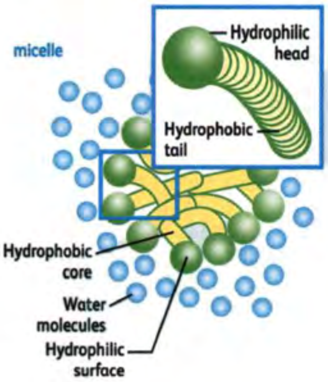


Figure 2.7 Position of Hydrophobic and Hydrophilic on detergents

2.6 Literature Review

Lin,C. et al. [6] studied the possibility of applying waste tire powder as a sorbent for the recovery of spilled oil was explored. The results indicate that 2.2 g of motor oil can be adsorbed to each gram of 20 mesh tire powder. Due to its elastic property, waste tire powder is re-usable for over 100 times without decreasing its oil absorption efficiency. Therefore, at least 220 g of motor oil can be recovered per gram of waste tire powder, which is very competitive to commercial sorbent.

The results of this study indicated that sorption efficiency increased as the tire powder particle size decreased, and decreased as the environmental temperature increases. When applying the waste tire powder to oil slicks on seawater, the oil sorption efficiency is shown to be better than if it was on fresh water. Efforts have been made to enhance the waste tire powder's oil sorption efficiency. Results indicated that the highest efficiency was obtained when the waste tire powder was pre-cleaned by n-hexane, followed by water cleaning > un-cleaned > dishwashing liquid cleaned > seawater cleaned. Compared to commercial oil sorbent, the result indicated that waste tire powder was economically more feasible, if it was re-used for 100 times. More efforts are encouraged to enhance the waste tire powder's oil sorption capacity without decreasing its re-usable characteristics.

Park, S.J. et al. [5] investigated the adsorption characteristics of activated carbon treated with 30 wt% HCl and 30 wt% NaOH were investigated. The acid and base values were determined by Boehm's method and the surface structures were studied by the BET method with N_2 adsorption and iodine adsorption capacity. Also the adsorption properties of the activated carbons treated with acid and base chemical solutions were investigated with CO_2 and NH_3 adsorptions. Different adsorption behaviors of CO_2 and NH_3 on the modified activated carbons were observed, even though the physical surfaces of the activated carbons (i.e., specific surface area, pore size, and pore volume) were not significantly changed.

Dias, J.M. et al. [18] reviewed the use of waste materials for the preparation of AC; however, these studies are restricted to either type of wastes, preparation procedures, or specific aqueous-phase applications. The present work reviews and evaluates literature dedicated both to the preparation of activated carbon (AC) by recycling different types of waste materials and also to its application in various aqueous-phase treatments. It is clear that conventional nonconventional wastes can be used to prepare AC, that can be applied in various aqueous treatment processes, namely to remove organic pollutants, dyes, volatile organic compounds, and heavy metals. Moreover, high surface areas can be obtained using either physical or chemical activation; however, combined treatments might enhance the surface properties of the adsorbent, therefore increasing its adsorption capacity. It is evident from the revision made that AC prepared from both conventional and non-conventional wastes might effectively compete with the commercial ones. This happens mostly when the activation procedures are optimized considering both the raw material used to produce the carbons and the contaminants to be removed.

Murillo, R. et al. [19] studied the valorize pyrolytic of tire char by means of the production of a useful adsorbent for air purification. An activation process with CO_2 was chosen to control the process of microporosity generation. The activation reaction and the textural properties were followed to achieve the understanding of porosity evolution. A change in the reaction rate in the first steps of the process was observed, followed by a linear relationship between activation time and burn off. Microporosity is generated in two main processes. At the beginning, narrow microporosity is formed, and later, a widening of the micropores is taking place. The performance of the new obtained samples for hot gas cleaning was tested by a process of Phenanthrene (Phe) adsorption in a fixed bed reactor with a process temperature of 150 °C at low inlet concentrations. It was concluded that the porosity development, both micro- and non-microporosity, increases the adsorption capacity of activated carbons, likely due to a multilayer adsorption process

Gunasekara, A.S. et al. [20] used the ground discarded tires adsorb naphthalene, toluene, and mercury ions (Hg^{2+}.) from aqueous solutions. Their sorption properties and kinetics were determined by batch equilibration techniques at 20°C. The isotherms were linear for naphthalene and toluene and their sorption coefficients were about 1340 and 255 (ml/g), respectively. Sorption of the organic compounds by the ground rubber particles was relatively fast (within 30 min). However, the mercury isotherms were non-linear, and its sorption was slow as compared to the sorption of the organics.

The rubber particles had a strong affinity for Hg^{2+}. These results show that ground discarded tires are effective in removing organic compounds and Hg^{2+} from wastewater and other contaminated environments. In addition it would be a useful, environmentally friendly use of discarded tires.

Ahmad, A.L. et al. [21] studied the adsorption of residual oil in palm oil mill effluent (POME). POEM is the wastewater produced by the palm oil industry. It is a colloidal suspension which is 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids originating in the mixing of sterilizer condensate, separator sludge and hydrocyclone wastewater. POME contains 4000 $mg.dm^{-3}$ of oil and grease, which is relatively high compared to the limit of only 50 $mg.dm^{-3}$ set by the Malaysian Department of Environment. A bench-scale study of the adsorption of residual oil in POME using synthetic rubber powder conducted using a jar test apparatus. It was found that almost 88% removal of residual oil was obtained with an adsorbent dosage of 30 $mg.dm^{-3}$ and mixing speed of 150 rpm for 3 hours at a pH 7.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1) Tire powder was obtained from Polymer Technology Workshop, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang
2) Pure vegetable oil
3) Hexane, (C_6H_6), analytical grade from Sigma Chemical Company
4) Sulfuric acid, (H_2SO_4), analytical grade from Lab System Company
5) Sodium hydroxide, (NaOH), analytical grade from Lab System Company
6) Deionized water

3.2 Apparatus and Instruments

1) Beaker 100 ml, 250 ml and 500 ml
2) Erlenmeyer flask 250 ml
3) Volumetric flask
4) conical flask
5) Volumetric cylinder 100 ml
6) Seperatory funnel 250 ml
7) Funnel
8) Burette
9) Pipette
10) Dropper
11) Stirring rod
12) Deionized water bottle
13) Analytical balance
14) Sieve

15) Desicator

16) Vacuum filtration and filter paper no. 4

17) Horizontal shaker

18) Scanning Electron Microscope (SEM)

3.3 Experimental Procedure

3.3.1 Adsorption experiment without pretreatment of tire powder

The adsorption experiment used was the batch equilibrium technique at room temperature. The step of experiment listed as below:

1) Weight the initial oil. Mix oil and water by percent volume per volume and in the 5 Erlenmeyer flasks, each containing 100 ml of oil-water mixture. Present by volume of oil in each flask was 5%, 10%, 20% and 30% (weigh and record the weight of oil used in each flask before mix with water).
2) Add tire powder (non-treated) that known exactly weight in oil-water mixture. Percent by weight of tire powder in 100 ml of liquid mixture were 0.5%, 1.0%, 2.0% and 3.0%.
3) Place stopper on Erlenmeyer flasks and shake at constant speed by using horizontal shaker until required contact time. The adsorption time were studied at 30, 60, 90, 120, 180 and 240 minutes.
4) Remove the remained tire powder by using vacuum filtration.
5) Hexane extraction was used to analyze the remained oil in the filtrate (3.3.2).

3.3.2 Oil extraction by Partion-Gravimetric Method

1) Weight the empty flask.
2) Pour oil-water mixture into seperatory funnel and follow with 30 ml hexane.

3) Place stopper on seperatory funnel then shake it severely for 2 minutes and wait until the mixture separate into 2 layers.

4) Drain the water layer and extract it with 20 ml and 10 ml hexane respectively, then collect oil layer in beaker.

5) Evaporate hexane out from oil layer at 105 °C for 1 hour after that keep it at room temperature in desiccators for 1 hour.

6) Weigh the weight of remained oil.

3.3.3 Adsorption experiment with pretreatment of tire powder

The aim of this experiment was studied the pretreatment processes of tire powder in order to improve the adsorption efficiency. The method of pretreatment tire powder consisted of acid treatment with H_2SO_4, base treatment with NaOH and organic treatment with hexane. The adsorption condition was obtained from section 3.3.1.

The step of experiment listed as below:

- Prepare treated tire powder by immersed the tire powder that known exactly weight in the pretreatment solution for 24 hours. Hexane, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used as pretreating solvent.

- After 24 hours, separated the pretreating solution from tire powder by filtration and evaporate the solvent out and keep treated tire powder in desicator.

- Repeat the experiment in section 3.3.1

3.3.4 Adsorption experiment with pretreatment of tire powder in acid-base condition

The objective of this experiment is to determine the oil removal efficiency of the best pretreatment of tire powder in section 3.3.3 with acid-base optimum condition: pH 3 and pH 9, 1%wt. of tire powder, 20%vol concentration of oil in 90 minutes. The experiment step listed as below

1) Prepare water to pH3 by using H_2SO_4 and pH9 by NaOH using then checking it with pH Meter.
2) Repeat the experiment as section 3.3.3 with pretreated tire powder.

3.3.5 Calculation

3.3.3.1 The amount of oil adsorbed calculate by using material balance

$$V(C_i - C_f) = G(q_f - q_i) \tag{3.1}$$

Where C_i and C_f are the initial and final concentration of oil (g/mL)

q_i and q_f are the amount of oil adsorbed per gram of adsorbent (g/g)

V is the total volume of oil and water mixture (mL)

G is the amount of tire powder added to oil-water mixture (g)

3.3.3.2 Removal efficiency (RE)

$$RE = \frac{C_i - C_f}{C_i} \times 100 \tag{3.2}$$

Where RE is removal efficiency (%)

C_i is initial concentration (g/mL)

C_f is final concentration (g/mL)

3.3.6 Determination of Iodine Number of filtrate solution

3.3.6.1 Preparation of Solutions

1) Hydrochloric Acid Solution (5% by weight)
2) Sodium Thiosulfate (0.100N)

3) Standard Iodine Solution (0.100+-0.001N)

4) Potassium Iodate Solution (0.1000N)

5) Starch Solution

3.3.6.2 Standardization of Solutions

1) Pipet 25.0 mL of potassium iodate (KIO_3) solution into a 250 mL titration (or wide-mouthed Erlenmeyer) flask.
2) Add 2.00±0.01g of potassium iodide (KI) to the flask and shake the flask to dissolve the potassium iodide crystals.
3) Pipet 5.0 mL of concentrated hydrochloric acid into the flask
4) Titrate the free iodine with sodium thiosulfate solution until a light yellow color is observed in the flask.
5) Add a few drops of starch indicator and continue the titration dropwise until one drop produces a colorless solution.

3.3.6.3 Standardization of 0.100 ± 0.001N Iodine Solution

1) Pipet 25.0 mL of iodine solution into a 250-mL wide-mouthed Erlenmeyer flask.
2) Titrate with standardized sodium thiosulfate until the iodine solution is a light yellow color.
3) Add a few drops of starch indicator and continue titration dropwise until one drop produces a colorless solution.

3.3.6.4 Procedure

1) Dry the tire powder in accordance with Test Method D2867. Cool the tire powder to room temperature in desiccators.
2) Pipet 10.0-mL of 5 wt % hydrochloric acid solution into each flask containing carbon.

3) Pipet 100.0 mL of 0.100N iodine solution into each flask. Standardize into iodine solution just prior to use.

4) For each filtrate, use the first 20 to 30 mL to rinse a pipet. Discard the rinse portions. Use clean beakers to collect the remaining filtrates. Mix each filtrate by swirling the beaker and pipet 50.0 mL of each filtrate into a clean 250-mL Erlenmeyer flask.

5) Titrate each filtrate with standardized 0.100N sodium thiosulfate solution until the solution is a pale yellow.

6) Add 2 mL of the starch indicator solution and continue the titration with sodium thiosulfate until one drop produces a colorless solution.

7) Record the volume of sodium thiosulfate used.

3.3.7 Calculation of Iodine Number Test

3.3.7.1 Determine sodium thiosulfate

$$N_1 = \frac{(PR)}{S}$$

Where N_1 is sodium thiosulfate, N

P is potassium iodate, mL

R is potassium iodate, N

S is sodium thiosulfate, mL

3.3.7.2 Determine the iodine solution

$$N_2 = \frac{(SN_1)}{I}$$

Where N_2 is iodine, N

S is sodium thiosulfate, mL

I is iodine, mL

3.3.7.3 Calculations are required for each carbon dosage, as $\frac{X}{M}$ and C.

To calculate the value of $\frac{X}{M}$:

$$A = (N_2)(12693.0)$$

$$B = (N_1)(126.93)$$

$$DF = \frac{(1 + H)}{F}$$

Where DF is dilution factor

H is 5% hydrochloric acid, mL, and

F is filtrate, mL

$$\frac{X}{M} = \frac{[A - (DF)(B)(S)]}{M}$$

Where $\frac{X}{M}$ is iodine absorbed per gram of carbon, mg/g

S is sodium thiosulfate, mL

M is carbon used, g

To calculate the value of C as follows:

$$C = \frac{N_1 S}{F}$$

Where C is residual filtrate, N

3.4 Measurement of Physical Properties and Chemical Characterization

1) The surface of tire powder was imaged by Scanning Electron Microscope (SEM).

Figure 3.1 The Scanning Electron Microscope (SEM)

2) To mix water and oil in this experiment, horizontal shaker are used.

Figure 3.2 The Horizontal Shaker

3) Solvent recovery can be done by evaporator by using liquid-liquid extraction technique.

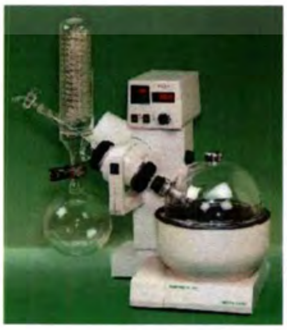


Figure 3.3 The Rotary Evaporator

3.5 Experimental Design

The unavailable experiment was designed for study the effect of process variables on oil removal. The concentrations of oil in water, dosage of non-pretreated tire powder and adsorption time were firstly studied. The maximum adsorption condition of each parameter was also used for study the effect of pre-treatment of tire powder. The experimental condition was shown in table 3.1 to 3.4.

Table 3.1 Experimental conditions for study the effect of concentration of oil on oil removal with non-pretreated tire powder

Oil concentration (volume%)	Dosage of non-treated tire powder (wt%)	Adsorption time (minute)
5	1	240
10	1	240
15	1	240
20	1	240
25	1	240
30	1	240

Table 3.2 Experimental conditions for study the effect of non-treated tire powder dosage on oil removal

Oil Concentration (volume%)	Dosage of non-treated tire powder (wt%)	Adsorption time (minute)
20	0.5	240
20	1	240
20	2	240
20	3	240

Table 3.3 Experimental conditions for study the effect of adsorption time on oil removal

Oil concentration (volume%)	Dosage of non-treated tire powder (wt%)	Adsorption time (min)
20	1	30
20	1	60
20	1	90
20	1	120
20	1	180
20	1	240

Table 3.4 Experimental conditions for study the effect of pretreatment method of tire powder dosage on oil removal

Pretreatment Method	Oil concentration (volume%)	Dosage of tire powder (wt%)	Adsorption time (min)
Non-pretreatment	Best condition from Table 3.1	Best condition from Table 3.2	Best condition from Table 3.3
Hexane			
H_2SO_4			
NaOH			

CHAPTER 4

RESULT AND DISCUSSION

This special project was studied to determine the oil removal efficiency in synthetic oil-water mixture by using non-pretreated and pretreated waste tire powder. The results as described into three parts. First, the adsorption experiment without pretreatment of tire powder was performed to determine the suitable condition for oil removal. To determine the suitable condition, the effects of adsorption time, concentration of oil and tire powder dosage on oil removal were studied. Second, the adsorption experiment with pretreatment of tire powder was aimed in order to improve the adsorption efficiency. The method of pretreated tire powder consisted of acid treatment with H_2SO_4, base treatment with NaOH and organic treatment with hexane. Finally, the effect of pH of synthetic-oil water on oil removal was carry out by using tire powder which improved by suitable pretreatment method. The adsorption experiment used was the batch equilibrium technique at room temperature.

4.1 Adsorption experiment without pretreatment of tire powder

Tire powder is a flexible and hydrophobic (oil-philic). Then, adsorption of residue oil from water by using waste tire powder as absorbent was studied to determine the oil removal efficiency. The effect of adsorption time, concentration of residue oil and tire powder dosage on oil removal were investigated for finding the suitable condition for further experiments.

4.1.1 Effect of adsorption time on oil removal

Adsorption time is an important factor that affected the oil removal efficiency. Figure 4.1 shows the effect of adsorption time on the adsorption of residue oil by using 1wt% of tire powder without pretreatment and 20%v/v of oil concentration.

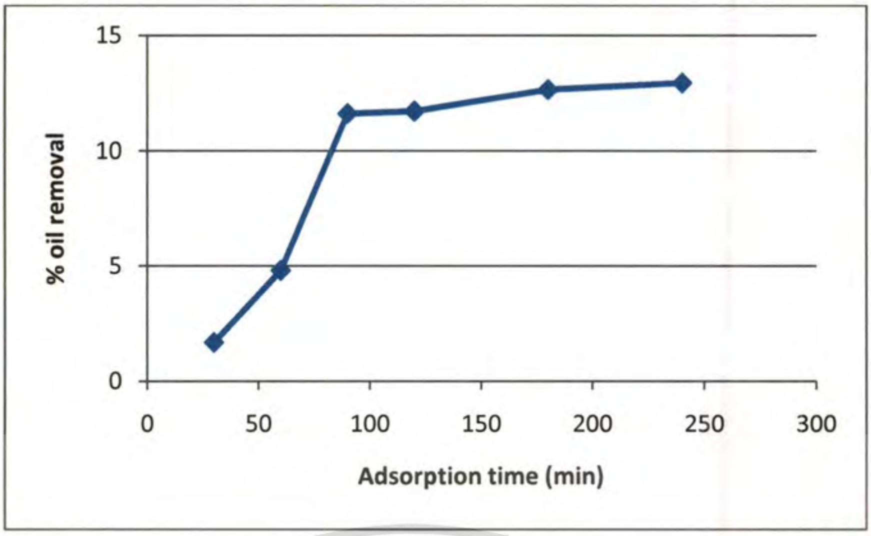


Figure 4.1 Effect of adsorption time on oil removal efficiency by using tire powder without pretreatment as absorbent

From figure 4.1, it is shown that the oil removal efficiency was sharply increased within 90 minutes. When the adsorption time over 90 minutes, the percentage of oil removal remained constant, implying equilibrium has been reach. The optimum adsorption time for removal residue oil by using waste tire powder without pretreatment as absorbent is 90 minutes.

4.1.2 The effect of tire powder dosage on oil removal

The experimental results using four dosages of tire powder without pretreatment were 0.5, 1, 2 and 3wt% and 20%v/v of oil concentration with adsorption time of 90 minutes was shown in figure 4.2.

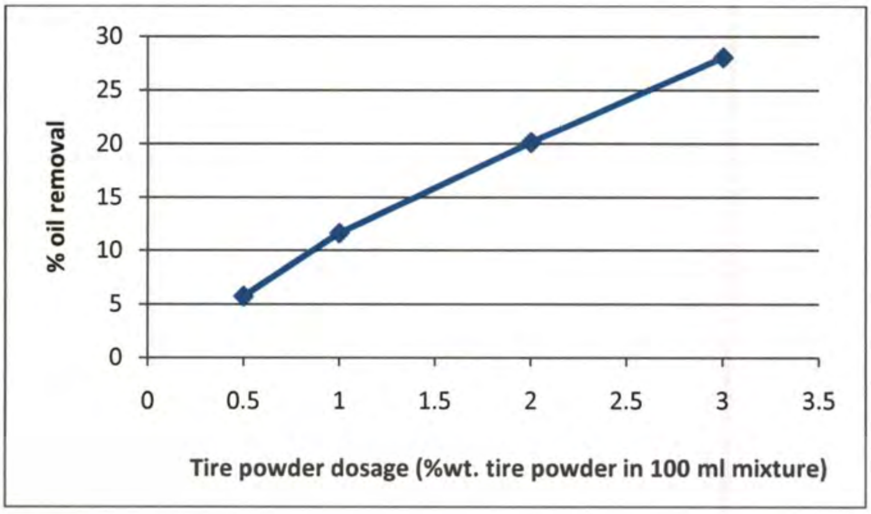


Figure 4.2 Effect of tire powder dosage on oil removal efficiency by using tire powder without pretreatment as absorbent

Table 4.1 The ratio of oil removal to tire powder dosage (without pretreatment)

Tire powder dosage (%wt)	Oil removal (%)	Ratio of oil removal to tire powder dosage
0.5	5.76	11.52
1	11.65	11.65
2	20.15	10.08
3	28.07	9.36

Figure 4.2 shows the effect of tire powder dosage toward the percentage of residue oil adsorption by using waste tire powder without pretreatment as absorbent. It was noticed that when the weight dosage of non-pretreated tire powder increased, the percentage of residue oil adsorption improved as well. Whereby, about 28.07% of residue oil had been adsorbed with an addition of tire powder 3wt% while 11.65% of residue oil was removed by tire powder dosage of 1wt%. When compare the ratio of oil removal to tire powder dosage as shown in table 4.1, at tire powder dosage of 1wt% of had the highest ratio of oil removal to tire powder dosage. It can be concluded that the suitable tire powder dosage for oil removal at this operating condition was 1wt%.

4.1.3 Effect of initial concentration of residue oil

This experiment was performed by using the optimum conditions in previous parts. There is 1%wt. of tire powder and adsorption time 90 minutes, the initial concentration of residue oil were varied. The effect of initial concentration of residue oil on percentage of oil removal was shown in figure 4.3.

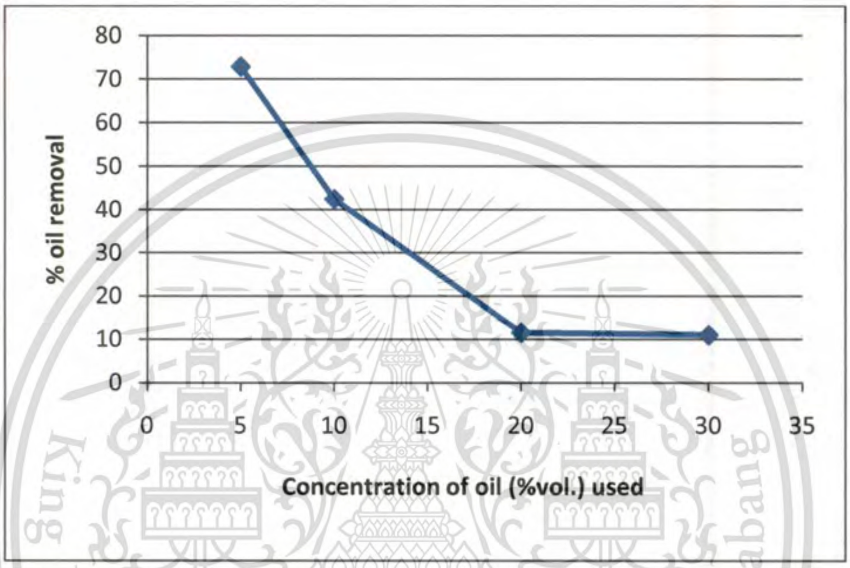


Figure 4.3 Effect of initial oil concentration on percentage of oil removal using non-pretreated tire powder as absorbent

From figure 4.3, it can be seen that the percentage of oil removal decreased with increasing the oil concentration in water. When oil concentration was increased from 5% to 20%, the oil removal was dropped from 73.02% to 11.65%, after that the percentage of oil removal remained constant or adsorption between tire powder and residue oil was saturated. Then, the best condition for studying the effect of concentration of oil by using waste tire powder without pretreatment as absorbent was 0.5% of residue oil in synthetic oil-water mixture with 73.02% in oil removal.

These three previous parts: study the effect of adsorption time, concentration of oil and tire powder dosage were performed to determine the optimum condition. Next, the section 4.2

(adsorption experiment with pretreated tire powder) and section 4.3 (adsorption experiment with pretreatment of tire powder in various pH solution) were study further to improve the adsorption capability of tire power in oil removal. Thus, to clearly observe the effect of pretreatment method of tire powder, the initial concentration oil was chosen at 20%v/v.

4.2 Adsorption experiment with pretreated tire powder

This experiment was focused on the pretreatment tire powder method to improve the adsorption efficiency of tire powder for removing oil residue in water. There are three pretreatment methods were studied in this part including acid-cleaned, base-cleaned and organic solvent-cleaned. The pretreatment of tire powder was performed by dipping tire powder in 0.1M H_2SO_4, 0.1M NaOH and hexane for 1 day. Then, the adsorption experiment was performed as previous section with optimum condition. Effect of pretreatment method of tire powder on percentage of oil removal was shown in figure 4.4.

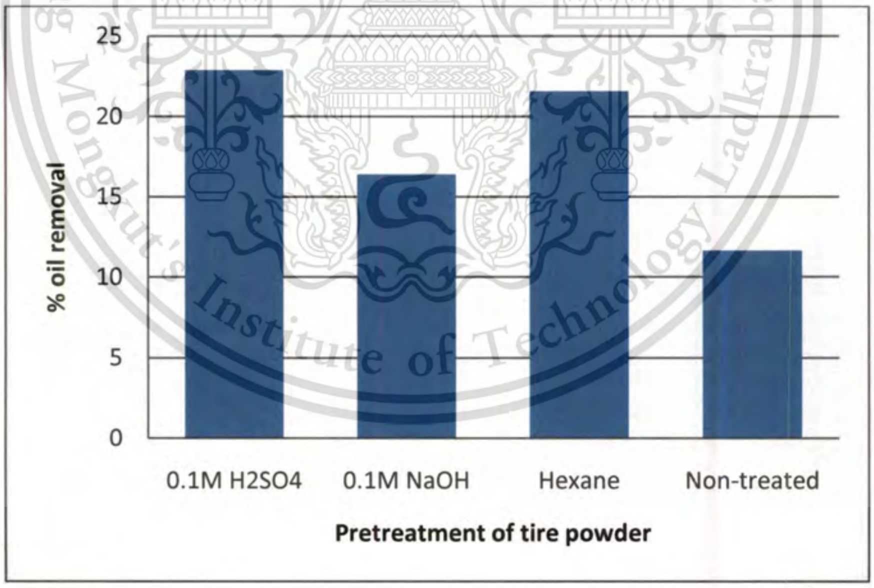
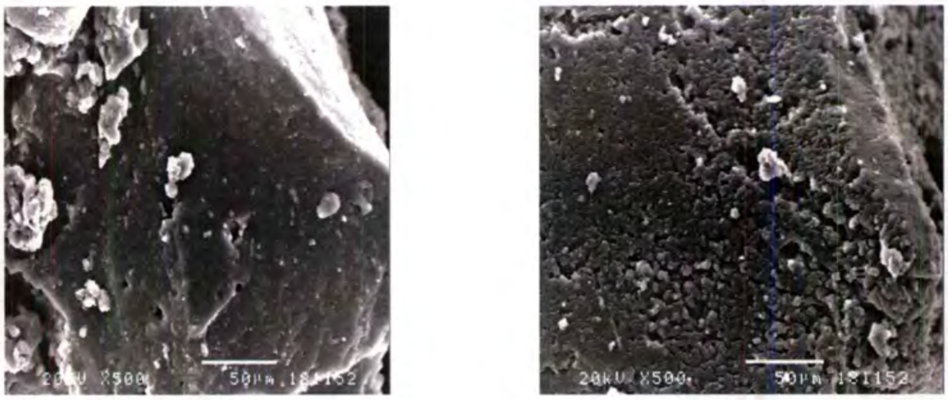


Figure 4.4 Percentage of oil removal by using different pretreatment methods of tire powder

Figure 4.4 compares the effects of different ways of waste tire powder pretreatment on the adsorption capacity. The results indicated that acid (0.1M H_2SO_4) and hexane cleaned waste tire powder had the best sorption capacity followed by base (0.1M NaOH) cleaned. However, the percentage of oil removal from all three pretreatment methods of tire powder was better than that of untreated tire powder.

Untreated waste tire powder was contained coke and some aqueous soluble impurities. Hexane can wash out a layer of brownish constituents to expose the hydrophobic surface of the rubber tire powder. Acid and base solution consisted of water as major composition then, water cannot wash out the brownish constituents, but it does wash out some hydrophilic impurities to allow the oil to pass more easily through the tire powder. In addition, acid and base components may increased the surface area of tire powder by its ion transferred from bulk solution to surface of tire powder, then acid or base ion reacted with tire surface to generated the porous surface as seen from the SEM micrographs in figure 4.5.

(a) (b)



(c) (d)

Figure 4.5 SEM micrographs of untreated and treated tire powder surface at 2000 magnification

(a) Untreated tire powder

(b) Tire powder cleaned by H_2SO_4

(c) Tire powder cleaned by NaOH

(d) Tire powder cleaned by hexane

It can be seen from SEM micrographs that after cleaning tire powder with H_2SO_4 and NaOH, the porosity of tire surface was developed while the number of small particles on the surface of hexane cleaned tire powder has been reduced.

4.3 Adsorption experiment with pretreated tire powder in various pH of oil solution

pH of oil solution adjustment was done to study the effect of removing the residue oil using pretreated tire powder. The effect of pH was conducted by adjusting the pH of oil solution from 3,7 and 9 and using the dosage of treated tire powder 1wt%, initial oil concentration of 20%v/v and mixing time 90 minutes. The results were shown in figure 4.6.

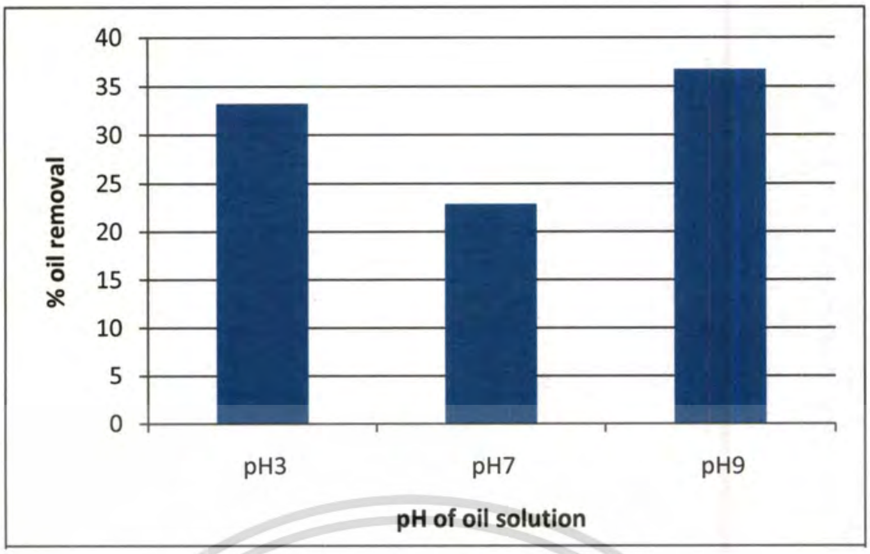


Figure 4.6 Effect of pH of oil solution on percentage of oil removal by H_2SO_4-cleaned tire powder

Figure 4.6 shows that H_2SO_4 cleaned tire powder has a good removal of residue oil at solution condition of pH 3 and pH 9. It can be suggested that after pretreatment of tire powder with H_2SO_4, the generation of pore rubber was basic occurred. Moreover, strong acidic and basic conditions of oil solution could be break long chain of triglycerides to short chains by hydrolysis reaction. From this reason, short chain oil can be easily adsorbed on external and internal surface of tire powder.

The interaction between surface of tire powder and oil molecule in case of acid-treated tire powder may be physical adsorption by interacting between polar active site generated from acid or base treated tire powder and the hydrolyzed residue oil.

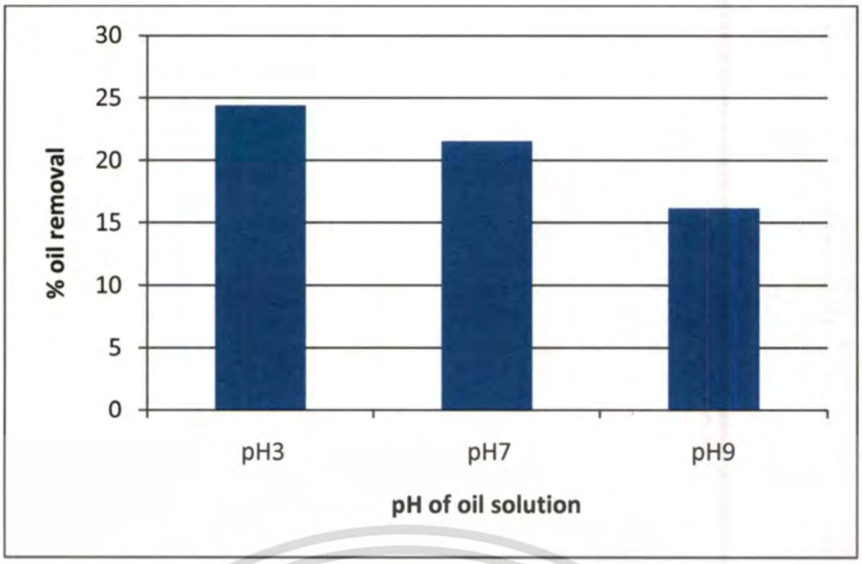
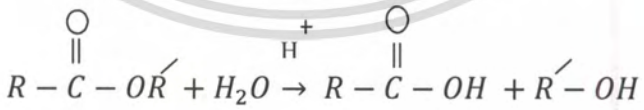


Figure 4.7 Effect of pH of oil solution on percentage of oil removal by hexane-cleaned tire powder

Figure 4.7 is also shown that hexane-cleaned tire powder has a higher removal of residual oil than untreated tire powder at pH 3 while at pH 9, hexane-cleaned tire powder has lower capacity for oil adsorption than untreated tire powder.

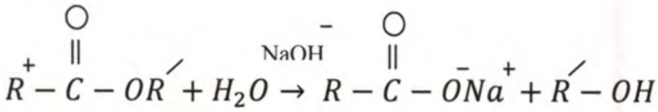
The hydrolysis of ester in acid and base solution were shown in the equation (4.1) and (4.2)

Acid solution:

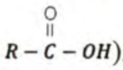


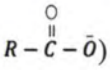
$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OR' + H_2O \xrightarrow{H^+} R - \overset{\overset{\displaystyle O}{\|}}{C} - OH + R' - OH \quad (4.1)$$

Base solution:



$$R^+ - \overset{\overset{\displaystyle O}{\|}}{C} - OR' + H_2O \xrightarrow{NaOH^-} R - \overset{\overset{\displaystyle O}{\|}}{C} - O^-Na^+ + R' - OH \quad (4.2)$$

The product from acid hydrolysis of oil was triglyceride that had carboxyl group in the molecule ( $R-\overset{\overset{O}{\|}}{C}-OH$). This molecule has strong polarity then, it can adsorbed on some polarity site of tire powder surface.

For basic hydrolysis of oil, the carboxylate salt of triglyceride was generated in the reaction. This molecule consisted on carboxylate ion ( $R-\overset{\overset{O}{\|}}{C}-\bar{O}$) and cation ($Na^+$). The adsorption of residue oil in basic medium was low because Na^+ barrier around solid tire powder was occurred then, carboxylate ion of triglyceride difficultly adsorbed on surface of adsorbent.

4.4 Determination of Iodine Number

Iodine number is a measure of the iodine absorbed in a given time by chemically unsaturated material, such as vegetable oil or rubber. The theory illustrates that the more the Iodine Number, the more the porosity or total surface area of absorbent.

Thus, this experiment that used waste tire powder as absorbent was performed, aimed to determine the porosity or total surface area of non-pretreated and three different pretreated tire powder. The experiment was carried out by using 1 gram of non-pretreated or three different pretreated tire powder immersed in 10 ml of 0.0952 N iodine solution titrate against 0.1026 N sodium thiosulfate.

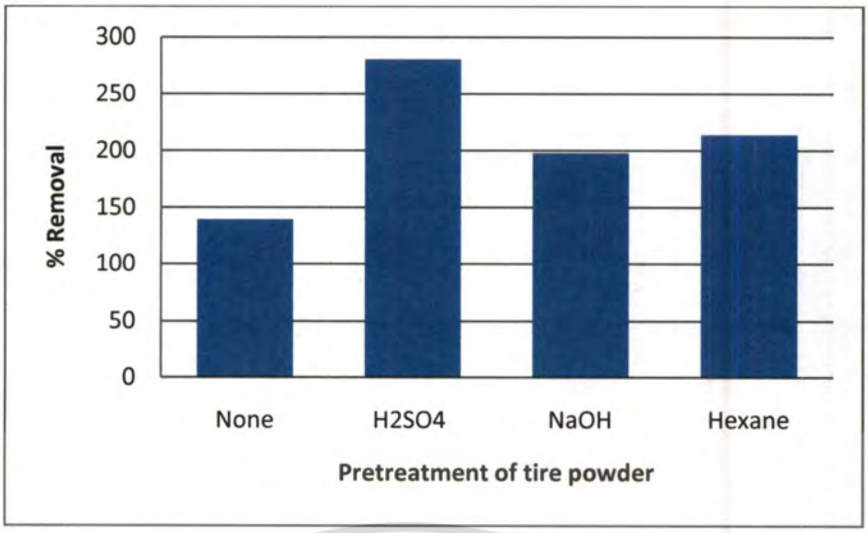


Figure 4.8 Determination of Iodine Number

Figure 4.8 compares the Iodine Number of non-pretreated and three different pretreated tire powder. The results indicated that acid (0.1M H_2SO_4) pretreated tire powder had the best Iodine Number followed by hexane pretreatment and the values of Iodine Number were 281.12% and 214.10% respectively. However, the efficiency increased of Iodine Number of all three pretreatment methods of tire powder were better than that of untreated tire powder. The efficiency increased of H_2SO_4 pretreated, hexane pretreated and NaOH pretreated tire powder compared to non-pretreated tire powder was 50.31%, 34.77% and 29.48% respectively.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The experiment was studied to determine the oil removal efficiency in synthetic oil-water mixture by using non-pretreated and pretreated waste tire powder. The adsorption experiment used was the batch equilibrium technique at room temperature.

5.1 Conclusion

- The oil removal efficiency was sharply increased within 90 minutes. When the adsorption time over 90 minutes, the percentage of oil removal remained constant, implying equilibrium has been reach. The optimum adsorption time for removal residue oil by using waste tire powder without pretreatment as absorbent is 90 minutes.

- The experimental results using four dosages of tire powder without pretreatment were 0.5, 1, 2 and 3wt%. About 28.07% of residue oil had been adsorbed with an addition of tire powder 3wt% while 11.65% of residue oil was removed by tire powder dosage of 1wt%. When compare the ratio of oil removal to tire powder dosage, at tire powder dosage of 1wt% of had the highest ratio of oil removal to tire powder dosage. It can be concluded that the suitable tire powder dosage for oil removal at this operating condition was 1wt%.

- The initial concentrations of residue oil were varied. When oil concentration was increased from 5% to 20%, the oil removal was dropped from 73.02% to 11.65%, after that the percentage of oil removal remained constant. The best condition for studying the effect of concentration of oil by using waste tire powder without pretreatment as absorbent was 0.5% of residue oil in synthetic oil-water mixture with 73.02% in oil removal.

- The section 4.2 (adsorption experiment with pretreated tire powder) and section 4.3 (adsorption experiment with pretreatment of tire powder in various pH solution) were study further to improve the adsorption capability of tire power in oil removal. Thus, to clearly observe the effect of pretreatment method of tire powder, the initial concentration oil was chosen at 20%v/v.

- There are three pretreatment methods were studied in this part including acid-cleaned, base-cleaned and organic solvent-cleaned. The results indicated that acid (0.1M H2SO4) and hexane cleaned waste tire powder had the best sorption capacity followed by base (0.1M NaOH) cleaned which were 22.92% and 21.60% respectively. However, the percentage of oil removal from all three pretreatment methods of tire powder was better than that of untreated tire powder.

- The effect of pH was conducted by adjusting the pH of oil solution from 3, 7 and 9. H2SO4 cleaned tire powder has a good removal of residue oil at solution condition of pH 3 and pH 9 which were 33.24% and 36.76% . Hexane-cleaned tire powder has a higher removal of residual oil than untreated tire powder at pH 3 while at pH 9, hexane-cleaned tire powder has lower capacity for oil adsorption than untreated tire powder.

- The determination of Iodine Number was done to determine the porosity or total surface area of non-pretreated and three different pretreated tire powder. The results indicated that acid (0.1M H_2SO_4) pretreated tire powder had the best Iodine Number which was 281.12.

5.2 Recommendation

1. Using MSDS of each solution was concerned in the experiment to prevent any accidents.
2. In this experiment, synthetic oil-water mixture was used thus, if this special project has longer time than this, the experiment with real oil residue in waste water should be performed.
3. We have to control all available and experimental method to more perfectly.

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Appendix A-1

Adsorption experimental data

For all adsorption experiments, the percentage of oil removal or removal efficiency is calculated by the equation below;

$$RE = \frac{C_i - C_f}{C_i} \times 100$$

Where RE is removal efficiency (%)

C_i is initial concentration of residue oil (g/mL)

C_f is final concentration of residue oil (g/mL)

A-1.1 Adsorption experiment without pretreatment of tire powder

Table A-1.1 Experimental data from the study about effect of adsorption time on oil removal

Tire powder dosage (%wt. tire powder in 100 ml mixture)	Concentration of oil (%vol.)	Adsorption time (min)	Average of initial concentration of oil (g)	Average of final concentration of oil (g)	Removal efficiency (%)
1	20	30	17.4530±0.0155	17.1557±0.0274	1.70
		60		16.6102±0.0514	4.83
		90		15.4190±0.0325	11.65
		120		15.3957±0.0678	11.75
		180		15.3918±0.0757	11.81
		240		15.3831±0.0698	11.86

Table A-1.2 Experimental data from the study about effect of tire powder dosage on oil removal

Tire powder dosage (%wt. tire powder in 100 ml mixture)	Concentration of oil (%vol.)	Adsorption time (min)	Average of initial concentration of oil (g)	Average of final concentration of oil (g)	Removal efficiency (%)
0.5	20	90	17.0538ฑ0.0245	16.4477ฑ0.0441	5.76
1			17.4530ฑ0.0155	15.4190ฑ0.0325	11.65
2			17.0538ฑ0.0245	14.7771ฑ0.0542	20.15
3			17.0538ฑ0.0335	12.2668ฑ0.0602	28.07

Table A-1.3 Experimental data from the study about effect of initial concentration of oil on oil removal

Tire powder dosage (%wt. tire powder in 100 ml mixture)	Concentration of oil (%vol.)	Adsorption time (min)	Average of initial concentration of oil (g)	Average of final concentration of oil (g)	Removal efficiency (%)
1	5	90	3.1827ฑ0.0456	0.8588ฑ0.0211	73.02
	10		6.3528ฑ0.0522	3.6497ฑ0.0623	42.55
	20		17.4530ฑ0.0155	15.4190ฑ0.0325	11.65
	30		25.7329ฑ0.0673	22.8858ฑ0.0787	11.06

A-1.2 Adsorption experiment with pretreated tire powder

Pretreatment methods of tire powder	Tire powder dosage (%wt. tire powder in 100 ml mixture)	Initial concentration of oil (%vol.)	Adsorption time (min)	Average of initial concentration of oil (g)	Average of final concentration of oil (g)	Removal efficiency (%)
0.1M H_2SO_4	1	20	90	16.3709ฑ0.0189	12.6190ฑ0.0581	22.92
0.1M NaOH					13.6818ฑ0.0223	16.42
Hexane					12.8351ฑ0.0551	21.60
Non-treated				17.4530ฑ0.0155	15.4190ฑ0.0325	11.65

A-1.3 Adsorption experiment with pretreatment of tire powder in various pH of oil solution

pH of solution	Pretreatment of tire powder	Tire powder dosage (%wt. tire powder in 100 ml mixture)	Initial concentration of oil (%vol.)	Adsorption time (min)	Average of initial concentration of oil (g)	Average of final concentration of oil (g)	Removal efficiency (%)
3	0.1M H_2SO_4	1	20	90	16.6822ฑ0.0235	11.1376ฑ0.0651	33.24
	Hexane				16.4707ฑ0.0221	12.4437ฑ0.0549	24.45
7	0.1M H_2SO_4				16.3709ฑ0.0437	12.6190ฑ0.0730	22.92
	Hexane				16.3709ฑ0.0256	12.8351ฑ0.0592	21.60
9	0.1M H_2SO_4				16.0583ฑ0.0328	10.1547ฑ0.0677	36.76
	Hexane				17.5888ฑ0.0387	14.7485ฑ0.0368	16.15

Appendix A-2

Determination of Iodine Number

A-2.1 Determine sodium thiosulfate ($Na_2S_2O_3$) normality

Run	Volume of $Na_2S_2O_3$ used (cm^3)
1	24.3
2	24.6
3	24.2
Average	24.37

$$N_1 = \frac{P \times R}{S}$$

Where N_1= Normality of Sodium thiosulfate ($Na_2S_2O_3$), N

P = Potassium iodate (KIO_3), mL

R = Normality of Potassium iodate (KIO_3), N

S = Sodium thiosulfate, mL

Example :

$$N_1 = \frac{25 \times 0.1}{24.37} = 0.1026\,N$$

A-2.2 Determine iodine solution normality

Run	Volume of $Na_2S_2O_3$ used (cm^3)
1	23.9
2	24.1
3	23.4
Average	23.8

$$N_2 = \frac{S \times N_1}{I}$$

Where N_2 = Normality of Iodine, N

S = Sodium thiosulfate ($Na_2S_2O_3$), mL

N_1 = Normality of Sodium thiosulfate ($Na_2S_2O_3$), N, and

I = Iodine, mL

Example :

$$N_2 = \frac{23.8 \times 0.1}{25} = 0.0952\, N$$

A-2.3 Determination of Iodine Number of tire powder

For all determination of Iodine Number, the equation is described below;

Iodine Number = $\frac{X}{m}D$

$$\frac{X}{m} = \frac{A - (2.2B \times mL\ of\ Na_2S_2O_3 used)}{wt.\ of\ absorbent\ (g)}$$

$$C = \frac{1}{2}\frac{N_2 \times mL\ of\ Na_2S_2O_3 used}{mL\ of\ filtrat}$$

Where $\frac{X}{m}$ = Milligram of iodine absorbed per gram of absorbent

N_1 = Normality of iodine solution

N_2 = Normality of $Na_2S_2O_3$ solution

A = $12693.0N_1$

B = $126.93N_2$

C = Residual filtrate normality

D = Correction factor

Example (To calculate the Iodine Number by using non-treated tire powder):

$$\frac{X}{m} = \frac{(0.0952 \times 12693) - (2.2 \times 0.1026 \times 126.93 \times 37.35)}{1} = 138.2722$$

$$C = \frac{1}{2}\frac{(0.1026 \times 37.35)}{10} = 0.190$$

Given D value in Correction Factor table, D = 1.0100

$$\therefore\ Iodine\ Number = \frac{X}{m}D = 138.2722 \times 1.0100 = 139.65$$

Table A-2.3.1 Determination of Iodine Number of non-pretreated and pretreated tire powder

Type of tire powder	Average of $Na_2S_2O_3$ used (mL)	$\frac{X}{m}$	C	D	Iodine Number	Efficiency increased (%)
None	37.35	138.2722	0.190	1.0100	139.65	-
H_2SO_4	32.65	272.9302	0.170	1.0300	281.12	50.32
NaOH	35.40	194.1410	0.180	1.0200	198.02	29.48
Hexane	34.85	209.8988	0.180	1.0200	214.10	34.77

Appendix A-3

Correction Factor

Residual Filtrate Normality,C	0.0000	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0009
0.0080	1.1625	1.1613	1.1600	1.1575	1.1550	1.1538	1.1513	1.1500	1.1475	1.1463
0.0090	1.1438	1.1425	1.1400	1.1375	1.1363	1.1350	1.1325	1.1300	1.1288	1.1275
0.0100	1.1250	1.1238	1.1225	1.1213	1.1200	1.1175	1.1163	1.1150	1.1138	1.1113
0.0110	1.1100	1.1088	1.1075	1.1063	1.1038	1.1025	1.1000	1.0988	1.0975	1.0963
0.0120	1.0950	1.0963	1.0925	1.0900	1.0888	1.0875	1.0630	1.0850	1.0838	1.0820
0.0130	1.0800	1.0788	1.0775	1.0763	1.0750	1.0738	1.0725	1.0713	1.0700	1.0688
0.0140	1.0675	1.0663	1.0650	1.0625	1.0613	1.0600	1.0588	1.0575	1.0563	1.0550
0.0150	1.0538	1.0525	1.0513	1.0500	1.0488	1.0475	1.0463	1.0450	1.0438	1.0425
0.0160	1.0413	1.0400	1.0388	1.0375	1.0375	1.0363	1.0350	1.0333	1.0325	1.0313
0.0170	1.0300	1.0288	1.0275	1.0263	1.0250	1.0245	1.0238	1.0225	1.0208	1.0200
0.0180	1.0200	1.0188	1.0175	1.0163	1.0150	1.0144	1.0138	1.0125	1.0125	1.0113
0.0190	1.0100	1.0088	1.0075	1.0075	1.0063	1.0050	1.0050	1.0038	1.0025	1.0025
0.0200	1.0013	1.0000	1.0000	0.9998	0.9975	0.9975	0.9963	0.9950	0.9950	0.9938
0.0210	0.9938	0.9925	0.9925	0.9913	0.9900	0.9900	0.9988	0.9875	0.9875	0.9863
0.0220	0.9863	0.9850	0.9850	0.9838	0.9825	0.9825	0.9813	0.9813	0.9800	0.9788
0.0230	0.9788	0.9775	0.9775	0.9763	0.9763	0.9750	0.9750	0.9738	0.9738	0.9725
0.0240	0.9725	0.9708	0.9700	0.9700	0.9688	0.9688	0.9675	0.9675	0.9663	0.9663
0.0250	0.9650	0.9650	0.9638	0.9638	0.9625	0.6925	0.9613	0.9613	0.9606	0.9600
0.0260	0.9600	0.9588	0.9588	0.9575	0.9575	0.9563	0.9563	0.9550	0.9550	0.9538
0.0270	0.9538	0.9525	0.9525	0.9519	0.9513	0.9513	0.9506	0.9500	0.9500	0.9488
0.0280	0.9488	0.9475	0.9475	0.9463	0.9463	0.9463	0.9450	0.9450	0.9438	0.9438

Correction Factor (Continues)

Residual Filtrate Normality,C	0.0000	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0009
0.0290	0.9425	0.9425	0.9425	0.9413	0.9413	0.9400	0.9400	0.9394	0.9388	0.9388
0.0300	0.9375	0.9375	0.9375	0.9363	0.9363	0.9363	0.9363	0.9375	0.9375	0.9375
0.0310	0.9333	0.9333	0.9325	0.9325	0.9325	0.9319	0.9313	0.933	0.9300	0.9300
0.0320	0.9300	0.9294	0.9288	0.9288	0.9280	0.9275	0.9275	0.9275	0.9270	0.9270

Appendix B

ASTM D4607-94

Standard Test Method for Determination of Iodine Number of Activated Carbon

1. Scope

1.1 This test method covers the determination of the relative activation level of unused or reactivated carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed (in milligrams) by 1gram of carbon using test conditions listed herein is called the iodine number.

1.2 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

C819	Test Method for Specific Surface Area of Carbon or Graphite
D1193	Specification for Reagent Water
D2652	Terminology Relating to Activated Carbon
D2867	Test Method for Moisture in Activated Carbon
D3860	Practices for Determination of Adsorptive Capacity of Carbon by Isotherm Technique
E11	Specification for Wire-Cloth Sieves for Testing Purposes
E177	Practice for Use for the Terms Precision and Bias in ASTM Test Methods
E287	Specification for Laboratory Glass Graduated Burets

E288 Specification for Laboratory Glass Volumetric Flasks

E300 Practice for Sampling Industrial Chemcials

2.2 NIST Publication:

Circular 602---Testing of Glass Volumetric Apparatus

3. Summary of Test Method

3.1 This test method is based upon a three-point adsorption isotherm. A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The carbon treated solutions are filtered to separate the carbon from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of oil removed per gram of carbon is determined for each and the resulting data used to plot. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02N is reported as the iodine number.

3.2 Iodine concentration in the standard solution affects the capacity of an activated carbon for iodine adsorption. Therefore, the normality of the standard iodine solution must be maintained at a constant value (0.100ฑ0.001N) for all iodine number measurements.

3.3 The apparatus required consists of various laboratory glassware used to prepare solutions and contact carbon with the standard iodine solution. Filtration and titration equipment are also required.

4. Significance and Use

4.1 The iodine number is a relative indicator of porosity in an activated carbon. It does not necessarily provide a measure of the carbon’s ability to absorb other species. Iodine number may be used as an approximation of surface area for some types of activated carbons. However, it must be realized that any relationship between surface area and iodine number cannot be generalized. It varies with changes in carbon raw material, processing conditions, and pore volume distribution.

4.2 The presence of adsorbed volatiles, sulfur, and water extractables may affect the measured iodine number of an activated carbon.

5. Apparatus

Note-All volumetric measuring equipment should meet or exceed the requirements of NIST Circular 602. Volumetric glassware meeting those specifications is generally designated as “Glass A”. See also Specifications E287 and E288.

5.1 Analytical Balance, accuracy ฑ0.0001g.

5.2 Buret, 10-mL capacity or 5-mL precision buret

5.3 Flasks, Erlenmeyer 250-mL capacity with ground glass stoppers.

5.4 Flask, Erlenmeyer wide-mouthed, 250-mL capacity.

5.5 Beakers, assorted sizes

5.6 Bottles, amber, for storage of iodine and thiosulfate solutions

5.7 Funnels, 100-mm top inside diameter.

5.8 Filter paper, 18.5-cm prefolded paper, Whatman No. 2V or equivalent.

5.9 Pipets, volumetric type, 5.0, 10.0, 25.0, 50.0 and 100.0-mL capacity.

5.10 Volumetric Flasks, 1L

5.11 Graduated Cylinders, 100-mL and 500-mL.

6. Reagents

6.1 Purity of Reagents---Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 Purity of Water---References to water shall be understood to mean reagent water conforming to Specification D1193 for Type II reagent water.

6.3 Hydrochloric Acid, concentrated.

6.4 Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)

6.5 Iodine, United States Pharmacopeia, resublimed crystals

6.6 Potassium Iodide

6.7 Potassium Iodate, primary standard

6.8 Starch, soluble potato or arrowroot.

6.9 Sodium Carbonate

7. Hazards

7.1 Several potential hazards are associated with conducting this test procedure. It is not the purpose of this standard to address all potential health and safety hazards encountered with its use. The user is responsible for establishing appropriate health and safety practices before use of this test procedure. Determine the applicability of federal and state regulations before attempting to use this test method.

7.2 Personnel conducting the iodine number procedure should be aware of potential safety and health hazards associated with the chemicals used in this procedure. The "Material Safety Data Sheet" (MSDS) for each reagent listed in Section 6 should be read and understood. Special precautions to be taken during use of each reagent are included on the "Material Safety Data Sheet" (MSDS). First aid procedures for contact with a chemical are also listed on its

“MSDS”. A “Material Safety Data Sheet” for each reagent may be obtained from the manufacturer. Other safety and health hazard information on reagents used in this procedure is available.

7.3 Careful handling and good laboratory technique should always be used when working with chemicals. Avoid contact with hydrochloric acid or acid vapor. Care should also be taken to prevent burns during heating of various solutions during this test procedure.

7.4 The user of this test method should comply with federal, state, and local regulations for safe disposal of all samples and reagents used.

8. Preparation of Solutions

8.1 Hydrochloric Acid Solution (5% by weight)--- Add 70ml of concentrated hydrochloric acid to 550ml of distilled water and mix well. A graduated cylinder may be used for measurement of volume.

8.2 Sodium Thiosulfate (0.100 N)--- Dissolve 24.820g sodium thiosulfate in approximately 75ฑ2.5mL of freshly boiled distilled water. Add 0.10ฑ0.01g of sodium carbonate to minimize bacterial decomposition of the thiofulfate solution. Quantitatively transfer the mixture to a 1-L volumetric flask and dilute to the mark. Allow the solution to stand at least 4 days before standardizing. The solution should be stored in an amber bottle.

8.3 Standard Iodine Solution (0.100ฑ0.001 N)--- Weigh 12.700g of iodine and 19.100g of potassium iodide (KI) into a beaker. Mix the dry iodine and potassium iodide. Add 2 to 5 mL of water to the beaker and stir well. Continue adding small increments of water (approximately 5 mL each) while stirring until the total volume is 50 to 60 mL. Allow the solution to stand a minimum of 4h to ensure that all crystals are thoroughly dissolved. Occasional stirring during this 4-h period will aid in the dissolution. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. It is important that the standard iodine solution has an iodide-iodine weight ratio of 1.5 to 1. Store the solution in an amber bottle.

8.4 Pottassium Iodate Solution (0.1000 N)--- Dry 4 or more grams of primary standard grade pottasium iodate (KIO_3) at 110ฑ5 °C for 2 hours and cool to room temperature in a desiccator. Dissolve 3.5667ฑ0.1mg of the dry potassium iodate in about 100-mL of disstilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Mix thoroughly and store in a glass-stoppered bottle.

8.5 Starch Solution--- Mix 1.0ฑ0.5g of starch with 5 to 10 mL of cold water to make a paste. Add an additional 25ฑ5 mL of water while stirring to the starch paste. Pour the mixture while stirring, into1 L of boiling water and boil for 4 to 5 min. This solution should be made fresh daily.

9. Standardization of Solutions

9.1 Standardization of 0.100 N Sodium Thiosulfate --- Pipet 25.0 mL of potassium iodate (KIO_3) solution from 8.4 into a 250 mL titration (or wide-mouthed Erlenmeyer) flask. Add 2.00ฑ0.01g of potassium iodide (KI) to the flask and shake the flask to dissolve the potassium Iiodide crystals. Pipet 5.0 mL of concentrated hydrochloric acid into the flask. Titrate the free iodine with sodium thiosulfate solution until a light yellow color is observed in the flask. Add a few drops of starch indicator (8.5) and continue the titration dropwise until one drop produces a colorless solution. Determine sodium thiosulfate normality as follows:

$$N_1 = \frac{(PR)}{S}$$

Where N_1 is sodium thiosulfate, N

P is potassium iodate, mL

R is potassium iodate, N

S is sodium thiosulfate, mL

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.001 N.

9.2 Standardization of 0.100ฑ0.001 N Iodine Solution---- Pipet 25.0 mL of iodine solution (8.3) into a 250-mL widemouthed Erlenmeyer flask. Titrate with standardized sodium thiosulfate (9.1) until the iodine solution is a light yellow color. Add a few drops of starch indicator and continue titration dropwise until one drop produces a colorless solution. Determine the iodine solution normality as follows:

$$N_2 = \frac{(SN_1)}{I}$$

Where N_2 is iodine, N

S is sodium thiosulfate, mL

I is iodine, mL

The titration step should be done in triphcate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.003 N. The iodine solution concentration must be 0.100ฑ0.001N. If this requirement is not met, repeat 8.3 and 9.2.

10. Procedure

10.1 The procedure applies to either powdered or granular activated carbon. When granular carbon is to be tested, grind a representative sample (see Practice E300) of carbon until 60 wt% (or more will pass through a 325-mesh screen) and 95wt% or more will pass through a 100-mesh screen (U.S. sieve series, see Specification E11). Carbon received in the powdered form may need additional grinding to meet the particle size requirement given above.

10.2 Dry the ground carbon from 10.1 in accordance with Test Method D2867. Cool the dry carbon to room temperature in a desicator.

10.3 Determination of iodine number requires an estimation of three carbon dosages. Section 11.4 describes how to estimate the carbon dosages to be used. After estimating carbon dosages, weigh three appropriate amounts of dry carbon to the nearest milligram. Transfer each weighed sample of carbon to a clean, dry 250-mL Erlenmeyer flask equipped with a ground glass stopper.

10.4 Pipet 10.0-mL of 5 wt % hydrochloric acid solution into each flask containing carbon. Stopper each flask and swirl gently until the carbon is completely welted. Loosen the stoppers to vent the flasks, place on a hot plate in a fume hood, and bring the contents to a boil. Allow to boil gently for 30ท2s to remove any sulfur which may interfere with the test results. Remove the flasks from the hot plate and cool to room temperature.

10.5 Pipet 100.0 mL of 0.100 N iodine solution into each flask. Standardize into iodine solution just prior to use. Stagger the addition of iodine to the three flasks so that no delays are encountered in handling. Immediately stopper the flasks and shake the contents vigorously for 30ท1s. Quickly filter each mixture by gravity through one sheet of folded filter paper (Whatman No.2V or equivalent) into a beaker. Filtration equipment must be prepared in advance so no delay is encountered in filtering the samples.

10.6 For each filtrate, use the first 20 to 30 mL to rinse a pipet. Discard the rinse portions. Use clean beakers to collect the remaining filtrates. Mix each filtrate by swirling the beaker and pipet 50.0 mL of each filtrate into a clean 250-mL Erlenmeyer flask. Titrate each filtrate with standardized 0.100N sodium thiosulfate solution until the solution is a pale yellow. Add 2 mL of the starch indicator solution and continue the titrtion with sodium thiosulfate until one drop produces a colorless solution. Record the volume of sodium thiosulfate used.

11. Calculation

11.1 The capacity of a carbon for any adsorbate is dependent upon the concentration of the adsorbate in solution. The concentrations of the standard iodine solution and filtrates must be specified or known. This is necessary to determine an appropriate carbon weight to produce final concentrations agreeing with the definition of iodine number. The amount of carbon sample to be used in the determination is governed by the activity of the carbon. If filtrate normality are not within the range of 0.08 N to 0.04 N, repeat the procedure using different carbon weights.

11.2 Two calculations are required for each carbon dosage, as X/M and C.

11.2.1 To calculate the value of X/M, first derive the following values:

$$A = (N_2)(12693.0)$$

$$B = (N_1)(126.93)$$

$$DF = \frac{(1 + H)}{F}$$

Where DF is dilution factor

H is 5% hydrochloric acid, mL

F is filtrate, mL

$$\frac{X}{M} = \frac{[A - (DF)(B)(S)]}{M}$$

Where $\frac{X}{M}$ is iodine absorbed per gram of carbon, mg/g

S is sodium thiosulfate, mL

M is carbon used, g

To calculate the value of C as follows:

$$C = \frac{N_1 S}{F}$$

Where C is residual filtrate, N

11.3 Using logarithmic paper, plot X/M (as the ordinate) versus C (as the abscissa) for each of the three carbon dosages (see Fig.1). Calculate the least squares fit for the three points and plot. The iodine number is the X/M value at a residual iodine concentration (C) of 0.02 N. The regression coefficient for the least squares fit should be greater than 0.995.

11.4 Carbon dosage may be estimated as follows:

$$M = \frac{[A - (DF)(C)(126.93)(50)]}{E}$$

Where M = carbon, g

A = (N2)(12693.0),

DF = dilution factor (see 11.2.1)

C = residual iodine, and

E = estimated iodine number of the carbon

Three carbon dosages are calculated using three values of C (usually 0.01, 0.02 and 0.03).

12. Report

12.1 The reports should include the following:

12.1.1 Complete identification of the sample, including source, manufacturer's lot number, and carbon type.

12.1.2 The iodine number adsorption isotherm, the iodine value with a 95% confidence limit for the determination.

13. Precision and Bins

13.1 Interlaboratory precision for this test method was determined by a round robin in which six laboratories participated. Activated carbon made from five different raw materials was used in the round robin.

13.2 The following criteria should be used in determining the acceptability of the results:

13.2.1 Repeatability (Within Laboratories)---- Precision of this test method in the determination of iodine number of activated carbons ranging from 600 to 1450 iodine number is ฑ5.6% of the average value measured in milligrams iodine absorbed per gram of carbon. This range corresponds to 2 S, or the 95% confidence limits, as defined in Practice E177. If two results determined in the same laboratory differ by more than 5.6%, they should be considered suspect.

13.2.2 Reproducibility (Between Laboratories)---- The between laboratory precision of this test method in the determination of iodine number of activated carbons ranging from 600 to 1450 iodine number, is ฑ10.2% of the average value, as measured in milligrams of iodine absorbed per gram of carbon. This range corresponds to 2 S or the 95% confidence limits. Results obtained by two different laboratories which differ by more than 10.2% should be considered suspect.