Treatment of Petroleum Contaminated Water Using Peat



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Abstract

The goal of this project was to investigate the ability of peat moss to remove crude oil from water. Because peat is an organic substance, it has been shown to absorb other organic substances, such as oil. This report will investigate peat's ability to absorb oil from oil-contaminated water. The absorption of crude oil was measured through various experiments. The data collected was then analyzed in order to design a full-scale treatment system.

The first goal of our MQP was to acquire an understanding of crude oil including: chemical composition, origin, and other important preliminary information. The second goal was to design, produce, and evaluate the efficiency of feasible and simple processes to separate crude oil from water using peat. Through experiments, these simple designs were evaluated. By experimenting with the purification of water containing any amount of crude oil, a simple system was designed that could help with both present and future oil spills.

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Background

Crude Oil

Crude oil, or petroleum in its natural state, is the unprocessed fossil fuel extracted from the ground. It is an oily, toxic, flammable, yellow-to-black liquid that forms naturally beneath the earth's surface. When an organism dies and is covered by silt and sands over long periods of time, the pressure and the heat from the surrounding environment turn the organism into oil and gas. Petroleum contains mixtures of hydrocarbons, which are organic compounds composed of only carbon and hydrogen. Petroleum can also contain some sulfur and nitrogen compounds (Viswanathan, 2006).

Crude Oil and the Environment

Oil is a naturally occurring substance that is located under the Earth's surface. Occasionally, the oil finds its way from its depth to the earth's crust, forming oil sands, oil shale, tar pits, and other forms of surface oil. These types of apparent oil are not harmful to the environment because they are rare, contained more, and located in a naturally occurring situation.

When there is an oil spill due to various circumstances, crude oil leaks into the surrounding environment, negatively affecting the ecosystem and most likely threatening the survival of the organisms in the surrounding environment. An oil spill can consist of a few hundred barrels of drilled and contained oil to over half a million gallons or more of uncontained and uncontrolled oil leakage. Each oil spill has its own implications depending on certain factors. Some of these factors include the type of oil that spilled, the location of the spill, the species of wildlife in the spill area, the timing of breeding cycles and seasonal migration of wildlife, and the

weather at the time of the spill (Australian Maritime Safety Authority, *The Effects of Oil on Wildlife*, 2010).

Once the oil spills into the environment, it makes contact with many things. The longer the oil remains uncontained, the more difficult it becomes to rid the spill site from the hazardous material. The wildlife in the affected areas is unable to avoid the oil spill and becomes coated with the oil. The fish may confuse the oil for food. Once any living creature digests oil, the health risks could lead to death. The birds feed in the water and end up covered in the oil. The oil on their bodies can cause them to drown because the oil prevents them from flying, or hypothermia due to the effect crude oil has on their feathers (Australian Maritime Safety Authority, *The Effects of Oil on Wildlife*, 2010).

Immediate contact with an oil spill is not the only danger in this type of situation. Oil spills become somewhat of a ripple effect. Oil can also affect next generations of animals; for instance, any consummation of wildlife that has been infected by the oil spill in some way can then pass on contamination to the next animal. Even the quantity of eggs hatched can be reduced. On the shoreline, oil spills are lethal to breading turtles. For example, because turtles breed on shorelines, oil spills are lethal to breading turtles and their offspring (Australian Maritime Safety Authority, *The Effects of Oil on Wildlife*, 2010).

Crude Oil & Health Hazards

Exposure to crude oil in the air can be toxic and hazardous to the human body. Some symptoms of exposure may include: breathing problems, headaches, nausea, dizziness, and brief confusion. A person with asthma or any respiratory problems may experience side effects of crude oil toxins just by brief exposure. Long-term effects may include respiratory damage, liver, blood, and kidney damage, along with immune and nervous system damage. Exposure to crude oil can also be the cause of cancer and birth defects. The extent of reaction toward the toxins depends on the conditions of exposure and any other unique factors. Children are at a higher risk of negative side effects along with pregnant woman and their babies (*Dispersants* 2004). In order to prevent exposure to these dangerous toxins one must be aware of unusual odors, pollution alerts, air pollution, oil-ridden sand, oil-ridden animals, and oil-ridden plants.

Types of Crude Oil Light Crude Oil:

Light crude oil is liquid petroleum that contains a low density and viscosity, along with a low specific gravity and high API gravity. API gravity is the measure of heavy petroleum liquid is compared to water. Lighter crude oil is worth a higher price than heavy crude oil because more fuel can be extracted at the refinery.

Heavy Crude Oil:

Heavy crude oil does not flow easily at room temperature and has a higher density and specific gravity than light crude oil. Heavy crude oil is usually a result of exposed crude oil that is exposed to bacteria, water, and air. These surface conditions cause the loss of its lighter fractions leaving only the heavy fractions remaining.

Sweet Crude Oil:

Crude oil, or petroleum, is considered sweet if its sulfuric content is below 0.5%. It also has traces of hydrogen sulfide and carbon dioxide within its composition. This type of crude oil is used for the production of gasoline and has a sweet aroma to it. To determine the quality of crude oil, testers would taste the oil to see if it was sweet or not. In any case, a lighter, sweeter crude oil would be the best conditions for production.

Sour Crude Oil:

Petroleum is considered sour if its sulfuric content is above 0.5%. It's quite frequent that crude oil will contain certain impurities that need to be extracted before it can be processed into fuel, but at a higher price. This is the reason why sour crude oil is most commonly processed into diesel and fuel oil instead of a lighter oil to maximize efficiency and profit. This type of oil can be very toxic if it is inhaled at a high concentration.

Crude Oil Constituents

Crude oil consists of several chemical elements that include carbon, nitrogen, sulfur, hydrogen, and oxygen along with other various metals. The chemical elements in crude oil are listed below:

Elements	Range (% Composition)
Carbon	83% - 87%
Hydrogen	10% - 14%
Nitrogen	0.1% - 2%
Oxygen	0.1% - 1.5%
Sulfur	0.5% - 6%

Table 1: Crude Oil Constituents (Grace 2007)

In its purest form, petroleum is only made up of crude oil. Crude oil contains six main elements. The order of greatest abundance of these six elements is: carbon, hydrogen, nitrogen, oxygen, sulfur, and various metals including: iron, nickel, copper, and vanadium. But in the form of common usage, it contains both crude oil and natural gas (both mainly consisting of hydrocarbons). There are four different types of hydrocarbons in crude oil; paraffins, aromatics, naphthenes, and asphaltics (Viswanathan, 2006).

Type	Average	Range (% Composition)
Paraffins (Alkanes)	30%	15% - 60%
Aromatics	15%	30% - 60%
Naphthenes (Cycloalkanes)	49%	3% - 30%
Asphaltics	6%	Remainder

Table 2: Elemental Composition of Crude Oil (Grace 2007)

The average amount of each hydrocarbon is displayed first, including Paraffins, Aromatics, Naphthenes, and Asphaltics. Along with that information is a range percentage that could be found in any petroleum product. Petroleum can also be found in medicines, solvents, fertilizers, plastics, and pesticides.

Petroleum is a mixture of hydrocarbons, whose most commonly found molecules are alkanes (also referred to as Paraffins). This molecule has straight or branched chains that are only made of carbon and hydrogen. They usually have from five to forty carbon atoms per molecule. Those molecules with four or less carbons are found in a gaseous state at room temperature. This gas can be liquefied under pressure and sold, used for the factory's energy, or just burned away. The cylcoalkanes have similar properties to the alkanes except for their boiling points (higher B.P. than alkanes). The aromatic hydrocarbons are unsaturated with one or more rings with six carbons that attach to hydrogen atoms. The different types of molecules can be discovered in a science lab by extracting them in a solvent, separated, and deciphered using the proper processes (Viswanathan, 2006).

A hydrocarbon is an organic compound containing only hydrogen and carbon molecules. Naturally occurring hydrocarbons are most commonly found in crude oil. These hydrocarbons form from decomposing organic matter where hydrogen and carbon are abundant (Viswanathan, 2006). Benzene (C_6H_6), is a colorless and sweet smelling liquid or vapor that is volatile and dissolves in water. Acute health risks of benzene include: vomiting, dizziness, and sleepiness. Chronic health risks associated with benzene include: bone marrow weakening, leukemia, and death (Centers for Disease Control 2010).

Figure 1: Benzene Chemical Structure



Taken from: http://csrchem2005.bootsglobal.com/main.asp?pid=684

Hydrogen sulfide (H_2S) is a poisonous, flammable, colorless gas that produces a smell comparable to rotten eggs. Acute health risks of hydrogen sulfide include: eye and throat irritation and loss of consciousness. Chronic health risks associated with hydrogen sulfide include: permanent headaches and impaired attention span, memory, or motor function (Centers for Disease Control 2010).





Taken from: http://www.chemeddl.org/alfresco/service/org/chemeddl/ttoc/ttoc_results/?id=27899&mode=primary&type=molecule&num_results=§ion=& sectitle=&guest=true

Ethylbenzene ($C_6H_5CH_2CH_3$) is a colorless fluid that is highly flammable and smells like gasoline. It is commonly found in coal tar and petroleum. Acute health risks associated with ethyl benzene include: irritation of the eyes and throat, dizziness, and vertigo (Centers for Disease Control 2010).





Taken from: http://www.kutztown.edu/acad/chem/instruments_html/nmr.htm

Toluene (C_7H_8) is a clear and colorless liquid or vapor that smells like gasoline. Toluene naturally occurs in crude oil. Acute health risks associated with toluene in low and moderate levels include: tiredness, confusion, weakness, impaired memory and motor control, nausea, loss of appetite, hearing and color vision. Acute health risks associated with high exposure to toluene can include: light-headedness, dizziness, unconsciousness, and fatalness. Chronic health risks associated with toluene include damage to the nervous system or kidneys (Centers for Disease Control 2010). **Figure 4: Toluene Chemical Structure**



Taken from: http://www.knowledgerush.com/kr/encyclopedia/Aromatic_hydrocarbon/

Xylene is a colorless and sweet-smelling liquid or vapor. It is extremely flammable and volatile. It occurs naturally in petroleum and coal tar. Acute health risks associated with high levels of xylene include: headaches, lack of coordination, dizziness, confusion, impaired balance, and irritation to the skin, eyes, nose, throat, and stomach. Exposure to very high levels of xylene can cause unconsciousness and death. Chronic health risks associated with exposure to xylene include: changes in the liver or kidneys, impaired reaction time, impaired concentration, and impaired memory (Centers for Disease Control 2010).

Figure 5: Xylene Chemical Structure



Taken from: http://syoknews.com/

Naphthalene is a colorless to white or brown solid or vapor that smells like mothballs. It is volatile and soluble in water. 1-Methylnaphthalene is a clear liquid and 2-Methylnaphthalene is a solid. Acute health risks associated with exposure to naphthalene include: vomiting, diarrhea, rashes. High exposure to naphthalene can be fatal. Chronic health risks associated with exposure to naphthalene include hemolytic anemia, which is a disorder of red blood cells. Symptoms of this anemia include fatigue, lack of appetite, restlessness, and pale skin (Centers for Disease Control 2010).

Figure 6: Naphthalene Chemical Structure



Taken from: http://www.aanda.org/index.php?option=com_article&access=standard&Itemid=129&url=/articles/aa/full/2005/47/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa3508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa508-05/aa

Generic alkanes (including octane, hexane, nonane) are colorless liquids or vapors that smell like gasoline. They are present in crude oil and petroleum products. They are highly flammable and volatile. Acute health risks associated with medium-sized alkanes include numbness in the feet and hands and muscle weakness in the feet and lower legs. Inhaling high levels of some alkanes can cause asphyxiation. Chronic health risks vary with the type of alkane and the duration of exposure (Centers for Disease Control 2010).

History of Oil Spills

With the production and distribution of crude oil, there comes a certain amount of risk in the transportation aspect. As many precautions that can be taken to make a safe and fault free delivery, there is always that slight chance that something unexpected and unavoidable can come up. In the past, there have been many instances where the worst occurs, and the crude oil spills out of the transport container and contaminated the surrounding environment. Some of these instances are described below.

For one example, on January 18th, 2000, 343,000 gallons of heavy oil spilled into Guanabara Bay, Rio de Janeiro, Brazil. The source of the spill was from a broken pipeline belonging to the Duque de Caxias refinery. The owner of the refinery was responsible for finding the proper groups to control the contamination of the environment. The environmental worry was for birds and the aquatic life. Despite the efforts of the groups involved in containing the spill, unfortunately, there were still casualties of marine wildlife such as different types of whales that washed up on the shore soon after the spill (Kirwan, 2000).

Another instance is the spill in Calcasieu River, Louisiana, where approximately 71,000 barrels (about 3,000,000 gallons) were spilled due to a strong storm on June 19th, 2006. It was

assumed that floating booms contained the oil spill, but something went wrong and the oil escaped into the Calcasieu River and into the Calcasieu Lake. It is estimated that 2.25 million gallons was contained, but 730,000 gallons did escape into the water causing serious contamination. Because of this, recreational and commercial marine traffic needed to be rerouted. Along with any oil spill, there comes a certain amount of wildlife casualties along with it (United States Department of Commerce, *Large Oil Spill in Calcasieu River*, 2006).

In Houston Texas, January 23, 2010, an oil tanker and a towing vessel crashed in the port of Port Arthur. The oil tanker was bound for Exxon Mobil Corp.'s Beaumont refinery and the towing vessel was carrying barges. It is reported that approximately 450,000 gallons of crude oil (about 11,000 barrels) spilled into the surrounding area. Luckily, the location of the crash was a heavy traffic area for marine vehicles and very little wildlife was polluted by the spill. In this instance, the oil contamination was contained before it could do any widespread damage. It did delay the traffic of about 150 barges and 15 tankers per day of clean up (Wall Street Journal, *Collision Causes Crude Oil Spill in Texas*, n.d.).

Cleaning Oil Spills

There have been various methods to clean up oil spills in the past. A common method of cleaning up oil spills is using dispersants. Dispersants act by reducing the surface tension between oil and water to stop them from mixing. This causes the formation of oil droplets, which are then rapidly diluted by water movements and consumed by naturally occurring bacteria. Dispersants are most effective when used within one or two hours after the spill. In the Cosco Busan oil spill of 2007, mushrooms and hair were used soak up the oil on top of the water. The mushrooms and hair were made from a mixture of organic material. Bacteria were also used to clean up oil spills. In a process called bioremediation, naturally present organisms living in the

ocean eat up the oil when it enters their natural habitat. If sulfate or nitrate is fed to the bacteria, they multiply up to five times the rate that they would without assistance. Skimmer equipment is also used to clean up oil spills from the water's surface. Skimmers float across the water surface and suck or scoop the oil into storage tanks on nearby vessels located on the shore. Burning oil is another method used to remove oil from the water surface and keep it away from the shoreline. In certain cases, if the oil has no possibility of the oil polluting the coastline, it is just left to break down by natural methods (wind, sun, currents, and waves) (CNBC.com, *17 Ways to Clean Up the Gulf Oil Spill*, n.d.).

Oil Spills in Developing Countries

There are about six million tons of crude oil is transported around the world on a daily basis. Although the majority of countries have some form of equipment stockpiles in the case that an oil spill occurs, there are still many countries (mostly developing) where there is a heavy reliance on local resources to clean up oil spills. Most vulnerable countries are those with no significant oil production, and in turn, little oil spill response infrastructure. While oil spills also occur in countries that produce and export oil, there is often poor oil spill cleanup equipment maintenance. Factors that contribute to the risk of oil spills in developing countries include: high traffic density, bad weather conditions, and navigational obstacles. The response of oil spills varies greatly in developing countries. Because of the cheap cost of labor, but the lack of capital, most laborers are hired for shoreline cleanup. This introduces the need for improved, and economical, technological methods to clean up the water surfaces (Wagstaff, 1999).

Peat Moss

Peat is a type of partially decomposed organic vegetable matter. Because peat is produced in the natural process of coal making, peat deposits possess the ability to change into coal deposits over time. Peat forms at a rate of an inch every 15 to 25 years, so the formation of peat is a relatively slow process. In order for the formation of peat to occur, environmental conditions must be cold and wet, and the soil must be acidic, lacking in oxygen, and lacking in nutrients. A large component of peat is moss, specifically Sphagnum moss. Other components include plant matter such as grasses and shrubs and decomposed animal matter. Peat can be found in bogs, swamps, and wetlands - mostly in the northern hemisphere. Peat covers about two percent of the land on earth. About two-thirds of the world's supply comes from Russia, and one quarter is found in Canada. About two-thirds of the world's wetlands are composed of peat, and about seven percent of that peat is used for agriculture (The Heart of New England, *What is Peat Moss?*, 2004).

Throughout history, peat has been used for many purposes from fuel to fertilizer. In Europe, peat was harvested for many uses. It was cut from bogs in "bricks", dried, and used both for insulation and burning for fuel and heat. Peat moss was also used as a wound dressing in both World War I and II due to its absorbent and antiseptic qualities. Peat's antiseptic properties are due to its acidity, which prevents the growth of bacteria and fungi. Another advantage of peat is that it can hold about twenty times its dry weight in water. This is why peat is used for fertilizer in certain areas. Peat can also be used for paper and pulp production and in packing products for shipments. Due to its low operation and maintenance requirements, peat has been used for wastewater treatment filtration processes since 1891 (The Heart of New England, *What is Peat Moss?*, 2004).

Methodology

Standard Curve

Before the experiments began we created a standard curve using Potassium Hydrogen Phthalate in order to measure the concentrations of crude oil in water in our experiments and express our results in COD rather than an absorbance reading. To create the curve we started by measuring out 425 mg of Potassium Hydrogen Phthalate and mixed it with 1000 ml of distilled water. We then diluted the sample by 50% each time to generate four standard solutions: 0, 125, 250, and 500 mg/L. 2.5 ml of each sample was placed in a test tube and digested in a heater block for two hours. An image of the digester has been provided below:



Figure 7: Digester

Once the heating concluded, the samples were cooled and then analyzed in the spectrophotometer. Using the results from these solutions a standard curve was then created plotting absorbance levels along the y-axis and COD levels along the x-axis. This standard curve was crucial for later results throughout this experiment. The standard curve allows us to find the COD levels of given solutions by measuring an absorbance level determined by the spectrophotometer and matching it to our curve.

COD / Absorbance Testing

A Chemical Oxygen Demand (COD) test is used to indirectly measure the amount of organic compounds in water. A strong chemical oxidant is used along with acid and heat to oxidize the organics. It also measures the amount of oxidant consumed in the breakdown of organic matter, which indirectly gives the amount of crude oil our samples (Droste, 1996).

The first step before any testing could begin was to create a mixture of oil and water that would be used as our solution for sample testing. To do so we mixed 500 ml of motor oil with 500 ml of distilled water. The mixture was placed on a mixing plate for 24 hours. Using this solution we were then able to begin removal using peat.

The next step in our experiment was to measure the amount of oil absorbed by mixing the solution with peat moss. We designed our experiment to test different ratios of peat-to-water in order to find the most efficient ratio to rid contamination from the water. We also recorded the amount of time used for mixing and use time as a variable in a second set of tests.

We next measured out different amounts of water and mixed them with one gram of peat. However, we needed a way to mix the oil and water completely. To ensure that the solution got completely mixed with the peat, we placed the mixture in a rotator that continuously rotated to make certain the contaminated water contacted with the peat. An image of the rotator is provided below:

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Figure 8: Rotator

Then, we extracted a sample of the solution that was previously mixed with the peat. A major concern of ours was being able to extract a sample without any trace of peat ending up in it. To eliminate any concern we will test blank samples of distilled water with peat so that in the end we can subtract the results of the blanks from the results of our samples. By doing so we will have eliminated (to our fullest potential) the amount of natural organic matter contamination brought upon by the mixing of peat.

Being that we rotated the solution in the peat for at least 2 hours, we needed to come up with a alternative to get the peat to settle within the solution. We solved this problem by using a centrifuge that rotated our samples at 2500 rpm and forced all the peat to settle to the bottom of the vial. Doing this made it easy to use a pipette and allowed us to obtain a clear sample of solution that we needed for testing. An image of the centrifuge is provided below:



Figure 9: Centrifuge

Using a pipette we will extract different amounts of solution and diluted each sample by 90% so that our results would be visible on our standard curve. This was achieved by mixing distilled water with our extracted solution. Once the diluting process concludes the next step will be to extract 2.5 ml of each solution, including the blanks with distilled water and peat, and place them in 20-900 mg. COD/L range test tubes to be digested in the digester for 2 hours. The samples are heated for 2 hours on a timer at 150°F. Following the 2 hours of digestion, we allowed the samples to cool before transferring them to a cuvette. Once this step was completed, we were able to test our samples using a spectrophotometer.

In our experiments we used a spectrophotometer to get absorbance readouts. The spectrophotometer functions by sending a laser beam through a sample, which is then reflected back to give a measure of the amount of dissolved constituent. The spectrophotometer measures the amount of absorbed light passing through the sample. Before testing any of the samples we set the wavelength of the spectrophotometer to 600 nm and using a procedural blank, zeroed the absorbance reading. The value calculated is expressed in abs (absorbance). Using our standard curve we generated COD values using the absorbance readings of our samples that were produced by the spectrophotometer. Below is an image of the spectrophotometer:



Figure 10: Spectrophotometer

To summarize the methodology of the experiment, a flow chart is displayed that contains the procedural steps outlined throughout this section. After the completion of the experimental procedure, we then collected and analyzed the data in order to produce a clear and accurate conclusion.



Figure 11: Summarized Experimental Procedure

Results and Discussion

Standard Curve

Table 3, shown below, contains the absorbance readings of potassium hydrogen phalate that was used to create our standard curve. The standard curve is used to convert our absorbance readings of experimental samples into COD readings.

COD (mg/L)	Absorbance (cm ⁻¹)
0	0.0001
125	0.0466
250	0.0726
500	0.1466

Table 3: Dilution for Standard Curve

Using the data displayed in the table above, a standard curve was then constructed and a linear regression performed. Each point on the standard curve graph, Figure 12, represents a COD value correlating with the absorption factor after fifty percent dilution. The orange line shows how we found the COD value from the absorbance reading. By locating given absorbance levels on the y-axis and connecting them to the line of best fit, we were able to determine a corresponding COD level.



Figure 12: Standard Curve: Absorbance vs. COD

Initial COD

After completing our graph for our standard curve, we created a batch of oil contaminated water. After digesting a sample of the contaminated water we then used the spectrophotometer to provide us with an initial absorbance value. Using the same sample we took four absorption readings and found an average. The average absorbance was calculated to be 0.1787 (abs).

After reviewing our data we concluded that our average absorbance reading was too large to fit on our standard curve. Due to this we were then forced to dilute our sample 90 percent to place the result on the standard curve. This absorbance value of our sample after dilution was calculated to be .0957. From this absorption value we were able to draw a line connecting this point to a corresponding COD value. We discovered that the initial actual COD value of our contaminant was 3050 mg/L.

COD Testing: Water to Peat Ratios

In the next table, Table 4, you will notice different water to peat ratios that we used in our experiments. The purpose behind this approach was to be able to identify a reliable and efficient ratio of water to peat in order to absorb the largest amount of contaminate. We decided to keep

the amount of peat used in our experiments constant at 1 gram so that water would remain our only variable needing to be altered. In Table 4, the experimental absorption column is divided into two columns: distilled water with peat and contaminated water mixed with peat. For experimental purposes we diluted the oil contaminated water ninety percent in order to graph our results. The purpose behind testing distilled water and contaminated water and finding the difference between them was to determine the amount of contamination the peat itself was causing. The actual absorbance displays the difference between the distilled water mixed with peat and the contaminated water mixed with peat. After calculating the difference we were able to generate COD values for each experimental ratio.

Peat (g)	Oil/Water (ml)	Ratio	Experimental Abs.		Actual Abs.	COD (90%	Actual COD
						Dilution)	
			Distilled Water + Peat	Cont. Water (90% dilution) + Peat			
1	2	1:2	0.1609	0.2520	0.0911	300	3000
1	3	1:3	0.1530	0.2141	0.0611	200	2000
1	4	1:4	0.2576	0.0386	-0.2190	N/A	N/A

Table 4: COD Readings for Peat to Contaminated Water Ratios

Our most successful ratio came out to be one gram of peat for every three ml of oilcontaminated water. The 1:2 ratio proved to be successful having a COD value lower than the initial COD of the contaminated water. We believe that the 1:2 ratio was the most successful because there was less oil-contaminated water and less peat. With more peat, there is a greater risk of natural organic matter being released from the peat. Comparably, with a larger volume of water, the risk of the natural organic matter floating around the water is greater. This is why we believe that the 1:4 ratio provided negative absorbance results. The negative absorbance value could also be caused by an insufficient amount of peat, so the sample was still fairly contaminated. In order to graphically represent our results the graph below represents the different experimental ratios that were provided in the previous table, Table 4.



Figure 13: COD Results: Peat-to-Water Ratio Testing

Figure 13, above, is the standard curve results from of the peat-to-water ratio testing. The blue line represents the 1:2 peat-to-water ratio and the green line represents the 1:3 peat-to-water ratio. The 1:4 peat-to-water ratio provided a negative result which is the reason that there is not a line on the graph to represent it.

COD Testing: Time as a Variable

The next step in our experiment was to investigate the effect time had on the results. To do so, four samples were mixed in the rotator, each for a different amount of time. Each sample

contained the same amount of contaminated water and peat but was mixed for different durations of time. We analyzed the data to provide an optimal contact time for peat and contaminated water to mix. The following table displays the results:

Time (hr)	Abs	COD (90% Dilution)	Actual COD
2	0.0123	30	300
4	0.0149	35	350
8	0.0294	90	900
24	0.0724	230	2300

Table 5: COD Readings for Time Variations

Based on this information, the longer the oil-contaminated water was mixed with peat, the greater the contamination. This is due to natural organic matter that was released from peat into the water. We also found that the difference in COD levels between mixing the samples for two hours and four hours was very small. One can see that there are major differences in the COD levels between mixing for two hours and twenty-four hours.

Conclusions and Recommendations

In this project we explored the ability of peat moss to extract crude oil from contaminated water. Peat moss is a relatively cheap and an abundant material to think about when considering absorbance. To explore the ability peat has in absorbing contaminants in water; an experiment was designed to mix peat with the oil-contaminated water in order to get a COD reading similar to that of distilled water. From our experiments, we concluded that the 1:3 ratio, of peat most to mL distilled water, showed the most promising results with an approximate COD reading of 200 mg/L. The 1:4 ratio resulted in a negative absorbance level based on the calculations mentioned previous to Table 4. We also concluded that mixing the samples of contaminated water with peat between two and four hours produced the most appropriate COD for this experiment.

For future experiments using peat, we first recommend the development of an analytical method that separates the natural organic matter that is released from the peat into the petroleum. This will allow for more a more accurate measurement of the ability of peat the absorb oil from oil-contaminated water. Next, based on our results, we recommend less mixing time of peat and contaminated water. Lastly, we recommend a comparison of peat moss with other effective oil absorbents. These include the various methods of oil spill clean ups mentioned previously such as mushrooms and hair and dispersants.

Capstone Design

The treatment system we are designing must handle 100 gallons per minute (GPM). There is one main water line used in this design that enables influent-contaminated water to flow into a grit chamber. From there, the influent water flows through a primary clarifier into trickling filters. After the trickling filters, the water travels into an aeration tanks. The water is then pumped once again through a clarifier prior to contacting peat. The total amount of peat needed to treat contaminated water in a system this size is 400, 580 pounds of peat per day (See Appendix 2 for calculations). This value represents the amount of peat needed if this system were to treat oil-contaminated water 24 hours a day. The treated water then flows into a holding tank. The size of the settling tanks could be anywhere from 3,000-4,500 gallons depending on the given system and available space. Our system is also equipped with all the necessary components for operation including transfer pumps, hoses and fittings, and distribution headers.

To complete all aspects of the Major Qualifying Project, a capstone design was applied to the project. The capstone design description was based off of previously learned material in the classroom and relative engineering standards. Also integrated were realistic stipulations such as; economic, environmental, sustainability, constructability, ethicality, health and safety, social, and political. The descriptions of how each one applies are discussed below.

The first stipulation is economics. When applying this theory of decontamination, cost is a factor to be examined. Peat is a relatively cheap resource to use for the purpose of absorbing contamination in polluted water. Since contact time is a factor to consider, the longer the necessary contact time, the more peat needed and the higher the cost will climb. Also the size of the contaminated area contributes to the required amount of peat used. The more peat used, the greater the cost.

The second concern is constructability. In this project, a process of decontamination needed to be created. A design was necessary for contacting peat with contaminated water, the extraction process of water samples, and the output of the disinfected water. The size of the design process depends on the location and conditions of the polluted area.

Another factor to consider is health and safety. In terms of health risks, to leave an oil spill uncontained would cause obvious concerns for the wildlife in the surrounding areas and the human population if the contamination reached any type of water supply. Safety control is just as important for anyone involved in the decontamination process. It is important that when any organization is in control of cleaning a spill that they themselves do not get infected from the pollution.

Lastly, sustainability is incorporated into the design of the project. To keep the cleansing process continuous, the peat being used needs to be switched out with fresh peat. The design requires the upkeep of manual labor or the design of an automatic process of switching utilized peat with a fresh batch of peat. Eventually the process should reach a point where it has done as much as it can and can be shut down until the next instance where it is necessary.

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Appendices

Appendix 1: COD Procedure

- 1. Preheat the COD heater block to 150 degrees Celsius. (Dod not use oven)
- 2. Remove the cap from a COD twist-cap vial.
- 3. Carefully add 2.5 ml of sample into the vial.
- 4. Twist the cap.
- 5. Thoroughly mix the contents of the sealed vial by shaking
- 6. Process standards and blanks exactly as the samples
- Place the twist-cap vial in a COD heater block capable of maintaining 150 degrees +/- 2 degrees for 2 hours
- 8. Remove the vial from the heater block and allow to cool.
- 9. Allow any suspended precipitate to settle
- 10. Method A: Standard Range reagent (20-900 mg/l COD)
 - Set the wavelength of the spectrophotometer to 600 nm, and, using a procedural blank, zero the absorbance reading.
 - 2. Read and record the absorbance of the standard and sample on the spectrophotometer.

Appendix 2: Peat Calculations & System Diagram

- 1. 100 gallons per min = 378,541.178 ml per min
- 2. 378,541.178 * 60 min/hour * 2 hour mixing time = 45,424,941.36 ml/min (2 hours)
- 3. 45,424,941.36 / 3 (1:3 ratio) = 15,141,647.12 grams of peat needed every two hours
- **4.** 15,141,647.12 grams per 2 hours * 12 ==181,699,765.4 grams of peat per day
- 5. Grand total of peat needed per day = 400, 580 pounds of peat/day

