RESEARCH PLAN

PURIFYING OIL-CONTAMINATED WATER

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PURIFYING OIL-CONTAMINATED WATER

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ABSTRACT

Regretfully, the world continues to pump underground oil for heating, transportation, and petrochemicals without regard to the extensive environmental damage being caused. This damage includes our drinking water. Still ongoing is the U.S. Navy spill of jet fuel into the drinking water in Hawai'i [ref.1]. Nigeria has extensive oil-contamination in their drinking water, [ref.2], which has resulted in many serious health problems.

This study identifies a simple way to purify water from oil contaminants. Bentonite clay is used to purify water contaminated with actual samples of crude oil. First, samples of distilled water are contaminated with the crude oil and the initial "time-zero" concentration of oil contamination of each is documented. Then laboratory-grade powdered Bentonite clay is added to each sample and the samples are stirred frequently. At the times of 1 hour, 2 hours, 3 hours, etc., one sample is filtered to remove the Bentonite clay and the oil it has adsorbed on its surface, before documenting the concentration of the remaining oil in the water. This purification process is documented hourly, and graphed, to show the reduction of oil concentration versus time.

This study proved that Bentonite clay is effective as a decontaminant of oil-contaminated water.

INTRODUCTION

From [ref.2], oil can cause many extensive health problems. "Petroleum products are a complex mixture of hydrocarbons, consisting of both aromatic and long- and short-chain aliphatic hydrocarbons. Components of crude and refined petroleum, namely volatile organic compounds (VOCs), such as benzene, toluene and xylenes, and polycyclic aromatic hydrocarbons (PAHs), have independently been associated with adverse human health effects. Acute exposures to high concentrations of VOCs cause central nervous system toxicity, resulting in symptoms such as headaches, fatigue and dizziness. Chronic exposure to VOCs can impair the immune system via oxidative stress and decreases in white blood cell count. Benzene in particular is strongly associated with disorders of the hematopoietic system such as aplastic anemia. Benzene is also classified as a known human carcinogen based on occupational studies in humans. Polycyclic aromatic hydrocarbons cause symptoms such as nausea, vomiting and skin and eye irritation following acute, high-level exposures. Exposures to PAHs during pregnancy have been linked to decreased birth weight and impaired development in off- spring. Chronic occupational exposures are associated with dose-dependent increased risks of certain types of cancers, including lung, skin and bladder cancer. Naphthalene, a low molecular weight PAH that was detected in Ogale water samples, can adversely affect the hematopoietic system, damaging and killing red blood cells, causing symptoms such as shortness of breath and fatigue. Alkylated PAHs comprise the majority of PAHs detected in petroleum products and are particularly persistent. Although the health effects of alkylated PAHs have not been well studied, limited evidence suggests that they may be more toxic and carcinogenic than their parent PAH compounds."

Thus, there is an urgent need to decontaminate oil-contaminated water.

PROBLEM

The problem is to identify a safe method of decontaminating water from contaminated oil. This is very much needed by the Navajo Nation as our water has been contaminated with oil, [ref.3]. Another example: it's not clear why the water line broke on a Sunday in February 2019, [ref.4] but by the time someone noticed and stopped the leak, more than 1,400 barrels of fracking slurry mixed with crude oil had drained off the wellsite owned by Enduring Resources and into a snow-filled wash. From there, that slurry – nearly 59,000 gallons – flowed more than a mile downstream toward Chaco Culture national historical park before leaching into the stream bed over the next few days and disappearing from view. The rolling, high-desert landscape where this happened is Navajo Nation off-reservation trust land, in rural Sandoval county, New Mexico. Neighbors are few and far between, and they didn't notice the spill. The extra truck traffic of the cleanup work blended in with the oil and gas drilling operations along the dirt roads in that part of the county. Then three days after the spill, something ignited and exploded 2,100 feet away on another wellsite owned by Enduring Resources, starting a fire that took local firefighters more than an hour to put out. The two accidents account for just 1% of oil- and gas-related incidents in north-western New Mexico in 2019, according to statistics kept by the New Mexico oil conservation division (OCD). Since those two, there have been another 317 accidents in the region as of 29 March, including oil spills, fires, blowouts and gas releases. There were 3,600 oil and gas spills over the previous decade, both smaller and larger. In both cases in February 2019, the people living closest to the accident sites were among the last to know what happened.

HYPOTHESIS

Can oil which is contaminating water be removed with safely, with powdered Bentonite clay?

VARIABLES

The variables in my experiment are:

- Oil contamination, measured in either (a) parts per million, (b) absorbance "A" percentage, or (c) retardation factor "Rf"
- Laboratory-Grade Powdered Bentonite Clay ($Al_2H_2Na_2O_{13}Si_4$)
- Crude Oil: 35-40 API (light crude) Light Sweet Naphthenic Azeri Crude Oil and/or Below 20 API (heavy crude) Heavy Aromatic-Naphthenic Azeri Crude Oil
- Distilled Water
- Duration in time of application of Bentonite Clay to the contaminated water
- Water Temperature

BACKGROUND RESEARCH

There are many sources of oil contamination, Figure 1, [ref.5]. It is my goal to find a solution to the removal of oil contamination from our drinking water.

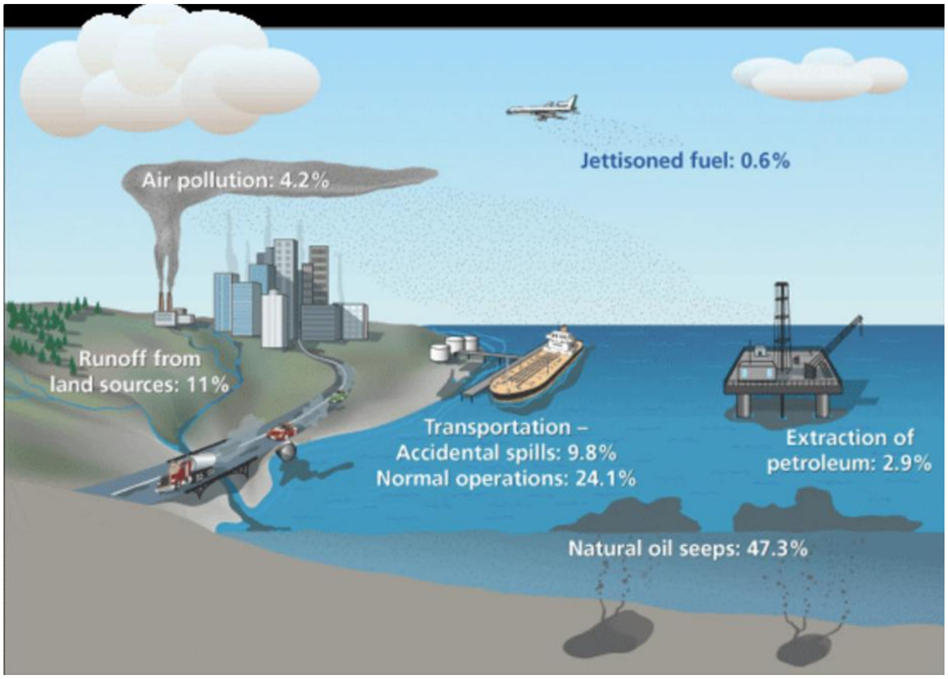


Figure 1. Sources of Oil Contamination [ref.5]

MATERIALS AND EQUIPMENT

The following are the materials and equipment and experimental procedures used.

- Distilled Water
- Crude Oil: 35-40 API (light crude) Light Sweet Naphthenic Azeri Crude Oil and/or Below 20 API (heavy crude) Heavy Aromatic-Naphthenic Azeri Crude Oil
- Laboratory-Grade Powdered Bentonite Clay
- Beakers, Stir Rods
- Optional surfactant (a phosphate) to help oil and water mix
- Unico S2150 UV/Vis Spectrophotometer
- Paper Chromatography or Thin-Film Chromatography (UV Light Required)

EXPERIMENTAL PROCEDURES – Stir Method

A. Mix crude oil samples into distilled water. Use a surfactant, if necessary, to help oil and water mix together. A phosphate might be a good choice for a surfactant, followed by a sulfate as a possible second choice.

B. Measure the initial concentration of oil in the distilled water. Use either the Unico S2150 UV/Vis Spectrophotometer to measure absorbance "A" versus wavelength from 190nm to 1100nm, or use Paper Chromatography or Thin-Film Chromatography to measure the retardation factor, Rf.

C. Add laboratory-grade powdered Bentonite clay to the contaminated water. Stir frequently.

D. After 1 hour, filter a sample of contaminated water to remove the Bentonite clay particles and the attached oil.

E. Measure the concentration of oil in this treated sample. Use either the Unico S2150 UV/Vis Spectrophotometer to measure absorbance "A" versus wavelength or use Paper Chromatography or Thin-Film Chromatography to measure the retardation factor.

F. Repeat steps D and E hourly, to be able to graph the purification of water versus time.

G. If the Unico S2150 Spectrophotometer is used, apply the Beer-Lambert law $A = \varepsilon LC$ to derive the ratio of the concentrations "C/C_initial" versus time. L is the dimension of the cuvette, which is 1 cm and a constant for all measurements. For a specific wavelength, ε is a constant. Thus, C/C_initial = A/A_initial, namely the ratio of the concentrations is the ratio of the absorbances A, for a given wavelength.

EXPERIMENTAL PROCEDURES – Funnel Method

Same as above "stir method" except Steps C and D replaced by putting Bentonite in a Funnel and gently pouring the oil-contaminated water into the funnel, to be filtered by the Bentonite. Then measure the filtrate (liquid passing through the Bentonite) with either chromatography or the Unico Spectrophotometer. That is trial-1. Starting with a fresh funnel and fresh Bentonite, pass the previous filtrate through the new funnel and measure the new filtrate with either chromatography or the Unico Spectrophotometer. That is trial-2. You keep passing the liquid filtrate through fresh Bentonite, to keep purifying it, for trials n, n+1, n+2, etc. The advantage to this funnel method is that you can cycle through your trials more quickly (hopefully) than the one-hour-per-trial for the stir method. You would need a large sample of oil-contaminated water, as each fresh Bentonite would absorb some water.

DATA, DIAGRAMS, AND OBSERVATIONS

The following figures are illustrative of the experimental procedure that was followed.

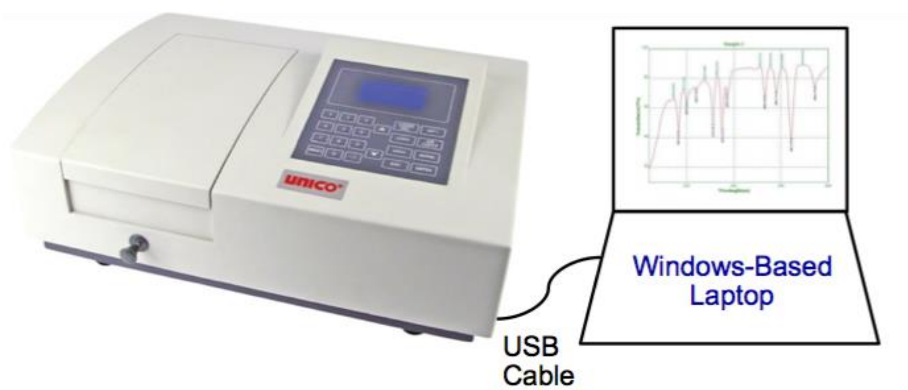


Figure 2. Unico S-2150 UV/VIS Spectrophotometer and Laptop

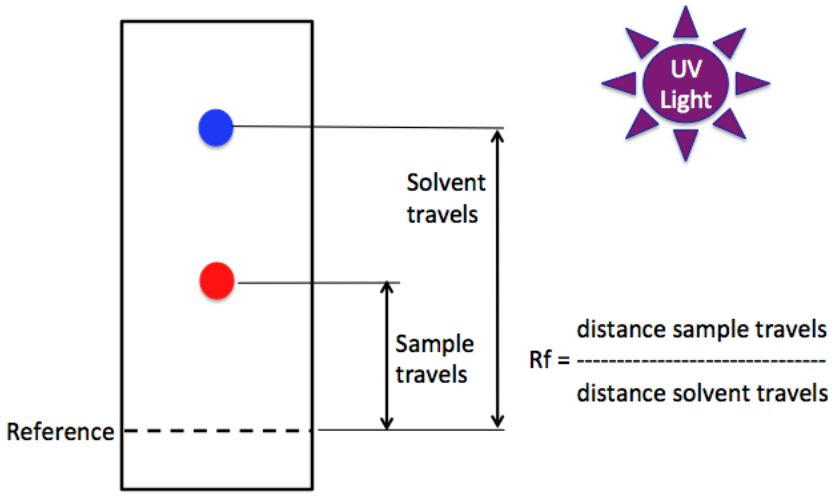
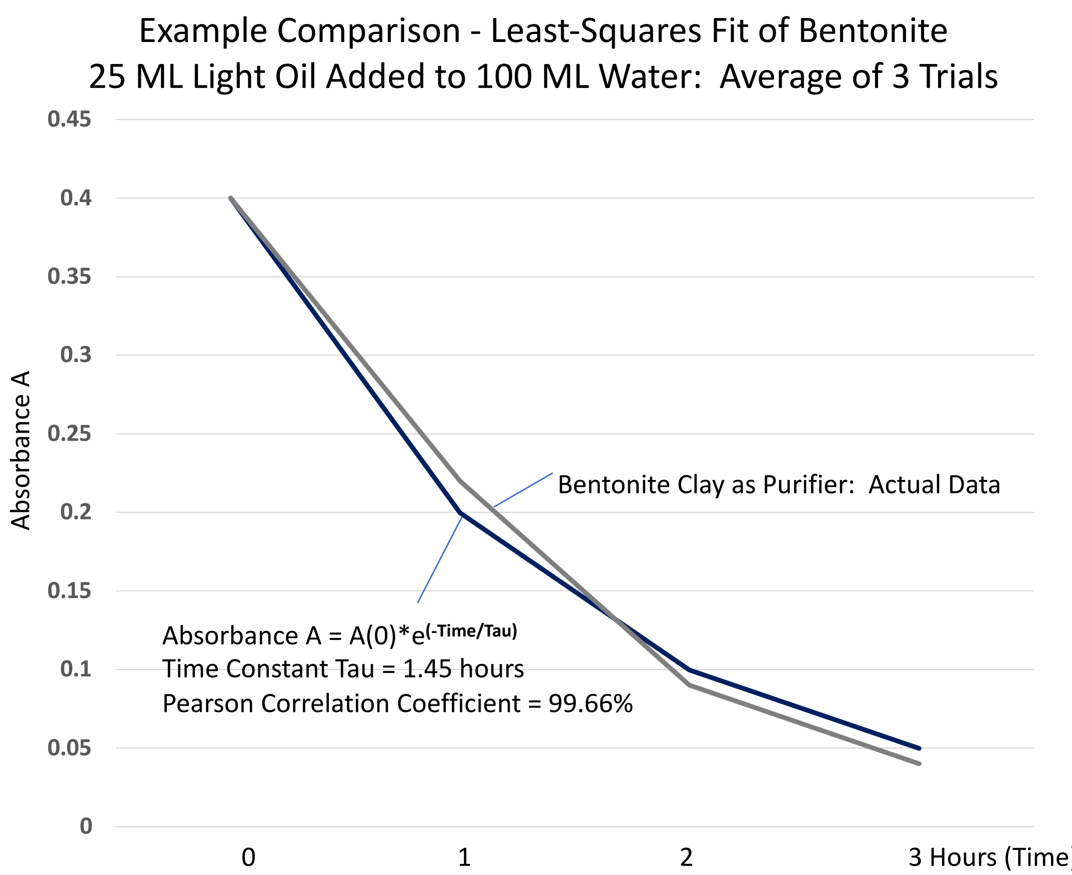


Figure 3. Retardation Factor Rf for Liquid Chromatography



Least-Squares Fit Summary Tables

Oil Absorbent 25 ml Light Oil	Time Constant Tau (hours)	3 hours / Tau (Unitless)	1 - $e^{(-3/Tau)}$	Pearson Correlation Coefficient
Sand	1.22 hours	2.46	91.4%	99.51%
Bentonite	1.45 hours	2.07	87.4%	99.67%
Kaolinite	1.46 hours	2.05	87.2%	92.97%
Illite	0.71 hours	4.23	98.5%	98.79%

Oil Absorbent 50 ml Light Oil	Time Constant Tau (hours)	3 hours / Tau (Unitless)	1 - $e^{(-3/Tau)}$	Pearson Correlation Coefficient
Sand	0.81 hours	3.70	97.5%	97.38%
Bentonite	1.08 hours	2.78	93.8%	85.13%
Kaolinite	0.65 hours	4.62	99.0%	94.83%
Illite	0.49 hours	6.12	99.8%	97.94%

Oil Absorbent 25 ml Heavy Oil	Time Constant Tau (hours)	3 hours / Tau (Unitless)	1 - $e^{(-3/Tau)}$	Pearson Correlation Coefficient
Sand	0.49 hours	6.12	99.8%	89.32%
Bentonite	1.03 hours	2.91	94.6%	83.98%
Kaolinite	2.00 hours	1.5	77.7%	94.92%
Illite	0.69 hours	4.35	98.7%	98.26%

Discussion of Least-Squares Fit Summary Tables

Column 1 shows the oil type (light or heavy) and volume (ml), as well as the absorbent. Column 2 shows the time constant Tau (in hours) for the least-squares fit of Absorbance A = A(0)*$e^{(-Time/Tau)}$, where A(0) is the absorbance at time zero.

Column 3 divides the duration of the experiment (3 hours) by the time constant Tau, to create a non-dimensional ratio of (3 hours) divided by Tau (hours).

Column 4 calculates 1-$e^{(-3/Tau)}$, which is the "completeness" of the experiment for each oil and each absorbent, based on the number of time constants Tau in the 3 hour test duration. My three hour testing duration was between 1.5 and 6.12 time constants long. Some standard values used in statistics are: 1-$e^{(-1)}$ = 63.2% (one time constant) and 1-$e^{(-2)}$ = 86.5% (two time constants).

Column 5 gives the Pearson Correlation Coefficient, which is a statistical measure of the agreement between the empirical absorbance data and the theoretical equation A(0)* $e^{(-Time/Tau)}$. 100% denotes a perfect fit and 0% denotes no correlation. All of my correlations showed excellent agreement between my data and my theoretical equation. My highest correlation was 99.67%. I used the PEARSON function in Excel to calculate all correlations.

Observations

Time	25ML Light Oil Results	50 ML Light Oil Results	25 ML Heavy Oil Results
1 Hour	Illite Clay had best purification. Sand had second best purification. Bentonite Clay had third best purification. Kaolinite Clay had worst purification.	Sand and all 3 clays had nearly the same absorbance at 1 hour. Kaolinite had slightly the best absorbance, followed by Illite Clay and Bentonite Clay. Sand had slightly the worst absorbance.	Sand had best purification overall. Illite Clay had second best purification. Bentonite Clay had third best purification. Kaolinite Clay had worst purification.
2 Hours	Illite and Kaolinite Clays had best purification (nearly equal) and best overall purifications. Sand and Bentonite had second best purifications (nearly equal).	Large divergence in absorbance. Illite Clay showed slightly improved absorbance, as did Sand. Kaolinite Clay and Bentonite Clay showed dramatically worse absorbance.	Illite Clay had best purification. Bentonite Clay had second best purification. Kaolinite Clay had third best purification. Sand had worst purification.
3 Hours	Third hour has mixed results: Illite and Kaolinite Clays had slightly less purification than at 2 hours. Sand and Bentonite had slightly better purification than at 2 hours.	Absorbance more converged. Bentonite had the best absorbance, followed by Kaolinite, then Sand. Illite Clay had the worse absorbance.	Third hour saw loss of purification from second hour for all purifiers. Illite Clay had best purification. Kaolinite Clay and Sand had second best purifications (nearly equal). Bentonite Clay had worst purification.

CONCLUSIONS

My project showed that clay was very successful in separating oil from water. However, Bentonite was not a universal solution, but part of an overall solution. Kaolin and Illite clay were the star winning clays that effectively removed at least 80-90% of the oil from the contaminated water; making clean water. There were advantages to all the clays and even advantages to sand which mimics bodies of water. Thus, my hypothesis was accepted.

FUTURE DIRECTIONS

In the future, I will expand my data taking to contaminated regions of the Navajo Nation. This could include discarded oil from abandoned gas stations, repair shops, and junk yards. The old oil may be abandoned and mentally forgotten, but it is still mobile and working its dangerous way into our water supply.

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