Rice Husk Use In Oil Spills Demonstrated With Cod And Phytotoxicity Tests

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Abstract

Motivated to develop faster and faster contemporary society has been using more and more fossil and energy resources that can, unfortunately, cause environmental accidents. Petroleum is responsible for providing different products derived as lubricating oil widely used in different production chains and object of study of the work in question. Many environmental problems faced by the Oil and Gas Industry are associated with leaks, accidents and irregular discharges. Thus an alternative for cleaning and adsorption of oil spilled in the sea is presented the validity in this article: the rice husk, being the main objective of this article to prove its effectiveness with lubricant oil adsorbent. It was used as a low cost alternative adsorbent. Performing physical order treatments such as heating and using acid and base that could increase their efficiency. Some COD and Fitoxicity tests of the generated effluent were performed and analyzed during the work, generating excellent results related to the adsorption of lubricating oils, showing a total adsorption of 6.15 g / g when treated in basic medium and 4.7 g / g in acid medium.

Statement Of Novelty

This work is an original contribution that allows to quantify the efficiency of the use of rice husk as an adsorbent for oil and petroleum products, thus proving it results in a greater viability of using this low-cost material as an alternative to clean oil spills. In addition, the phytotoxicity test and COD applied for different contact times and Hydrogen Potential are scarce data in the scientific literature, but they are extremely necessary to conceive a process of reusing a raw material (which should be wasted) in a sustainable way. The language used is easy to understand and the paper content has a big social impact, affecting researchers to even agricultural producers.

1 Introduction

According to the AAPG (American Association of Petroleum Geologists), petroleum is a thick, flammable, yellow-to-black mixture of gaseous, liquid, and solid hydrocarbons that occurs naturally beneath the earth's surface, can be separated into fractions including natural gas, gasoline, naphthalene, kerosene, fuel and lubricating oils, paraffin wax, and asphalt and is used as raw material for a wide variety of derivative products. The word petroleum comes from the Latin *petra*, meaning "rock," and *oleum*, meaning "oil." Each composition model and fraction, beyond the oxygen and carbon, characterizes different oils with different impacts on the environment.

Oil spills are serious issues nowadays with the worldwide industrialization process that accelerates and grows the demands for energy increasingly and can be described as large amounts of petroleum (or some of its derivatives) spilled due any failure on the petroleum extraction or transportation process. These spills, if wrongly characterized, when in contact with the environment can link serious damage to the local fauna and flora, in addition to various economic expenses, which can not always repair the damage already caused. So over the years many works have been developed to ensure and investigate

environmental regularity in the oil sector, such as an article written by Lessard & Demarco (2000) that shows a study reporting that the use of dispersants to counter the effects of an oil spill can result in lower overall environmental impact than relying on other countermeasures and it was supported by numerous international organizations and large multinational companies in the industry.

Therefore, predicting the potential long-term impact of spilled oils on their environment and selecting mitigating, preventive or spill containment and cleaning actions are essential and need to be further refined and studied. Wang, Fingas & Page (1999) stated that the accuracy and precision of analytical data has been improved and optimized by a series of quality assurance or control, and the laboratory data handling capability has been greatly increased through new advances.

According to Raiomondo (2017), the value of models linking organism-level impacts to a population's responses to Ecological Risk Assessments (ERAs) has been shown to be extensively necessary in recent decades. There is little discussion about the usefulness of these models for translating multiple organism-level endpoints into a holistic interpretation of population effect, and there is limited guidance on when models should be used and their application in the scientific context. This reflects the work in question that discusses the possible risks to society if oil spills are not effectively remedied and cleaned up. In view of this, phytotoxicity tests can be done to monitor the quality, in this case of contaminated water, and to prevent possible impacts from affecting the population around the spill area. The plant toxicity test, known as the phytotoxicity test, has the advantage that no sample pretreatment is required. The germination rate, the gain of biomass, root elongation and biochemical aspects associated with low cost and reproducibility make this type of laboratory test a great ally in the process of pollutant analysis.

One the matter of quality waters tests, one of the most significant for determining the degree of pollution, following the same subject, is the Chemical Oxygen Demand (COD), and based on Woodard et al. (2011) that is an indispensable parameter in the characterization studies of sanitary sewage and industrial effluents. It evaluates the amount of dissolved oxygen (DO) consumed in acid medium that leads to the degradation of organic matter. And the analysis of COD values in effluents and surfactants. These water body quality assessments are important, as written by Czerniawska-Kusza & Kusza (2011), when adhering to suspended solids, the contaminants present in the water column tend to be transported for long distances or sediment along the course, contaminating other regions at the water, raising greater concern about the polluting potential of water body sediments that receive domestic or industrial effluents.

So this paper aims to predict whether a water resource decontamination method using rice husk adsorption can be effective by performing phytotoxicity and chemical oxygen demand tests in the laboratory.

2. Materials And Methods

The experiments were conducted at the Water and Effluent Analysis laboratory and at the Analytical laboratory, at the Engineer's Center listed campus and at the Environmental and Sanitary Engineer

Laboratory, a building of the Federal University of Pelotas (UFPel) at the Engineering Center, in Pelotas, Rio Grande do Sul – Brazil.

2.1 Combings and Adsorbent Materials Used

For the experiment was used the new mineral based lubricating oil, multiviscous for gasoline, ethanol and CNG engines, with viscosity in SAE standard of 20W50, in the ratio of 10% oil to a certain amount of distilled water.

The rice husk provided by industries in the region of the municipality of Pelotas was used as adsorbent material. Thus, for the experimental part, the adsorbent materials were divided into 4 subgroups in which three treatments were made:

Husk A, heat treated: a physical treatment, keeping the adsorbent material in a greenhouse at a temperature ranging from 110 to 115 ° C;

Husk B, with basic treatment: a 1h stirring chemical treatment of a 30% mass / mass solution of sodium hydroxide;

Husk C, with acid treatment: chemical treatment under stirring for 1h in a solution with 30% mass / mass concentration of hydrochloric acid, and;

Husk D, fresh: that has not received any treatment.

After chemical treatments, the materials were washed for 4 hours constant.

2.2 Physicochemical Analysis

Samples were taken from the supernatant at the end of each adsorption time and in the extract COD analyzes were performed as described in the Water and Wastewater Analysis Manual (2016).

Phytotoxicity tests were applied to cucumber seeds and seeds. The seeds and samples were prepared as follows:

- The seeds (20 Lettuce and 10 Cucumber) were separated in 9 cm diameter petri dishes lined with filter paper (Whatman No. 3);
- 5 mL of each effluent sample was applied to identified plates containing cucumber and lettuce seeds;
- 5 mL of distilled water was applied to identified plates containing the seeds, this being the test control;
- The plates were sealed with parafilm paper, and then incubated at 20°C for 48h for lettuce and 72h for cucumber;
- The number of germinated seeds of each plate was counted, measuring the average length of each plate in order to verify the GI (germination index).

The germination index was calculated using the formula $IG = (G * Lm / Lc)$ described by Zucconi et al (1981), in which:

IG = germination index;

G = number of germinated seeds in the sample divided by the number of germinated seeds in the control;

Lm = mean length of sample roots (mm);

Lc = mean longitude of control roots (mm);

3. Chemical Oxygen Demand (Cod)

After performing the COD procedure with all rice husk samples with the different treatments and contact times, it was possible to draw a graph (Fig. 1) to better interpret the results obtained. And was also made a basic statistics to define which treatment and time has the best efficiency.

Table 1
– Correlation Between the Contact Time and the Type of Treatment

Treatment	Average Cod	Best Contact Time	Worse Contact Time
In Natura	479,98	15 min	0 min
Termic	457,69	15 min	0 min
Acid	388,47	15 min	0 min
Basic	734,77	5 min	120 min

Can be observed at the Table 1 that the only treatment the wasn't the most effective one at the time of 15 minutes of contact is the Basic one, which also has the least favorable results for de average percentual of COD. In counterpoint the acid treatment has achieved the best COD results, and was twice time more efficient than the rice rusk COD without treatment, but the most consistent results were obtained at the in natura rice rusk,due the fact that standard deviation calculated was also the smaller number founded. The oil adsorption expressed in terms of organic matter was maximum within the first 5 minutes for the basic treatment. After this period occurs the desorption phenomenon, which for the basic treatment is irreversible, demonstrated by the increase of COD concentration in the solution at constant rate until reaching the initial concentration, as can be seen at the Fig. 1.

The adsorbent materials that underwent the acid, heat and in natura adsorbent treatments reach the maximum adsorption capacity in 30min, period when the system reaches the kinetic equilibrium, that is, the adsorption rate is equal to the desorption rate. At equilibrium the material treated with acid, heat and

in natura obtained the maximum adsorption capacity, obtaining at equilibrium COD removal efficiency of 76.44%, 54.46% and 55.20%, respectively.

The difference in efficiency between treated materials and fresh adsorbent material may be related to oil hydrolysis. It can be said that the adsorbent material with basic treatment favored alkalization of the solution, thus also favoring oil hydrolysis, increasing the concentration of COD in solution and the tendency to remain dissolved. Abdel-Halim and Al-Deyab (2011) also concluded that treating the commercial sodium alginate, with a very simple acidification treatment with alcoholic HCl solution, it was converted into water insoluble material through and the so-obtained acidified sodium alginate (ASA) was found to exhibit complete water insolubility and to have a carboxyl content of 465 mequi./100 g sample.

For the other used materials, it provided a more selective adsorption, that is, possibly split the organic matter into two fractions: one hydrophobic (most of the fractionation and susceptible to adsorption by fresh material, heat treated material and hydrochloric acid material). or the adsorbate surface interaction which may be chemical or covalent) and another hydrolyzed or water soluble (non-adsorptive fraction). According to Aquino et al (2006), hydrophobic compounds tend to present much lower COD because it is adhered to the solids surface.

3.1 Phytotoxicity

Germination rates were compared with the distilled water control, generating an IG of 1 or 100%, which is the standard for 100% germination. Treatments using fresh husk showed the lowest germination rates with averages between 70% at 60 minutes and 108% at 15 minutes. The time of 30 minutes presented lower germination index than the other contact times, which may be justified by an error during the analysis or by an anomaly in the seeds used during this time. According to Zucconi et al. (1981), the absence of phytotoxicity would be reached with germination indexes above 50%.

Knowing the germination indexes of each seed with its respective time and treatment, two graphs were generated that demonstrate how this behavior was, separately for lettuce (Fig. 2) and cucumber (Fig. 3).

It is interesting to analyze that both graphs show similar behavior in germination with time, especially until 50 min, where heat treatment excels in germination, indicating better decontamination of the medium by rice husk.

Analyzing Fig. 2, it is evident that there is a line inversion and that the most promising treatments after 50 min are, first the basic and second the thermal. But when it comes to Fig. 3, the basics didn't do as well as expected, as the heat treatment outperformed it in seed growth. And the notoriety of acid treatment after 200 minutes is still valid, which almost reached the maximum potential of the basic treatment in the last moments of germination.

Moreover, it is common to both graphs the presence of sharp germination peaks, for all treatments previously performed, around 120 minutes, demonstrating, until then that this can be the optimal time of oil adsorption and remove much of the aggregate pollutants. to spilled oil.

The heat treatment presented the best germination indexes, with indexes above 100% in 3 of the analyzed times. The time of 60 minutes presented an index of 21%, being the only time with germination below 80%. The acid treatment presented germination rates higher than 100% in the first two contact times, afterwards there was a decrease in the values and in the 60 minutes contact time the germination index was zero, which may have been caused by some contamination of the sample or plate preparation as no root growth occurred in any of the 3 plates analyzed.

In the basic treatment, only the last time, 240 minutes, presented germination index higher than 100%. The contact times of 5 and 15 minutes presented, respectively, 75% and 46% of germination, being the lowest values found in this treatment. The other times presented germination rates between 80% and 100%.

Based on Zucconi et al (1981) the absence of phytotoxicity would only be achieved with germination rates above 50%. Saviozzi et al (1992) states that it would take germination rates between 80% and 90% to consider the stability of organic material. Regardless of the divergence from the recommended minimum values for germination indices, recent studies tend to adopt higher indices in order to increase biosecurity.

4 Conclusions

Rice husk, being a cheap and residual material, proved to be able to be reused for various purposes and, mainly, validated its performance to that used as adsorbent material for all that has been argued so far. Therefore, it is concluded that it can be well used in the oil and gas industry to avoid major environmental damage as a means of containment and mitigation.

As a promising adsorbent of organic compounds or effluent oil, it presented a high percentage of oil removal associated with water, but analyzing residual COD, the effluent treatment process can be interrupted at 15 minutes, since its values in solution are 208., 150.94 and 94.92 mg / L, correspond to a removal percentage of 77.95%, 84% and 89.93% for the in natura, heat treated and acid treated husk respectively.

Taking into account total adsorption, the peel that underwent basic treatment had one of the best oil retention scenarios with a rate of 5.16 g / g adsorption, and seeking effective adsorption parameters in cheap materials, Dhir and Kumar (2010) indicates with *Salvinia* that the sorption values of this material can vary from 8.3 g to 10.8 g of oil adsorbed per gram of biomass, but this result will depend on the type of oil.

The contact times of oil-treated shells could guide us to a narrower range, which facilitates the applicability and creation of a peel utilization model, especially with basic treatment, as oil adsorbing material in future spills. As well as being cheap, the method described here enables the recovery of all oil adsorbed by the shell, further reducing the damage associated with such environmental accidents.

4.1 Future Considerations

The use of different treatments can be studied, aiming at reducing costs and even altering the optimum rice husk adsorption times. In addition, oil companies could conduct more incentives and field trials to improve the technique presented here.

Declarations

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Highlights

The rice husk proved to be able to be reused for the cleanup of oil spills purpose.

The percentage of oil removal associated with water depends on the previous treatment applied to the rice rusk.

The adsorption process was effective and it is associated to the contact times of treated rusks with the oil and water solution.

Figures

Figure 1

Removal Efficiency

Figure 2

Germination Index for Lettuce

Figure 3

Germination Index for Cucumber

Supplementary Files

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