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RESEARCH ARTICLE

Rice Husks (Oryza sativa) as a Bio-Adsorbent For Pollutants in Water: A Vision for the Mining Industry

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ABSTRACT

This research evaluates the efficiency of rice husks as a bio-adsorbent in wastewater treatment to reduce the concentration of pollutants such as Total Petroleum Hydrocarbons (TPH) and oils and greases, generated in industrial processes such as mining where fuel and lubricants are used for machinery, equipment, gear systems and mineral treatment such as flotation. The water samples were characterized using standard method 5520-F for TPH and 5520-D for oils and greases. The particles of the bio-adsorbent material had a size of 0.3 mm without any chemical modification, obtaining 12 doses (4 of 50 g, 4 of 60 g and 4 of 70 g) to be applied in 3 treatments with 4 repetitions for each parameter. This resulted in the removal of approximately 70% on average in the concentration of TPH and 67% of oils and fats with treatment 1 (T1), with 50 g of rice husks being the optimum adsorption dose in this study. These results indicate that the increase in the amount of adsorbent material would not necessarily be the main factor to improve the efficiency of the process, there are other important variables such as the size of the adsorbent particle and the agitation time. Due to the efficiency found, rice husks could be incorporated in the mining industry as an alternative for the treatment of wastewater with high concentrations of these parameters.

1. INTRODUCTION

The mining industry is not exempt from the use of hydrocarbons, oils and greases, as they are essential inputs for the operation of machinery, equipment lubrication, gear systems and certain mineral treatment processes such as flotation, which could cause water resource contamination by spillage, mainly originating in the storage and handling areas of these compounds. Generally, in the industrial sector it is very common to generate wastewater with high concentrations of Total Petroleum Hydrocarbons (TPH) and oils and fats, with values that can reach up to 31 458 mg/l and 87 000 mg/l, respectively, being one of the main sources of water pollution (Quintero, 2017; Torres & Reyes, 2021). One of the most serious environmental problems in Ecuador's water resources is precisely the use of freshwater bodies as recipients of these discharges and even the sewage system, mostly without any prior treatment (ECLAC, 2012; Lara-Basantes & Andrade, 2022; Andrade at al., 2022). Something similar occurs in vehicle establishments dedicated to oil changes, washing and greasing services, an activity that is increasing in Ecuador according to the National Institute of Statistics and Census (INEC, 2022).

TPH are petroleum-derived compounds found in crude oil and consist of a mixture of various hydrocarbon fractions. Although some of these fractions can be degraded by microorganisms, aliphatic and long-chain aromatic hydrocarbons tend to persist in the environment, generating negative impacts, and when TPH enter aquatic ecosystems they can alter their quality, due to their toxicity (Kuppusamy et al. 2020). In addition to causing nuisance in surface waters, they can bioaccumulate in aquatic biota mainly in larger organisms through trophic transfer by ingestion of lower organisms or through direct ingestion by adsorption on organic matter, with effects ranging from acute to chronic, depending on the metabolism of each species (Ihunwo et al. 2021).

In the industrial sector, modern machines need special lubricants to operate in extreme conditions and challenging environments, which has prompted the development of a wide variety of advanced lubricants that meet today's technological requirements. Lubricating oils due to their toxic nature and resistance to biodegradation pose a threat to the environment, endangering water, water and air quality, threatening the health of ecosystems. Assessing the biodegradability and toxicity of lubricants is crucial to meet eco-labelling criteria, ensuring environmental protection and promoting sustainable practices. Biodegradability can be assessed in a variety of environments, such as aerobic, anaerobic, freshwater and marine environments, using specific approaches that consider the unique conditions of each environment.

Given this problem, rice husk ash (*Oryza sativa*), considered as a waste generated in the milling process of the crop, has been considered as an alternative for water treatment in the mining industry (Adlim et al., 2018). The use of this waste and its derivatives as an adsorbent has been the subject of studies to remove different types of environmental pollutants such as dyes, phenols, organic compounds and heavy metals, and also because crude adsorbents have been classified as fast and economical treatments of contaminated water .

This work evaluates the adsorption capacity of rice husks in wastewater with high concentrations of TPH and oils and greases from industrial processes where fuels and lubricants are used, as an alternative for water treatment in the mining sector, in order to reduce the negative impact on the quality of water resources.

MATERIALS AND METHODS

Water characterization

This procedure was carried out before and after treatment. The wastewater samples were taken from an establishment that works with machinery and vehicles that handle fuels and lubricants, applying the sample collection, preservation and storage techniques established by the American Public Health Association. Standard method 5520-F was used for TPH analysis and 5520-D for oils and greases.

Bio-adsorption process

The rice husk type SFL 011 was obtained from a pilar located in the city of Guayaquil - Ecuador, the adsorbent material did not undergo any chemical modification. It was left to dry in the environment for 15 days to eliminate humidity and in the laboratory it was crushed, then sieved to obtain a particle size of 0.3 mm, obtaining 4 doses of 50 g, 4 of 60 g and 4 of 70 g. Each dose was added to 100 ml of

100 ml of water. Each dose was added to 100 ml of wastewater in a jar test apparatus (Velp Scientific, Spain) for 20 minutes at 150 rpm. Then it was left to stand for 10 minutes and finally through a 0.20 mm filter the particles were removed from the treated water (Banchon et al., 2017).

Experimental design

In the present work, 3 treatments were carried out for each parameter with 4 replicates, to find the optimal dose of bio-adsorbent (Table 1).

Table 1. Treatments to assess the reduction of TPH and Oils and Fats concentrations by rice husks

Treatment	Particle size of bio-adsorbent (mm)	Dose (g)	Waste water (ml)	Time (min)	Repetitions
T1		50	100	30	4
T2		60	100	30	4
T3	0,3	70	100	30	4

Statistical analysis

Descriptive and inferential statistics of parametric and non-parametric test were applied because it corresponds to a set of values where the data obtained have a normal distribution and another group of data where the results according to the Shapiro-Wilks normality test have a free distribution. The resulting data were processed by analysis of variance (ANOVA), using Tukey's test, with a 5% significance level for data with normality, and the Kruskal-Wallis test for data without normal distribution.

RESULTS

Effect of bio-adsorbent doses

Figure 1 shows the concentrations of TPH and oils and fats in the water samples before (Mi) and after (Mf) the bio-adsorption process in each treatment with replicates. The results for Mi were 101.053 mg/l for TPH and 200.35 mg/l for oils and fats. TPH concentrations with T1 decreased to 31.59 mg/l on average between replicates, followed by T3 (39.55 mg/l) and T2 (61.46 mg/l). For oils and fats T1 was also the most effective, decreasing to 65.45 mg/l, followed by T2 (74.37 mg/l) and T3 (157.5 mg/l).

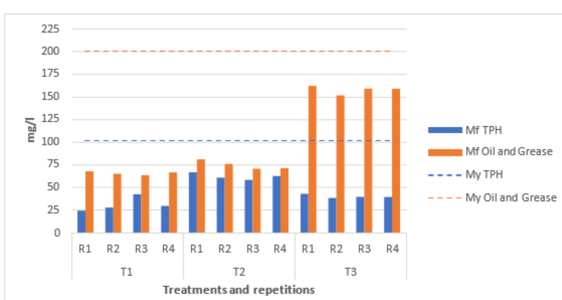

Figure 1. Treatments and replicates for the bio-adsorption experiment with rice husk doses: treatments T1-50 g; T2-60 g; T3-70 g. Initial TPH: 101.053 mg/l. Initial oils and fats: 200.35 mg/l.

According to the Shapiro-Wilks normality test (Table 2), the results of TPH have a normal distribution, because the p-statistic exceeds the significance level of 0.05. While for oils and fats the null hypothesis is rejected, as they do not have a normal distribution

Table 2. Shapiro-Wilks Normality Test of the study parameters

Variable	N	Media	D.E.	W*	P
TPH	13	48,26	20,96	0,88	0,15 45
Oils and Fats	13	106,89	50,18	0,75	0,00 08

Based on Tukey's test for TPH, a significant difference is observed between T2 and the other treatments. In addition, T1 and T3 do not show significant differences, suggesting a similar adsorption capacity (Table 3).

Table 3. Tukey's test for Total Petroleum Hydrocarbons parameter

Treatme nt	Media	N	E.E.		
T2	61,46	4	2,54	A	
T3	39,55	4	2,54		B
T1	30,59	4	2,54		B

Table 4 shows the Kruskall-Wallis test for oils and fats, significant differences between treatments. The adsorption capacity differs between the groups.

Table 4. Kruskall Wallis test for the parameter Oils and fats

Treatment	Stockin gs	Ranks		
T1	65,45	2,50	A	
T2	74,37	6,50	A	B
T3	157,50	10,50		B

DISCUSSION

With the results of the EH results, it is possible to demonstrate the non-compliance with the maximum permissible limits for discharge, both in fresh water bodies (TPH: 0.5 mg/l; Oils and Fats: 0.3 mg/l) and in the public sewage system (TPH: 20 mg/l; Oils and Fats: 70 mg/l) according to the environmental regulations of Ecuador. This seems to be common in industries using fuels and lubricants, attributed to the lack of infrastructure such as grease traps. After the bio-adsorption process, an average of approximately 70% removal of TPH concentration was obtained with T1, 39% with T2 and 61% with T3. For oils and fats an average removal rate of 67% was achieved with T1, 63% with T2 and 21% with T3. This could indicate that increasing the rice husk dosage does not necessarily improve the adsorption capacity, mainly for oils and fats where it gradually decreases as the dosage increases.

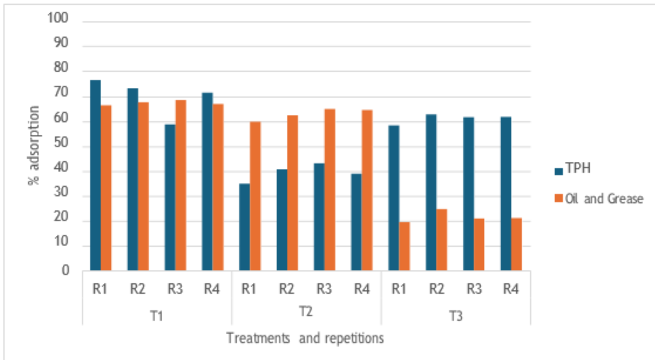

Figure 2. Percentage of adsorption in each treatment and repetition with rice husk doses: treatments T1-50 g; T2-60 g; T3-70 g. Average % TPH reduced: 70% with T1; 39% with T2; 61% with T3. Average % oils and fats reduced: 67% with T1; 63% with T2; 21% with T3.

The removal rates in other studies are similar, Castaño et al. (2017) obtained between 40% to 90% removal of TPH and for oils and fats Razavi et al. (2014) achieved decreases from 30% to 70%, stating that the removal of contaminants is mainly due to the silica, cellulose, hemicellulose and lignin content of rice husk (Babiker et al., 2020; Wang et al. (2018). Hossain et al., (2020) observed that the performance as a bio-adsorbent was also influenced by the reduction in size of the rice husk particle, which favored homogeneity in pore distribution by its total volume and average width. According to Banchon et al. (2017) a smaller particle size of plant adsorbents increases the contact surface area, reducing the drag forces and improving the agglomeration forces to adsorb microdroplets of the contaminants.

Stirring time would also be an influential factor, even more so than resting time. Banchon et al. (2017) observed that the capacity of their bio-adsorbents decreases without agitation, this process would be increasing mass transfer, adhesion forces and chemical affinity (dipole-dipole); a key factor if one wants to elaborate rice husk-based filters, where other filtering compounds such as polyethylene glycol and clay are generally added to improve the reduction of hydrocarbons but increasing the levels of phosphates and nitrates (Madu et al., 2021). In the present study no chemical compound was added to the adsorbent material, however, there is research where phosphoric acid or sodium hydroxide is added, the latter with the best result (Rodriguez et al., 2012). This combination will depend on the type of wastewater and the pollutants to be treated.

The use of this type of vegetable waste could be an economical alternative to activated carbon, according to Wagih et al. (2024) rice husks have a higher oil removal efficiency compared to sawdust and sugar cane bagasse. Norizan et al. (2012) indicate that rice husks can be more efficient adsorbents for motor oils as the sorption can exceed 5 g/g, while for hydrocarbon derivatives the sorption process can be affected by the presence of water, as this could be saturating the adsorbent material before the pollutant. Other studies mention that there are no ideal plant species to treat wastewater, the selection of biomass depends on several factors, such as the specific characteristics of the wastewater, the environment where the adsorbent is located and the climatic conditions (Gill et al., 2013).

CONCLUSION

Rice husks were used as an adsorbent for TPH and oils and fats. The interaction of this material with these pollutants reduced their concentration in the water by an average of 39% to 70% of TPH and 21% to 67% of oils and fats. The best results were obtained with 50 g of bio-adsorbent.

The use of 3 types of adsorbent material dosage allowed to determine that the increase in its quantity is not necessarily the main factor to improve its efficiency. The size of the adsorbent particle would be another factor to consider, since the smaller the particle, the more homogeneously it would be distributed in surface contact area, reducing the drag forces and improving the agglomeration forces to adsorb contaminants. In turn, agitation time would be another factor to be analyzed in future research.

The search for a suitable adsorbent requires a continuous selection process. In the mining industry, wastewater is sometimes not suitable for human consumption after treatment, but it can at least be suitable for another purpose according to Ecuador's environmental regulations. If these waters are subjected to this type of treatment, costs could be reduced in the execution of the company's environmental management plan, and water recirculation processes could even be implemented in the company's facilities.

AUTHORS' CONTRIBUTION

	CLB	JCLA	JCFA	DNVU	MATP
Conceptualization	■				■
Formal analysis	■	■	■	■	
Research	■	■	■	■	■
Methodology	■	■	■	■	■
Resources	■	■	■	■	
Validation		■	■	■	
Writing, proofreading and editing	■				■

All authors declare that they have read and approved the final manuscript.

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