International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.05, pp 105-112, 2018

Evaluation of Cedar Sawdust (*Cedrela Odorata L.*), Camajón (*Sterculia apétala*) and Ceiba Amariila (*Hura Crepitans L.*) for the Removal of Heavy Oil in Aqueous Solution

Angel Villabona Ortíz[1], María Villadiego[2], Candelaria Tejada Tovar[3], Gustavo Padilla[4], Diofanor Acevedo*[5]

[1,2,3,4]Faculty of Engineering, Chemical Engineering program, Research Group IDAB, University of Cartagena Av. El Consulado, St. 30 No. 48-152. Colombia.
[5]Faculty of Engineering, Research Group Innovation, Agricultural and Agro-industrial Development, University of Cartagena Av. El Consulado, St. 30 No. 48-152. Colombia.

Abstract : The present research work was carried out with the objective of determining the potential for the removal of diesel in seawater solution from sawdust from three native forest species of the Colombian Caribbean Coast: Cedar (Cedrela Odorata L), Camajón (*Sterculia apétala*) and yellow Ceiba (*Hura Crepitans L.*), for which first the physicochemical characterization of wood samples obtained in carpentry workshops of the Departments of Sucre and Bolívar was carried out; experimenting with Diesel as heavy oil, being the contact time 10 min. Following separation of the sawdust from the solution, the samples were subjected to gas chromatography to determine the amount of adsorbed oil, which varied in the three sample types due to the physicochemical composition in each type of wood. The maximum adsorption capacity was cast per cedar (58.51%), followed by the yellow Ceiba (58.13%), and finally the camajón (34.15%); the best removal conditions were obtained under the conditions of 5g of sawdust and particle size 1 mm. Finally, the adsorption potential of cedar was evaluated, reaching a saturation point of approximately 13.13 mg L^{-1}. Presenting this residual biomass as a possible solution to the environmental problems of heavy oils in water, showing at the same time the possibility of valorizing this type of organic materials catalogued as waste.
Keywords : Adsorption, sawdust, heavy oil, residual biomass.

1. Introduction

Water is a fundamental resource in the development of human life and industry, the vast majority of water bodies are increasingly polluted, product of poor disposal and inappropriate treatment of industrial waste; this implies the need to implement environmentally friendly processes [1].

Heavy oil pollution in aquatic environments is a problem given that this floats on the surface forming a film of variable thickness preventing the entry of light and gaseous exchange, producing the solubilization of

International Journal of ChemTech Research, 2018,11(05): 105-112.

DOI= http://dx.doi.org/10.20902/IJCTR.2018.110512

water-soluble compounds and affecting different populations, including plankton, macroinvertebrates and benthos or macroinvertebrates, which live on the bottoms of rivers and swamps. Excessive use of fossil-based resources and petrochemical by-products contributes to the increase of pollutants in water, such as accidents or oil spills in oceans and rivers that often occur affecting the aquatic ecosystem. Industries are another source of pollution, since washing with water from pipes and industrial equipment generates effluents with high concentrations of heavy oils [2].

This problematic has greatly boosted the study of new low-cost alternatives, effective and most importantly, clean technologies, as the treatments traditionally used are not environmentally friendly; most dispersants are potentially flammable and toxic, contributing to the dirt in coastal areas and contamination of drinking water, skimmers (skimmer), absorbents, among others, present similar problems [3].

The search for new materials, organic in nature, has contributed to remedy environmental problems such as water pollution, achieving a better disposal and use of solid waste, for our case in particular sawdust, considered waste in woodworking factories, since it will be used to reduce the concentration of oils in water sources [4]. Different researchers have used bamboo sawdust [5], pine [6],mixed with bentonite [7], impregnated [8], sawdust and neem dust [9], for the adsorption of dyestuffs and heavy metals such as Ni (II), Cr (VI) in tannery wastewater [10] and Zn (II), Cu (II), as it has a polymer structure consisting of cellulose lignin, capable of carrying out the mechanism of adsorption of protons from contaminants.

Other sources demonstrated that treated sawdust can be used effectively as a raw material for the extraction of methylene blue dye in aqueous solution over a wide concentration range [11]. In addition, the adsorber potential of sawdust is not only used to adsorb ions, but also to adsorb oils in the combination process of sawdust adsorption and energy recovery through the combustion of impregnated sawdust, in the treatment of olive oil wastewater [8, 12].In the United States and China, a mixture of bentonite and sawdust was used for coagulation of oil in water, obtaining an efficiency of 92% or more [13].

To investigate the possibility of exploiting sawdust from different types of wood, is an innovative idea for the Colombian oil industry, because it can reduce the concentration of heavy oil, discharged into water sources, furthermore, sawdust in woodworking factories is the most abundant by-product considered as waste, but in the treatment of aqueous effluents with heavy oil content, has a significant value to be able to use it as waste, as the basis for these will be an easily replaceable and affordable material, in addition to the aforementioned environmental benefits.

A sawdust filter adapted to an oil-contaminated water drain pipe, in addition to contributing to the environment, gives the company the opportunity to comply with environmental regulations, reducing fines and legal aspects. The purpose of this research focused on evaluating the capacity to remove heavy diesel-type oils in aqueous solution of sawdust, from three forest species native to the Colombian Caribbean Coast: Cedar, Camajón, Ceiba Amarilla, as well as its physical and chemical characterization.

2. Experimental

A quantitative research of an experimental type was carried out, where the dependent variable was the amount of diesel adsorbed, the independent variables were particle size and sawdust quantity and finally the variables involved were: time, temperature, pH, solution concentration, sample volume, hydrocarbon type [3, 8, 10, 14, 15, 16, 17, 18, 19, 20].

2.1 Preparation of adsorbents

Cedar, camajon and yellow ceiba sawdust of different sizes were used in the best possible condition. The sample was sorted in a sifter in order to choose appropriate particle sizes for testing; it was washed several times with distilled water until the brown color of the water disappeared, dried at 80°C for 24 h.

2.2 Characterization of sawdust

Once the sawdust was prepared, the functional groups responsible for adsorption by infrared spectroscopy using an infrared spectrum equipment preheated to 70°C was characterized in order to be identified, for which each sample is mixed with KBr (20 mg) in an agate mortar to obtain the fine powder that will be pressed and placed in a sample holder for analysis [3].

2.3 Determination of the quantity of adsorbed oil.

Once the time was over, the sawdust was removed from the solution, allowed to drain and the Soxhlet analysis was performed with chloroform as a corresponding solvent, to verify the effectiveness of the sawdust [8, 10, 16, 18, 19, 20].

The experimentation was carried out in glass jars. The amount of seawater and diesel used was kept constant, the concentration chosen being 20 mg L^{-1} because in each glass flask, the prepared heavy oil and seawater solution was poured, a dosage of 2 g and 5 g was added, and the particle size of 1 mm and 2 mm, corresponding to each batch experiment, for each type of sawdust a maximum contact time of 10 min was maintained, and a pH of 7.6; it is higher than the established concentration of 10 mg L^{-1}[21]. Twelve bottles containing 400 mL of synthetic sea water from Marbella beaches and diesel were used in the experiment. It was used a random block design in factorial layout of 3 x 2 x 2, obtaining a number of 12 experiments.

3. Results and discussions

3.1 Species characterization

After removing dirt such as dust and lumps from the samples, physicochemical characterization of the sawdust was carried out. The camajón sawdust had no characteristic smell or taste, with a pale yellow color and light brown or reddish yellow heartwood and slightly visible pores, a % of humidity: 79.12%. Figure 4 shows the corresponding infrared spectroscopy (FTIR) analysis to determine the functional groups that favour the diesel adsorption process.

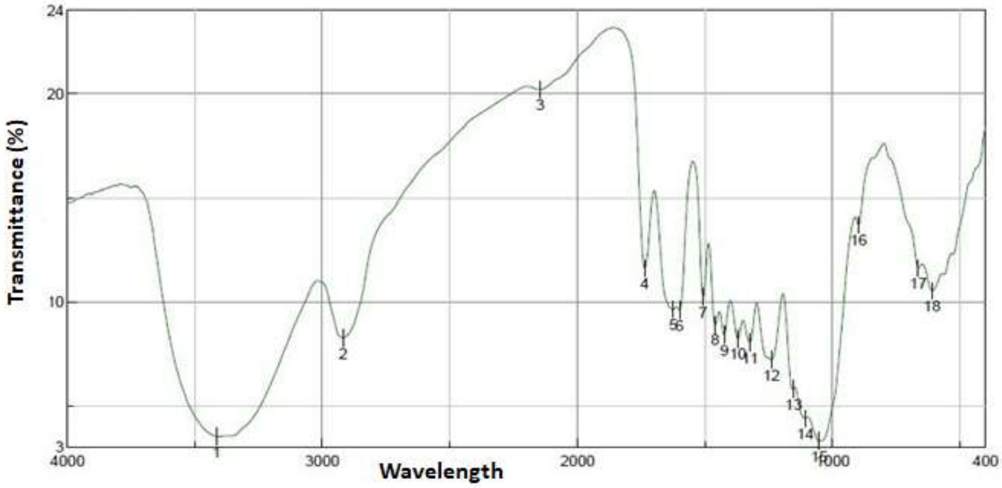

Figure 4. Spectrum of Sterculia Apétala (Camajón)

The spectrum shown in Figure 4 shows 18 peaks. The most important located in the range between 3600-3100 cm^{-1} corresponds to the vibrations of the O-H group due to the stretching of the existing hydroxyl alcohols, phenols and carboxylic acids in cellulose and hemicellulose and lignin [22].In addition, it shows a marked peak between 2880 $cm^{-1}$and 2150 cm^{-1} related to the CH zone, produced the polarity of the bond and the hybridization of carbon, corroborating the presence of hydrocarbons of alkanes, fatty acids, alcohols of high molecular mass, aldehydes, ketones and N-alkyl esters, ratify the presence of vegetable wax, substance that favors the interaction with apolar compounds. A marked peak in the bands around 1736.58 cm^{-1}, related to carbonic esters due to the low-medium adsorption intensity of the COOO-group.

Ceiba Blanca sawdust does not have a characteristic colour or flavour, it may or may not have sapwood to heartwood colour marking with diffuse pores of little abundance and slightly visible to the naked eye and a moisture (%): 80.15%.

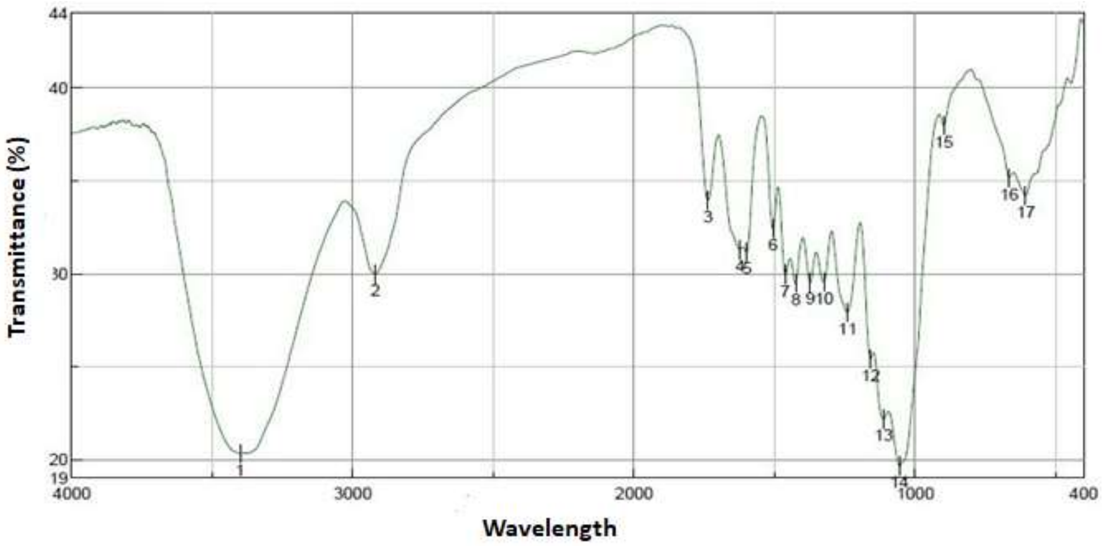

Figure 5.Spectrum of Hura Crepitans L. (Ceiba Blanca)

Looking at the FTIR in Figure 5, marked peaks are observed between the bands of 3600 cm^{-1} to 3200 cm^{-1} corresponding to the O-H vibrations, and are manifested with a blunt band which can be reflected in fatty acids, divided into two regions, a water repellent hydrophobic apolar that repels water, and interacts with apolar compounds such as oils, and a hydrophilic polar [22]. The peaks around 3000 cm^{-1} indicate symmetrical and asymmetrical aliphatic hydrocarbons (CH_2) and stretching hydrocarbons (CH_3), showing the presence of alkanes, fatty acids, alcohols of high molecular mass, aldehydes, ketones and N-alkyl esters, confirming the presence of vegetable wax. In addition, white ceiba sawdust has esters, olefins, waxes, alcohols, ethers, carboxylic acids, anhydrides and acetyles due to the presence of cellulose, lignin and hemicellulose in its structure.

For its part, cedar sawdust has a very characteristic pleasant smell, with a slightly bitter taste, brown-red-greyish coloration, diffuse pores and 79.89% moisture. The characteristic bands of the chemical groups of C. Odorata L are illustrated in Figure 6 by means of an FTIR analysis.

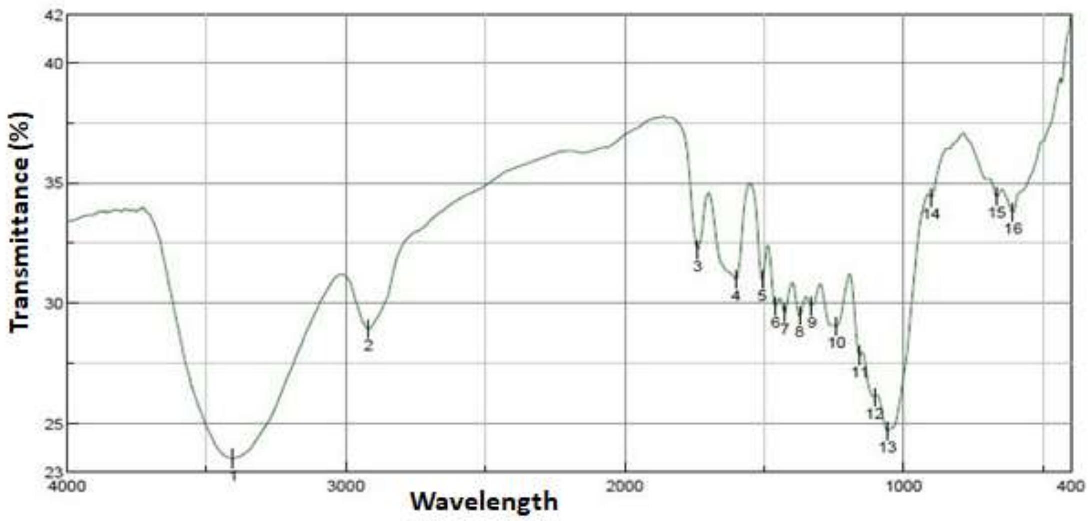

Figure 6.Spectrum C. Odorata L. (Cedar)

In the spectrum the wide and marked peaks located in the band 3403.74 cm^{-1} correspond to the vibrations of the OH group, due to the stretching of carboxylic acids concentrated by the ease of the link between the carboxyl (CO) and hydrogen (H) groups, which can be reflected in fatty acids. In addition, CH2 has symmetrical and asymmetrical aliphatic CH_2, esters and lactones, conjugated dyes, aliphatic aldehydes, ketones, tertiary alcohols, phenols, carboxylic acids and ethers due to the presence of cellulose, lignin and hemicellulose in its structure.

3.2 Adsorption and diesel removal capacity.

The adsorption capacity of the three types of sawdust: cedar, camajon and yellow ceiba as determined by gas chromatography are shown in Figure 7:

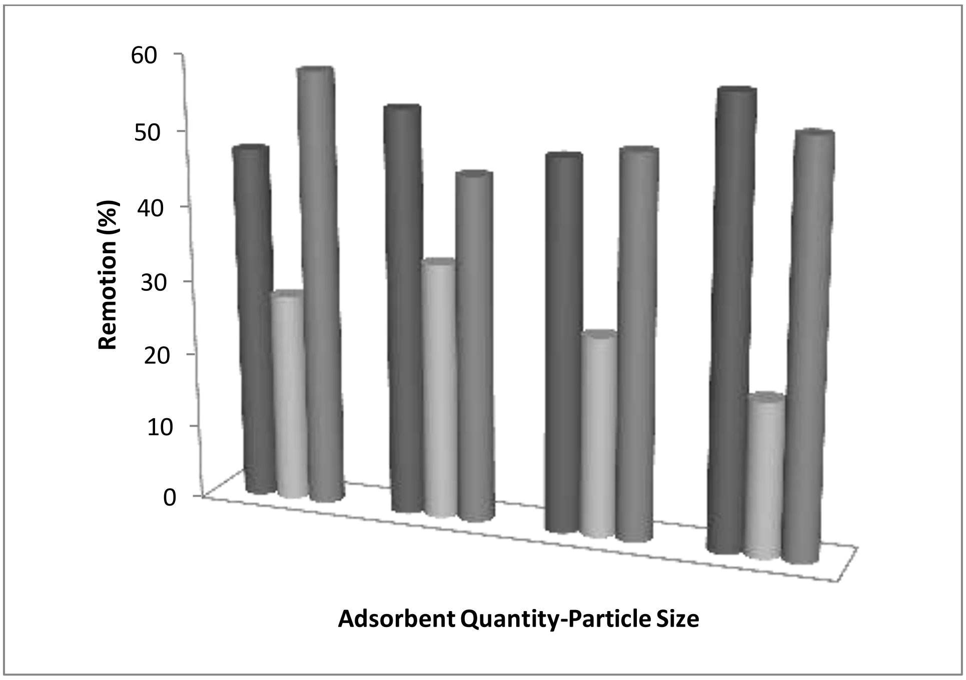

Figure 7.Adsorbate Removal Percentage (Diesel). (■) Cedar, (■) Camajon and (■) yellow ceiba

The best result was the cedar sawdust, with a removal rate of 58.49% with an amount of 5 g and a particle size of 1 mm and, very close, under the same conditions is found the yellow ceiba sawdust obtaining results of 58.13% of removal amount, as predicted in the FTIR analyses performed. For a better analysis of the results, a comparative graph was made of the amount of adsorbate removed in the three types of sawdust, under each of the established conditions of adsorbent quantity and particle size.

The best result was the cedar sawdust, with a removal rate of 58.49% with an amount of 5 g and a particle size of 1 mm and, very close, under the same conditions is found the yellow ceiba sawdust obtaining results of 58.13% of removal amount, as predicted in the FTIR analyses performed. From the two groups of quantities of 2 g and 5 g, as the quantity of sawdust decreases, the amount of removal decreases, because when you have high quantities of sawdust, the contact area between it and the suspended oil is larger, that is, the sawdust spreads and occupies the entire cross-sectional area of the container containing the oil. On the other hand, a higher percentage of removal occurs when the particle is smaller. It was observed that the size of 1 mm generated a significant increase in oil removal since, the smaller a particle is, the higher the contact area, allowing adsorbate to achieve maximum adsorption capacity.

The cedar sawdust is distinguished as the most advantageous among the three studied, followed by the yellow ceiba and camajon. Although the three types of sawdust have a similar chemical structure, the cedar sawdust presented a more hydrophobic behavior due to a greater intensity of adsorbance in the known hydrophobic zone, which ranges from 1600 cm^{-1} to 1030 cm^{-1} where the presence of lignin, a hydrophobic and oleophilic compound attributable to its waxy surface is identified, as well as the cellulose located around point 3400 cm-1 [18, 20].

3.3 Adsorption potential of *Cedrala odorata L.*

To determine the adsorption potential, the concentrations of the prepared solution were varied to establish the adsorption capacity; for this reason, tests were carried out only with the sawdust of *Cedrela Odorata L.*, at different concentrations (40,60 and 80 ppm), selected because it yielded better results at a concentration of 20 ppm among the three sawdust types, as can be seen from the results shown in Figure 8, the removal rate increased from 58.50% to 62.17% when the concentration doubled. Then, the difference between 60 ppm and 80 ppm was minimal, remaining around 65%.

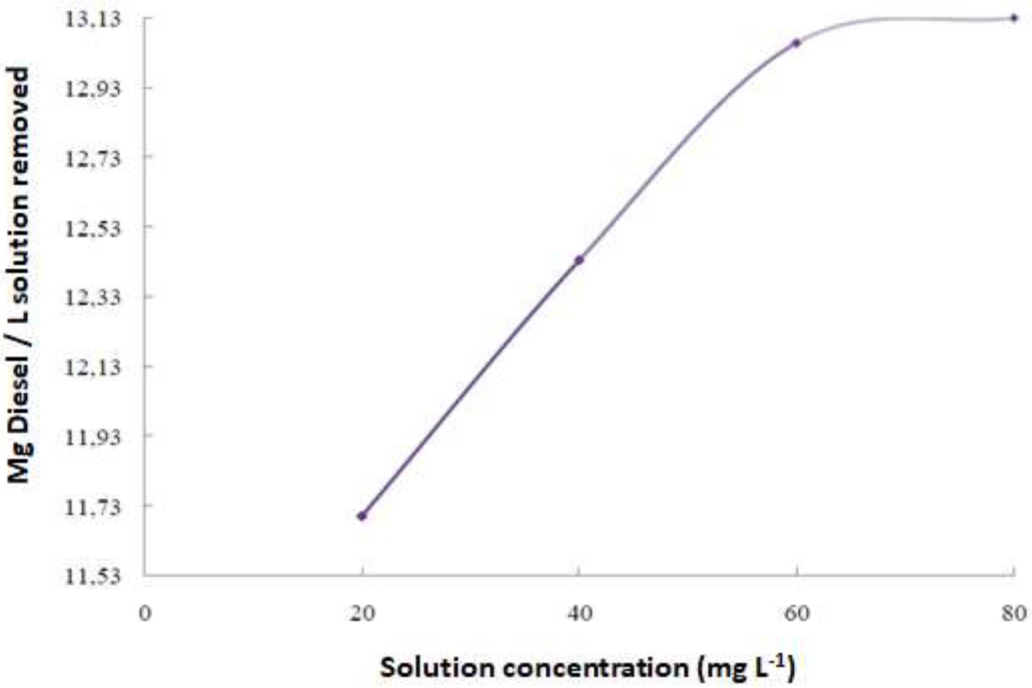

Figure 8. Adsorption potential of *C. Odorata L*

Figure 8 shows the behavior of the adsorption potential of *C. Odorata L.*, for the conditions in which greater diesel removal occurred, with a quantity of 5g and a particle size of 1mm, in different concentrations (20,40,60 and 80 ppm) of diesel solution in seawater. The amount of Diesel removed tends to stabilize around 13 mg L^{-1}, showing saturation of the material at these concentrations.

4. Conclusions

In the physical and chemical characterization of three types of sawdust, using FTIR for each, it was observed that they have similar chemical compositions, but differ in the concentration of some functional groups, reflected in the intensities and proximity to the bands that represent hydrophobic and hydrophilic zones. It was established that the sawdust with the highest yield was *C. odorata L.* with 58.49%, followed by *H. crepitans* with 58.13% and finally *S. apétala* with 34.14%. It was determined that the removal percentage yield increases as the particle size decreases, in the same way the amount of sawdust dosage. When establishing the adsorption capacity of *C. odorata L.* sawdust at concentrations of 40, 60 and 80 ppm, it was observed that it had good diesel removal capacity, and its saturation was close to 13 mgL^{-1}, as the concentration increased.

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