TREATMENT OF WASTEWATER GENERATED FROM AUTOMOBILE SERVICE STATIONS USING CORN COB AS ADSORBENT

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ABSTRACT
Automobile wastewater is one among the heavily contaminated wastewater consisting of harmful elements such as surfactants, oil and grease, dust particles, and various dissolved and suspended solids. In this study, car wash water from an automobile wash center in Chennai, Tamil Nadu was collected and treated with waste from corn crops that is inedible. The increase in automobile industries and similar wash centers is contributing to environmental contamination. Due to the low cost and availability, the efficiency of removal of pollutants, and since it promotes environmental sustainability, natural materials are adopted more than chemicals. The study adopted using a column adsorption process and it showed good results in the physiochemical characteristics where it has adsorbed oil and grease, TDS, and TSS. Oil and grease removal by 71.4% was observed whereas the biochar was found to be effective with an 89% reduction in total dissolved solids and more than 50% decrease in parameters such as TSS, COD, conductivity, oil and grease, and total alkalinity. The adsorption isotherm was studied with varying particle size and bed height along with the comparison of removal efficiency of various parameters in this experimental investigation.

Keywords: Automobile Wastewater, Biochar, Adsorption, Physio-Chemical Characteristics, Sustainability, Corn Cobs.

INTRODUCTION
Water is one of the basic essential substances for human livelihood. The significance and role of water cannot be replaced with any other substance in its form. The increase in industrialization and urbanization has caused a huge number of harmful effects on water life and water bodies. This leads to being a threat to the nature and environment, generally referring to the level of contamination caused to its water bodies. The disposal of wastewater effluents from industries and other sources should be treated before letting out them into the atmosphere. The wastewater disposed into the environment consists of harmful pollutants that are treated with various technologies for a sustainable environment and human life. Contamination of water is not a new alarm to the globe, subsequently, prevention and control for the same have been practiced for years. Color, turbidity, pH, nutrients, odor, turbidity, and coliform count are some of the major factors that affect the quality of clean water. The strong development and growing industrialization due to the increase in the population worldwide leads to environmental pollution in a sizable manner. There are several methods adopted to treat wastewater using chemicals as well as natural materials. In recent times, an idea for using natural adsorbents that are safer and also inexpensive such as sugarcane bagasse, rice shell, neem bark, sawdust, oil palm shield, coconut shell, nonliving plant materials like potato peal, sawdust, black gram shell, egg shield, seed shields, coffee shell, sugar-beet pectin sets, and citrus peel, etc., in favor of the elimination of heavy poisonous metal ions from effluent and it has been determined fruitfully. In this study, one of the cheapest and easily available crops, corn cobs is used for treating wastewater. Maize is scientifically known as Zea mays, and it is a widely farmed crop plant. It is used as a staple meal as well as for manufacture. Around 85% of the nation’s maize is produced in nine major states Karnataka, Andhra Pradesh, Tamil Nadu, Rajasthan, Maharashtra, Bihar, Uttar Pradesh, Madhya Pradesh, and Gujarat, with Andhra Pradesh being the main producer.
There have been studies made in which corn cobs were used for various dye removal and it was mostly used in tanneries. Few studies also showed how it efficiently removed toxic metals like chromium, and mercury, and removed excess contamination from wastewater.\textsuperscript{11-13} Among several types of wastewater, automobile service station wastewater is categorized as one of the heavily contaminated wastes with high impurities\textsuperscript{14,15}. Automobile wash centers is booming in today’s world with the increase in demand, population, and change in lifestyles. The majority of the time, untreated car wash effluent is released into sewer systems. The direct discharge of this car-washed wastewater into the sewerage system may have a bad impact on the efficiency of sewage treatment operations due to heavy toxic elements and metals present, or at the very least place a burden on the sewage treatment facility.\textsuperscript{16,17} These wastewaters are the water coming out of car wash centers which contains harmful contaminants like detergents, high amounts of oils, grease, petrol and diesel residues, metals, organic matter, and particles such as dust which is directly let out in the open sewers and water bodies.\textsuperscript{18,19} The presence of suspended solids and other dissolved solids must be treated consciously before letting them out into the environment to prevent pollution and contamination. A study carried out on how huge car wash centers use heavy equipment’s with electrocoagulation, and membrane bioreactor treatment processes which is expensive and unaffordable for the small-scale centers.\textsuperscript{20-23} Hence the need for treatment in a sustainable and natural form is a better alternative for sustainability and better use of waste developed from agricultural wastes.\textsuperscript{24,25} Thus, the use of natural adsorbents is the need of the hour based on the economic, social, and environmental demands.\textsuperscript{26-28}

**EXPERIMENTAL**

**Materials**

Corn cobs were collected from local vendors in Koyambedu market, Tamil Nadu. These cobs were cleaned well by washing them in running tap water to remove the dust and impurities. The whole point of this experiment was to conduct it chemically free and hence no chemical treatment was done. The corn cobs were then sundried and once again washed using distilled water. Further oven-dried at 110° C to remove moisture content, then crushed in a grinder to obtain a powdered form which is shown in Fig.-1. The pH of corn cobs was found to be acidic with a pH value of 6.7. The wastewater was collected from a car wash center in Chennai, Tamil Nadu. It was found that there are no proper facilities to treat the wastewater before letting it out into drains, nearby water bodies, or even in barren lands. The influent water was collected in a 2L can and initial characterization was carried out for those samples. Physio-chemical parameters like pH, turbidity, total dissolved solids, total suspended solids, COD, BOD, Total alkalinity, oil and grease, conductivity, and Total hardness were determined.

**Preparation of Biochar**

After cleaning the cobs and drying them in the oven, a sizeable amount of it was used to prepare biochar. The corn cobs were cut into small pieces and it was kept in a muffle furnace. From the cycling experiment, it was found that 400°C seems to be the most suitable temperature to obtain biochar. The cobs were placed in porcelain bowls at 400 °C for 30 minutes. It was taken out and placed in a desiccator until it cools. The obtained form was then crushed by hand and washed in distilled water to remove dust. Further, it was oven dried at 105 °C. Repeat washing until the substance is dust free or it will affect the treatment and make the water dark in color if not cleaned properly. A sieve/filter was used to wash to separate black dust particles. The remaining solid dust-free black material is the biochar of corn cob shown in Fig.-1.
Characterization of Corn Cobs
The raw powdered form of corn cobs and biochar were taken for surface morphological analysis using a scanning electron microscope. The samples were configured with 10 kV voltage and an operating distance of 10 μm and 20 μm and then followed with EDS analysis. The raw corn cobs were kept in an oven at 110 °C for 24 hrs and the moisture content was determined. Further, the biochar form was used to determine the biochar yield.

Column Adsorption
Column adsorption methods were adopted for this experimental investigation. Column tubes of 36cm depth with a diameter of 2.3 cm in the upper end and 1.4 cm in the lower opening were used for this study. There were two different materials used for treatment which are (i) raw form and (ii) biochar form. Firstly, raw treatment was conducted with a column filled with sand as the filter media at the bottom. The depth of the filter media was 5.5 cm in height. On top of the sand filter, the dried powdered raw form of corn cobs was filled into the column tube at a depth of 100 mm. They were compacted and filled to be free from voids. The automobile wastewater was poured into the column tube for a period of 10 minutes and 100 ml of wastewater was filled. It was observed that water took time to come to the bottom of the column noted to be 35 minutes when the first drop of water came out. It was observed that the water had a pale-yellow color while the cobs in the tube had a layer of black-colored dust particles as shown in Fig-2. The collected water was then tested for physical and biological characteristics. The second part of the experiment was the same process using biochar. Here the prepared biochar was further sieved using sieves of size 150 μm and 600 μm. The biochar was filled to 100 mm, 150 mm, and 200 mm depth, and a sand filter of height same as in the raw treatment was used here. The flow rate was kept for 10 minutes for 100 ml of wastewater. It was observed from the experiment that the time taken for water to flow out was much less compared to raw filtration of 3 minutes. The results in biochar were seems to be good as compared to raw treatment and resulted in clear water.

![Fig.-2: Experimental Setup for Column Study using Corn Cob](image)

SEM Analysis
The below given table shows the elemental composition of corn cob with both the raw as well as biochar form obtained from EDS analysis. It was observed that the carbon and oxygen content is higher in biochar when compared with the raw form. The presence of P and Cl is higher in raw form whereas Fe is not detected in it. Meanwhile, Mg was detected in biochar while not present in the raw one which may be due to the biochar preparation process. The Fig.-3 shows images obtained From SEM Analysis that show a heterogeneous structure in both materials. Biochar shows a porous structure compared to raw form which favors adsorption process.

<table>
<thead>
<tr>
<th>Element</th>
<th>Raw (%)</th>
<th>Biochar (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>71.95</td>
<td>75.14</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.94</td>
<td>16.76</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.82</td>
<td>1.34</td>
</tr>
<tr>
<td>Silica</td>
<td>5.31</td>
<td>0.49</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>2.15</td>
<td>0.30</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.55</td>
<td>0.93</td>
</tr>
<tr>
<td>Iron</td>
<td>Not detected</td>
<td>1.51</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.91</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Table–1: Composition of Corn Cob in Raw and Biochar using EDS analysis
RESULTS AND DISCUSSION

The collected automobile wastewater was tested for initial characterization and it was observed that it consisted of heavy contamination with TDS being 1938 mg/L, which after treatment with raw and biochar was 270 mg/L and 212 mg/L respectively. The initial TSS was a very high value of 10000 mg/L, which decreased to 8000 mg/L after raw treatment and to 2000 mg/L after biochar treatment. The collected water was brown and after treatment with biochar, clear water was obtained. The biochar shows an effective outcome in the removal of turbidity, conductivity, TDS, and TSS compared to the raw form. The Table-2 shows the results of all parameters before the treatment process and after the filtration with raw and biochar forms.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Initial Characterization</th>
<th>Raw (average)</th>
<th>Biochar (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
<td>6.43</td>
<td>7</td>
</tr>
<tr>
<td>Turbidity</td>
<td>126 NTU</td>
<td>107 NTU</td>
<td>73 NTU</td>
</tr>
<tr>
<td>TDS</td>
<td>1938 mg/L</td>
<td>270 mg/L</td>
<td>212 mg/L</td>
</tr>
<tr>
<td>TSS</td>
<td>10000 mg/L</td>
<td>8000 mg/L</td>
<td>2000 mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>260 mg/L</td>
<td>160 mg/L</td>
<td>128 mg/L</td>
</tr>
<tr>
<td>BOD</td>
<td>58 mg/L</td>
<td>27 mg/L</td>
<td>18 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>2840 μs/cm</td>
<td>1400 μs/cm</td>
<td>600 μs/cm</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>7 mg/L</td>
<td>&lt; 2 mg/L</td>
<td>&lt; 2 mg/L</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>413 mg/L</td>
<td>200 mg/L</td>
<td>150 mg/L</td>
</tr>
<tr>
<td>Total hardness</td>
<td>130 mg/L</td>
<td>75 ppm</td>
<td>80 ppm</td>
</tr>
</tbody>
</table>

The removal efficiencies were found to be more than 50% with the biochar-treated ones with more efficient and effective adsorbent. The Fig.-5 shows removal efficiencies of the parameters tested and a comparative graph showing the percentage of decrease in characteristics with raw and biochar treated with the effluent water. There is a noticeable difference in TDS removal and a huge difference in biochar, while oil and grease show an equal amount of removal in both cases.

Adsorption Isotherm

The experiment was carried out with column adsorption and the Thomas model was used for the adsorption studies. It is a theoretical model commonly applied in column adsorption data analysis. Since from the study biochar proved to be efficient among the two materials and so isotherm studies were done for the same with the use of linear equations. The bed heights were changed from 100mm to 200mm, the isotherm studies showed 150 mm to have a K_TH value maximum of 1.54 whereas 200mm had adsorbed more of value 10.014, where q_0 is the maximum equilibrium capacity and K_TH is the rate constant in Thomas model. The Fig.-6 shows the breakthrough curve based on the effect of particle size and bed height.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Particle size</th>
<th>Bed height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thomas</td>
<td>parameters</td>
<td>150 μm</td>
<td>300 μm</td>
</tr>
<tr>
<td>model</td>
<td>K_TH (ml/min mg)</td>
<td>2.46</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>q_0 (mg N/g)</td>
<td>5.64</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.984</td>
<td>0.975</td>
</tr>
</tbody>
</table>

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CONCLUSION

The initial characteristics of automobile wastewater were determined along with that of adsorbent. The biochar form compared to raw corn cobs provided remarkable results in reducing the parameters that were found to be in excess leading to environmental contamination. It was observed from the adsorption studies that adsorption was effective in a bed height of 150 mm. The parameters after treatment with adsorbent were within the permissible values. The maximum removal efficiency was attained in parameters influencing the contamination of water bodies and the environment. It was derived from the experiment that the removal efficiency of 71.4% in oil and grease and almost 90% TDS were removed effectively with the treatment process. The objective was to remove the former parameters but it was noticed that corn cob biochar was an effectual adsorbent as it helped decrease parameters like COD, TSS, and conductivity. The progress shown in the study when treated with biochar is satisfying and viable. It can be suggested from the experimental works that a filter can be made and attached to the outlet of the pipe from automobile stations resulting in letting out treated water into the sewers which are fit for further treatment with the other water as this adsorbent proved best in oil and grease removal as well as dissolved solids. The results predict that adverse changes in properties make corn cob a proficient natural adsorbent which also is easily available, and the cheapest material as it is a waste that is converted and used for treatment purposes.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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