e-ISSN No.: 2582-4228

Journal of Indian Association for Environmental Management

Journal homepage: www.http://op.niscair.res.in/index/php/JIAEM/index

Activated Rice Husk as Chemical Oxygen Demand Reducing Agent in Petroleum Contaminated Water

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Submitted: February 02, 2021 Revised: October 17, 2021 Accepted: October 20, 2021

Abstract: **Water contaminated by petroleum products contains many harmful carcinogenic wastes, which prove to be fatal for living beings. Treatment of such water is of paramount importance. Areas around Belagavi in Karnataka state (15.87°N 74.5°E) have rich alluvial soil known for its commercial crops sugar cane and paddy. The rich mills are a source of rice husk, and rice bran powder finds utility as a fodder and fuel source. The proposed work envisages the usage of low cost, readily available material, rice husk, as an adsorbent in treating petroleum contaminated water [PCW]. Water samples were obtained from 50 different locations in close vicinity of petrol filling stations, vehicle servicing points, garages in Belgaum city four times at regular intervals of six months (before and after monsoons). Samples are subjected to tests like alkalinity, calcium hardness, chemical oxygen demand, electrical conductivity, magnesium hardness pH, total dissolved solvents, and total hardness. It was found that COD was higher for these samples and even higher for samples obtained after monsoons. Rice husk was used by considering pH, particle size, time, and dosage as the four parameters that govern its efficiency as adsorbent, thus reducing the COD of the samples.**

***Keywords*:** **Activated rice husk Petroleum derivatives Water and waste water Chemical Oxygen Demand**

I. INTRODUCTION

One of the major problems our world is currently suffering from is the pollution of water. Contaminants in organic and inorganic materials are the primary forms of pollutants that add to water pollution. Rice husks, the protective layer of rice, are used as fertilizers, fuel, insulation boards, building material, etc. The proposed study assesses the impact of petroleum contaminated water and activated rice husk as an adsorbent to reduce the petroleum components from water. The chemical pollutants directly contribute and increase the chemical oxygen demand (COD). The efficiency of treatment is evaluated using COD analysis.

Guo, Y et al. state the utilization of activated rice husk adsorbent (ARHA) to reduce hexavalent chromium from industrial effluents. During the study, the parameters were adsorbate concentration, contact temperature, contact time, pH, and pore structures. Treatment and reduction of heavy metal ions by activated rice husk were reported [19]. Many techniques are available to separate impurities from petroleum-contaminated water, but the more efficient reduction of dissolved organic pollutants from petroleum-contaminated water is adsorption. This study reported that adsorption of contaminated petroleum water carried out using different adsorbents such as activated carbon, bentonite, and results showed an efficient reduction of dissolved organics from PCW [20].

Attempts for Treatment of Pollutants

Mercury is a hazardous element that proves to be a toxic material. Removal of Hg^{2+} using silver nanoparticles, supported on activated alumina and protected by dimercaptosuccinic acid (MSA), is stressed [1]. Carbonaceous materials derived from varied sources have been activated and used exhaustively in sewage, industrial effluent, and water purification [2, 3]. Activated carbon prepared from lignin, a waste obtained during the kraft pulping process, has proved to be very efficient adsorbent compared to other activated carbon forms. The kraft liquor lignin was acid activated by organic phosphoric acid [4]. Studies also indicate using adsorption with activated carbon to treat and reduce phenolic derivatives [5-10]. Materials obtained by pyrolysis treatment and chemical activation on sewage sludge have a high surface area and significant porosity, which can be further used to treat and reduce organic wastes from municipal sewage and industrial effluents [11].

Industries, domestic wastewater, and agriculture are the three primary reasons that contribute to phosphorous as a pollutant in water bodies. Water hyacinth wastes were used as an adsorbent in combating swine wastewater pollution due to phosphorous [12]. Fluoride removal is facilitated by alum-impregnated activated alumina as in [13].

Usage of Rice Husk as Adsorbent

Heavy metals located in 4-6 period, 11-15 group of the periodic table, possessing relatively higher density are generally known to be toxic. Cd, Cu, Pb, and Zn in wastewater can be reduced in a controlled pH range on treatment with ARHA and Carbonized Rice Husk (CRH). At pH 7, the adsorbent showed a more remarkable ability to remove some water [14]. A similar review in managing industrial wastewater using rice husk is proposed [15]. Studies report rice husk carbon utilization to purify biodiesel obtained from the processing of remnants of edible oil during frying operations in the food industry [16].

Petroleum Contaminated Water (PCW)

Wastewater contaminated by petroleum sources until and unless fully treated is not usable for gardening / or any other application due to trace impurities have potent of being toxic and carcinogenic. The common scenarios where water bodies come into contact with petroleum derivatives are leakages from pipelines, storage tanks for storing petroleum products, transportation, overfill and spill while filling tanks, automobile service centers, accident spots, and equipment breakdown installation of storage systems. Such water has detrimental impacts on life. Many measures are undertaken to surmount this exceptional problem. Bioremediation process powered with acclimatized bacterial consortium aids in the reduction of petroleum products from water [17]. Ultrafiltration processes for the reduction of petroleum hydrocarbons (PHCs) are tested as in [18].

II. MATERIALS AND METHODS

As a part of the investigation, the authors identified potential locations to collect water samples. Water samples from 50 open and bore wells in the near vicinity of garages, petrol fillings stations, vehicle washing/servicing stations within 10 km from Udyambag, and Belagavi as the focal point were identified. Water samples were collected in sterilized bottles as per specifications laid down AWHA in APPA in pre-monsoon and post-monsoon seasons. Grab sampling of samples from recognized sources likely to be contaminated was carried out starting from the first quarter of 2011. Laboratory reagents of LR grade obtained from SD Fine Chemicals (SDFCL), namely sulphuric acid (1N), sodium thiosulfate (0.1N), sodium hydroxide (1N and 0.5 N), potassium dichromate (0.25N), phenolphthalein indicator, methyl orange indicator, mercuric sulfate, KCl (0.1N) solution, ferrous ammonium sulfate (0.25N), ferroin indicator, buffer solution of pH, were utilized for the adsorption study.

The water samples were characterized at onsite for pH by a portable device pH/EC/TDS meter (ELICO & Naina Solaris Limited - Npc 361D). The collected samples were transported to the laboratory in insulated intermodal containers. The rest of the water parameters were tested in the laboratory using the procedure specified in APHA, 1985. The total hardness (TH), magnesium (Mg), COD, and calcium (Ca) were analyzed by the volumetric method. The COD tests were conducted as per the standard potassium dichromate technique mentioned in ASTM D 1252-67 (modified and reapproved, 1974). Higher COD values were observed in post monsoons samples, comparable to visual inspection results of other parameters such as turbidity. Similar inferences can be made concerning the other seven parameters tested.

The collected water samples treatment involved administering ARHA, and adsorption studies were carried by varying each of the variables in succession. The key factors affecting rice husk adsorption efficiency are contact time, dosage, particle size, and pH.

Effect of Contact Time

A mixture of ARHA (0.2 gram) with 200 ml of the test water sample is mixed and taken in an Eppendorf cups and intricately gently agitated by a variable speed wrist shaker. Total samples of 50 samples from identified collection spots were shaken for 150 minutes. After the predetermined shaking time, the contents are centrifuged, filtered using ashless Whatman filter paper No. 41, and the collected filtrate is preserved in a bottle. It is observed that the slope of the curve for COD versus contact time approaches zero beyond 70 minutes. Figure 2 shows the graphical representation of the effect of time on COD values. It is observed COD is inversely proportional to time, and beyond 70 minutes, there is no significant change in COD, and hence 70 minutes is inferred as saturation time. Further experimentations for COD reduction are repeated at a fixed contact period of 70 minutes.

Effect of pH

200 ml of sample from the 50 test samples collected were collected in different containers, 0.2 gram of activated rice husk as adsorbent is added to each of the samples, and adsorption experiment were performed for p^H of 2, 4, 6, 8,10, and 12. The sample bottles were shaken using a wrist shaker for an optimal time duration of 70 minutes. The contents are centrifuged, filtered using Whatman filter paper, and the filtrate collected is stored in a bottle. The observed results indicate a minimum COD of 50 ppm is observed in the acidic reason at a pH of 2.0. Thus the further experimentation is carried out at a pH of 2.0 and contact time of 70 minutes.

Effect of Particle Size

The standard screen screened adsorbent samples of ARHA as per the Tyler series on a rotap shaker. Three different sized particles having a particle size of 212, 425, and 500 microns were classified. 200 ml of sample and 0.2 grams of ARHA are taken in sample bottles. The p^H of the mixture is adjusted using $NaOH/H_2SO_4$ used as alkalinity regulators. The contents are shaken with a wrist shaker for 70 minutes, centrifuged, and filtered using Whatman filter paper, and COD was determined. The results of the effect of particle size are depicted in Figure 4. The minimal COD value was observed for the particle size of 212 microns. It is clear and inferred that as the surface area increases, the particle size decreases and leads to better adsorption efficiency. Hence, further studies were carried out at 212 microns particle size of ARHA, 70 minutes of contact time, and an acidic range p^H of 2.0.

Effect of Dosage

The final variable study was that of adsorbed ARHA dosage at 70 minute residence time, acidic pH of 2, and 212 microns ARHA particle size. 200 ml of water sample was taken in a sample bottle, and ARHA is added at various percentages. The sample bottles are shaken using a wrist shaker for 70 minutes. The sample was centrifuged and filtered with Whatman filter paper, and the optimal dosage was determined. The experimental analysis results are shown in figure 5, and it is inferred that the optimal reduction of COD occurs at a dosage of 0.1 grams per 100 ml of the water sample.

III. Results and Discussion

Four key factors analyzed rice husk's role as an adsorbent, which is contact time, pH, particle size, and dosage. It was observed from the results that 70 minutes of contact time was found to be optimal for shaking the water samples (Figure 2), pH value of 2 (Figure 3), the particle size of 212 micrometers (Figure 4), and dosage of 0.1g/100ml (Figure 5). Figures 6a-6g show the tests for impact assessment of the petroleum contaminated water for 50 samples taken before and after the monsoons. As a result, there is a higher magnitude of diluted wastes from different sources percolates through the soil and reaches the water aquifers during the post monsoons. The presence of these contaminants can be seen in the water samples collected from open and bore wells in around Udyambag, Belagavi. The experimental batch results show that ARHA can be one of the prominent low-cost adsorbents that can reduce the COD. The authors identify the need for studying adsorption for COD reduction in a continuous system, and due efforts are needed in the direction of desorption and regeneration of ARHA.

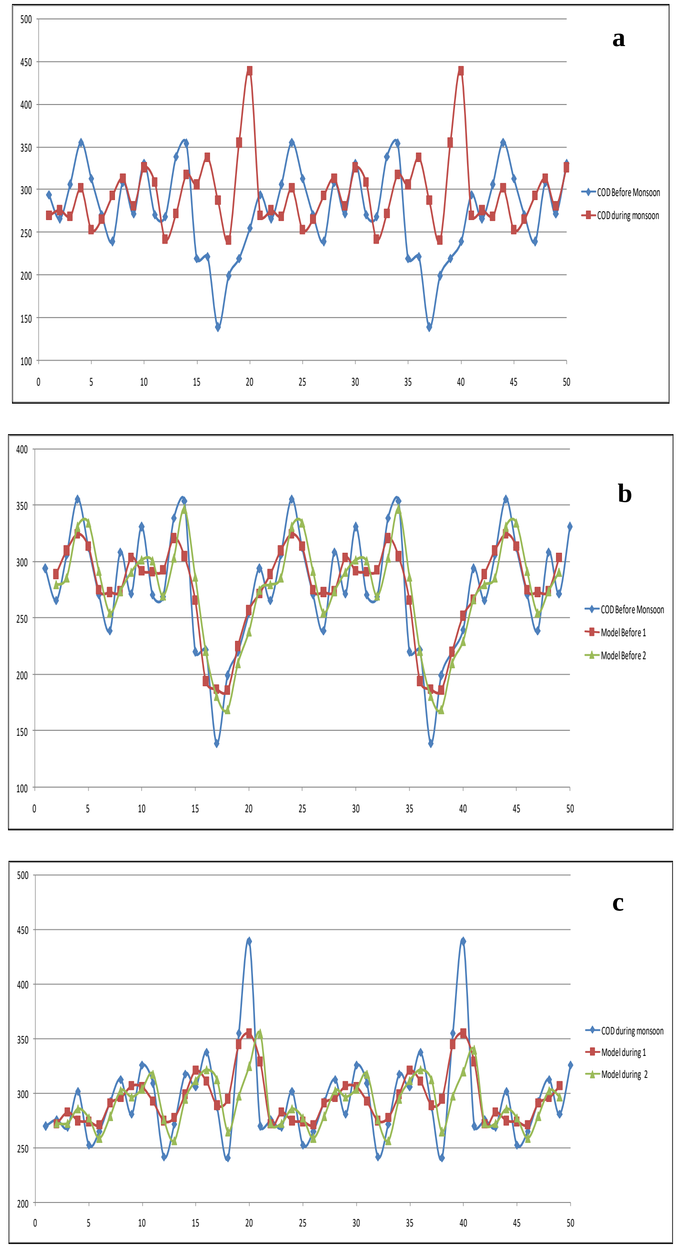

Figure 1: Graphs showing COD values of samples collected before the monsoons and during the monsoons **a** Graph showing the COD values before the monsoons and during monsoons **b** Graph showing the COD values before the monsoons and during monsoons **c** Graph showing the COD values during the monsoons and models

Figure 1(a), (b), and (c) represent the COD values of samples collected before the monsoons and during the monsoons. The classical moving average 2 point and 3 point technique (MAT) is employed to obtain an overall idea of trend cycles in the data. MAT indicates average of subsets. The monsoon period indicates higher values of COD in the range of 241-439 ppm and that before monsoons is in the range of 139-356 ppm. The higher values of COD during rainy season in sub surface water aquifers may be attributed to contaminants from washing of roads and other sources and not necessarily due to petroleum origin.

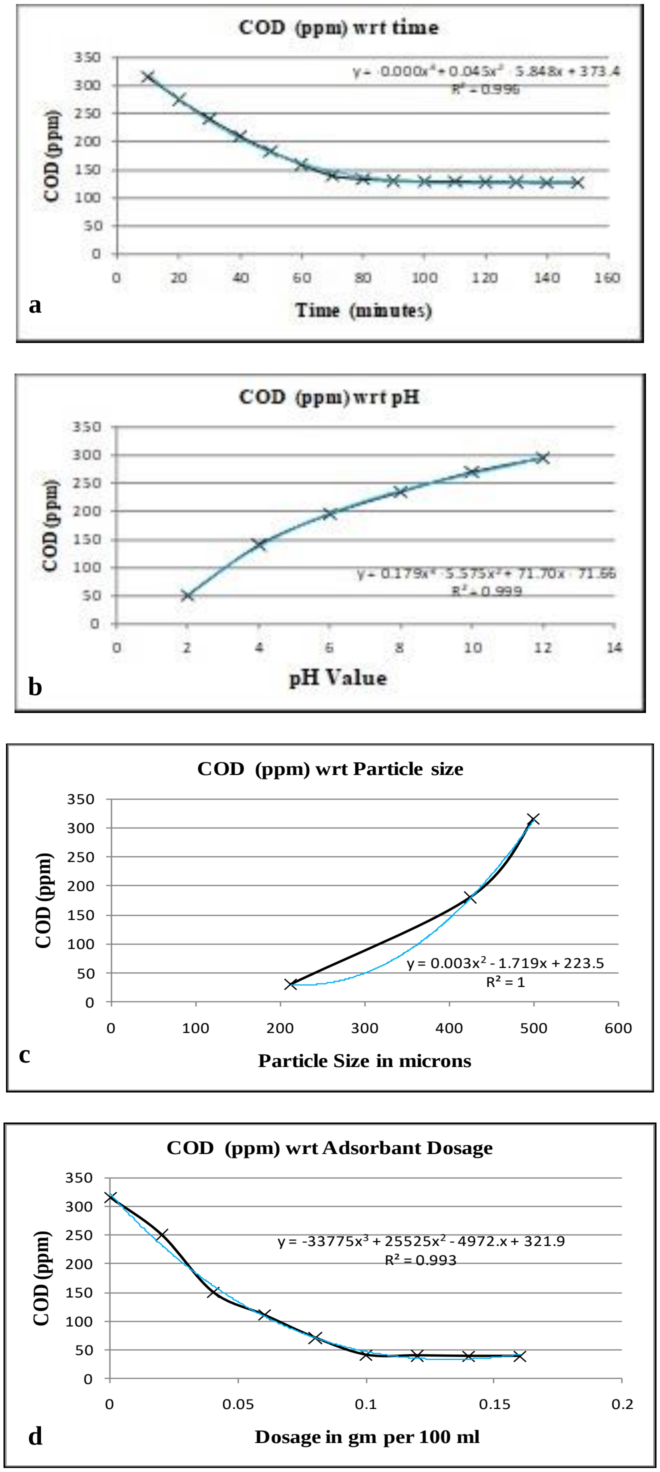

Figure 2: Graph showing COD versus other COD affecting parameters **a** Graph showing the variation of COD with respect to time **b** Graph showing the relation between COD and pH values **c** Graph showing the relation between COD and particle size **d** Graph showing the impact of rice husk (ARHA) dosage on COD

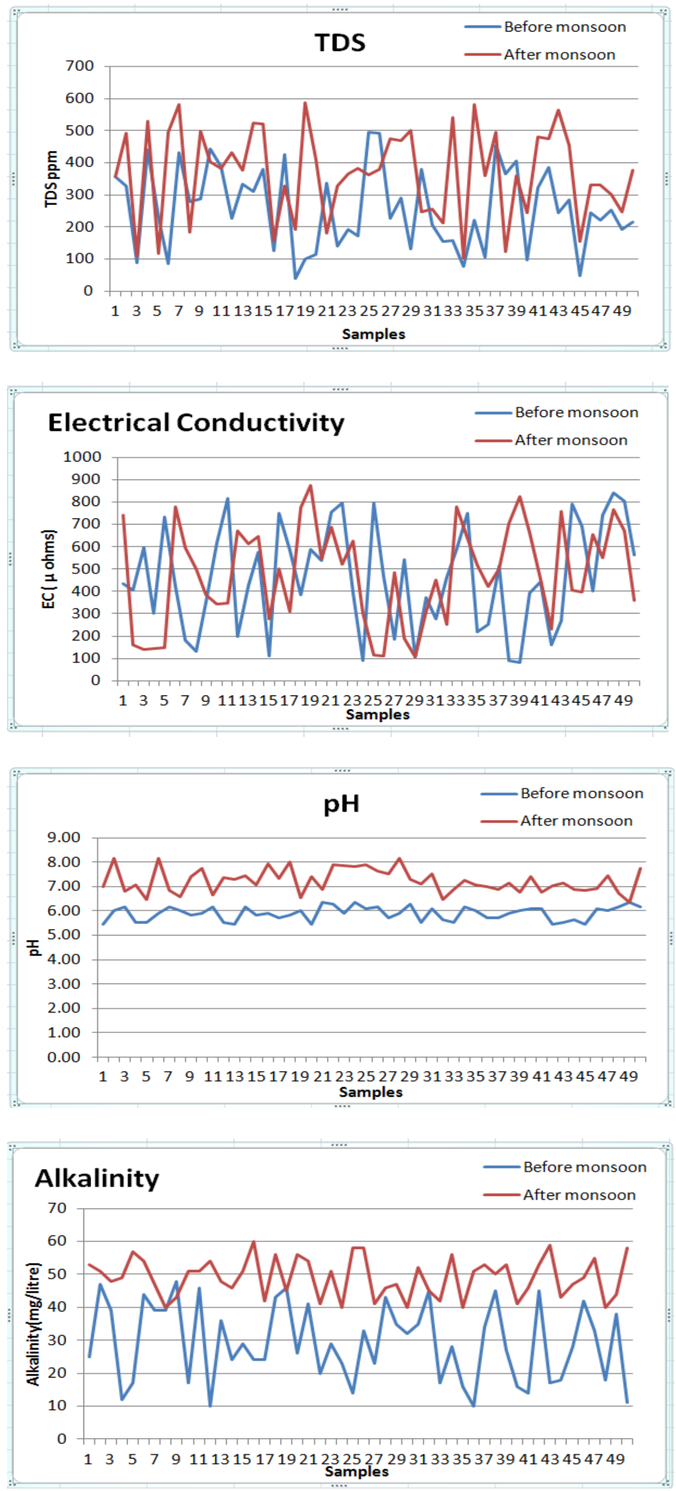

Figure 3: Figure showing **a** TDS **b** Electrical Conductivity **c** pH **d** Alkalinity of samples before and after monsoon

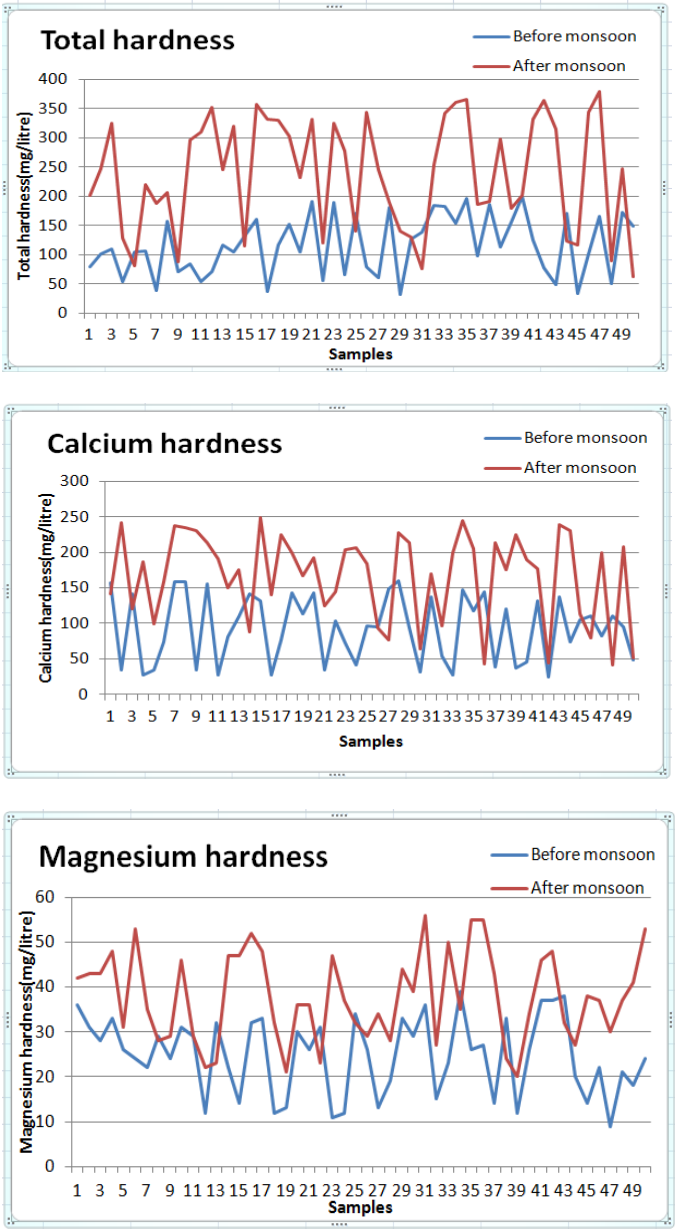

Figure 4: Figure showing **a** Total hardness **b** Calcium hardness **c** Magnesium hardness of samples before and after monsoon

IV. Conclusion

Water pollution due to petroleum products is a severe issue in the present era. The problem is unavoidable in most of the scenarios. So a robust technique for overcoming it is highly crucial. The proposed work focuses on utilizing rice husk as an adsorbent in treating petroleum contaminated water. The rice husk's performance characteristics were evaluated using time, pH, particle size, and dosage as the COD's key parameters. It was found that rice husk is a promising adsorbent agent in adsorbing petroleum products in water, which was evident from the obtained COD values.

V. Acknowledgement

The authors are indebted to Dr. MSS KLES College of Engineering and Technology, Belgaum, for all the necessary amenities provided for the experimentation.

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