

Suitability of Rice Husk as Bio Sorbent for Removal of Dyes from Aqueous Solution on the basis of Chemical Oxygen Demand Analysis

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Abstract

Researchers are investigating the various biomaterials as an effective alternative to the activated carbon for removal of dyes from aqueous solution. Some of the biosorbent have shown extremely high capacity for removal of dyes. But being a biomaterial, consists of organic molecules, they also contribute organic matter to the solution during adsorption process and thus contribute to the COD of the treated solution. There is a very strong and strict restriction on the value of COD of the industrial waste water before discharging into environment. So the biomaterial which is capable of removing the dyes below the prescribed limit, if increases the COD then it is not suitable for use in the adsorption process for removal of dyes from industrial effluent. In this paper the suitability of raw rice husk, sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk has been examined and found that raw rice husk is not suitable biosorbent where as treated rice husk are the promising biosorbent.

Index terms— rice husk, biomaterials, activated carbon, biosorbent, effluent.

1 Introduction

Chemical oxygen is an important parameter to determine the quality of water. It is the amount of oxygen consumed to oxidize the organic substances present in the waste water into carbon dioxide. Almost all the organic substances get oxidized into carbon dioxide by strong oxidizing agent. It differs from BOD in the sense that BOD stands for biochemical oxygen demand which is defined as the amount of dissolved oxygen consumed by the microorganism present in the waste water responsible for aerobic decomposition of the degradable organic substances present in the waste water. The BOD test involves taking an initial dissolved oxygen (DO) reading and a second reading after five days of incubation at 20°C whereas COD is a much faster, more accurate test and can be completed within 2-3 hours. The value of COD of waste water is always greater than the BOD of the same waste water. Higher the value of COD means more dissolved water will be consumed in oxidizing the pollutant in the water leaving less amount available for the aquatic life and thus lower the quality of water. Ministry of Environment and Forests, Government of India has laid the standard of COD as 250 mg/L for Common Effluent Treatment Plants.

At present millions of dyes are being used in leather, textile, pulp & paper, paints, medicines etc. As a rough estimate it has been reported that 12% of total dye lost during manufacturing storage and transportation to the end user. About 20 to 25% of dyes used in industries find its way into the effluent and finally enter into the environment. [3] Dyes are stable, incompatible with strong oxidizing agents, acids, light sensitive and combustible. [7] They are very toxic, extremely small amount produces intense colour and hence repulsive to our aesthetical sense, interfere with photosynthesis by obstructing the sunlight and so harmful to aquatic ecosystem. [9] Moreover it has a tendency to accumulate in the cell of living organism and thus enter into our food

chain. Since dyes are organic molecule and so their presence in waste water enhances its COD. Due to such evil consequences various governmental and environmental agencies have put extremely stringent regulation regarding the quality of effluent which has to be discharged into the natural water bodies. Their strict enforcement has drawn the attention of the researcher to find out the suitable and cost effective method for removal of dyes from aqueous solution. The dyes are very complex organic molecule, resistance to aerobic digestion and are stable to light, heat and oxidizing agents and hence their treatment are difficult. [8] Several methods like chemical precipitation, ion exchange, reverse osmosis; coagulations & Flocculation, solvent extraction, Oxidation and distillation etc., have been reported in the abundant available literature during the last three decades. But all these methods have limitation. Among them the adsorption is found to be the best available method as involves simple low cost technique and non generation of toxic products. [4] Activated carbon is the best known adsorbent. But due to its high cost and difficult to regenerate it has limited applicability. Researchers are now looking for alternative material which can be used as an effective alternative of activated carbon. Many biological and agricultural waste/by product like barley straw, waste tea leaves, sago waste, peanut hulls, hazel nut shell, saw dust, neem bark, chitin beads, thermally treated rice husk ash, waste banana, orange peels, cocoa shells, tree fern, coffee residue, palm kernel fibre, olive stone waste, grape stalk, bagasse, fly ash, etc., have promised to be a good alternative on the basis of their removal capacity. [6] But their impact over the COD of the waste water i.e., the overall quality of waste water has not been examined after the adsorption.

In the present study the suitability of Raw Rice husk, sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk as a biosorbent for the removal of MG and CV have been examined on the basis of their removal capacity as well as by observing the change in the COD value of dyes solution before and after the removal of dyes by adsorption process.

2 II.

3 Materials and Methods

4 a) Adsorption Experiment i. Preparation of adsorbent

The rice husk, collected from a rice mill in silchar, was passed through different sieve sizes. The fraction of the particle between 425 and 600micron (geometric mean size: 505 micron) was selected. This was washed thoroughly with distilled water several times for removing dirt and impurities. It was then first air dried and after that dried at temperature 60 °C. The dried rice husk was designated as Raw Rice Husk (RRH). It was then suspended in 0.1M potassium hydrogen phosphate (K_2HPO_4) solution and in 0.1M sodium carbonate solution in separate beaker. Both were kept in the incubator whose temperature and rotational speed were maintained at 40 °C and 100 rpm respectively, for about 2 hours. Then incubator was switched off. It was left at normal temperature for next 24 h. After that solution was filtered and the filtered rice husk was washed thoroughly with distilled water until the rice husk gave no color and the pH of the washed water was close to neutral. They were then dried at 60 °C for 6 h.

After drying, the adsorbents were stored in sealed glass containers and designated as potassium hydrogen phosphate treated rice husk (KHPRH) and sodium carbonate treated rice husk. They were now used in all the experiments.

ii. Stock Solution One gram each of commercial grade crystal violet and malachite green obtained from local chemist, were dissolved in one liter of distilled water to prepare the stock solution of 1000 mg/L. Experimental dye solution of different concentrations was prepared by adding the appropriate volume of distilled water in the stock solution.

iii. Batch Adsorption Experiments Three samples of 150 ml of both dyes solution of 50 mg/L concentration were taken in 250 mL glassstoppered, Erlenmeyer flasks. Now 1.5gm of RRH, NCRH and KHPRH to keep the dose 10 gm/L were added to the sample and marked the flask as RRH, NCRH and KHPRH. All these six flask were kept in incubator whose temperature and rotational speed were maintained at 30 °C and 200 rpm respectively, for about 90minutes. Samples from the flasks were collected after 90 minutes and the residual dye concentration in the solution was measured by using double beam UV/VIS spectrophotometer (Model 3501/0706). The percentage removal of dye by the adsorbent was using Equation 1: % Removal = $\frac{C_0 - C_t}{C_0} \times 100$ (1)

Where C_0 & C_t are initial concentration and concentration at any instant t of dye in mg/L. All the experiments were performed twice and the average values of results were taken.

5 b) Test for chemical oxygen demand measurement

The principle involves in the COD test is that all organic compounds can be oxidized to carbon dioxide, ammonia and water. The oxidation reaction can be expressed as $C_nH_aO_bN_c + ?n + a/4 + b/2 + 3/4c + O_2 \rightarrow nCO_2 + ?a/2 + 3/2c + H_2O + cNH_3$

This expression includes the oxygen demand caused by the oxidation of ammonia into nitrate through the process of nitrification represented by the following equation $NH_3 + 2O_2 \rightarrow NO_3^- + H^+$

Dichromate does not oxidize ammonia into nitrate, so this nitrification can be safely ignored in the standard chemical oxygen demand test. [10] For the test COD block digestion system (model Pelican Kelplus -08L CAC) were used for the test. The test was started with switching on the digestion system and set the temperature 150

0 C in the temperature controller. Now mercuric sulphate was added to each digestion tubes and took 50ml of sample in it. After that standard $K_2Cr_2O_7$ (potassium dichromate of strength 0.125N) was added in it. At this stage the digestion tube was kept in plastic tray with water to cool the tube during addition of sulphuric acid. Now 50 ml of Sulphuric acid as reagent was added slowly and carefully. Then the solution was mixed thoroughly. After mixing the digestion tubes were placed properly in the COD digester. The air condensers were kept on the digestion tubes and reflux the mixture for 90 minutes by setting the time in timer. At the end of the digestion the air condensers were separated from the digestion tube. The tube were now removed and kept over tube support rack and left them to cool at room temperature. Finally the tube was taken one by one for titration for determination of COD. The titration was done against 0.1 M Ferrous Ammonium sulphate solution by adding 1-2 drops of Ferroin indicator. [??] The amount of COD was calculated from equation 2 Table 1 shows that raw rice husk; sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk are able to remove the crystal violet from aqueous solution up to 40.63%, 90.6 % and 89.6% respectively through the process of adsorption. Similarly they can remove malachite green up to 51.38%, 98.4% and 97.3 % respectively.

6 COD (in

7 Results and Discussions

It can be seen from table ?? that the COD of the CV solution after adsorption onto raw rice husk increased from 127.84 before adsorption to 133.76 after adsorption of CV onto RRH. Similarly the COD of the MG solution after adsorption onto raw rice husk increased from 116.52 before adsorption to 121.11 after adsorption of MG onto RRH. The increase in the COD after adsorption onto RRH may be due to the fact that the RRH which was made of various organic molecules likes cellulose (25 to 35%), hemicelluloses (18 to 21%), lignin (26 to 31%), soluble (crude protein) (2 to 5%) [5] though remove the dyes from aqueous solution but it also contributes the organic matter to the solution. During the process of adsorption onto RRH the addition of organic molecule is much more compare to the removal of dyes then there is an increase in the COD. In case of the treated rice husk the value of COD decreased after adsorption but the decreased was not proportional to the % removal of the dyes. The same reason may be preferred here also. In this case the contribution of organic matter by the rice husk was less compare to the raw rice husk as during treatment most of the weakly attached organic matter got washed away. So the COD analysis suggests that raw rice husk is not appropriate biomaterial for adsorption of CV and MG in waste water whereas sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk can be used as adsorbent for CV and MG dyes although they all show removal capabilities of dyes from the waste water.

IV.

8 Conclusion

The adsorption experiments suggest that raw rice husk, sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk may be used as biosorbent for removal of CV and MG from aqueous solution. But COD analysis suggests that RRH cannot be a suitable biosorbent as it increases the COD of the treated waste water through the process of adsorption of dyes onto RRH. However sodium carbonate treated rice husk and potassium hydrogen phosphate treated rice husk may be used as biosorbent for removal of CV and MG from aqueous solution. As they not only remove the dyes from waste water but also reduce the COD of the treated waste water. This result suggests that COD analysis has to be made in deciding the suitability of the biosorbent. ¹

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and potassium hydrogen phosphate treated rice husk									
DYES				Percentage removal by					
				RRH		NCRH		KHPRH	
Crystal violet				40.63		90.6		89.6	
Malachite green				51.38		98.4		97.3	
Table 2 : COD of the various solutions									
COD Before				COD of CV solution				COD of MG solution	
(mg/L)				after adsorption onto				after adsorption onto	
COD of solution									
CV sol		MG sol		RRH		NCRH KHPRH		RRH NCRH KH-PRH	
127.84		116.52		133.76		66.88		81.65 121.11 43.27 50.66	

Figure 1: Table 1 :

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