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Adsorption Study of Algal Biomass Cultivated at Carbon Sequestration Plant and its Potential to Treat Industrial Effluents

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Abstract: Algal Biomass procured from carbon sequestration plant of NALCO at Angul, India, was evaluated for its possible application as an industrial adsorbent. The algal biomass (AB) and carbonized algal biomass (CAB) were taken for the adsorption characteristics. A comparative study of adsorption capacity with commercial activated charcoal (CAC) has been reported in the present work. X-Ray Diffraction and FTIR study were carried for the structural analysis. The BET method was carried out for surface area analysis of the samples. The removal of Methylene Blue (MB) dye has been studied for all the samples and it is observed that the maximum dye removal (98%) occurs with activated carbonized algal biomass. Color reduction potential of the adsorbents was studied on wastewater effluent from paper mill, beverages and steel industries. A maximum of 85.7% of color removal was noted from paper mill effluent that was higher comparable to that with commercial activated charcoal.

Keywords: Adsorbent; Methylene Blue dye; Algal Biomass; Carbon Sequestration; Waste water effluent.

1. INTRODUCTION

Industries such as textile, leather, paper, plastics, food, cosmetics etc. use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. Methylene blue is one such commonly found dye in the effluents discharged from such industries. Discharge of colored wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body and an increase in toxicity. Many dyes may cause allergic dermatitis, skin irritation, and dysfunction of kidney, liver, brain, reproductive system and central nervous system [1]. Other problems associated with colored effluent are lowering light penetration, affecting photosynthesis activity of aquatic life and degrading aesthetic nature of the water surface [2-4]. Moreover, their degradation products may be mutagenic and carcinogenic [5-7]. Here by it is indispensible to treat these colored effluents to ensure the welfare of environment and human health.

With everyday rising levels of pollution from such effluents, considerable attention has been focused on its removal using adsorbent derived from low cost materials. Prevalent technologies for color removal such as coagulation, flocculation [8], biological oxidation [9] and chemical precipitation [10] have the limitations due to their high energy demand, high cost, requirement of large number of chemicals and hazardous by products. It is rather difficult to treat dye effluents because of their synthetic origins and mainly aromatic structures, which are biologically non-degradable. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [11].

Various studies have been done to establish the adsorbent characteristics of waste materials and biomass such as silica and iron oxide [12], bamboo dust [13], bagasse fly ash [14], polyvilnyldienefluoride fibers [15], waste apricot [16], olive seed waste [17], vetiver roots [18], Hevea brasilienis seed coat [19], peach stones [20] and peanut husk [21] . All these studies concluded excellent ability and economic promise of the activated carbons prepared from biomass samples.

Algal biomass (AB) being one of the most efficient photosynthetic and CO_2 sequestering organism on earth, its adsorption potential can be enhanced considerably in a CO_2 rich environment [21]. Bio-fixation of carbon dioxide using microalgae is becoming a potential option as they have the ability to fix CO_2 using solar energy with efficiency ten times greater than that of terrestrial plants; with numerous additional technological advantages one such is the adsorption capacity [22]. Algae are ubiquitous naturally and serve as one of the biomaterials with high capacity for removing dye from contaminated waters [23]. Compare to physicochemical processes, Biological processes have potential to convert or degrade the pollutant into water, carbon dioxide and various salts of inorganic nature. The isolation of potent species and there by degradation is one of the interest in biological aspect of effluents treatment [24].

In the present study the adsorption of methylene blue (MB) dye on the algal biomass (AB) cultivated at the carbon sequestration plant was compared with the carbonized algal biomass (CAB) and commercially available commercial activated charcoal (CAC). The effect of change of adsorbent dose (AB, CAB, and CAC), solution pH and adsorption kinetics have been studied.

2. MATERIALS AND METHODS

2.1 Biosorbents

The biosorbents used in this study was obtained from the carbon sequestration plant, NALCO, India. To prepare the

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sample; firstly it was grinded and screened through 200 BSS sieve. The powered algae were washed with distilled water and dried in a convection oven at 50℃ or 6 h. Further it was treated with 0.1 M HCl and dried at 50℃ for 2 h. The acid protonation using 0.1 M HCl was performed to increase algae adsorption capabilities and to remove any ions.

2.2 Surface area analysis

The surface area of the biosorbents was determined by BET method in a surface area analyzer (Smart Instrument Co. Pvt. Ltd.). Surface area of the algae after washing was 7.92 m^2/g; determined by BET method.

2.3 Characterization of the adsorbents

The biomass samples (AB and CAB) were analyzed for total fat, total protein, and total carbohydrate. Proximate analysis was done to determine its moisture content, volatile matter, ash content and fixed carbon.

2.4 Activation of the algal sample

The AB was activated by physical activation method by direct heating it In Tubular furnace (ACMS -91009) up to 650℃ for a period of 1hr.

2.5 Preparation of MB solution

MB stock solution of 50mg/l was prepared by dissolving a known weighed quantity of solid methylene blue in distilled water. MB solutions of 10, 20, 30, 40 mg/l were obtained by diluting the stock solution.

2.6 Adsorption capacity studies on the samples

Batch mode experiments were carried out to study the adsorption capacities of the adsorbents AB, CAB and CAC. For each experiment, 400 ml of stock solution was taken. pH of the MB solution was adjusted to 6.0, by adding 0.1M HCl or 0.1M NaOH solutions. MB has the highest dissociation at pH 6.0. pH measurements were made using a pH meter (PSAW Digital pH meter) 0.25, 0.5, 1.0, 2.0 gms of the adsorbent was added and the suspension was stirred in a magnetic stirrer at 200 rpm of 10 min. Samples of 15ml were taken and centrifuged (Weber Lab Centrifuge ,Model-ACM-67891-C) for 5, 10, 15, 20 min at 4000rpm.

2.7 Color removal study with industrial waste water effluent

Waste water effluents from various industries located in the state of Odissha were collected to check the percentage color and total dissolved solid (TDS) removal using the adsorbent samples. Effluents from paper mill, beverage factory and steel plant were collected from J.K.Paper mill at Rayagada, Parle Agro at Khurda and Rourkela Steel Plant respectively. 400 ml of each of the samples were treated with 2 gm of the adsorbent samples AB, CAB and CAC. After the suspensions were kept in a shaker for a period of 1hr; 15ml of each of the samples were centrifuged for 15mins. The supernatant was removed for analysis of MB. MB concentration was determined by measuring the absorbance at 660 nm (wavelength corresponds to maximum absorption peak of the MB) by using UV-vis, spectrophotometer. The percentage removal of MB $=100\times (C_i–C_f)/C_i$ Where C_i and C_f are the initial and final MB concentrations in the solution (mgl^{-1}). Total dissolved solid (TDS) content of the effluent samples were checked in a Hanna Hi 2300 TDS meter both before and after the treatment with the adsorbent samples AB, CAB and CAC.

3. RESULTS AND DISCUSSION

3.1 X-Ray diffraction and FTIR analysis

The X-Ray diffraction study of the raw algae is shown in the Fig. 1 and the result was analyzed by X'Pert High Score software. The X-ray diffraction confirms the presence of complex mineral salt within the algae samples. The main salts are Cadmium Nickel aluminum oxide (JCPDS PDF Number 77-1881), barium gallium oxide (JCPDS PDF Number 23-1021) and monoclinic iron neodymium molybdenum oxide (JCPDS PDF Number 46-0475). The result as observed there is a slight shifting in d-spacing data with the standard data. Raw algae and algae biomass after proximate analysis was characteristics by FTIR analysis to get an idea about the presence of surface groups and bonding in the algae sample. The Fig.2 and Fig 3 show the FTIR image of raw algae and algae after proximate analysis respectively. In the raw algae several peaks are observed at different wave number at 3685 cm^{-1} primary alcohol O-H stretching, at 3200-3400 cm^{-1} normal "polymeric" OH stretching, at 2926-2928 cm^{-1} methylene

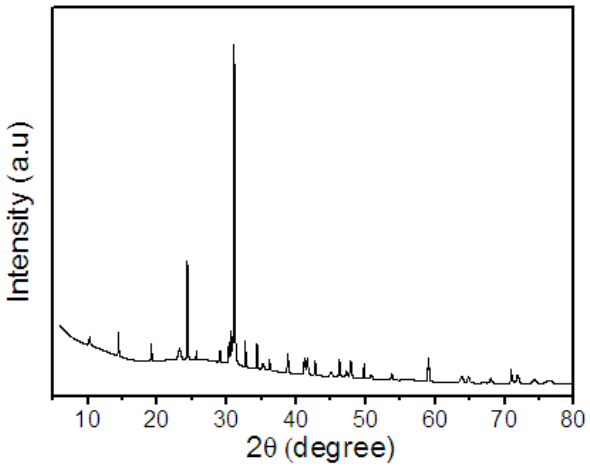

Fig. 1: X-Ray diffraction study of raw algae

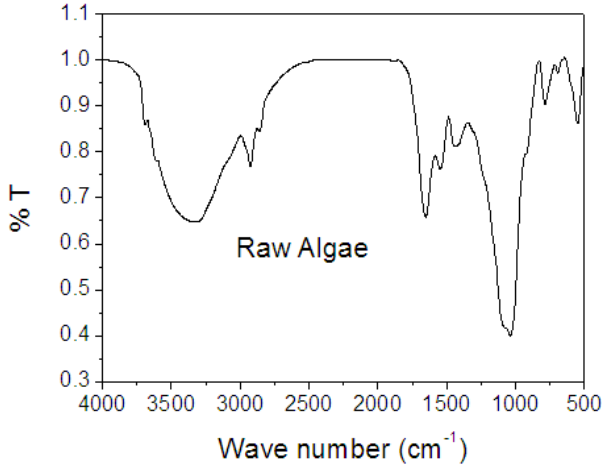

Fig.2: FTIR image of raw algae.

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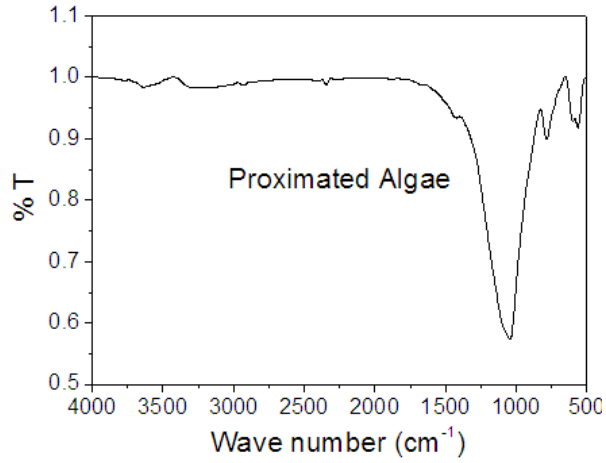

Fig. 3: FTIR image of biomass after proximate analysis

C-H stretching, at 1660 cm^{-1} alkenyl C=C stretching, at 1605 cm^{-1} conjugated C=C, 1410-1440 cm^{-1} methyl C-H symmetric and asymmetric bending respectively. But most interestingly these above peaks are not observed after proximate analysis that mainly because of the complete burning of hydrocarbon related all group during the ash analysis. But comparing these two figures it was observed some peaks are present in both samples these are mainly for the inorganic salts such as at 1040 cm^{-1} for sulfate ions, and 790 cm^{-1} for carbonate ion and at 550 cm^{-1} polysulfide groups.

3.2 Effect of pH on adsorption

The pH of the system exerted a profound influence on the absorptive capacity of the adsorbate molecule, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Fig. 4 shows the variations in the removal of the dye from waste water at different system pH. From the figure, it is evident that the maximum removal of MB color was observed at pH 6.0. A similar trend of pH effect was observed for the adsorption of MB on activated carbon prepared from fly ash [25] and biosolids [26] .This may be attributed to the hydrophobic nature of the developed carbon, which led to the adsorption of hydrogen ion (H^+) into the surface of the carbon when immersed in water, making it positively charged.

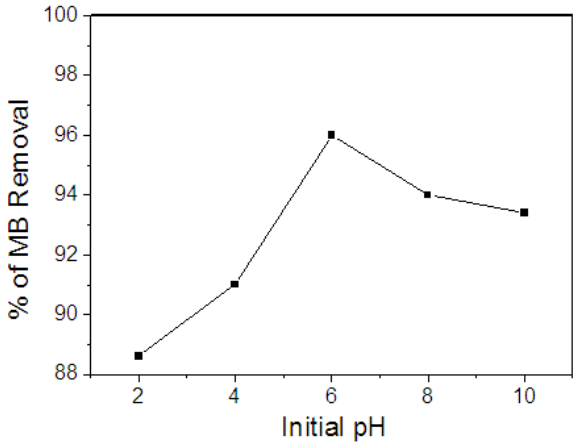

Fig. 4: Percentage removal of MB with variation of pH

A low pH value (1.0 to 3.0) leads to an increase in the H^+ ion concentration in the system, and the surface of the activated carbon acquires a positive charge by absorbing H^+ ions. On the other hand, an increase of the pH value from 6; led to an increase of the number of negatively sites. As the biomass surface is negatively charged at pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecules, leading to maximum adsorption of MB [27]. Moreover, the increasing adsorption of MB with increasing of pH value is also attributed to the attraction between cationic dye and excess OH^- ions in the solution.

3.3 Effect of adsorbent dose on MB adsorbent

The adsorption of MB on AB, CAB and CAC was studied with different dose (0.25, 0.5, 1.0, 2.0 gms) onto 50 mgl^{-1} of initial MB solution at temperature (27±2℃) and the pH to 6.0 is shown in Fig. 5. , for an overall contact time of 30 min. including 10 min. of stirring and remaining 20 min. of centrifuging process. The maximum removal obtained was 94%, 98%, 96% for AB, CAB and CAC respectively with 2.0gms of the adsorbent dose. The increase in the adsorption of MB with the adsorbent dose can be attributed to increase in surface area of the adsorbents.

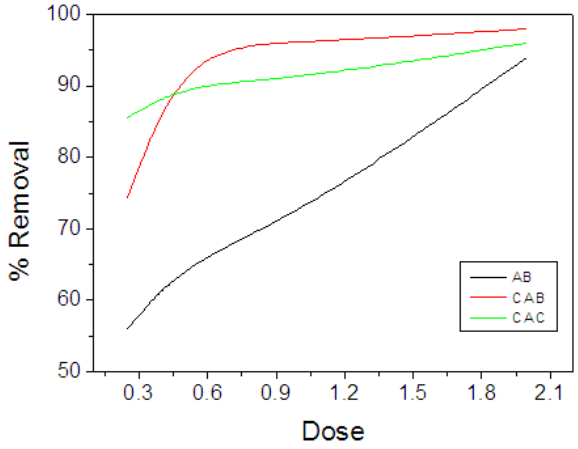

Fig. 5: Dose effect on 400ml of MB (50 mg/l) after 30 min of contact time at room temperature

3.4 Effect of contact time on MB removal

The relation between percentage removal of MB with overall contact time was studied. The result of removal of MB at pH 6.0 with 2gm of each of the adsorbents (AB, CAB and CAC) is presented in Fig. 6. It was found that that more than 70% removal of MB occurred in first 10min by just stirring the suspension. More than 90% of the MB was removed in next 5min by centrifuging the samples. Thereafter the adsorption rate was found to slow down. This is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species on to the surface of the adsorbents and the available cationic adsorbate species in the solution, as well as the slow pore diffusion of the solute into the bulk of the adsorbent. The equilibrium was attained at 30 min when the maximum MB adsorption was achieved. In the process of MB adsorption initially dye molecules have to first encounter the boundary layer effect, than they diffuse

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from boundary layer on to adsorbent surface, and then finally diffuse into the pores.

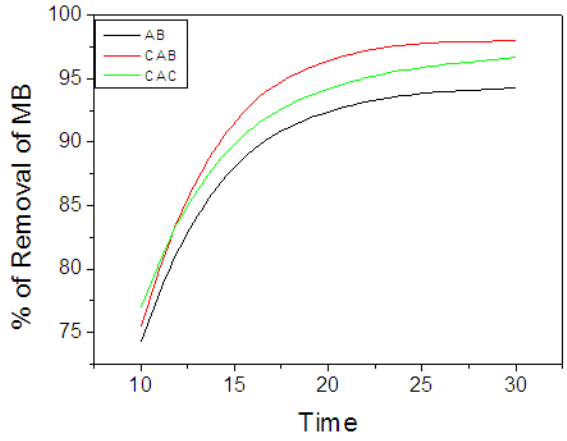

Fig. 6: Effect of contact time on the removal of MB (50gm/L) with 2 gm of different adsorbent samples

3.5 Color and TDS removal of industrial waste water effluent

The removal of color and TDS from the paper mill, beverage and steel plant effluent is shown in the Fig. 7 and Fig. 8. Maximum percentage of color removal that was noted with the adsorbent CAB as shown in the Figure 6 shows 85.7%, 78.6%, and 47.7% respectively from paper mill, beverage and steel plant effluent.

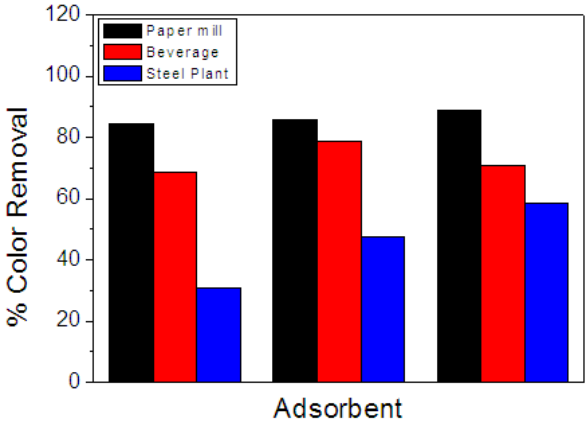

Fig. 7: Percentage of color removal with absorbent at various industries

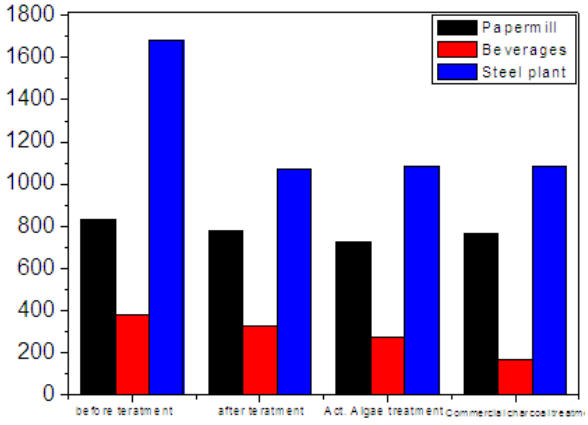

Fig. 8: TDS of different industrial effluents

The values were quiet comparable to that obtained with CAC; that gave 88.7%,70.9% and 58.3% color removal respectively from paper mill, beverage and steel plant effluent. A TDS removal of 12%, 28.01% and 35.47% was noted from paper mill, beverage and steel plant effluent respectively with the adsorbent CAB that was again comparable to that with CAC as shown in the Figure 8.

4. CONCLUSIONS

The adsorption study of the algae biomass and carbonized algae biomass has been analyzed for the removal of MB from the industrial effluents. The structural analysis was carried out by the XRD and FTIR analysis. The removal of MB has been done by varying the pH and doses. The investigations showed that the activated carbon developed from algae has a very good adsorption capacity for the removal of MB from aqueous solutions. The equilibrium adsorption was practically achieved in 30 min. pH of the solution is one of the major parameter that effects the % removal of MB. The optimum conditions for removal of methylene blue dye at a concentration of 50 mg/l from an aqueous solution at room temperature 27 °C were; adsorbent dose of 5 g/l, contact time of 30 min., and pH of 6.0. From the results it is also observed that the removal of the dye is at par with the CAC. The activated algae can be employed as low cost adsorbent as an alternative to CAC for the removal of color and dyes from industrial waste water effluent. Also the adsorbent sample have a great potential as a low waste and cost effective adsorbent and can be further explored for their application in second stage adsorption.

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