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Adsorption Efficiency of Carbon Prepared from Agricultural Waste Materials in Removing Basic Dye From Aqueous Solution

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Management of solid waste is the burgeoning issue of the current times. Agriculture waste is rich in organic material like cellulose, lignin *etc*. and can be of great use if utilized as right resource at right time and right place. In the current study agriculture waste material has been used for adsorption of colour from waste water. Sugarcane bagasse and paddy straw have been recycled to activated carbon and have been utilized and compared as the adsorbent for the removal of basic dye from aqueous solution. A basic dye, methylene blue has been used as the adsorbate. Two different mineral acids have been used for activation of raw material and it was observed that both H_3PO_4 and HNO_3 were good activating agent but impregnation efficiency was in following order $H_3PO_4 > HNO_3$. Adsorption experiments were conducted by varying several parameters namely pH, adsorbent dose, initial concentration of dye and contact time. It was observed that colour was effectively removed at all selected pH and the increase in activated carbon dose showed an increase in its adsorption efficiency. The percentage of colour removal decreased with an increase in the initial dye concentration. More than 90 % adsorption efficiency of dye from solution containing 10 mg/L of dye was attained with an adsorbent dosage of 0.1 g after 45 min of contact time at all pH. Results obtained indicate that agriculture waste material could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for dye removal and can thus be a good example of wealth from waste.

Key Words: Activated carbon, Adsorption, Methylene blue, Paddy straw, Sugarcane bagasse.

INTRODUCTION

Water pollution and improper waste management is an issue of global concern. A large part of every country's wealth is being used up for both liquid and solid waste management but anything sustainable is still not achieved. Coloured effluent is one of the major problems which is released from textile industries. This coloured wastewater is produced due to maximum use of dyes by textile industries to colour their products. The discharge of highly coloured effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Among the various classes of dyes, basic dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high[1]. Methylene blue is one such basic dyes which causes eye burns and may be responsible for permanent injury to the eyes of human and animals. It gets dissociated into methylene blue cation and chloride anion. Dissociated methylene blue is preferentially adsorbed onto many solids[2]. It is difficult to remove the dyes from effluent since the dyes are stable to light and heat and are also biologically non-degradable. Coagulation and flocculation are the two commonly used treatments methods for the removal of dyes. However these methods are very expensive. Adsorption processes using activated carbons are widely used to remove pollutants from wastewaters. It is one of the effective methods for removal of dyes from waste effluent. Adsorption is a good alternative for industrial waste streams containing a high percentage of molecules that are not readily biodegradable. Experience has shown, however, that molecular weight is the principal factor and that molecules possessing three or more carbon atoms usually respond favourably to adsorption treatment[3]. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions[4]. Activated carbon is widely used as an adsorbent for many species of pollutants because of its high and wide affinity. However, commercially available activated carbon is expensive. Thus other cheap alternatives should be tested for dye removal from waste waters. Recycling of agriculture waste material which is a natural renewable resource that can be converted into useful materials and energy can be a solution to waste management and an alternative to expensive activated carbon. Thus in the current study activated carbon prepared from waste sugarcane bagasse and paddy straw were experimented for removal of dye from aqueous solutions. In agricultural countries where abundant source of biomass is available biosorption is becoming more and more attractive because plant residues are cellulosic materials which have an inherent ability to adsorb waste chemicals such as dyes and cations in water due to the columbic interactions[5]. So the aim of the present study is to compare the efficiency of both sugarcane bagasse and paddy straw in removing colour from aqueous solutions.

EXPERIMENTAL

Preparation of adsorbents: Agriculture wastes have been used as a raw material for activated carbon mainly because of their abundance. Production of activated carbon from this source may reduce the cost of wastewater treatment and at the same time can be a step towards sustainable waste management as it will open new market for recycled agricultural waste product.

Control sugarcane bagasse carbon (CSAC): Sugarcane bagasse was collected from local markets of Bangalore. It was washed thoroughly to remove dust and was then dried under sunlight until all the moisture evaporated. The material was ground to fine powder. It was then carbonized at 300 ºC in muffle furnace for 3 h. The carbonized material was then powdered using a mortar and pestle to size that could be sieved through ASTM sieve No. 20 and was used for the further study.

Orthophosphoric acid treated sugarcane bagasse carbon (OSAC): Sugarcane bagasse was collected from local markets of Bangalore. It was dried under sunlight until all the moisture evaporated. The material was ground to fine powder. The ground powder was treated with 25 % orthophosphoric acid in the ratio of 1:10 (bagasse:acid w/v) for 1 h. After 1 h the sugarcane bagasse was filtered out, washed with distilled water to remove free acid and activated at 300 ºC in muffle furnace for 3 h. The heated material was washed with distilled water to remove residual acid. The material was dried in an oven at 120 ºC for 24 h and then powdered using a mortar and pestle to size that could be sieved through ASTM sieve No. 20.

Nitric acid treated sugarcane bagasse carbon (NSAC): The preparation method of NSAC was similar to OSAC except that it was soaked in 25 % nitric acid in the ratio of 1:10 (bagasse:acid w/v) at for 1 h.

Control paddy straw carbon (CPAC): Paddy straw was collected from local markets of Bangalore. It was washed thoroughly to remove dust and was then dried under sunlight until all the moisture evaporated. The material was ground to fine powder. It was then carbonized at 300 ºC in muffle furnace for 3 h. The carbonized material was then powdered using a mortar and pestle to size that could be sieved through ASTM sieve No. 20 and was used for the further study.

Orthophosphoric acid treated paddy straw carbon (OPAC): Paddy straw was collected from local markets of Bangalore. It was dried under sunlight until all the moisture evaporated. The material was ground to fine powder. The ground powder was treated with 25 % orthophosphoric acid in the ratio of 1:10 (paddy straw:acid w/v) for 1 h. The straw was then filtered out, washed with distilled water to remove free acid and activated at 300 ºC in muffle furnace for 3 h. The heated material was washed with distilled water to remove residual acid. The material was dried in an oven at 120 ºC for 24 h and then powdered using a mortar and pestle to size that could be sieved through ASTM sieve No. 20.

Nitric acid treated paddy straw carbon (NPAC): The preparation method of NPAC was similar to OPAC except that it was soaked in 25 % nitric acid in the ratio of 1:10 (straw:acid w/v) at for 1 h.

Adsorbate solution: An aqueous solution of 1000 mg/L methylene blue dye was prepared by dissolving required amount of dye in double distilled water. The samples of required concentration were prepared by diluting the stock solution of dye. The pH of the solutions were adjusted by adding an appropriate volume of 0.1 N solution of HNO_3 and 0.1 N NaOH, respectively.

Experimental methods and calculations

Batch mode studies: Adsorption experiments were performed in a set of conical flasks (100 mL) where solutions of methylene blue dye (100 mL) with different initial concentrations (5 -20 mg/L) were placed in these flasks. Equal mass of 0.1-1.0 g of particle size (ASTM sieve No. 20) prepared activated carbon from all the mentioned sources was added to dye solutions and kept in a shaker for time period varying from 0.5-2.0 h to reach an equilibrium. The flasks were then removed from the shaker and the final concentration of dye in the solutions was analyzed using a spectrophotometer model Shimadzu 6400 at 665 nm. The samples were filtered prior to analysis in order to minimize interference of the carbon particles with the analysis. The adsorption efficiency of all the type of adsorbents was calculated according to the expression:

$$\text{Adsorption efficiency (\%)} = \frac{(C_o - C_f)}{C_o} \times 100$$

where C_o = initial concentration of dye (mg/L) and C_f = final concentration of dye (mg/L) after the treatment process was over.

RESULTS AND DISCUSSION

Activated carbon can be considered as a material of phenomenal surface area made up of millions of pores-rather like a "molecular sponge"[6]. It is commonly used in separation processes involving organic compounds and is widely used in fields such as medicine, water and air treatment, the food and beverage industry and industrial processes. The methods for preparing activated carbons are often classified as chemical and physical activation methods. Chemical activation method consists of carbonizing a raw material after adding substances that restrict tar formation[7]. In this work chemical activation of the raw materials was done using 25 % H_3PO_4 and 25 % HNO_3. Two types of chemical activating agents were used to study that which acid is a better activating agent. Activated carbons made by chemical activation have a porous and very open structure, ideal for adsorption of big molecules[7]. The acid introduced within the material plays a dual role. Firstly it produces hydrolysis of the lignocellulosic material with subsequent partial extraction of some components, thus weakening the particle which swells and secondly the acid occupies a volume which inhibits the contraction of particle during the heat treatment, thus leaving a porosity when it is extracted by washing after carbonization[8]. For this study a type of carbon was prepared by burning the raw materials at 300 ºC without chemical activation and was compared for dye removal efficiency. Removal of pollutant by carbon is based on a simple fact that when a liquid containing impurities is brought into contact with carbon, the attraction of the carbon for the impurity is greater than the attraction of the liquid for the impurities. The carbon therefore adsorbs the impurities such as colouring matter until equilibrium is reached after which the carbon will no longer remove these substances from the particular solution. The rate of removal of impurities from a solution by carbon is very rapid during the first interval of contact and gradually reaches a point where increased time of contact gives no further decolorization[9]. The mechanism for the removal of dye by adsorption may be assumed to involve the following four steps: (a) migration of dye from bulk of the solution to the surface of the adsorbent (activated carbon), (b) diffusion of dye through the boundary layer to the surface of the adsorbent, (c) adsorption of dye at an active site on the surface of activated carbon and (d) intra-particle diffusion of dye into the interior pores of the activated carbon particle. The boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption. Since, the uptake of dye at the active sites of activated carbon is a rapid process, the rate of adsorption is mainly governed by either liquid phase mass transfer rate or intraparticle mass transfer rate[10]. Adsorption of dye on activated carbon depends on various parameters which have been considered in the current study and their effect on adsorption efficiency has also been discussed. One result which was common to all sets of experiments was that post treatment with control paddy straw carbon the solution turned black in colour for all adsorbent dosage and all adsorbate concentrations at all pH. Thus due to this reason the efficiency of control paddy straw carbon in adsorbing dye from aqueous solutions has not been discussed. The carbonizing temperature for all types of carbon was constant 300 ºC. Girgis *et al.*[11] studied that essentially microporous carbons with narrow micropres are formed at 300 ºC, but widening of the micropores with appearance of some mesopores is believed to occur when the temperature of carbonization is increased.

Effect of initial dye concentration: The influence of the initial concentration of methylene blue in the solutions on the adsorption efficiency of CSAC, NSAC, OSAC, NPAC and OPAC was studied. The experiments were carried out at fixed adsorbent dose (0.1 mg/100 mL) in the test solution, pH (4.0) and at different initial concentrations of methylene blue (5, 10, 15 and 20 mg/L) for different time intervals (30, 45, 60, 90 and 120 min). Results are shown in Fig. 1. It is evident that the per cent adsorption efficiency of CSAC, NSAC, OSAC, CPAC, NPAC and OPAC decreased with the increase in initial dye concentration in the solution. The lowest dyes removal for all types of carbons was measured for initial dye concentration of 20 mg/L and 0.5 h contact time. For all the concentrations of the adsorbent the efficiency of dye removal increased as the contact time between all the adsorbents and adsorbate

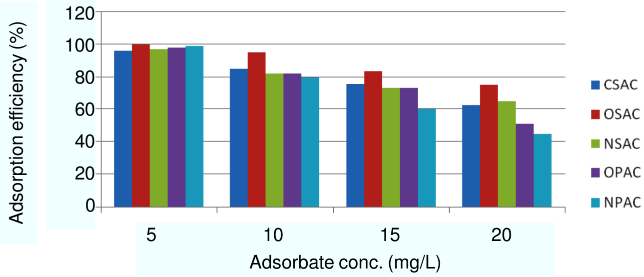

Fig. 1. Effect of adsorbate concentration on the adsorption efficiency of carbon

solution increased. As a comparison, activated carbon from sugarcane bagasses which was treated with orthophosphoric acid (OSAC) and one which underwent physical treatment (CSAC) had shown better result in the dye adsorption compared to carbon from sugarcane bagasse which was treated with nitric aid (NSAC). Also for paddy straw, orthophosphoric acid treated paddy straw gave better results than nitric acid treated paddy straw (Fig. 1). According to Girgis *et al.*[11] who prepared activated carbons from sugar cane bagasse impregnated with 50 % inorganic acids. The effectiveness of such impregnation was in the following order: $H_3PO_4 > H_2SO_4 > HCl > HNO_3$. Similar results were obtained in this study. For paddy straw carbon OPAC showed more than 90 % dye removal at low concentration but as the dye concentration increased its efficiency reduced. It was also observed that for all concentrations of dye carbon from paddy straw showed lower efficiency when compared to carbon from sugarcane bagasse.

Effect of adsorbent dose: The adsorption of methylene blue on CSAC, NSAC, OSAC, CPAC, NPAC and OPAC were studied by changing the quantity of adsorbent (0.1, 0.2, 0.5 and 1.0 g/100 mL) in the test solution while keeping the initial dye concentration (10 mg/L) and pH (4.0) constant. Experiments were carried out at different contact times for 2 h. As shown the percentage adsorption increased with increasing adsorbent doses. For the adsorbent dosage of 1.0 g/100 mL of all types of adsorbents, it was found that after a contact of 45 min the amount of dye being adsorbed by all the types of carbon was nearly 100 % (Fig. 2). As for orthophosphoric acid treated sugarcane bagasse carbon (OSAC), 100 % removal of dye was obtained with a dosage of as low as 0.2 g. For all other types of carbon though there was more than 75 % removal with a dosage of only 0.1 g, the percentage efficiency increased to more than 95 % with application of 0.5 g of the adsorbents which is due to the increase in adsorbent surface area and availability of more adsorption sites.

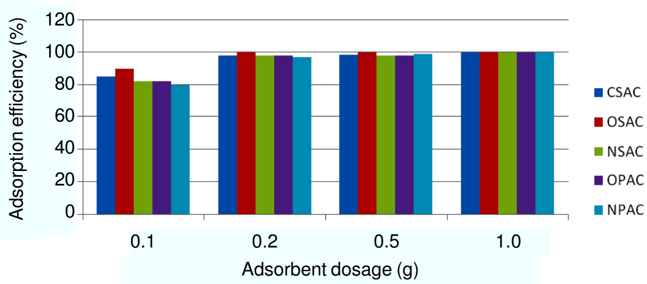

Fig. 2. Effect of adsorbent dosage on adsorption efficiency of carbons

Effect of contact time: For most efficient work, the manner and type of agitation to produce the proper contact between the activated carbon and the material treated are of great importance. Decolorizing, purifying and deodorizing results are greatly affected by the degree of contact, which in turn is a function of the fineness of the carbon, its effective surface area and the manner and continuity of agitation[9]. The results of the study (Fig. 3) show that the amount of the adsorbed dye from solution containing 10 mg/L of dye onto 0.1 g of all types of activated carbon increases with increase in agitation time and reaches 100 % by 2 h. The removal of methylene blue from aqueous solutions by adsorption on carbonized paddy straw and sugarcane bagasse increases with time, but with lower values this may be related to the fact that in the beginning of the adsorption process, the methylene blue is adsorbed on the external surface of particles which increases the local concentration of methylene blue on the surface and leads to formation of methylene blue aggregates[12]. Methylene blue molecules are known to form dimers and aggregates, depending on the conditions of solution such pH, concentration and presence of other ions. Methylene blue aggregates can migrate from the external surface of the adsorbent material to the inner pores, resulting in de-aggregation of the methylene blue aggregates and restoring monomers. In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the species from the outer sites to interior sites of the adsorbent particulars[13].

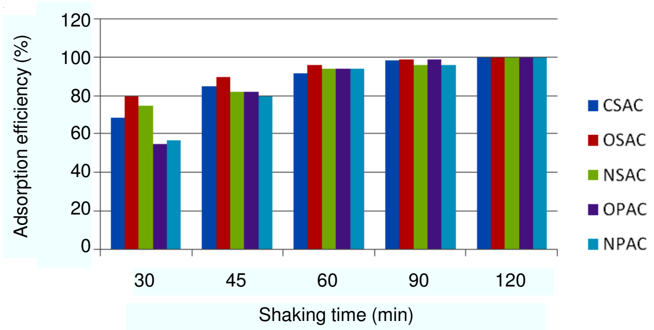

Fig. 3. Effect of contact time on adsorption efficiency

Effect of pH: In general, initial pH value may enhance or depress the uptake. This is attributed to the change in pH value. As the pH increases, it is usually expected that adsorption also increases. But in the current study it was found that adsorption of dye is not much affected by change in pH of the solution. More than 50 % dye was adsorbed in the initial 0.5 h regardless of the pH of the solution. Later by 45 min almost 100 % removal was observed in all carbon samples and at all pH values. Dyes can be adsorbed regardless of solution pH and corresponding electrostatic repulsion because in addition to electrostatic interactions, a fraction of dye adsorption appears to occur *via* chemical adsorption that is of high binding strength. It is probable that some components of the dye molecules such as N, S, O and benzene rings can perform hydrogen bonding or ligand exchange with the surface functional groups[14]. Also, a very strong reason for complete removal of dye could be that OSAC, NSAC, OPAC and NPAC all were activated with acids which changed the surface charge of the carbon samples thus increasing their affinity for the basic methylene blue dye. Methylene blue dye as cationic organics is preferentially adsorbed on negatively charged acidic surfaces[15]. Solids which are normally negatively charged in water, such as silica and carbon, readily adsorb cationic dyes[16].

Conclusion

Sugarcane bagasse and paddy straw are a very common biomass waste material and are easily available at a low price. The study showed that for all types of carbon the adsorption of methylene blue was dependent on the adsorbent dose and the concentration of methylene blue in the wastewater. The results show that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of methylene blue even with lower dosages of carbon. Orthophosphoric acid treated sugarcane bagasse and paddy straw showed a better performance compared to nitric acid treated sugarcane bagasse. CSAC, NSAC, NPAC have a lower adsorption efficiency compared to orthophosphoric acid treated sugarcane bagasse and paddy straw carbons (OSAC and OPAC resly) at the any given initial dye concentration. This study also shows that all types of carbon have well developed micro and mesopores as methylene blue adsorption occurs best at these sites. McConnachie *et al.*[17] in their study discussed that conventionally the pores of activated carbon are divided into three groups, micropores of less than 2 nm in "width", mesopores of 2-50 nm and macropores of greater than 50 nm. Phenol molecules can penetrate down to the lower range of micropores whereas methylene blue requires pores of about 1.3 nm so can only enter the largest micropores and the mesopores. In general terms, to effect adsorption it is necessary to present the molecule to be adsorbed to a pore of comparable size[6]. The advantages of activation with phosphoric acid include a high yield and lower working temperature. Well developed porosity together with high cation exchange capacity makes phosphoric acid activated carbons from lignocellulosic precursors (sugarcane bagasse, paddy straw) promising material for applications involving metal ion adsorption[18]. The adsorption efficiency can be arranged in the following order

OSAC > OPAC > CSAC > NSAC > NPAC > CPAC

Studies conducted by other scientists show that vegetable fibers can be good precursors for producing highly porous activated fibers by simple preparative methods[12].

Thus the study proved that sugarcane bagasse and paddy straw, both can be an attractive option for dye removal from dilute industrial effluents. As both sugarcane bagasse and paddy straw are easily and freely available in countries like India where agriculture is among the major businesses and also and show good sorption capacities when properly treated they can be an efficient alternative to expensive sources of activated carbon. Similarly, Castro *et al.*[19] also concluded that phosphoric acid activation of agricultural residues and bagasse from sugar cane processing, as precursors, resulted in activated carbons with good surface properties and ability to remove some species from aqueous solution.

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