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Pineapple peel waste activated carbon as an adsorbent for the effective removal of methylene blue dye from aqueous solution

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Abstract: In present study, the use of low-cost, locally available, highly efficient, and eco-friendly adsorbent pineapple peel has been investigated as an ideal alternative to the current expensive methods of removing Methylene Blue from aqueous solution. Chemical modification of the adsorbent was done for enhancing its sorption capacity by increasing its chelating power using sulphuric acid. Various factors which control the rate of sorption process like; initial dye concentration, adsorbent dose, contact time, agitation time and pH have been studied. The results showed that as the amount of the adsorbent increased, the degree of adsorption increased accordingly and equilibrium adsorption was attained in 30mins. Desorption studies were carried out using HCl for regenerating adsorbent. The results revealed that pineapple peel waste activated carbon (PPWAC) is an effective sorbent and can be used for removing cationic dyes like Methylene Blue from waste water.
Keywords: pineapple, sorbent, adsorption, aqueous, dye.

1. Introduction:

Organic dyes are the major pollutants which are generally create pollution in the ecosystems and they are difficult to treat because of their different and complicated molecular structures. Many industries, such as textile, dyestuff manufacturing, leather tanning, food preparation, paper production, and printing, use dyes that produce highly colored waste effluents. These dyes are directly or indirectly toxic to microbial populations and can even be carcinogenic to mammals by consume the dissolved oxygen required by aquatic life[1]. Textile industry use dyes and pigments to colour their products. There are more than 100,000 commercially available dyes with over 7x105 tonnes of dyestuff are produced annually[2].

Methylene Blue (MB) is a cationic dye. It is generally used for dying cotton, wood and silk. Its chemical formula is $C_{16}H_{18}N_3SCl.3H_2O$[3]. Methylene blue has wide applications, which include paper coloring, temporary hair colorant, dying cottons, and wools. Although not strongly hazardous, it can cause some harmful effects in humans such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis[4].

Various methods adopted for colour removal from industrial effluents include coagulation, floatation, biological treatment, hyper filtration, adsorption and oxidation[5]. Among these options, adsorption is most preferred method and activated carbon is most effective adsorbent widely employed to treat wastewater containing different classes of dyes, recognizing the economical drawback of commercial activated carbon[6,7].

Many researchers have studied the applicability of the biological products like Some of the materials which are used for the preparation of activated carbon in the recent past are, Coir pith[8,9], passion fruit and mandarin peels[10], rice husks[11], linseed straw, saw[12], rice hulls[13], cashew nut hull, coconut shells and husks, eucalyptus bark[14], orange peel[15], linseed cake, tea waste, shale oil ash, palm kernel fiber[16], and silkworm pupa[17] etc as the raw materials for the production of activated carbon. Different adsorbents such as zeolite, perlite, benotite, kaolite, rice husk, maize cob, coconut coir, bagasse pith, etc. have been employed for removal of dyes from effluents[18-21]. Clays, metal hydroxides, sunflower stalks, hardwood, fertilizer, fly ash, coal, peat, sawdust, lignite, coal, cotton, bark, wood and steel wastes were also used as adsorbents[22,23,31-36] for the removal of different dyes from aqueous solution. Still there is a need for identification of virgin low cost precursor for the production of activated carbon.

The main objects of this paper are: (i) to study the feasibility of using Pineapple peel waste as an precursor for the production of activated carbon (ii) to determine efficiency of Methylene dye removal from aqueous solution (iii) to determine the effect of the various parameters affecting sorption, such as contact time, adsorbent dose and pH (iv) to explore the desorption efficiency of sorbent by using HCl.

2. Experimental

2.1 Adsorbent preparation

The pineapple peel wastes were collected from fruit stalls of Coimbatore districts. The collected pineapple wastes was cut into small pieces and sun dried, until all the moisture was evaporated. The dried pineapple wastes were further used for the preparation of activated carbon. Pineapple wastes was completely mixed with concentrated sulphuric acid in the ratio 1:1 and maintained in a Muffle furnace at 300^{o}C at 3 hrs for activation. The material was taken out and washed with distilled water till the pH reached 7. It was then sieved for the particle size of 150-250 µm and then stored in plastic containers for further studies. Basic characteristics of adsorbent (PPWAC) like pH, conductivity, moisture etc were analyzed by standard procedures [24]. The scanning electron microscope (SEM) analysis was carried out to study the surface texture before and after methylene blue adsorption using Joel 6400 model,Tokyo.

2.2. Adsorption study

Analytical grade Methylene Blue dye was obtained from Loba Chemie and used for the adsorption study. Batch mode experiments was carried out using PPWAC as an adsorbent to investigate the factors influencing the rate of extent of uptake of dyes by varying the parameters such as agitation time, dosage of the adsorbent pH and initial dye concentration. The concentration of the dye in the solution was determined using UV-VIS spectrophotometer (Cyber lab UV 100). The wavelength of maximum adsorption (λmax) was used as the monitoring wavelength. From the absorbance values of the dye solution before and .after treatment, the percent color removal was calculated. Methylene Blue = λmax = 665 nm.

2.2.1 Contact time and initial dye concentration studies

The Study was carried out by shaking (Neolab- Orbitol) at 200 rpm, the adsorbent (0.1g) with 50 ml aqueous solutions of dyes of different concentrations at their natural pH and at room temperature 30±2 0C in 100 ml conical flasks. Then the adsorbent was then separated by centrifugation and concentration of the dye in the supernatant was estimated at their corresponding λmax.

2.2.2 Adsorption equilibrium studies

Equilibrium experiments were carried out by agitating 100 mg of activated pineapple waste carbon with 50 ml of the dye solution of different initial dye concentrations (10- 40 mg/L) for 1 hrs, which is more than the sufficient to reach equilibrium.

2.2.3 Adsorption dose studies

Effect of the adsorbent dose was studied by agitating at 220 rpm 50 ml of 40 ppm of dye solutions with different doses of the adsorbent (25-200 mg) for a time greater than the equilibrium time. After that the adsorbent was separated by centrifugation and the concentration of the dye in the supernatant was estimated spectrophotometrically.

2.2.4 pH studies

The effect of pH on the removal f dyes was studied by agitating 50 ml of 40 ppm dye solutions adjusted to desired initial pH values (2-10) with known amount of the carbon for a time interval greater than the equilibrium time. The pH of the dye solution was adjusted to desired values using diluted HCl or diluted NaOH. After the agitation time the adsorbent was separated by centrifugation and the concentration of the dye in the supernatant was estimated spectrophotometrically.

2.3 Batch Desorption studies

After adsorption experiments with desired concentration of the dye solution and known amount of the carbon, the dye laden carbon was separated by centrifugation and the supernatant was discarded. The carbon was then given a gentle wash with double distilled water to remove any unabsorbed dye molecules. Desorption studies were carried out by shaking the dye laden carbon with 50 ml of distilled water adjusted to a desired pH (2-10) for a time greater than the equilibrium time and the desorbed dye was estimated spectrophotometrically. Desorption was also carried out with HCL of various concentration ranging from 0.05M to 1M.

3. Results and Discussion

3.1. Physico-Chemical characteristics of pineapple waste activated carbon

Physico-chemical characteristics values of pH, conductivity, moisture, water soluble materials, apparent density, Ion exchange capacity and zero point charging were observed as 5.7, 0.099, µs/cm, 19.09 %, 53.3%, 0.593 g/ml, 0.06 meq / g and 4.32 respectively (Table 1). The ion exchange capacity of the adsorbent indicates the involvement of Na^+, Ka+ and Ca^{2+} ions in the adsorption process. The apparent density of 0.593 indicates that the adsorbent could be separated effectively treatment. The pHZpc indicates that surface is positively charged below 4.32 and negatively charged above 4.32 thus indicating the usage of adsorbents in the removal of anionic and cationic species. SEM analysis of pineapple peel waste activated carbon (PPWAC) showed the heterogenous adsorption of dyes (Figure 1). It is clear that pineapple waste as considerable number heterogenous layer of pores where there are good possibilities of dye adsorption[25].

Table: 1 Physico-Chemical characteristics of Pineapple peel waste activated carbon.

Parameters	Values
pH	5.75
Conductivity (µs/cm)	0.099
Moisture (%)	19.09
Water soluble matter (%)	53.3
Apparent density (g/ml)	0.593
Ion exchange capacity (m eq/g)	0.06
Zero point charge	4.32

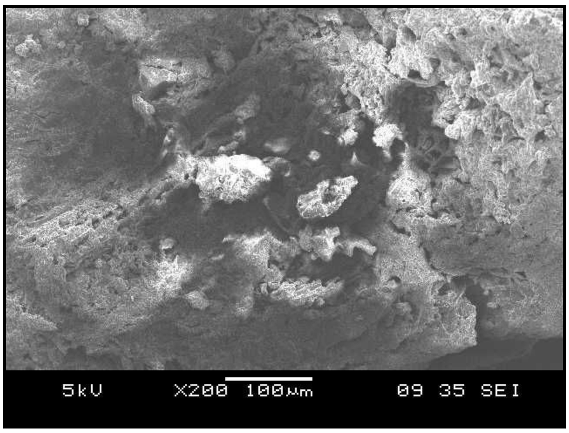

Figure: 1 SEM analysis of pineapple peel waste carbon

3.2 Effect of contact time on methylene blue adsorption

Effect of contact time on the adsorption of methylene blue on PAWAC from solutions, with methylene blue concentration of 20, 40 & 60 mg/L are shown in Figure 2. Methylene blue adsorption increase sharply at short contact time and slows down gradually until it reaches saturation. Equilibrium was attained at 30 min for 20, 40 and 60 mg/L. No appreciable increase in adsorption was observed beyond the maximum equilibrium time. The data further revealed that with an increase in the initial dye concentration, although the percentage removal of dye decreased, the amount of dye adsorbed per unit / weigh of adsorbent (mg/g) increased in the range of dye tested, suggesting that removal of dye is concentration dependent. The curves showed that although the equilibrium adsorption of dye increases with increasing initial dye concentration, extend of such an increase in q_e was not proportional to the magnitude of increase in initial concentration of dye solution. This might be due to an increase in availability of adsorption sites at lower dye concentration which might have decreased, as dye concentration had increased. The removal curves were smooth and continuous leading to saturation suggesting the possibility of formation of monolayer coverage of zye on the surface of the adsorbent [26,27].

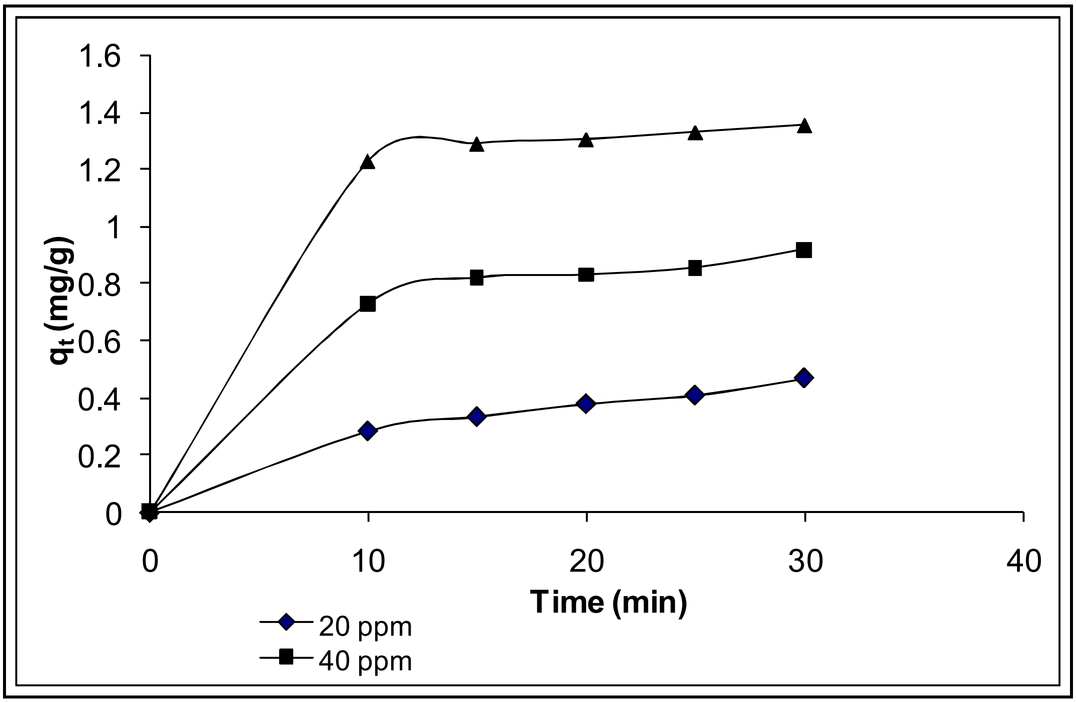

Figure: 2 Effect of agitation time and initial dye concentration on adsorption of methylene blue on PPWAC

3.3. Effect of adsorbent dose on percentage removal and maximum adsorption capacity (q_e)

The effect of sorbent dose on percent removal is illustrated in Figure 3. Removal percentage increased from 86.56 to 100% as the dose of the adsorbent increased from 25 to 200 mg / 50 ml of adsorbate. The percent removal increased with an increase in sorbent dose which might be due to an increase in the number of sorption site available for adsorption. The maximum sorption q_e (mg/g) decreases with an increase in dye concentration which might be due to aggregation of solute for the sorption site, which led to a decrease in total surface area of the sorbent and an increase in diffusional path length[28,3]. The number of sorption site available for the sorbent solute interaction increases with an increase in sorbent dose weight.

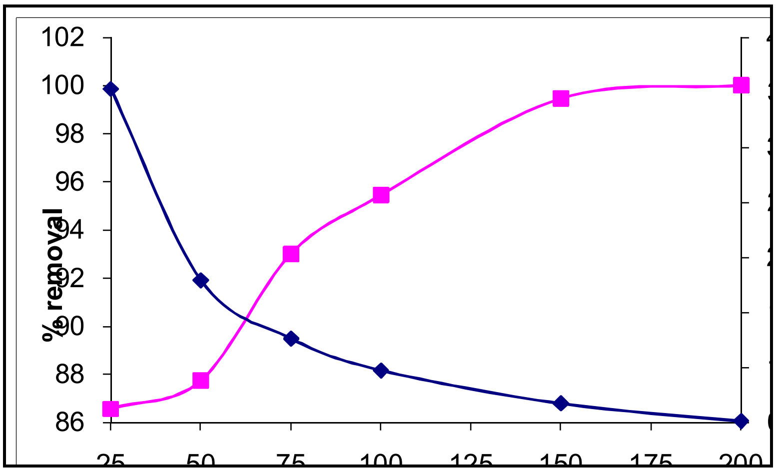

Figure: 3 Effect of adsorbent dose on percentage removal and maximum adsorption capacity (q_e)

3.4 Effect of pH

The methylene blue adsorption increases with increase in pH and the uptake of dye increase from 35.27% to 100% as pH increased from 2 to 10 (Figure 4). The final pH of the solution increased from 2.32 to 6.32 as the initial pH increased from 2 to 10 which might be due to the release of OH^- ions which has exchanged the site for methylene blue. The PK_a of methylene blue is 0.04. Hence methylene blue is completely ionized at pH greater than 0.04 and serves as a cationic species [29]. At low pH 2, the surface might be positively charged thus creating a competition between H^+ ions and cationic dye thus decreasing the amount of dye adsorbed. At higher pH the surface of activated pineapple wastes carbon may be negatively charged which enhances the positively charged dye cation adsorption through electrostatic force of attraction. The pH_{zpc} was found to be 4.32. The activated pineapple waste carbon has a positive surface charge at pH less than pH_{zpc}. On the contrary, when the pH is greater than pH_{zpc} the surface is negatively charged which favour the adsorption of cationic methylene blue [2].

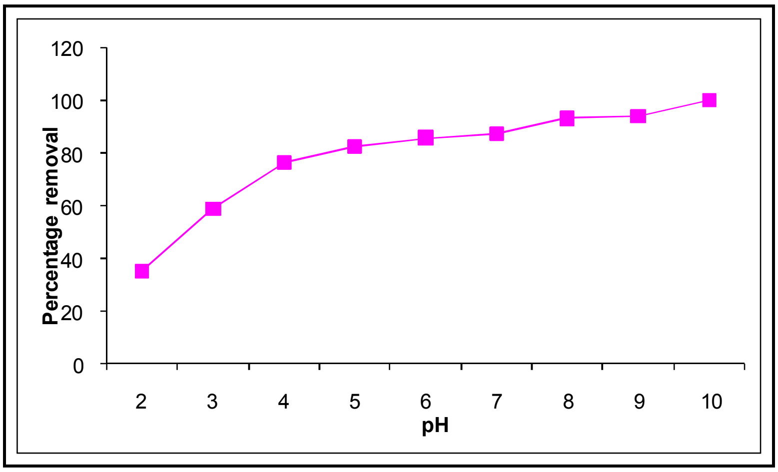

Figure: 4 Effect of pH on methylene blue adsorption on PPWAC

Table: 2 Effect of desorption on methylene blue adsorption of PPWAC

Initial dye concentration (mg/g)	% Desorbed
0.05	92
0.10	92
0.50	94
0.75	95
0.1	96

3.5 Desorption

Desorption process helps in the regeneration of the adsorbent and recovery of adsorbate (dye) from liquid phase. The percent desorption range from 92 to 96 % for the cations (Table 2). Under acidic conditions H^+ ions protonate the adsorbent surface thereby reflecting the dye from adsorption surface leading to desorption of positively charge dye ions [30]. Quantitative desorption at pH 2 indicate that the adsorption is mainly ion exchange. As the concentration of hydrochloric acid increase from 0.05M to 1M, the percent desorption ranges from 92 to 96%.

4. Conclusion

The present study explored the possibilities of utilizing the Pineapple waste activated carbon as an adsorbent for the effective removal of methylene blue. Pineapple waste carbon is prepared by chemical modification with concentrated sulphuric acid in the ratio 1: 1. Batch adsorption study was carried out to find the effect of contact time adsorbent dosage pH and adsorbate concentration on dye removal. The amount of dye adsorbed for unit weight of adsorbent mg/g increased with increase by dye concentration. The amount of dye adsorbed increased with adsorbent dose, as the surface area increased with increasing adsorbent mass.

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