"Adsorption Studies of Methylene Blue Dye on Activated Carbon Derived From Biowaste Material"

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ABSTRACT

Activated carbon synthesized from chayote (Sechium edule) by phosphoric acid (H_3PO_4) activation was used as adsorbent for the adsorption of methylene blue from aqueous solution. Batch adsorption technique was carried out to evaluate the effect of initial concentration (5-45mg/L) on the removal of methylene blue. The experimental data showed that the amount of methylene blue adsorbed by the activated carbon was increased from 0.4 to about 4.0 with increasing initial methylene blue concentration from 5 to 45 mg/L. Highest removal of methylene blue was achieved at initial concentration of 5 mg/L (98.69 %). The results indicate that the Sechium edule carbon activated with H_3PO_4 could be employed as low cost adsorbent in wastewater treatment for the removal of colour and dyes.

Keywords: Activated carbon; Sechium edule; Adsorption; Methylene blue.

I. INTRODUCTION

Manufacture and use of synthetic dyes for fabric dyeing has become a massive industry today with the emerging of fashion industry. Textile dyeing industries though small plays an important role in developing countries in terms of economy. India's contribution is found to be more than 5 percent. However, it also consumes high quantity of water and subsequently produces high discharge of wastewater with high amount of contaminants. This has an adverse effect on the health of the human beings as well as the environment. Over the last few decades wastewater from textile industries has become one of the biggest challenges. Due to rapid changes in the customer`s demands the textile dyeing and finishing industries use wide variety of dyestuffs [1]. More than 100,000 commercially available dyes are known till date [2] and the world annual production of dyestuffs account to more than 7×10^5 tones. Textile effluents vary from mill to mill and one process to another. However, mills having complex processes consume more water. So an average mill producing 60,000m of fabric per day is likely to discharge approximately 1.5 million liters per day of effluent [3]. About $10-15\%$ of the total dyestuffs used in dye manufacturing and textile industry are released into the environment during their synthesis and dyeing process [4]. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands, suspended solids, content in toxic compounds but also for color, which are the first contaminant to be recognized by the human eye [5]. Colors in water affect photosynthetic phenomenon due to reduced light penetration and adversely affect aquatic life [6, 7]. Some of the dyes are toxic and carcinogenic. Thus, uses of dye contaminated water without any treatment may cause adverse effect on human health, domestic animals, wildlife and on the environment. Thus, textile effluent needs to be treated for the protection of human health and environmental safety. However, the treatment of dyes in industrial wastewater presents several problems since dyes usually have a synthetic origin and complex aromatic molecular structures which make them very stable and generally difficult to be biodegraded and photodegraded [8]. Various treatment techniques have been conducted on a broad range of water and wastewater contaminated with dyes including physical or chemical treatment processes [9]. These include chemical coagulation, flocculation [10, 11], oxidation, ozonation and adsorption. Amongst the various techniques of treatment of wastewater, adsorption technique has proven promising due to its simplicity, effectiveness, low cost and efficiency [12]. Adsorption has been found to be a successful technique for controlling the extent of water pollution due to dyes, metallic species, surfactants and other organic pollutants [13]. Adsorption is the process by which a solid adsorbent can attract a component in water to its surface and form an attachment via a physical or chemical bond, thus removing the component from the fluid phase [14].

When a solid surface comes in contact with a solution a layer of solute molecules accumulate at the interface due to imbalance of surface forces. Majority of the solute molecules, accumulated at the interface, is adsorbed onto the large surface area within the pores of adsorbent and relatively few are adsorbed on the outside surface of the particles. Adsorption from solutions is generally limited to mono-layer coverage of the adsorbent surface. The adsorptive forces are weak beyond the first mono-layer. Therefore, adsorption from solution beyond the first mono-layer occurs rarely. The equilibrium distribution of solute between the liquid and solid phases is an important property of adsorption systems that helps in defining the capacity of a particular system. The tendency of solute to get adsorbed is determined by the difference in the adsorption potential between the solute and the solvent when the solute-solvent affinity is large. In general, the lower the affinity of the adsorbent for the solvent, the higher will be the adsorption capacity for solutes. The adsorption involves two types of forces: physical forces and chemical forces. Depending upon the nature of the forces involved, the adsorption is of two types: physical adsorption and chemisorptions. In physical adsorption, the adsorbate is bound to the surface by relatively weak van der Walls forces. Chemisorptions, on the other hand, involve exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. Adsorbents such as activated carbon, polymeric resins, alkylsilane-modified silica, organoclays, zeolites, agricultural products/by-products and industrial products/by-products have been extensively used [15]. An excellent adsorbent should have a good adsorption capacity and be selective, and it should also have favorable adsorption kinetics and regenerability. To satisfy these requirements, the porous adsorbent has a high surface area as well as relatively large pore sizes to allow adsorbate molecule to enter the interior surface. Activated carbon is known for its porous structure, high surface areas and large sorption capacities [16]. Thus, adsorption onto activated carbon has proven to be the most efficient and reliable method for the removal of many pollutants, including different dyes [17]. Since 1940's, activated carbon has become the standard adsorbent frequently utilized for the removal of organic and inorganic pollutants in water industry [18]. Activated carbon can be prepared by a physical or chemical activation process. Physical activation consists of two steps: a carbonization process where a carbonaceous material is carbonized under the oxygen free atmosphere followed by activation process where the material is activated with an activating gas such as CO_2 and H_2O. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw materials used, the nature of the activating agent, and the conditions of the carbonization and the activation processes. In chemical activation both carbonization and activation processes occur simultaneously at lower temperature and a shorter time thus saving time and energy. In chemical activation, several types of chemicals are used as the activating agent including H_2SO_4, H_3PO_4, HNO_3, KOH and $ZnCl_2$. The greatest specific surface areas of activated were found to be obtained at the carbonization temperature of 600^0C. In contrast, the maximum surface areas of activated carbon were obtained at the carbonization temperature of 800^0C with alkali metal (KOH, NaOH, K_2CO_3 and Na_2CO_3) activation. The application of activated carbon as adsorbent mainly depend on pore structure and surface chemical functional groups of porous carbon [19]. However, despite its prolific use in treatment of wastewater, commercial activated carbon remains an expensive material. This has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products. Several researchers have studied the production of activated carbons from rubber seed coat [20], rice husk [21], rattan sawdust [22], bamboo [23], sugar beet bagasse [24], oil palm fiber [25] and buckwheat [26]. *Sechium edule* (common name – chayote) is a perennial vine of the gourd family, Cucurbitaceae, cultivated for its edible fruits. It has been introduced as a crop worldwide and ranks as one of the world's most versatile vegetables. The *Sechium edule* originated in Central America and it was spread to the Caribbean, South America and Europe by Eastern explorers and eventually introduced to Asia, Africa and Australia. The largest source of *Sechium edule* continues to be Central America, including Costa Rica, Mexico and the Dominican Republic. The crop requires minimum agronomic inputs and all the parts of the crop are used in various ways. It is known by various names in different languages viz: Chayote (Mexico/Latin America), Chow-Chow, Isqush (Nepali Language), Piskut (Khasi language), Squash (English) [27]. The plant is native to Mexico, but the North-Eastern part of India has considerable diversity of *Sechium edule* particularly in the states of Mizoram, Meghalaya and Sikkim [28, 29]. In North Eastern Hill region of India, it is widely cultivated by farmers in the backyards and jhum lands for its tender leaves, fruits, young shoots and tuberous roots. Although its tender leaves and young shoots are eaten as vegetables, the matured and dried leaves and stems are discarded as waste and as such a huge pile of it is either burnt or thrown away. In view of producing low cost, effective and efficient adsorbents and treating wastewater, in present study, activated carbon was prepared from *Sechium edule* and subsequently the adsorption studies of methylene blue dye on activated carbon was carried out. Methylene blue was selected as a model dye because it is widely used as a medication and dye. Methylene blue, prepared for the first time by Heinrich Caro in 1876, also called methylthionium chloride is a phenothiazine derivative having a heterocyclic aromatic structure. It is a cationic dye that appears as a solid, odourless, dark-green powder at room temperature and gives a blue solution on being dissolved in water. Methylene blue, most common among all other dyes of its

category, is generally used in textile industries for dying wool, cotton and silk. Though methylene blue is not strongly hazardous and has some medicinal value, it can cause harmful effects. Since dyes have a synthetic origin and complex aromatic molecular structures, are inert and difficult to biodegrade when discharged into water bodies. Methylene blue largely pollutes water resources and their high concentration in water may cause temporary or permanent allergic effect to skin, eyes and mucous membrane. Acute exposure to methylene blue can caused increased heart rate, vomiting shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [30]. In the present study, experiments were conducted using aqueous solution of methylene blue to evaluate the adsorption of methylene blue on activated carbon prepared from *Sechium edule*.

2. MATERIALS AND METHOD

2.1. Adsorbate:

A cationic dye methylene blue with molar mass 319.85 was chosen for the adsorption study. It is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}ClN_3S$. Though it is regarded as acutely toxic it can have various harmful effects. The structure of methylene blue is given below-
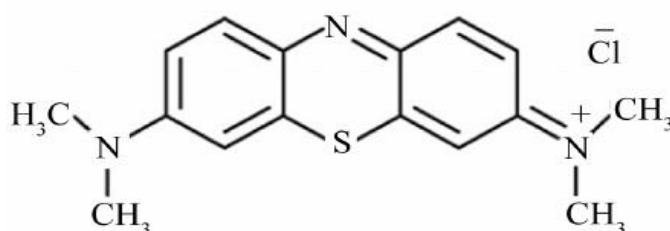
2.2. Preparation and chemical activation of the adsorbents
2.2.1. Preparation of activated carbon by pyrolysis:

The leaves and stems of chayote were collected from different parts of Nagaland and were used as a precursor for the preparation of activated carbon in this study. The precursor was first washed in water to remove dirt and dried in the sun. It was then collected in a stainless steel container and carbonized by electrically heating in a Muffle furnace at 600°C for 4 hours. After carbonization, the carbon prepared was cooled to room temperature and crushed into fine powder with mortar and pestle after which it was washed with distilled water several times to remove impurities. Finally the synthesized carbon product was dried in oven at 110°C for 12 h.

2.2.2. Chemical activation of the adsorbents:
The synthesized carbon products was then chemically activated with 0.1N solution H_3PO_4 under certain conditions to modify the chemical structure.
2.3. Characterization of activated carbon:
2.3.1 Determination of pH:
The pH of activated carbon of *Sechium edule* was determined using standard test method ASTM (American Society for Testing and Materials) D3838-80[31]. 1.0 gram of activated carbon of *Sechium edule* was transferred into 100 ml distilled water taken in a beaker and kept in a magnetic stirrer for one hour at 120 rpm. pH was then measured by digital pH meter. The samples were tested in triplicates.
2.3.2 Conductivity:
0.1 gram of activated carbon is mixed with 50 ml water and equilibrated for 1 hour by agitating at 120 rpm. The supernatant is then analyzed for conductivity using conductivity meter.
2.3.3 Apparent density:
To determine apparent density the standard test method ASTM D2854-96 was used [32]. In this method, a specific gravity bottle of 25 ml capacity was filled with the adsorbent and covered with a rubber stopper and weighed. The weight (g) divided by the volume (ml) gives the apparent density of the adsorbent.
2.3.4 Matter soluble in acid:
0.5 g of activated carbon is placed in an evaporating dish mixed with distilled water. 5-10 ml of concentrated HCl is added and digested by warming until sample is nearly dry. The digestion is repeated three times with 5 ml of the acid. Then it is diluted with 100 ml water and filtered using a previously weighed sintered crucible and the weight of the insoluble matter is calculated after drying for a constant weight at 103°C.
Calculation:
Matter soluble in acid (%) = [(C – D)/(C – B)] × 100 ……….. [33]

Where,

B = weight of crucible (g)

C = weight of crucible with original sample (g)

D = weight of crucible with cover plus dried sample (g)

2.3.5 Matter soluble in water:

1 g of activated carbon is added to 100 ml of distilled water and is shaken thoroughly for about 30 minutes and filtered. The residue is then dried, cooled and weighed [34].

Calculation:

Matter soluble in water (%) = [(C – D) / (C – B)] × 100

Where,

B = weight of crucible (g)

C = weight of crucible with original sample (g)

D = weight of crucible with cover plus dried sample (g)

2.3.6 Iodine number:

Iodine number is the mass (mg) of iodine adsorbed from a standard 0.1 N (0.05 M) iodine solutions, when the iodine concentration at equilibrium is exactly 0.02 N (0.01 M).To determine the iodine number, ASTM D4607-94(2006) [35] was used. In this method , 0.1 g of activated carbon was added with 10 ml of 5 % HCl and swirled in a conical flask until the entire activated carbon was wetted. The wetted solution was then boiled for exactly 30 seconds and the solution was cooled to room temperature. Then 100 ml of 0.1 N iodine solution was added to the contents of the conical flask. This solution was filtered using a Whatman 2V filter paper. Later 50 ml of the filtrate was then filtered against 0.10 N sodium thiosulphate solution until the yellow colour had almost disappeared. 1 ml starch indicator was added and the titration was continued until the blue colour just disappears. The equilibrium concentration is determined by calculation using the amount of sodium thiosulphate used in the titration.

Calculation:

X/M = A – (DF × B × S) / M

Where,

X/M = Iodine number (mg/g)

$A = 12693 N_2$, $B = 126.93 N_1$, $C = N_1 / (50 \times S)$,

C = residual iodine (N), S = Sodium thiosulphate (ml), M = carbon used (g), N_1 = concentration of sodium thiosulfate (N), N_2 = concentration of iodine (N)

DF = dilution factor

   = (I + H) / F

I = initial iodine (ml)

H = 5 % hydrochloric acid used (ml)

F = filtrate (ml)

2.3.7 Surface functional groups (Boehm's Titration):

The presence of surface functional groups in the activated carbons was quantified by Boehm's titration method [36, 37]. About 1.0 gram of activated carbon was mixed with each of 50ml solution (0.1 M) of NaOH, $NaHCO_3$ and Na_2CO_3 respectively, for 24 hours with continuous stirring. Then, the solid phase was separated from the aqueous solution by vacuum filtration. 10 ml of each filtrate was used for the excess acid titrat ion by 0.1 M HCl (hydrochloric acid). The phenolic group content on the carbon surface was determined as the amount of 0.1 M $NaHCO_3$ consumed by the sample. Lactonic group content was calculated as the difference between the amounts of 0.1 M Na2CO$_3$ and 0.1 M $NaHCO_3$ consumed by the activated carbon sample. Carboxylic group is obtained by subtracting the amount of 0.1 M Na2CO$_3$ consumed by the activated carbon from the amount of 0.1 M NaOH consumed. This method was used to calculate the concentration of acid groups on activated carbon surface under the following assumptions. Sodium hydroxide (NaOH) neutralizes carboxylic, phenolic and lactonic groups. Sodium carbonate (Na2CO$_3$) neutralizes only carboxylic and phenolic groups. Sodium bicarbonate ($NaHCO_3$) only neutralizes carboxylic groups.

2.3.8 Determination of zero point charge (pH$_{ZPC}$) :

pH$_{ZPC}$ of an adsorbent is important because it indicates the net surface charge of the carbon in solution [38,39]. To determine the pH of zero point charge, 0.1gram of activated carbon is added to 200 ml solution of 0.1 M

NaCl whose initial pH has been measured and adjusted with HCl. The containers were sealed and placed on a shaker for 24 hrs after which the pH was measured. The results are plotted with pH_{final}- $pH_{initial}$ against pH final. The point at which pH=0 is known as pH_{ZPC}.

2.3.9 Moisture content:

The moisture content of activated carbon samples were determined using standard test method [40]. The sample was put into a pre-dried crucible with lid, and the weight was taken to the nearest 0.5 mg. The lid was removed, followed by the heating of the crucible and the lid in a ventilated drying oven at 150˚C for three hours. After heating, the plate was quickly covered, cooled in desiccators and weighed. The loss in weight of the adsorbent represents the moisture content.
Calculation:
The moisture content is calculated as follows;
Moisture (weight %) = [(C – D) / (C-B)] x 100
Where,
B = weight of crucible with cover (g)
C = weight of crucible with cover plus original dried sample (g)
D = weight of crucible with cover plus dried sample (g)

2.3.10 Volatile matter content :

The volatile matter content of the activated carbons was determined using standard test method [41]. For which, 1 gm of activated carbon was taken in a pre-dried crucible which was covered with the lid and heated in a muffle furnace regulated at 950˚C for 30 min. after heating, the plate was quickly covered,cooled in desiccators and weighed.
Calculation:
The volatile matter content were calculated as follows:
Volatile matter (%) = [(C – D) / (C – B)] x 100
Where,
B = mass of crucible with cover (g)
C = mass of crucible with cover plus original sample (g)
D = mass of crucible with cover plus de-volatilized sample (g)

2.3.11 Ash content

The ash content of the activated carbon samples were determined using standard test method [42]. The crucible was ignited in the muffle furnace at 650˚C for 1 hour. After heating, the crucible was placed in a desiccator and cooled at room temperature. 1 gram of activated carbon pre-heated at 150˚C for 3 hours was taken in the crucible and heated in the furnace at 630˚C for 3hours. The crucible was kept in desiccators and cooled at room temperature and the weight was taken. The ash content of activated carbon was calculated as follows:
Total ash content (%) = [(D – B) / (C – B)] x 100
Where,
B = weight of crucible (g)
C = weight of crucible plus original sample (g)
D = weight of crucible plus ash sample (g)

2.3.12 Fixed carbon:

The fixed carbon content was determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The valued obtain was the amount of fixed carbon present in the sample expressed in percentage. The fixed carbon of activated carbon samples were calculated from the following equation.
% fixed carbon = 100 - (% moisture content + % ash content + % volatile matter content) Higher the percentage of fixed carbon, greater is the carbon content found in the material which is left after volatile materials are driven off. Hence better activated carbon is produced when percentage of fixed carbon is higher.

Table:1 Surface properties of the adsorbent

Sample SEAC (H_3PO_4)	
Matter soluble in acid (%)	5.2%
Conductivity (micromhos)	148.3
Matter soluble in water (%)	0.22%
Ph	8.4
Apparent Density(g/ml)	0.31
Iodine number (mg/g)	990.54
pHzpc	7.5
Moisture content%	2.5
Volatile matter content %	21.5
Ash content %	2.9
Fixed carbon %	73.1
Carboxylic (meq/g)	17.5
Phenolic (meq/g)	28.8
Lactonic (meq/g)	6.3
Total basic groups (meq/g)	11.3

2.4 Adsorption studies:

The adsorption capacity of activated carbon for methylene blue has been investigated using batch adsorption system. A stock solution of methylene blue (1000 mg/1) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature. The effect of initial concentration is studied by varying methylene blue concentrations between 5-45 mg/L in 100 ml of methylene blue dye solution and adding 1 g of adsorbent. Adsorption isotherm considers a relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature [43]. The percentage of the amount of dye adsorbed was calculated by the following equation,

Percentage removal $= 100 \frac{(C_i - C_f)}{C_i}$

Amount adsorbed (q_e) $= \frac{(C_i - C_f)V}{M}$

Where C_i and C_f are the initial and final equilibrium solution concentrations of the dye (mg/L), V is the volume of the solution (L) and M is the mass of the activated carbon (g). The data obtained is given in table 2.

Table 2: Effect of initial concentration of methylene blue with SEC (H_3PO_4).

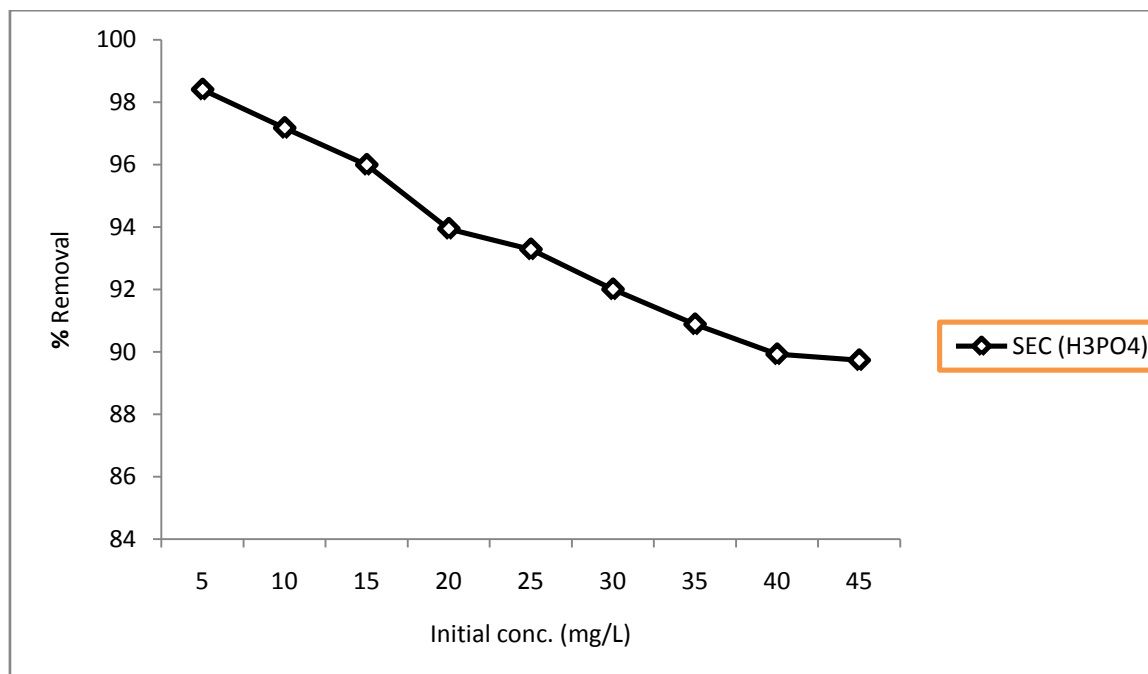| Adsorption sample	Initial Conc. [C_i]	Final Conc. [C_e]	Percent removal	Amount adsorbed [q_e]
SEC (H_3PO_4)	5	0.0758	98.40	0.4924
	10	0.2830	97.17	0.9717
	15	0.6012	95.99	1.4398
	20	1.2110	93.94	1.8739
	25	1.6800	93.28	2.3320
	30	2.4000	92.00	2.7600
	35	3.6201	90.88	3.1379
	40	4.0311	89.92	3.5968
	45	4.6210	89.73	4.0379

Fig 1: Variation of percent removal of methylene blue with increasing initial concentration.

Fig 2: Images of methylene blue dye solution of different concentration: (a)5mg/L, (b)25 mg/L.(Before and after adding adsorbent).

3.RESULTS AND DISCUSSION

pH of activated carbon is defined as the pH of a suspension of carbon in distilled water. The result show that the there is an increase in pH of the carbon sample. This increase in pH to about 7.7 indicates that the carbon sample may contain some water soluble alkaline substances. Conductivity measures the electrical current (EC), which is proportional to the mineral matter present in water. Thus conductivity depends on the total dissolved solutes (TDS). The results indicate that there is an increase in EC of the carbon sample. The result of apparent density of the carbon activated with H_3PO_4 is presented in Table 1. The result shows that the activated carbon synthesized have higher apparent density. If the density of activated carbon is high, then it provides greater volume activity and hence better quality of activated carbon. The amount of acid soluble matter of the adsorbent shows that the amount of acid soluble matter of the sample is less. This low value indicate that the carbon adsorbent is almost insoluble in acid; hence it may be used in treating water with acidic nature[44]. The water-soluble matter of the sample is determined and the result shows that water-soluble matter in the sample low. This low value indicate that the prepared activated carbon adsorbent are well suited for ground and surface water analysis as it may not alter the physical properties of water. Iodine number is the most fundamental parameter used to characterize activated carbon performance. The iodine number is a relative indicator of porosity in an activated carbon. The result for iodine number of the carbon adsorbent activated with H_3PO_4 is

presented in table 1. A higher value of iodine number for SEC (H_3PO_4) may be due to higher degree of activation which enables more adsorption of iodine molecule on the surface. Surface functional groups which have been determined by Boehm titration method here Phenolic groups were the major oxygen-containing surface functional groups on the SEC (H_3PO_4) surface. Only a small amount of lactonic groups were found. The neutralization with HCl revealed the total number of basic groups and showed that the acidic groups were more dominant at the surface of SEC (H_3PO_4). The initial pH_i and final pH_f and the values of $pH_f - pH_i$ are determined for the adsorbents the result shows the low pH_{ZPC} value which is consistent with the results of the Boehm titrations, which showed a dominance of acidic groups at the surface of SEC (H_3PO_4). The result of moisture content of the carbon activated with H_3PO_4 shows higher moisture content reduces the adsorption capacity of carbon by diluting the action of activated carbon. It could be seen in table 1 that the moisture content of the carbon adsorbent is less, hence the carbon activated with H_3PO_4 may be considered a better adsorbent. The volatile matter content results of the samples indicates that the carbon contain more volatile materials. These may be due to the extremely high surface area and high adsorption capacity of the activated carbon sample towards various volatile matters. A good activated carbon must have low ash content [45, 46]. The threshold limit of ash content should be less than 15% in activated carbon [47]. A small increase in ash content causes a decrease in adsorptive properties of activated carbon. With carbonization temperature increase, ash contents of the sample increases [48]. Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration of used activated carbon [49]. The result in the table 3.3.11 indicates that ash content in the sample is less, suggesting the fact that raw material used can be a good source for activated carbon. The fixed carbon of carbons activated by H_3PO_4 shows a high percentage 73.1%. The effect of initial concentration of methylene blue adsorption was evaluated at different concentration from 5 to 45 mg per L methylene blue solution. The graph shows that the removal percentage was decrease from around 98.40% to 89.73% when the methylene blue initial concentration was increased from 5 to 45 mg per L. This observation suggested limited numbers sorption sites available for sorption at higher methylene blue concentration.

4. CONCLUSION

Activated carbon was synthesized from *Sechium edule* and activated with phosphoric acid (H_3PO_4). Batch mode adsorption study of methylene blue on activated carbon was carried out. The effects of initial methylene blue was examined and the results showed that the amount of methylene blue adsorbed by the activated carbon was increased from 0.4 to about 4.0 with increasing initial methylene blue concentration from 5 to 45 mg / L. Highest removal of methylene blue was achieved at initial concentration of 5 mg per/L (98.69 %). Thus, activated carbon prepared from locally available *Sechium edule* can be proved as good ,effective and eco friendly adsorbent.

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