

# Preparation and Utilization of Corncob Activated Carbon for Dyes Removal from Aqueous Solutions: Batch and Continuous Study

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## Abstract

Commercial activated carbon and produced corncob activated carbon were used for the adsorption of methylene blue dye from aqueous solution using batch and continuous processes. Batch processes were conducted to study the effects of solution pH, contact time, adsorbent dose, agitation speed and initial dye concentration. The optimum values for methylene blue dye adsorption were: solution pHs of 6 and 7, contact times of 8 and 5 hr., adsorbent dosages of 1.5, and 0.5 gm, agitation speeds of 200 and 250 rpm and initial dye concentration of 50 mg/l calculated by commercial activated carbon and corncob activated carbon respectively. Two isotherm models, Freundlich and Langmuir fitted with the experimental data found from batch processes, the Langmuir model fitted well than the Freundlich, with maximum adsorption capacities of 16.21 and 30.95 mg/g and  $R^2$  of 0.952 and 0.992 predicted by commercial activated carbon and corncob activated carbon respectively. Radial and vertical flow regime reactors were conducted in column tests for the two adsorbent materials at different three flow rates (0.2, 0.3 and 0.4 L/min) and initial dye concentrations 15 mg/l, the same volume of (775 ml) from adsorbent materials used for both radial and vertical reactors to make a comparison between the capacity of the adsorbent materials each with another and between the performance of radial and vertical flow regime reactors configurations on breakthrough curves behavior. Radial flow regime reactor showed good results in comparison with vertical flow regime reactor.

**Key Words:** Methylene Blue, Adsorption, Radial Flow, Corncob Carbon

## المستخلص

تم استخدام الكربون المنشط التجاري وكاربون كوز الذرة المنشط كيميائيا لامتنزاز صبغة الميثيلين الزرقاء من المحاليل المائية باستخدام العمليات الدفعية والمستمرة. تم اجراء العمليات الدفعية لغرض دراسة تأثير حامضية الوسط، وقت التماس، جرعة المادة المازة، سرعة الخلط والتركيز الابتدائي للصبغة. القيم المثالية لامتنزاز صبغة الميثيلين كانت : حامضية الوسط ٦ و ٧، وقت التماس ٨ و ٥ ساعة، وزن مادة الامتنزاز ١,٥ و ٠,٥ غم والتركيز الابتدائي ٥٠ مغ/لتر لكل من الكربون المنشط التجاري و كاربون كوز الذرة على التوالي. الموديلان لانكمير وفرونديلج تطابقا مع النتائج الدفعية، الموديل لانكمير تطابق اكثر من فرونديلج مع قيم امتزاز عظمى ١٦,٢١ و ٣٠,٩٥ مغ/لتر وقيم  $R^2$  (0.992, 0.952) بواسطة الكربون المنشط التجاري و كاربون كوز الذرة على التوالي. سلسلة من فحوصات العمود اجريت للمادتين تأثير ثلاثة تصاريح مختلفة (٠,٢، ٠,٣ و ٠,٤ لتر/دقيقة)، تركيز اولي (١٥ مغ/لتر) مع نفس حجم المادة المازة (٧٧٥ مل) للمواد (الكربون المنشط التجاري و كاربون كوز الذرة) تم استخدامه لكل من الجريان الشعاعي والجريان العمودي لغرض اجراء مقارنة بين كفاءة المواد المازة من جهة وبين الجريان الشعاعي والعمودي في تقييم Breakthrough curves من جهة اخرى. الجريان الشعاعي بين نتائج جيدة مقارنة بنتائج الجريان العمودي.

**الكلمات المفتاحية:** صبغة الميثيلين، الامتنزاز، الجريان الشعاعي و كاربون كوز الذرة

## 1. Introduction

more people die from the consequences of unsafe water than from all forms of violence, including war. And, every year, water contamination of natural ecosystems affects humans directly by destroying fisheries or causing other impacts on biodiversity that affect food production. Contaminations due to industrial wastewaters has become a common problem for many countries. Dyes and pigments are one of the problematic

groups of pollutants. It is estimated that more than 100,000 commercially available dyes with over  $7 \times 10^5$  tons of dyestuff produced annually. Major problems associated with colored effluent are lowering light penetration, photosynthesis and damages the aesthetic nature of the water surface (Mohammed *et. al.*, 2014). Dyes have complex aromatic molecular structures which make them more stable and difficult to biodegrade. The direct discharges of the dyes into urban wastewaters in natural environments may cause the formation of toxic carcinogenic breakdown products. The presence of small amount of dyes (less than 1ppm) is highly visible and undesirable (Zainol, 2010). Methylene blue (MB) is an important basic dye widely used for coloring paper, temporary hair colorant, coating for paper stock, dyeing, printing cotton and tannin, dyeing leather, used as an antiseptic and for other medicinal purposes (Idris *et. al.*, 2012). MB can cause eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled. There for, the removal of such dyes from effluents prior to their final discharge is of significant environmental, technical, and commercial (Yan and Wang, 2013). Treatment of dye-based effluents is considered to be one of the challenging tasks in environmental fraternity (Himakshi *et. al.*, 2013). There are many removal techniques such as chemical oxidation, precipitation, filtration, aerobic and anaerobic microbial degradation, coagulation, membrane separation, electrochemical treatment, flotation, hydrogen peroxide catalysis, and reverse osmosis, ozonation and biological techniques can be employed to remove various pollutant form the textile industry wastewater (Gonawala and Mehta, 2014).

Some of these methods are non-economical and have many disadvantages such as high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. Among several chemical and physical treatment methods, the adsorption has been found to be superior to other techniques for the removal of dyes from aqueous solution in terms of methodology, operational conditions and efficiency (Fungaro *et. al.*, 2010). Activated carbon is widely used as an adsorbent due to its high adsorption abilities in removal of organic pollutants from wastewater (Olivella *et. al.*, 2012). The use of carbon as an adsorbent is limited because of its high cost. At present, there is a growing interest in using low cost adsorbents for dye adsorption. If an adsorbent is inexpensive and ready for use, the adsorption process will be a promising technique (Gong et al., 2008). The abundance and availability of agricultural by products make them good sources of raw materials for activated carbon (Taha *et. al.*, 2014). Corn is a significant crop which can be found all around the world. The annual production worldwide is about  $520 \times 10^9$  kg. Corn cob as a biomass and agricultural waste is an attractive candidate. Usage of these biomass wastes as a raw material for production of activated carbon is a highly beneficial (Wang *et. al.*, 2010).

In designing new internal arrangements to achieve a radial flow it is imperative that the flow distribution obtained in the radial inward flow direction is as near ideal as possible. This is harder than for a classic vertical flow reactor because of the increased problems of inlet flow distribution and also because of the inherently lower pressure drops through the bed. The advantages of radial over axial flow reactors are the high flow capacity, low pressure drop, and the possibility of using finely divided catalysts (Li and Zhu, 2011). The packed column of radial flow column (RFC) consists of two concentric porous cylindrical sieves, between which the stationary phase is filled with an adsorbent (Dia *et. al.*, 2009).

## 2. Experimental Work

### 2.1 Adsorbate

Methylene Blue (MB) dye was used as an adsorbate in the present study. The choice of MB dye as an adsorbate is due to its known strong adsorption on to solids. The MB dye used was supplied by Sigma-Aldrich, scientific bureaus in Iraq, Bagdad. A stock solution of methylene with 1000 mg/l concentration was prepared by dissolving 1 gm of powder in 1 L of distilled water, other required concentrations were prepared by diluting. Figure (1) shows MB powder



Fig. (1) MB Powder Used as an Adsorbate

### 2.2 Adsorbents

#### 2.2.1 Commercial Activated Carbon

#### 2.2.2 Corncob Activated Carbon

Corncob activated carbon was prepared as following (Rocha *et. al.*, 2015)

- Collection of the corncobs from Babylon Governorate.
- Cutting and sieving of collected corncobs to size near to 1 mm
- Washing and drying of sieved corncobs for two hours at 110°C.
- Soaking of dried corncobs with 0.85% solution of H<sub>3</sub>PO<sub>4</sub> at a ratio of one mile of H<sub>3</sub>PO<sub>4</sub> to one gram of dried corncobs for two hours
- Heating of soaked corncobs for two hours in an oven at 400 °C.
- Cooling and washing of produced activated carbon with distilled water until pH of washings reached to 6.
- Finally drying of product activated carbon at 110°C for two hours. The steps of experimental work of corncob activated carbon preparation are shown figure (2).



Fig. (2) The Steps of Corncob Activated Carbon Preparation

## 2.2 Experimental Arrangement

### 2.2.1 Radial Flow Reactor

Radial flow regime reactor with flow from external to center pipe was designed by perforated external and internal pipes located inside back house acrylic reactor. The external and the internal pipes have a diameter of 10 and 1cm respectively and a height of 16 cm. Back house acrylic reactor has an inner bottom and top diameters of 14.5 cm and 16.5 cm respectively. The adsorbent forced in between the external and internal pipes with effective depth (depth in the direction of the flow) equal to (radius of external pipe  $10/2$  – radius of internal pipe  $1/2$ ) 4.5cm and height equal to 10 cm. The same volume of (775 ml) from adsorbent materials (commercial activated carbon, corncob activated carbon and ion exchange resin) used for both radial and vertical reactors in continuous flow processes.

### 2.2.2 Vertical Flow Regime Reactor

Vertical flow regime reactor with down flow direction was established in a column of (8.5cm) inner diameter and (80cm) height. The two ends of column were provided with plastic sieve of (0.5cm) diameter followed by mesh layer of (0.2mm) diameter to provide good distribution of flow and to prevent materials from out flow respectively. The column was packed with the adsorbent of 13.7 cm height between two supporting layers. Above and bottom of the adsorbent there were (5cm) layer of gravel to prevent adsorbent from float and to provide a good distribution of flow, these two layers of gravel were washed after each run and used for all runs without replacing to ensure that there is no partition in adsorption process. Figures (4) show the pilot plant.

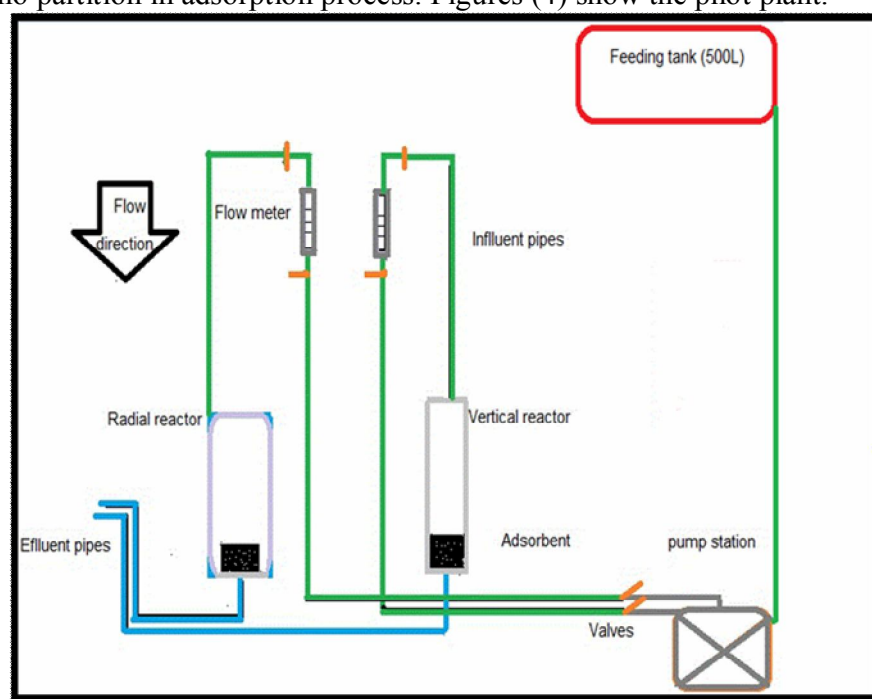


Fig. (3) Pilot Plant Adopted in the Present Study

## 3. Batch Experimental Results

Batch processes are important examples in which the adsorbent moves relative to the walls of the contaminated vessel. The simplest process involves a specific volume of

wastewater is mixed with a quantity of adsorbent into a container until the pollutant decreased to desired level for a certain period of time. Batch experimental processes were conducted to study the effect of various parameters, such as the pH, contact time, adsorbent dose, agitation speed and initial dye concentration for commercial activated carbon and corncob activated carbon. Batch experimental processes established in bottles of (250 ml) of volume, containing a (100 ml) of methylene blue solution.

### 3.1 Effect of Solution pH

One of the important factors that affecting the capacity of adsorbent in treatment is the solution pH. The efficiency of adsorption is dependent on the solution pH, since variation in value of pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Nandi *et. al.*, 2009). The effects of pH on adsorption of methylene blue (MB) dye for both commercial activated carbon and corncob activated carbon were evaluated at adsorbent dose of 0.5 g, agitation speed of 250 rpm, initial concentration of 100 mg/l and contact times of 10 and 5 hr. for both commercial activated carbon and corncob activated carbon respectively. It can be seen (Figure 5), for commercial activated carbon, when the pH increased from 2 to 6 caused an increase in removal efficiency from 74 to 79% respectively, decreasing in adsorption efficiency from 78 to 72 % when pH increased from 7 to 12, the maximum removal efficiency of 79% monitored at pH 6. For corncob activated carbon, when the pH increased from 2 to 7 caused an increase in removal efficiency from 80.6 to 94.3% respectively, decreasing in adsorption efficiency from 92.8 to 80.6 % when pH increased from 8 to 12, the maximum removal efficiency of 94.3% monitored at pH 7.

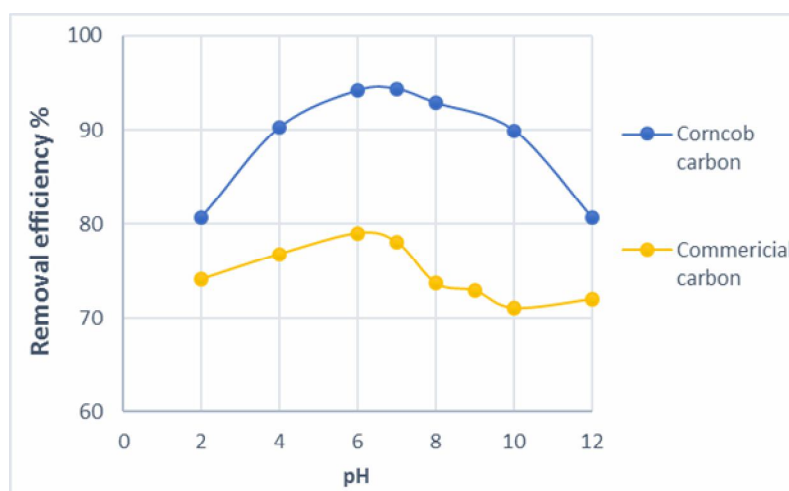


Fig. (4) the Effects of pH on MB Dye Adsorption onto Commercial Activated Carbon and Corncob Activated Carbon

### 3.2 Effect of Contact Time

The effect of contact time shown in figure (6) was investigated to find equilibrium time of adsorption using the parameters shown in table (1) except of time and pHs of 6,7 and 8 as optimum values for commercial activated carbon, corncob activated carbon and akualite respectively. It is clear for three adsorbent that the rate of adsorption is rapid at the beginning and becomes slow in later stages till saturation is reached. It is basically due to the saturation of the active sites which do not allow further adsorption to take

place. The equilibrium times are 8, 5 and 1.25 hr. for commercial activated carbon, corncob activated carbon and akaluite respectively.

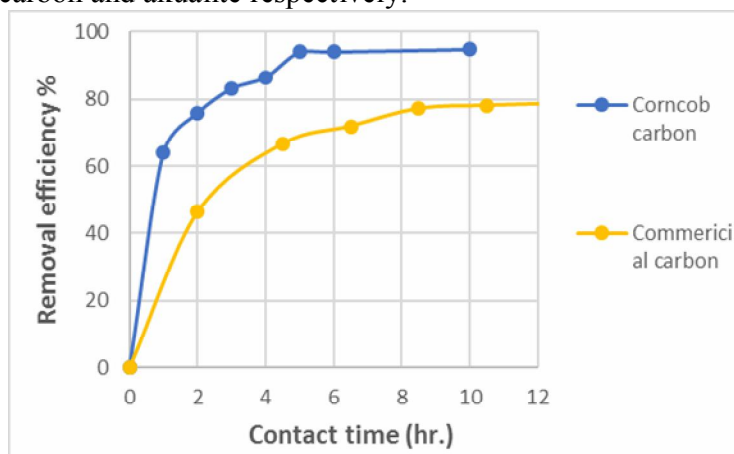


Fig. (5) the Effect of Contact Time on Adsorption of MB Dye onto Commercial Activated Carbon and Corncob Activated Carbon

### 3.3 Effect of Adsorbent Dosage

The effect of the amount dose on the MB dye adsorption was examined using the parameters shown in table (1) of the agitation speed and the initial dye concentration, with amount of dose from 0.25 to 1.5 g, optimum pHs values of 6 and 7 and contact times of 8 and 5 hr., for commercial activated carbon and corncob activated carbon respectively. As shown in figure (7) the increasing in adsorbent dosage from 0.25 to 1.5 mg and 0.25 to 1 resulted in an increase of removal efficiency from 59 to 98.56% and from 72.73 to 99.99 % for commercial and corncob activated carbon respectively.

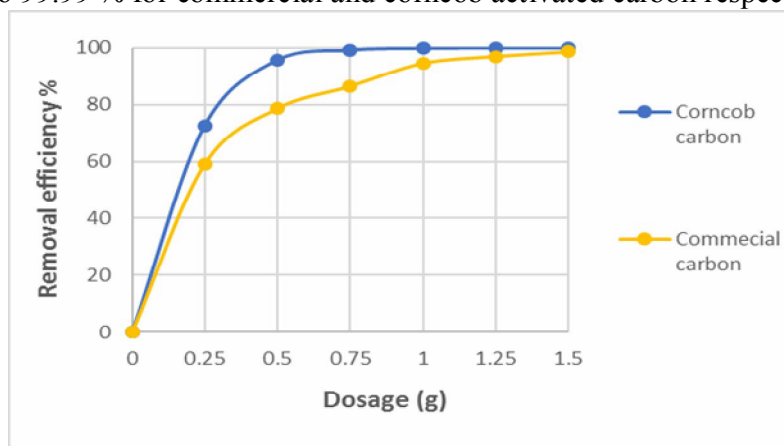


Fig. (6) the Effect of Amount Dosage on Adsorption of MB Dye onto Commercial Activated Carbon and Corncob Activated Carbon

### 3.4 Effect of Agitation Speed

The effect of agitation speed on the equilibrium adsorption was conducted as shown in figure (8) using the parameters shown in table (1) of the dosage and the initial dye concentration, optimum pHs and contact times found from pervious steps and different agitation speeds ranging from 50 to 300 rpm. For commercial activated carbon, when the agitation speed increased from 50 to 150 resulted in an increase of removal



efficiency from 43 to 75%, approximately constant removal efficiency of 78% in speeds above than 200 rpm. When the agitation speed increased from 50 to 150 resulted in an increase of removal efficiency from 51 to 88% and approximately constant removal efficiency of 93 in speeds above than 250 rpm for corncob activated carbon. This behavior due to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles.

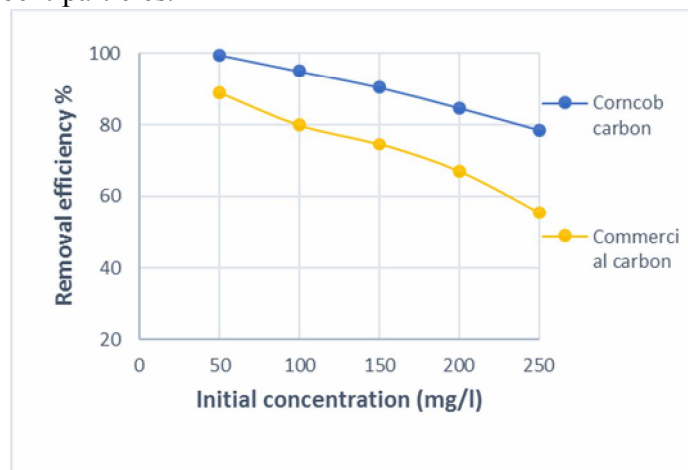


Fig. (7) the Effect of Agitation Speed on Adsorption of MB Dye Adsorption onto Commercial Activated Carbon, Corncob Activated Carbon and Akualite

### 3.5 Effect of Initial Dye Concentration

The effect of initial dye concentration on MB dye adsorption was evaluated as shown in figure (9) using the parameters shown in table (1) of the dosage and the agitation speed, optimum pHs and contact times found from pervious steps and different initial dye concentrations ranging from 50 to 250 mg/l. When the initial dye concentration increased from 50 to 250, the removal efficiency decreased from 89 to 55 and from 99.5 to 78.6 for commercial activated carbon and corncob activated carbon respectively.

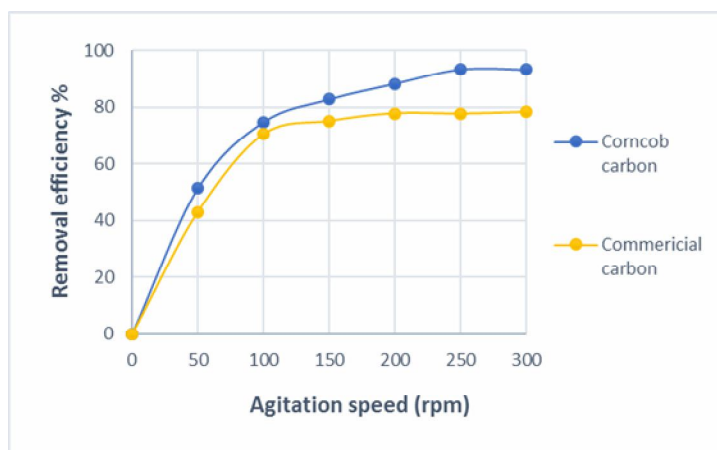


Fig (8) the Effect of Initial Dye Concentration of MB Dye Adsorption onto Commercial Activated Carbon and Corncob Activated Carbon



### 3.6 Adsorption Equilibrium Isotherms

The adsorption equilibrium isotherms were represented by the Langmuir and the Freundlich isotherm models for adsorption of MB dye on to commercial activated carbon and corncob activated carbon. Figure (10) shows the Langmuir isotherm reported for adsorption of MB dye on to commercial activated carbon at pH 6, contact time 8 hr., agitation speed 250 rpm, initial concentration 100 mg/l and dosage from 0.5 to 1.5 g. Langmuir isotherm conducted for adsorption of MB dye on to corncob activated carbon at pH 7, contact time 5 hr., agitation speed 250 rpm, initial concentration 100 mg/l and dosage from 0.5 to 1.5 g shown in figures (11).

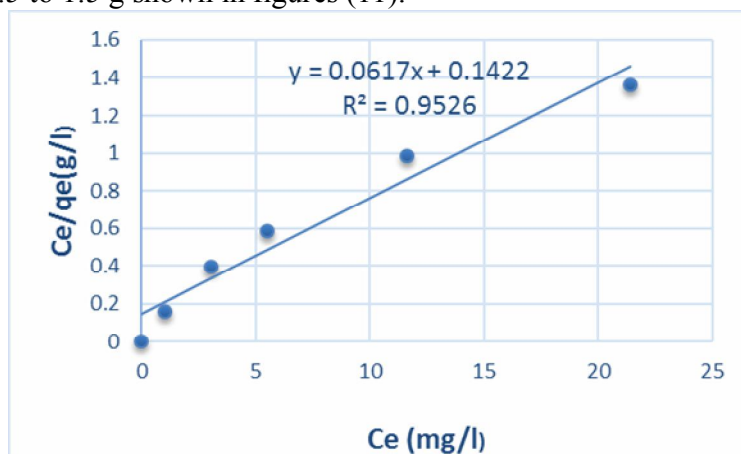


Fig. (9) Langmuir Isotherm for Adsorption of MB Dye onto Commercial Activated Carbon

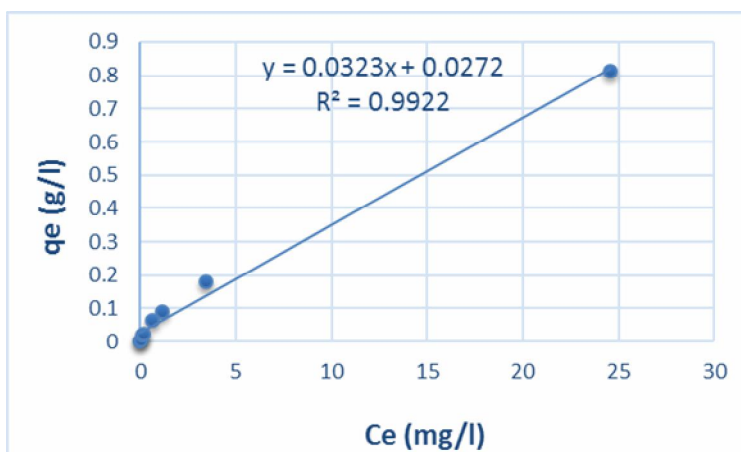


Fig. (10) Langmuir Isotherm for Adsorption of MB Dye onto Corncob Activated Carbon

### 4. Column Experimental Results

For the two adsorbents (commercial activated carbon and corncob activated carbon) and both the radial and vertical regime reactors, the flowrates  $Q = 0.2, 0.3$  and  $0.4 \text{ L/min}$  and a concentration dye  $C_0 = 15 \text{ mg/L}$  were studied as shown in figures (13), (14) and (15).

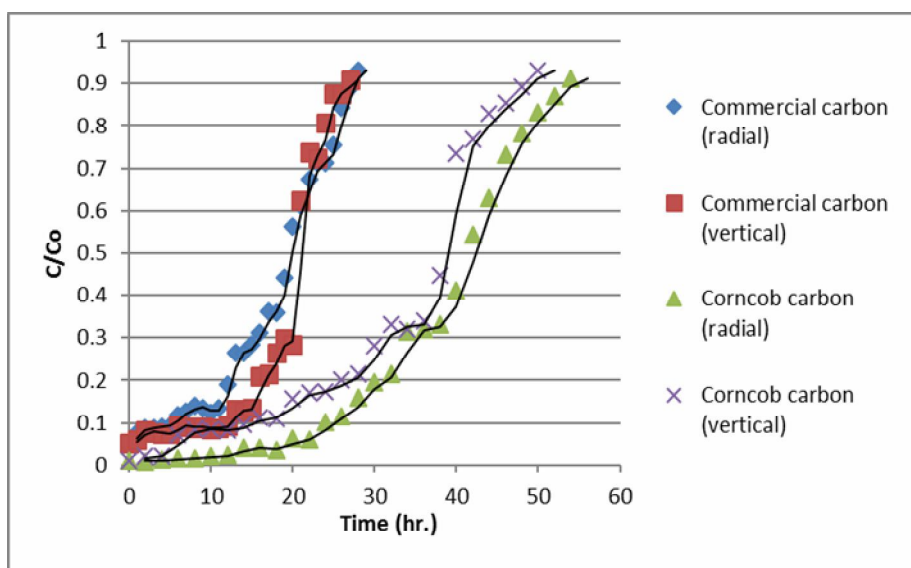


Fig. (12) Breakthrough Curve for Radial and Vertical Flow Regime Reactors at  $C_0=15$  mg/L,  $Q= 0.2$ L/min and pHs 6, 7 and 8 for MB Dye Adsorption onto Commercial Activated Carbon and Corncob Activated Carbon Respectively.

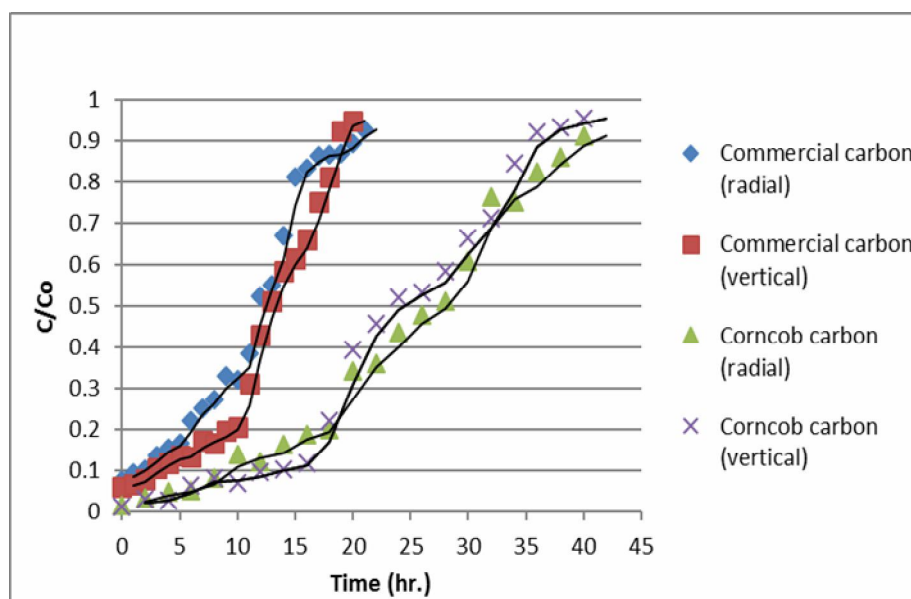


Fig. (13) Breakthrough Curve for Radial and Vertical Flow Regime Reactors at  $C_0=15$  mg/L,  $Q= 0.3$ L/min and pHs 6, 7 and 8 for MB Dye Adsorption onto Commercial Activated Carbon and Corncob Activated Carbon Respectively.

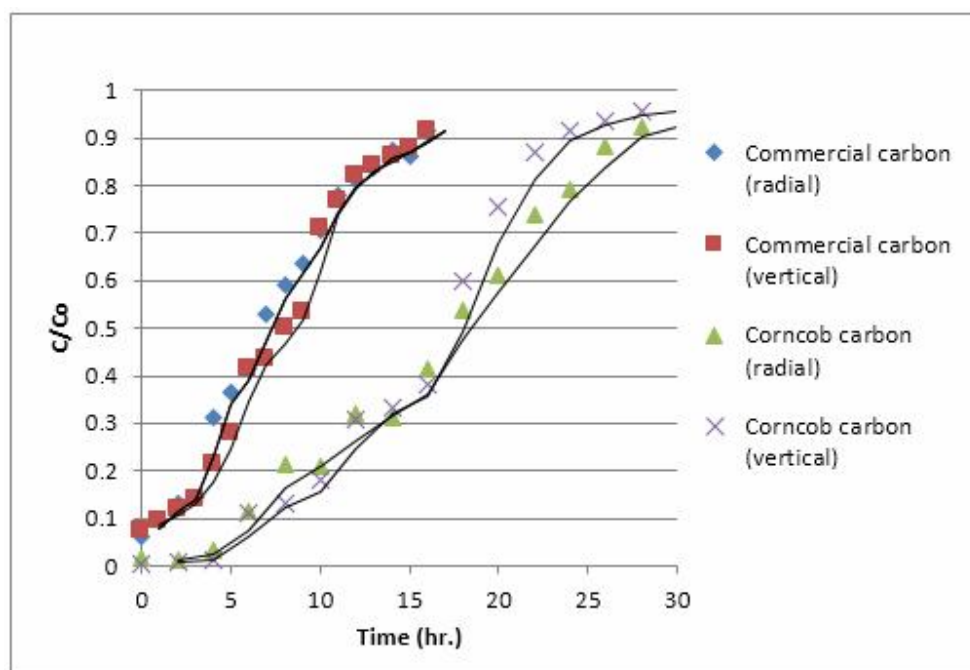


Fig. (14) Breakthrough Curve for Radial and Vertical Flow Regime Reactors at  $C_o=15$  mg/L,  $Q= 0.4$ L/min and pHs 6, 7 and 8 for MB Dye Adsorption onto Commercial Activated Carbon and Corncob Activated Carbon Respectively.

## 5. Conclusions

Based on results of batch and continuous processes and simulation of flow obtained from the present study, the following conclusions can be written:

- 1) The optimum achieved parameters for methylene blue dye adsorption are: solution pHs of 6 and 7, contact times of 8 and 5 hr., adsorbent dosages of 1.5 and 0.5 gm, agitation speeds of 200 and 250 rpm and initial dye concentration of 50 mg/l exhibited by commercial activated carbon and corncob activated carbon respectively.
- 2) Langmuir model fitted well with the experimental data, with maximum monolayer adsorption capacities of 16.21 and 30.95 mg/g and  $R^2$  of 0.952 and 0.992 predicted by commercial activated carbon and corncob activated carbon respectively.
- 3) In radial flow regime reactor, breakthrough curves showed that the outlet concentration of methylene blue dye at the beginning of run time is higher and the break point time is larger in comparison with vertical flow regime reactor for most figures of breakthrough curve.
- 4) The results of continuous flow processes showed that, when the flow rate or initial dye concentration increase, the time required reaching saturation decreases for both radial and vertical regime reactors.
- 5) Convergence in the time required reaching saturation between the radial and vertical regime reactors, as the flow rate or initial dye concentration increase in the results of continuous flow processes.
- 6) radial flow regime reactor may be a competitive installation over vertical flow regime reactor in removing of MB dye from aqueous solution.
- 7) For commercial activated carbon, the time required to reach the ratio  $C/C_o = 0.9$  is approximately 60% of the time required for corncob activated carbon to reach the same ratio of  $C/C_o$ .

- 8) Chemically activated corncob carbon showed good adsorption capacities in comparison with commercial activated carbon in both batch and breakthrough curve studies.
- 9) Corncob is a good agriculture source for activated carbon production utilized for MB dye adsorption in comparison with many agriculture materials utilized for dyes removal.

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