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Removal of Colour from Waste Water Using Coconut Shell Activated Carbon (CSAC) and Commercial Activated Carbon (CAC)

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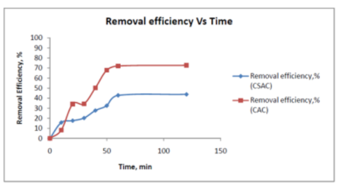
Graphical abstract



Abstract

In this study, series of batch adsorption experiment were conducted to examine the color removal efficiency of CSAC and CACs from waste water. The CAC is coal base activated carbon while the CSAC was manufactured in the laboratory. Yellow dye colour (Tartrazine E102) was utilized as the colourant. The adsorption efficiencies of the adsorbents were evaluated and compared by measuring the percentage of color removed. The effects of solution pH, adsorbent concentration, contact time as well as initial color concentration on the colour removal efficiency were also investigated. The optimum adsorption of color was achieved at low pH (pH 1.68), low initial color concentration (50mg/L) and 12g/l carbon dosage with removal efficiency of 75% for CAC and 45% for CSAC, with one hour agitation. Lower colour removal efficiency of 25% for CAC and 17% for CSAC were obtained at higher pH (pH 9-12), higher initial color concentration (100mg/L) and low carbon dosage, under the same retention time. A comparison of the Langmuir and Freundlich isotherm models of the adsorption data shows that Langmuir isotherm shows higher correlation coefficient, R2. The results indicate that CSAC has the potential as a low cost alternative for colour removal but the efficiency is lower than CSAC.

Keywords: Color removal; waste water; coal; coconut shell; activated carbon; adsorption isotherm

Abstrak

Dalam kajian ini, satu siri eksperimen penjerapan berkelompok telah dijalankan untuk menyiasat kecekapan penyingkiran warna oleh CSAC dan CACs daripada air sisa. Kecekapan penjerapan telah dinilai dengan mengukur peratus penyingkiran warna. Kesan larutan pH, kepekatan adsorben, masa betindak balas dan kepekatan warna asal terhadap kecekapan penyingkiran warna juga telah disiasat. Penjerapan warna optimum dicapai pada pH rendah (pH 1.68), kepekatan warna asal yang rendah (50mg/l) dan 12g/l dos karbon dengan kecekapan penyingkiran sebanyak 75% untuk CAC dan 45% bagi CSAC, dengan pergolakan selama satu jam. Kecekapan penyingkiran warna yang rendah iaitu 25% untuk CAC dan 17% untuk CSAC telah diperoleh pada pH tinggi (ph 9-12), kepekatan warna asal yang tinggi iaitu 100mg/l dan dos karbon yang rendah untuk tempoh penahanan yang sama. Perbandingan antara model isotherm Langmuir dan Freundlich ke atas data penjerapan menunjukkan bahawa model isotermal Langmuir menunjukkan keputusan yang lebih baik dengan pekali korelasi, R^2 yang lebih tinggi. Keputusan menunjukkan bahawa CSAC boleh digunakan sebagai alternatif kos rendah untuk CAC untuk menyingkirkan pewarna daripada air sisa tetapi kecekapannya penyingkirannya adalah lebih rendah berbanding CAC .

Kata kunci: Warna pengeluaran; air sisa; arang batu; kelapa shell; karbon teraktif; Adsorpsi sesuhu

1.0 INTRODUCTION

The extensive use of dyes in the textile, paper, rubber, plastic, cosmetics, food and pharmaceutical industries poses pollution problems in the form of coloured wastewater discharge into environmental water bodies. Intense colours of dye effluent have an adverse aesthetic effect which reduces aquatic diversity by blocking the passage of light through the water, therefore, reduces photosynthetic activity [1–3]. These colored waste waters are equally hazardous to the human health and therefore needs to be treated [1, 4–10]. Commercial activated carbon used in surface and wastewater treatment in Malaysia is largely derived from coal. The advantages of coal-based carbons can be seen in their ability to remove toxic organic compounds from industrial and municipal wastewater and potable water as well [1, 5–6, 10]. Another significant application of coal-based carbons is decolorization. The feedstock for these carbons, usually bituminous coal, is a non-renewable resource. The long-term availability of coal and its long-term environmental impact coupled with its potentially increasing cost has prompted researchers to consider renewable resources such as agricultural by-products as an alternative [3]. Malaysia is a tropical country where coconut is richly cultivated. The coconut shell is considered as an agricultural waste, therefore using it as a raw material for production of activated carbon is much more economical than the coal based activated carbon. Colorants typically have either a negative or neutral electric charge and are water soluble. In contrast, pigments are water insoluble and are accompanied by the coloring agents suspended in paint and ink. The difficulty in removing colorants in wastewater is primarily due to their extreme stability. The few oxidizing agents that are effective in reducing colorant contents, such as chlorine and ozone are expensive and do not significantly reduce the colorant content of wastewater unless added in very large quantities. Furthermore, these oxidizing agents have the potential for generating toxic organics that are harmful to both humans and the environment [1, 4–10]. Different methods have been recently developed for reducing some specific colorants. These methods include carbon adsorption, dye reduction, ozonations, electrochemical techniques, chemical pretreatments, aerobic and anaerobic treatments and powdered activated carbon-activated sludge system [11]. In this study, the carbon adsorption method is investigated for its efficiency in color removal from wastewater. The objectives of this research are to compare the adsorption efficiency of two types of activated carbons which are coconut shell activated carbon (CSAC) and coal based commercial activated carbons (CAC). The adsorption capacity is investigated by varying the adsorption parameters such as contact time, pH, carbon dosage and initial color concentration. The adsorption data were then modeled with Langmuir and Freundlich isotherms to study the adsorption process [2, 12–17].

2.0 MATERIALS AND METHOD.

2.1 Production of Activated Carbon

The activated carbon (CSAC) was produced by impregnating 40g of dried raw (or demineralized) coconut shell powder with 100 ml of 60% H_3PO_4 at room temperature for 12h. This was then thermally activated at 200^OC for 15mins and followed by carbonization at 450^OC for 45 mins in air. The sample was then cooled at room temperature and was thoroughly washed with distilled water to a neutral pH. This was then dried overnight at 105^OC in air. The Coal based commercial activated carbon (CAC) was purchased from market.

2.2 Waste Water Preparation and Adsorption Procedure

1000mg/L stock solution of synthetic waste water was prepared using yellow dye (tartrazine 19140) and from which other desired concentrations were obtained. Batch adsorption studies were carried out at room temperature (26^OC) by adding 100 ml of the colour solution to 2 g/l of activated carbon. This was then stirred for 1 hour at a constant agitation speed of 200 rpm. This solution was then filtered and then examined by using Ultra-violet spectrophotometer at 422 nm along with a blank solution as control. The percentage colour removal was then calculated as;

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100\%$$

Where, Ci is the initial colour concentration and Ce final colour concentration.

The above procedure was then repeated for different quantities of synthetic waste water sample, time, pH, carbon dosage and initial colour concentrations.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Contact Time

Contact time is a crucial sorption parameter that gives useful piece of information on the optimum adsorption time. From Figure 1, an initial rapid increase in the percentage removal of colour by either CSAC or CAC was observed which reached a steady state after one hour giving maximum colour removal efficiency for CAC and CSAC as 72% and 43% respectively. The removal rate was higher in the beginning due to larger adsorbent surface area. After adsorption, the rate of dye uptake was controlled by the rate of transport of dye from the exterior to the interior sites of the adsorbent particles which were nearly constant throughout the period of time.

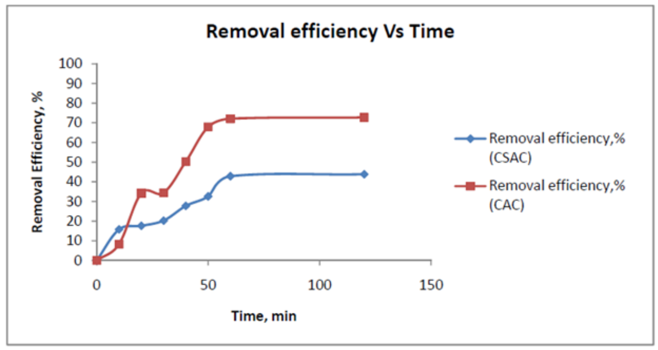


Figure 1 Removal efficiency versus time

3.2 Effect of pH

The pH of the solution influences adsorption by affecting the surface properties of the adsorbents and ionization or dissociation of the adsorbate molecules. Figure 2 shows that higher removal of color for both samples were observed at pH of 4 and below which is 75% and 45% respectively. As the pH of the solution increased, the dye adsorbed decreased considerably**.** This can be explained by the activated carbon characteristic during preparation. The activated carbon produced is hydrophobic in nature and take on a positive charge by absorbing hydrogen (H^+) ions when immersed in water. Low pH leads to an increase in H^+ ion concentration in the system. The surface of the activated carbon will possess positive charge by absorbing H^+ ions. As the carbon surface is positively charged at low pH, a significantly strong electrostatic attraction appears between the positively charged carbon surface and anionic dye molecule leading to higher adsorption of color dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the coconut shell based activated carbon and commercial activated carbon does not favor the adsorption of anionic dye molecules due to the electrostatic repulsion. For this reason, color adsorption efficiency drops in the alkaline medium [2, 18–19].

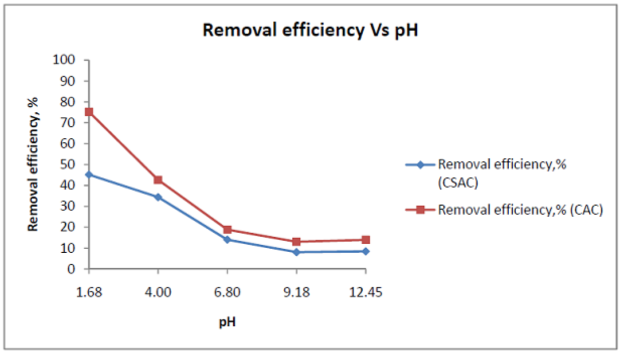


Figure 2 Removal efficiency versus pH

3.3 Effect of Carbon Dosage

From Figure 3, it was observed that the color removal efficiency increases when the carbon dosage increases. Up to 12 g/L of carbon dosage, the use of CAC is able to achieve 74% of removal efficiency compare to 44% of removal efficiency of CSAC. This increasing trend of efficiency is due to the increased active surface sites for adsorption and conglomeration of the adsorbent as the dosage of carbon increases [20–27].

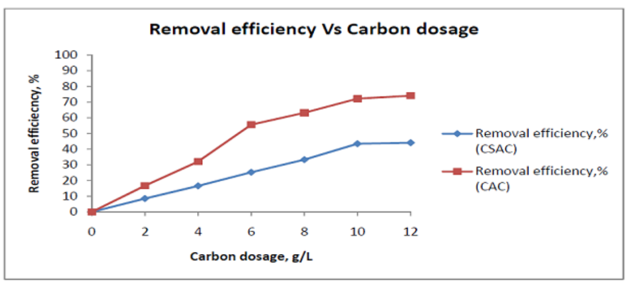


Figure 3 Removal efficiency versus Carbon dosage

3.4 Effect of Initial Color Concentration

Figure 4 presents the removal efficiency versus dye concentration. The percentage of color removal efficiency decreases with increasing dye concentration. This indicates that there is a reduction in adsorption, due to the lack of available active sites required for the high initial concentration of the colored solution.

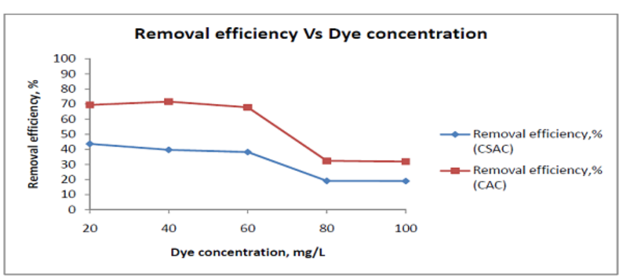


Figure 4 Removal efficiency versus dye concentration

3.5 *Langmuir Isotherm*

The Langmuir isotherm was evaluated using the model

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \qquad (1)$$

Where *Ce* is the equilibrium concentration (mg/ L), *qe* is the amount adsorbed at equilibrium (mg/ g), while, *a* (mg/ g), and b (L/ mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

The linear plots of *Ce*/*qe* against *Ce*, as shown in Figure 5, reveal that the adsorption obeys Langmuir isotherm model for all adsorbents. The values of *a* and *b*, shown in Table 3, were determined for all adsorbents from intercept and slopes of the linear plots presented in Figure 5.

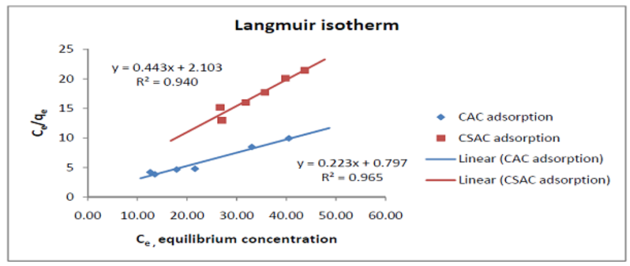


Figure 5 Langmuir isotherm graph

The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor or equilibrium parameter RL which is defined by

$$R_L = \frac{1}{1+bC_0} \qquad (2)$$

$$K_L = \frac{1}{ab} \quad (3)$$

Where *b* is Langmuir constant (L/mg) and C_O is initial concentration (mg/L). It has been shown using mathematical calculations that parameter R_L indicates the nature of adsorption process. From Table 1, it is observed that R_L values for CSAC and CAC fall in the range of 0-1, which is an indication of a favorable adsorption process as shown in table 2.

Table 1 Intraparticle diffusion rate parameter and diffusion coefficient at various dye concentration

Color concentration	R_L value	
(mg/L)	CSAC	CAC
10	0.3215	0.2632
20	0.1916	0.1515
30	0.1364	0.1064
40	0.1059	0.0820
50	0.0866	0.0667
80	0.0559	0.0427

Table 2 Nature of isotherms at different R values

Values (R)	Types of isotherm
R>1	Unfavorable
R=1	Linear
0<R<1	Favorable
R<0	Irreversible

3.6 *Freundlich Isotherm*

The Freundlich isotherm was determined using the model.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4)$$

Where K_F and $1/n$ are Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, while q_e is the colour adsorbed per unit weight of adsorbent (carbon). The amount of solute adsorbed and concentration of solute in solution can be represented by qe and Ce respectively. Eq. (4) can be linearized to the form shown in Eq. (5), and the constants can thus be determined numerically.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

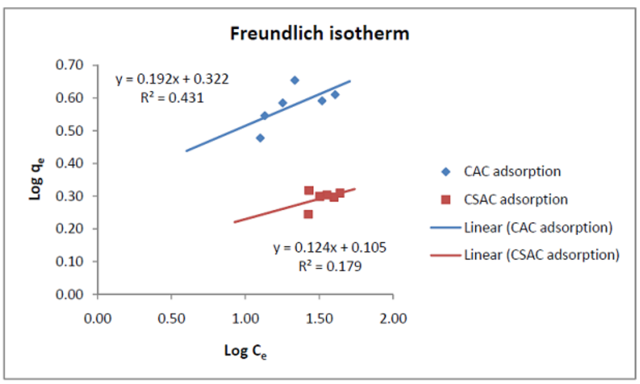


Figure 6 Freundlich isotherm graph

From Figure 6 above, a plot of log qe versus log Ce is a straight line with the interception at y-axis representing the value of log K_F with slope 1/n. The linear plot showed the applicability of Freundlich isotherm to both adsorbents. The value of 1/n which is closer to 0 means the adsorption is more heterogeneous. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is an indicative of cooperative adsorption. Table 5 below shows all the calculated isotherm constants.

Table 3 Effect of contact time

Adsorbent	Langmuir constants				Freundlich constants		
	a (mg/g)	K_L (L/g)	b (L/mg)	R^2	1/n	K_F	R^2
CSAC	2.257	2.100	0.211	0.940	0.124	1.274	0.179
CAC	4.484	0.796	0.280	0.965	0.192	2.099	0.431

From the study of the two sorption isotherms, it was observed that Langmuir isotherm with a better fitting model than Freundlich isotherm also had higher correlation coefficient, R^2 for both adsorbent graphs. This was further confirmed from the values of a (adsorption capacity) for CAC which was observed to be higher than CSAC.

4.0 CONCLUSIONS

The present investigation shows that activated carbon prepared from coconut shell is a promising adsorbent for the removal of color from aqueous solutions over a wide range of concentrations but the efficiency was less than the coal based activated carbon. The color removal efficiency was controlled by solution pH, adsorbent concentration and contact time as well as initial color concentration. The maximum adsorption of yellow dye occurred at low pH (pH 1.68) which is equivalent of removal efficiency up to 75% for CAC and 45% for CSAC at low colour concentration (50mg/L) and using 5g/L of carbon dose. The optimum contact time was observed after one hour for both adsorbents. The color removal increases with the increasing carbon dosages. However, color removal efficiency decreases with increasing initial color concentration. Adsorption data fitted well with the Langmuir isotherm than Freundlich isotherm as the former displayed a better fitting model because of the higher correlation coefficient exhibited. This shows that the colorants are covered on the surface of adsorbent in a monolayer form with homogeneous sites; and it was observed that the color removal by using CAC seems to be better than CSAC. This may be as a result of the fact that coconut based carbons are microporous and are classified as pores with a size less than 40 angstroms. Meanwhile colour molecules in waste water are much bigger than 40 angstroms. So even though coconut carbon has a large internal surface area, the pollutant cannot come in contact with most of it because it does not fit inside the pores. Therefore, the activity of coconut shell activated carbon is relatively low in colour removal to coal based AC which contains a large amount of pores that are between 40 and 5,000 angstroms (called the transitional pores). Though, coconut shell activated carbon is very effective in other applications like Trihalomethanes removal from waste water.

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