

Coconut Frond Activated Carbon as Adsorbent for Removal of Congo Red Dye

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Abstract: This study investigated the potential use of Activated Carbon from Coconut Frond (ACCF) as an adsorbent for the removal of Congo Red (CR) dye from aqueous solution. The effects of various operational parameters such as adsorbent dosage, initial dye concentration, contact time and pH were studied. The results demonstrated that up to 99.29% of CR removal could be achieved under optimum condition (adsorbent dosage: 3.0 g, initial dye concentration: 100 mg/L, contact time 24 h and pH). The experimental data were analysed using Langmuir and Freundlich adsorption isotherm models. The equilibrium data appeared to best fit the Langmuir isotherm model with a correlation coefficient of $R^2 = 0.9931$ and maximum adsorption capacity was 9.823 mg/g. This study indicates that ACCF has the potential in becoming a low-cost adsorbent for the removal of CR in water effluent.

Key words: Activated carbon from coconut frond, adsorption isotherm, congo red dye, dye removal, low-cost adsorbent, correlation

INTRODUCTION

Dyes are known to be particularly dangerous compounds for the environment as some dyes have carcinogenic properties and can be highly toxic to living beings (Acemioglu, 2004; Chaudhary *et al.*, 2002, Lee *et al.*, 1997). Dyes are classified based on their chemical structures and applications. Dyes contain chromophores which refer to a group of atoms that are attached to functional groups such as azo, anthraquinone, methine, nitro, arilmethane, carbonyl and others which are responsible for the colour of the dye. In textile industrial activities, azo dyes are the most important class of synthetic dyes and pigments (Van Der Zee, 2002). These azo dyes are highly used in food, paper and textile industries. In every industry related to dyes, 2-50% of the dyes are lost as waste effluents (Mabrouk and Yusef, 2008; Olukanni *et al.*, 2009). Most dyes released into the environment as waste effluents are not amenable to be degraded naturally due to their complex aromatic molecular structures (Mohan *et al.*, 2008). The dye effluent, then, pollutes the river and in some cases, the dye-containing industrial effluents can end up in the food chain and cause adverse effects if left untreated.

Congo Red (CR) or also known as benzidinediazo-bis-1-naphthylamine-4 sulfonic acid is a type of diazo dye that is mainly used for paper colouration and has been reported to be carcinogenic (Jalandoni-Buan *et al.*,

2010). The CR was first synthesised by Paul Bottiger in year 1883. The bright red colour of Congo has attracted manufacturers around the world to use it as the first choice to manufacture papers, textiles and imaging. The CR is water soluble and its solubility increases in organic solvents. The wide use of CR in biochemistry and histology cannot be denied. The CR has a unique characteristic that allows it to change its colour from red to blue when in contact with acid that is used as an acid-base indicator dye (Mera and Davies, 1984). In addition, CR is also used to stain tissues for microscopic examination (Vijayakumar *et al.*, 2009).

Currently, there are many treatment technologies, such as oxidation, bioremediation and chemical precipitation which have been designed to treat specific types of dye effluents. However, each technology has its own merits and limitation to its applications. The conventional methods such as oxidation process are expensive and inconvenient for small and medium-sized industries (Daneshvar *et al.*, 2004). Therefore, an alternative method of removing dye is sought for such condition. The adsorption technique seems to offer an alternative to substitute the existing treatment methods for dye removal as it has been proven to be effective, convenient and economical (Khan *et al.*, 2002). In recent years, agro-waste has drawn attention as one of the potential raw materials to function as adsorbent for dye removal. Countless researches have been performed to utilise agro-waste as adsorbent in removing dye.

Researchers, thus have begun focusing on agro-waste because it can be easily obtained, easy to handle and cheaper as compared to other adsorbents.

The adsorbent from agro-waste can be enhanced by using the activated carbon method. The activated carbon method once was a popular choice used to remove heavy metals and dyes from wastewater (Babel and Kurniawan, 2003). However, the cost to produce commercially available activated carbon is expensive due to the use of non-renewable and relatively expensive starting materials (Martin *et al.*, 2003). Therefore, an alternative way of producing activated carbon from cheaper materials such as agro-waste should be investigated.

At present, researchers have worked on the treatment of palm oil empty fruit bunch as an effective adsorbent for dye removal by modifying the palm oil empty fruit bunch with diethyldichlorosilane and trimethylchlorosilane (Rattanawong *et al.*, 2007). In another study, coconut coir dust was utilised as an adsorbent to remove cationic dye from aqueous solution (Etim *et al.*, 2016). However, no study has reported on the removal of CR using Activated Carbon from Coconut Frond (ACCF). Coconut fronds can be easily obtained throughout the year as the climate in Malaysia is suitable for the growth of coconut tree. Some researchers have stated that coconut fronds contain high amount of fibre, thus, it can be a potential raw material for adsorbent (Haddadian *et al.*, 2013). With that this study investigated the potential of producing low-cost ACCF as an adsorbent for CR dye removal.

MATERIALS AND METHODS

Preparation of activated carbon: Coconut frond which was used as raw precursor in this study had been collected from Jeli District located in Kelantan. The coconut frond was washed with water and dried under sunlight for 2 days. Next, the precursor was ground and sieved to a particle size of 0.125 μm . The precursor was then burnt in a furnace at 800°C for 2 h. After that the carbonised precursor was soaked in 0.2 M KOH solution with an impregnation ratio of 1:3 for 3 h. The carbonised precursor was washed with 0.1 M HCl and rinsed a few times with distilled water until pH 7 was attained. Finally, the ACCF was dried in an oven for 12 h.

Preparation of adsorbate and calibration curve: The CR (R&M chemicals) was used without any further purification. Certain amount of CR powder was weighed and dissolved in distilled water to prepare 1000 mg/L of stock solution. Meanwhile the calibration curve was prepared by diluting the CR stock solution with distilled

water to a few series of concentrations. Then, it was measured by using a UV-visible spectrophotometer at the wavelength of 497 nm.

Adsorption study: The adsorption study was conducted under different experimental conditions such as effect of various adsorbent dosages (0.1, 0.3, 0.5, 0.7, 1.0, 3.0 and 4.0 g), effect of initial dye concentrations (50, 100, 200, 300 and 400 mg/L), effect of contact time (4, 8, 12, 16, 20, 24, and 28 h) and effect of pH (pH 1-12). Basically, a certain dosage of ACCF was placed into a beaker that contained 200 mL of 100 mg/L CR solution. Next, the mixture was stirred well, covered with aluminium foil and left for 24 h at room temperature. After that, the mixture was filtered by using filter paper and the filtrate was measured by using a UV-visible spectrophotometer at 497 nm. The data were analysed based on the percentage of dye Removal (R) using the following equations as stated in a prior study (Nasuha *et al.*, 2010):

$$R\% = \frac{(C_o - C_e) \times 100}{C_o}$$

Where:

C_e = Equilibrium Concentration in the solution (mg/L)

C_o = Initial Concentration in the solution (mg/L)

RESULTS AND DISCUSSION

Effect of adsorbent dosage: Figure 1 illustrates the effect of adsorbent dosages on removal of CR dye using ACCF. The percentage of dye removal increased rapidly from 0.1-1.0 g of adsorbent and the percentage of dye removal slowly increased after it hit the equilibrium at 3.0 g of adsorbent. The percentage of dye removal became constant after 3.0 g of adsorbent dosage used. This indicates that the equilibrium phase was achieved after 3.0 g of adsorbent.

The removal efficiency increased as the adsorbent dosage increased. An adsorbent can only adsorb a certain amount of dye. Therefore, when the amount of adsorbent is increased, the amount of dye removed is increased as well, mainly due to more mass available that provides more contact surface for higher adsorption. In addition, higher dosage of adsorbent in the solution offers greater availability of the exchangeable site such as more available active sites for binding of CR molecules (Chakraborty *et al.*, 2011).

However, the removal efficiency starts to decrease when the adsorbent becomes saturated and further increment of the adsorbent dosage is insignificant for

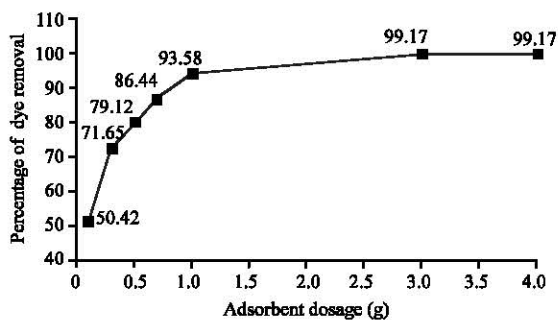


Fig. 1: Effect of adsorbent dosage on removal of CR dye using ACCF

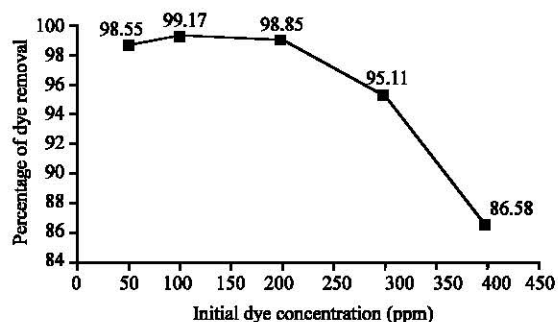


Fig. 2: Effect of initial dye concentration on removal of CR dye using ACCF

removal efficiency of the adsorbate. This is due to the attainment of equilibrium between the adsorbate and the adsorbent under the experimental condition (Chaari *et al.*, 2008).

Effect of initial dye concentration: Based on Fig. 2, the optimum percentage removal of CR using ACCF was at 100 mg/L of adsorbate concentration. Based on the data obtained, initial dye concentration of 100 mg/L gave 99.17% of removal after 24 h. Meanwhile initial dye concentration of 400 mg/L showed the lowest percentage of dye removal which was at 86.58% only. The percentage of dye removal seemed to increase when the initial dye concentration was set from 50-100 mg/L. However, the percentage of dye removal slowly decreased when the initial dye concentration was increased from 100-200 mg/L. Next, the percentage of dye removal rapidly decreased as the initial dye concentration increased from 200-400 mg/L.

High initial dye concentration can result in high mass gradient pressure between the solution and the adsorbent. This serves as a driving force to transfer the dye molecules from bulk solution to the particle's surface, thus resulting in lower mass transfer resistance between the aqueous phase and the solid phase (Vimonses *et al.*, 2009). In addition, the increase in initial dye concentration

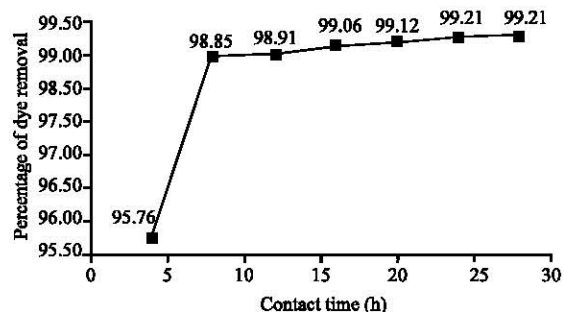


Fig. 3: Effect of contact time on removal of CR dye using ACCF

also enhances the interaction between the adsorbate and the adsorbent as the initial dye concentration is increased. Initial dye concentration is proportional to the number of dye particles in the aqueous phase which allows an increased rate of adsorption between the dye particles to bind to the active site of the adsorbent. Therefore, an increase in initial dye concentration will enhance the adsorption uptake of CR.

Effect of contact time: The effect of contact time was investigated at 4, 8, 12, 16, 20, 24 and 28 h. Figure 3 presents that the adsorption of CR using ACCF increased as the contact time was increased. The adsorption of CR rapidly increased for the first 4 h and then, displayed a steady increment until it reached 24 h of contact time. After 24 h, the adsorption process had attained its equilibrium state.

The rapid increment of CR adsorption rate for the first 4 h is because the CR molecules can attach freely with the ACCF active sites due to the vast vacant sites available (Toor and Jin, 2012). As contact time increased, the availability of the vacancy active sites becomes fewer, thus, slowing the adsorption rate of CR. The amount of ACCF adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under set of operating condition (Hashemian *et al.*, 2014).

Effect of pH: The CR dye is a diazo dye, thus, the initial pH influences the molecular structure of CR in aqueous solution. At around pH 7, the colour of CR in aqueous solution is solid red. The colour of CR changes to dark blue at acidic pH and to red at alkaline pH (10-12) but this red slightly differs from original red at the neutral pH. CR exists as an anionic form at basic pH (sulfonate groups) and as a cationic form at acidic pH.

Figure 4 shows that the percentage of dye removal on ACCF slightly decreased as the pH increased. The

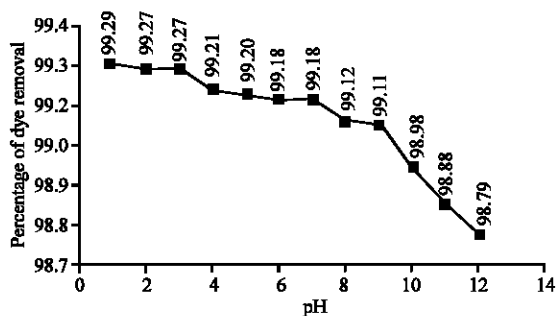


Fig. 4: Effect of pH on removal of CR dye using ACCF

percentage of removal decreased when the pH increased from 1-12. The colour of CR changed from red to dark blue when in contact with buffer pH 1-5. As the pH in the buffer increased from 6-12, the colour of CR changed from light red to a darker shade. Nevertheless, after the adsorption process took place, the solution turned colourless and no dye residue was observed for all pH buffers, hence, explaining the insignificant difference for the adsorption of CR from pH 1-12. This indicates that ACCF is indeed a good activated carbon due to the low acid/base reactivity that makes it more practical in removing CR (Hejazifar *et al.*, 2011).

Lower pH is favourable for removal of CR using ACCF. The interaction between more positive CR ion and ACCF is enhanced when ACCF acquires positive charges from the acidic solution. The surface of ACCF may become positively-charged when in contact with acid due to the hydrogen ions in the solution that carry positive charges, thus, favouring the adsorption of anionic dye with increased electrostatic force of attraction (Celekli *et al.*, 2011).

In contrast, when basic solutions are used, the surface of the ACCF may turn to be negatively-charged due to the accumulation of -OH in the solution, thus, leading to competition that disfavours adsorption of CR. When the ACCF surface is negatively-charged, the ions will have to compete for vacant active sites, thus, reducing the amount of CR being adsorbed by the ACCF (Yagub *et al.*, 2014). In addition, at higher pH, electrostatic repulsion appears to be higher between the CR and the ACCF, hence, decreasing the uptake of CR (Gupta *et al.*, 2012).

Adsorption isotherm study: Adsorption isotherm describes how solutes interact with adsorbents (Vinoth *et al.*, 2010). Two isotherm models, langmuir and Freundlich were chosen to fit the equilibrium data. Langmuir isotherm refers to homogeneous monolayer adsorption whereas the linear form of the Freundlich isotherm model is derived by assuming a heterogeneous

Table 1: Langmuir and Freundlich adsorption isotherms for removal of CR dyes using ACCF as adsorbent

Isotherm models	Values of constant	Best fitted isotherm model
Langmuir	$K_L(L/mg) = 10.18$ $q_{max}(mg/g) = 9.823$ $R^2 = 0.9931$	Langmuir
Freundlich	$K_F (mg/g) (L/mg)^{1/n} = 9.929$ $n = -20.04$ $R^2 = 0.9908$	

surface of adsorption capacity and adsorption intensity with a non-uniform distribution of heat from the adsorption (Soni *et al.*, 2012).

Based on the correlation coefficient (R^2) displayed in Table 1, the adsorption isotherm model for CR removal using ACCF appears to have better description in Langmuir equation. The adsorption of CR portrays a better fit with the Langmuir isotherm model at a higher R^2 . This indicates that the adsorption of CR using ACCF took place as monolayer adsorption on a surface containing a finite number of identical sites (Kaur *et al.*, 2014).

CONCLUSION

The ACCF appeared to be effective in removing CR dye from aqueous solution with the percentage of removal at 99% in which the red solution of the CR dye, after adsorption, turned colourless under optimum condition. Hence, it clearly displays a great potential to be applied as a low-cost adsorbent for removal of dyes in wastewater.

ACKNOWLEDGEMENT

The researchers are grateful to financial support given by the Ministry of Higher Education via. Research Acculturation Grant Scheme (RAGS), R/RAGS/A07.00/01095A/001/2015/000201.

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