RAW OYSTER SHELL SORBENT FOR REMOVAL OF CONGO RED DYE

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ABSTRACT

Raw oyster shell was successfully prepared as an adsorbent for removing Congo Red (C.R.) dye in an aqueous solution using an adsorption technique. The various parameters influencing this adsorption process, such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, pH, agitation speed and agitation time, were studied. The maximum percentage of dye removal of 96.3% was obtained at the optimised conditions of 75 µm of adsorbent size, 1.0 g of adsorbent dosage, 30 mg/L of initial dye concentration, pH 3, 110 rpm of agitation speed and 75 min of agitation time. The experimental data were analysed using two adsorption models, the Langmuir isotherm model and the Freundlich isotherm model. The adsorption data obtained well fitted for the Langmuir isotherm model indicate a monolayer adsorption reaction involved during the adsorption process. The result shows that raw oyster shells could be employed as a suitable alternative adsorbent to remove Congo red dye in an aqueous solution.

Keywords: *raw oyster shell, adsorption, congo red*

INTRODUCTION

Azo dyes are the largest group of colourants widely used in the textile, pharmaceutical, leather, paint, paper industry, drug, cosmetic and food processing due to their efficient cost and simplicity in synthesis action [1]. Recent studies show that azo dye is the most polluting dye in causing the environmental problem of aquatic contamination [2]. Congo red is an organic compound categorised as a direct dye with a chemical name sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid) and it is the first synthetic dye of anionic azo dyes [2]. Congo red dye is generated by cellulose industries, including wood pulp, cotton textiles, and paper. However, several reports describe it as a carcinogenic and mutagenic dye. Due to CR's structural stability, this dye is a major challenge for its removal from wastewater treatment. Presently, three main conventional methods are classified into physical, biological and chemical methods that are generally used as a treatment process for removing dyes in industrial wastewater. The adsorption method became one of the economical methods for removing dye pollutants due to the design, operation and regeneration efficiency of adsorbents compared to other methods. Moreover, the adsorption method effectively decreases unsafe organic or inorganic particles that are present in effluents [3]. Preparation of low-cost adsorbent from food waste could be potential since the debris is generated on a large scale and is known as inexpensive material. Food waste adsorbent is materials that are cost-effective, efficient and easy operation among low-cost materials [4]. Several adsorbents are commercially used to treat dye, including bamboo dust, durian peel, coir pith carbon, hazelnut shell, natural clay, and the seed of avocado [5]. The important properties of adsorbents are high porosity and larger surface area for effective dye adsorption in various ranges. Besides, the porous structure's larger surface area increased adsorption's kinetics [6]. Oyster shell is an abundant source material that can be obtained from food waste which is considered a potential precursor for the preparation of low-cost adsorbents. Low-cost and effective food waste material like oyster shells can be used as adsorbent for dye removal from wastewater. Besides, most oyster shells are usually dumped as waste along the beach coast and nearby restaurants without proper waste management. This research aims to determine the potential of oyster shells as an adsorbent from food waste to remove Congo red dye in an aqueous solution.

MATERIALS AND METHODS

Preparation of Activated Carbon

The raw oyster shells were obtained from a restaurant at Bachok, Kelantan, Malaysia. Firstly, the collected shells were thoroughly washed with distilled water to remove the impurities and then sun-dried for 24 hours. After that, the oyster shells were oven dried for 24 hr. When the oyster shells were completely dried, the shells were crushed using a mortar and pestle first before the shells were grounded into powder using a grinder and sieved to obtain the fine powder. Finally, the prepared oyster shell powder was stored in an airtight zipper bag for further experimental work.

Adsorption Experiments

The effects of adsorbent size, dosage, initial dye concentration, contact time, pH, agitation speed and agitation time were investigated to identify the adsorption uptake of the adsorbent used. The solution of CR dye was mixed with raw oyster shells adsorbent before it was filtered using filter paper. The filtrate was analysed with a UV-visible spectrophotometer at 497 nm. The result was reported based on the percentage of dye removal [7]. The efficiency of the dye removal percentage was measured by [8]:

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$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where C_e (mg/L) is the equilibrium concentration in the solution, C_0 (mg/L) is the initial concentration in the solution, V(L) is the volume of the solution and M(g) is the mass of the adsorbent.

Calculation of Adsorption Isotherms Parameters

Langmuir Adsorption Model

The Langmuir adsorption isotherm for all the parameters was calculated by:

$$q = \frac{q_{\max}\, b\, C_e}{1 + K_L C_e} \quad (2)$$

where q is the amount of dye uptake; $q_{\max}$ is the maximum dye uptake (mg/g); C_e is the equilibrium concentration (mg/L); K_L is the Langmuir equilibrium constant (L/mg).

The linearised Langmuir isotherm equation is given by using the following:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} = \frac{C_e}{q_{\max}} \quad (3)$$

where C_e is the concentration of Congo red at equilibrium (mg/L); q_e is the amount of Congo red at equilibrium (mg/g); $q_{\max}$ is the Langmuir constant-related adsorption capacity determined from the slope of $1/q_{\max}$ (mg/g); K_L is the Langmuir constant related to adsorption energy determined from the intercept of $1/b_{qm}$ (L/mg). Data obtained were used to construct a linear plot of C_e/q_e against C_e.

RESULTS AND DISCUSSION

Effect of Adsorbent Size

The effect of adsorbent size on the removal of CR dye was investigated by varying the adsorbent size from 75, 150, 300, 500, 710, and 1000 µm. Figure 1 showed that the percentage removal of CR dye decreased significantly with an increase in particle size of the adsorbent from 75 µm to 150 µm with 70.8-61.7% of CR dye removal. Higher adsorption was achieved with smaller particles size because of the larger surface area and the availability of more active sites for adsorption compared to the larger particles [9]. Further increase in adsorbent size from 150 µm, 300 µm, 500 µm, 710 µm and 1000 µm only show smaller changes in removal efficiency with the percentage of CR dye removal. This is because the active sites also decreased and were almost saturated with the increased adsorbent size.

Effect of Adsorbent Dosage

The effect of adsorbent dosage (0.1-2.0 g) on the removal of CR dye was studied. Figure 2 shows that a gradual increase in dye removal was observed from was from dosage 0.1 g (61.5%) until 1.0 g (81.7%). This is due to the high adsorptive surface area and the availability of more adsorption sites in raw oyster shells [10]. However, a non-significant increase was observed when the adsorbent dosages were increased from 1.0 g to 2.0 g, suggesting that the maximum adsorption is attained and the amount of ions bound to the adsorbent and the amount of free ions became decreased even with further addition of the adsorbent dosages. Hence, the maximum value for the optimum dosage of the raw oyster shell was found to be the best at a dosage of 1.0 g.

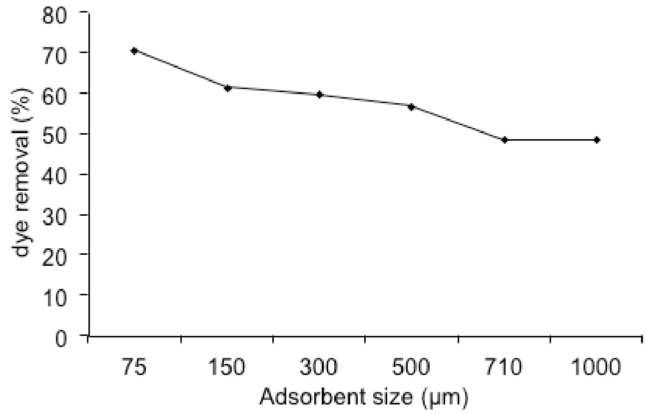

Figure 1 Effect of adsorbent size on the removal of CR (volume: 100 mL, concentration: 50 mg L^{-1} at 25°C)

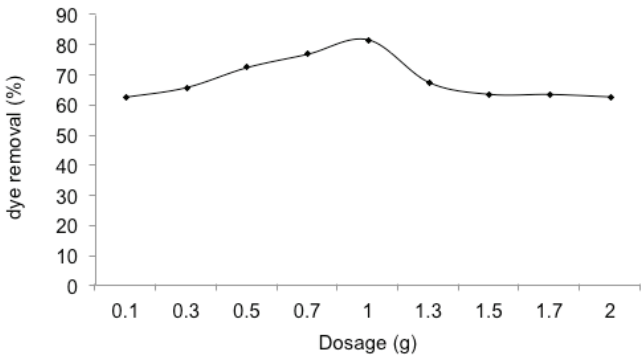

Figure 2 Effect of adsorbent dosage on removal of CR (volume: 100 mL, concentration: 50 mg L-1, adsorbent size: 75 µm at 25°C)

Effect of Initial Dye Concentration

The percentage removal of CR dye depends highly on the initial dye concentration. According to Figure 3, the percentage removal of dye is rapid in the initial stages, from 10 mg/L to 30 mg/L, but when it approaches equilibrium, the percentage of dye removal remains constant. This may be due to the availability of active sites during the initial stage of adsorption, and then, the vacant sites were occupied by CR molecules. This will cause a repulsive force between the dye and the sorbent surface in the bulk phase [12].

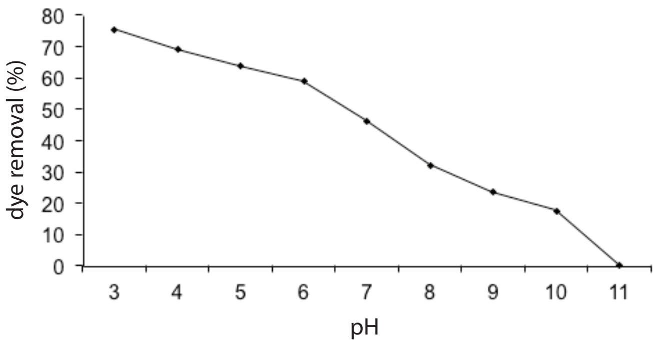

Figure 3 Effect of initial dye concentration on the removal of CR (volume: 100 mL; adsorbent size: 75 µm; dosage: 1.0 g, at 25ºC)

Effect of pH

Figure 4 shows that the percentage of CR removal decreased with an increase in pH from pH 3.0, pH 4.0, pH 5.0, pH 6.0, pH 7.0, pH 8.0, pH 9.0, pH 10 and pH 11. The percentage of CR removal was decreased with an increase in pH caused by the reduction of positively charged ions on adsorbents that weakened the electrostatic charge. Furthermore, at lower pH, the concentration of H^+ ion increases in the solution and the adsorbent surface acquires a positive charge [13]. Thus, the maximum adsorption of CR was obtained at pH 3.0 with maximum

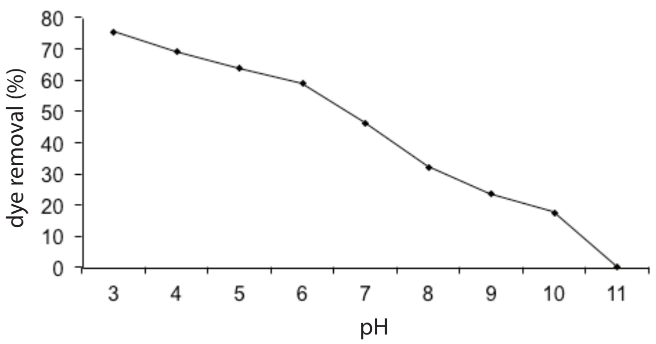

Figure 4 Effect of pH on removal of CR (Volume: 100 mL; adsorbent size: 75 µm; dosage: 1.0 g; initial dye concentration: 30 mg L-1; at 25ºC)

Effect of Agitation Speed

The effect of agitation speed on percentage removal CR was studied by varying the speed from 90 rpm to 170 rpm for 2 hours using an orbital shaker. Figure 5 shows that the percentage of CR removal increased from 84.9% at 90 rpm to a maximum of 92.2% at 110 rpm. However, increasing the agitation speed over 110 rpm affects the lower percentage of CR ion removal, decreasing from 92.1% at 110 rpm to 68.1% at 170 rpm.

The percentage removal was highly influenced by the agitation speed, which affects the distribution of solute in the bulk solution and the formation of the external boundary film [14]. At 90 rpm, the speed of the incubator shaker cannot distribute the particles properly in the adsorbent solution but accumulated. This condition occurred because some of the active sites of the adsorbent layer were covered, and only a certain part of the dye could adsorb the CR ions [14]. The maximum percentage of CR removal is 92.1% for the parameter of agitation speed at 110 rpm.

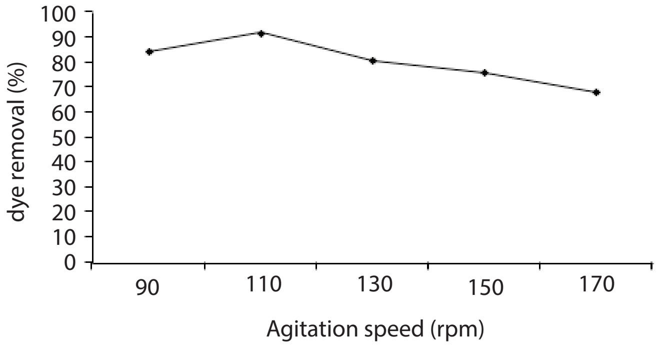

Figure 5 Effect of agitation speed on the removal of CR (Volume: 100 mL; initial dye concentration: 30 mg L-1; adsorbent size: 75 µm; dosage: 1.0 g, pH: 3; at 25ºC)

Effect of Agitation Time

Figure 6 shows that the percentage of CR removal increased significantly with the increase in agitation time. The percentage removal of CR dye increased during 15 90.3% to 75 min with a maximum of 96.3%; however, the percentage removal slightly decreased at 90 min with a 96.0% reduction. This trend was explained by Noreen et al. [15], where the increasing number of vacant sites gives more available active sites for the adsorption of dye at the initial stage. These binding sites were covered slowly with the dye, which created a lower adsorption rate before it reached the equilibrium phase. Therefore, the duration for the maximum percentage value on the removal of CR dye for agitation time was chosen at 75 min.

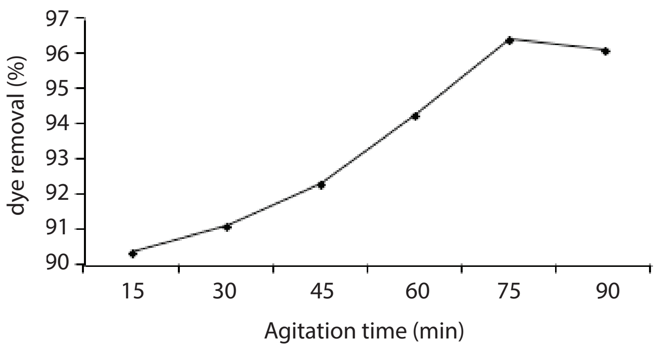

Figure 6 Effect of agitation time on the removal of CR (volume: 100 mL; 75 µm; dosage: 1.0 g; initial dye concentration: 30 mg L-1; pH: 3; agitation speed: 110 rpm at 25ºC)

Table 1 Isotherm constants for Congo Red adsorption onto a raw oyster shell

	Langmuir			Freundlich	
(mg.g)	(L.mg)	R2 ($mg.g^{-1}$)	KF	n	R^2
81.96	0.91	0.9995	5.77	1.72	0.9756

Adsorption Isotherms

The adsorption capacity of raw oyster shells onto CR was determined by measuring equilibrium isotherms. The predictive modelling procedures for analysing and designing an adsorption system can be determined using an adsorption isotherm [16]. Adsorption isotherms were analysed according to the linear form of Langmuir and Freundlich isotherms. Table 1 shows the results of the calculated isotherm constants. The experimental results are well fitted to the Langmuir model, with a higher correlation coefficient value. The maximum adsorption capacity estimated from the Langmuir model was 30.21 mg.g-1. This indicates that adsorption occurs on the monolayer surface of the sorbent. The sorbent surfaces reach complete coverage by CR in 24 h. After 24 h, no significant changes are shown in the amount of adsorbed CR and desorbed CR. This effect was also reported by Saha [17].

CONCLUSIONS

Raw oyster shell was successfully prepared as an adsorbent for the removal of Congo Red dye. The maximum percentage of dye removal of 96.3% was obtained at the optimised conditions of 75 µm of adsorbent size, 1.0 g of adsorbent dosage, 30 mg/L of initial dye concentration, pH3, 110 rpm of agitation speed and 75 min of agitation time, respectively. The adsorption data obtained well fitted for the Langmuir isotherm model indicate a monolayer adsorption reaction. The result shows that raw oyster shells could be employed as a suitable alternative adsorbent.

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