Preparation of raw oyster shell for removal of coomassie brilliant blue R-250 dye from aqueous solution

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Abstract. The removal of dye from textile wastewater effluent has become an important process nowadays. In this study, raw oyster shell was used as adsorbent for removal of Coomassie Brilliant Blue R-250 (CBB) dye by using the adsorption method in order to reduce the amount of waste oyster shells in waters and landfills which can cause pollution. Various parameters such as adsorbent size, adsorbent dosage, initial dye concentration, contact time and pH were investigated to study the potential of oyster shell as an adsorbent. The optimum adsorption was obtained at adsorbent size of 75 µm and 2.3 g of adsorbent dosage at 50 mg/L concentration of CBB dye. Optimum contact time of the dye adsorption was determined at 9 hours and the most effective condition for CBB dye removal was at pH 2. The removal efficiency was achieved at 99.64%. Thus, this study shows potential as an economical and environment friendly dye removal process for wastewater treatment.

1. Introduction
Synthetic dyes are organic pollutant found in the textile industrial effluents. The dyestuff used in dyeing process is discharged about 20% to the environment [1]. This can cause dye contamination in aqueous wastewater from industries due to dyes are not biodegradable. Dye present in the industry effluent are toxic, carcinogenic and mutagenic to human beings and aquatic life. It tends to reduce the photosynthetic activity in aquatic habitats by preventing the penetration of sunlight. Besides, most of these dyes can cause allergy when the water is used as a water source for drinking [2]. In textile industry, one of the largest classes of dye is acid dyes that used to give a broader range of bright colours on textiles. Acid dyes contain negative charge that normally forms ionic interactions when applied to fibres with positive charge such as leather, wool and silk during the dyeing process [3]. Most of the acid dyes are found to contain azo, anthraquinone and triphenylmethane compounds. Coomassie Brilliant Blue R-250 (CBB) is an acidic dye and widely used in textile and wool industry [4]. CBB dye from industrial effluent is toxic in nature when it gets accumulated in water bodies since it is difficult to biodegrade. Besides, it is used for protein staining in analytical biochemistry due to the attraction of anionic sulfonic acid groups to positive protein amine groups through Van der Waals attractions [5]. CBB is also a triphenylmethane azo dye which contains sodium salt that has greater solubility in water [6]. It has the molecular formula C₄₅H₄₄N₃O₇S₂Na and the molecular weight is 825.99 g/mol.

At present, various conventional techniques that are used to treat wastewater containing dye includes membrane filtration, adsorption, chemical coagulation, flotation, activated sludge, electrolysis and so on. Adsorption technique has been demonstrated as a potential method due to the high efficiency of dye removing, simplicity and low capital investment [7]. Adsorption is a separation process in which a solute or dye in a liquid is deposited on the surface of adsorbent [8]. Adsorbent acts as a filter material for the removal of hazardous compounds such as dye, heavy metal and grease during the process of wastewater treatment.
treatment. It can be derived from biomaterials such as agriculture and food waste in the form of raw or activated carbon. Thus, adsorbent is environmentally friendly and low cost to obtain. The high quantity of oyster shells is discharged from the restaurant as food waste cause the environmental problem as well. Therefore, raw oyster shell powder was studied as an adsorbent for removal of Coomassie Brilliant Blue R-250 (CBB) dye. Oyster shells were collected from Bachok, Kelantan. Several effective parameters such as adsorbent size, dye concentration, adsorbent dosage, contact time and pH was studied.

2. Methodology

2.1 Materials
Oyster shells were collected at Bachok, Kelantan, Malaysia. Coomassie brilliant blue R-250 (CBB) dye, hydrochloric acid (HCl), sodium hydroxide (NaOH) were purchased from Sigma Aldrich (USA).

2.2 Preparation of Adsorbent
The oyster shells were collected at Bachok, Kelantan, Malaysia. The collected oyster shells were washed with distilled water to remove the adhering dirt and soil. Then, the oyster shells were dried at 105 ºC in the oven for 24 hours in order to remove the moisture content. Next, the dried oyster shells were crushed into a smaller size by using a hammer. The smaller size of oyster shells was blended and sieved into different size to provide homogenous particle size. The different sizes of the oyster shell powder were stored in air-tight zipper bag for the further use.

2.3 Adsorption Study
Adsorbent (2.3g, 75 µm) was added into the 100 mL of the dye solution at 50 mg/L of dye concentration and pH 2 in 250 mL Erlenmeyer flask. The optimum contact time was determined at 9 hours and used throughout further adsorption experiments. After filtration, the absorbance reading for each particle size were recorded by using UV-visible spectrophotometer at 553 nm. The result was reported based on percentage dye removal [9]. The efficiency of dye removal percentage was measured by following equation (1).

\[ q_e = \frac{(c_0 - c_e)V}{M} \] (1)

where \( c_e \) (mg/L) is the equilibrium concentrations in the solution, \( c_o \) (mg/L) is the initial concentrations in the solution, \( V \) (L) is the volume of solution and \( M \) (g) is the mass of adsorbent.

3. Results and Discussion

3.1 Effect of Adsorbent Size
Different adsorbent size (45, 75, 150, 250, 425 and 710 µm) of the raw oyster shell were studied. The percentage removal of CBB dye increased from 45 µm (87.47%), to 75 µm (87.47%) and then started declined till 710 µm (71.43%) (Figure 1). The highest percentage removal of CBB dye by raw oyster shell powder was obtained at the particle size of 75 µm. This is can be explained by the relationship between the particle size and surface area. The relatively higher adsorption of dye with the smaller particle size of the adsorbent is due to the small particle size has greater surface area for adsorption of dye molecules [10]. The smaller the particle size of adsorbent with high surface area contain a large number of available active sites to react with the CBB dye molecule. The decreasing of the percentage removal of CBB dye when increasing of adsorbent size was due to the active site on the adsorbent was limited to the adsorption process. Besides, the smaller particle sizes of adsorbent may reduce internal diffusion and mass transfer limitation to penetrate the dye molecules into the adsorbent [11]. The
equilibrium was achieved in faster rate and higher adsorption capability of CBB dye was attained with smaller adsorbent particle size.

![Figure 1](image1.png)

**Figure 1.** Effect of adsorbent size of CBB dye removal. (concentration: 50 mg/L; volume: 100 mL; temperature: 25˚C; adsorbent dosage: 0.5 g; contact time: 24 hours)

3.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied by using various dosages (0.1, 0.5, 1.0, 1.5, 2.0, 2.3, 2.5 and 2.7 g). The efficiency of dye removal increases as the adsorbent dosage increases (Figure 2). The percentage of removal almost constant at the dosage of 2.3 g, 2.5 g and 2.7 g in which the percentage of the removal was 97.37%, 97.50% and 97.15%, respectively. The equilibrium was achieved with 2.3 g of adsorbent due to the active surface area was fully occupied [12]. The adsorption increased with the increase in adsorbent dosage. This may due to the higher amount of adsorbent provide more available adsorption sites and increased the surface area of the raw oyster shell powder that enhance the adsorption of dye molecule [13]. Besides that, the reduction of the percentage of removal of CBB dye when the adsorbent continues to increase leads to the transportation of dye molecules to active sites in the adsorbent was limited due to overlapping of adsorption sites [14]. The decrease of the adsorption efficiency may also cause by the adsorption sites remain unsaturated after the adsorption process. The unsaturated of active sites can result to the decrease of adsorption capacity.

![Figure 2](image2.png)

**Figure 2.** Effect of adsorbent dosage of CBB dye removal, (concentration: 50 mg/L; volume: 100 mL; temperature: 25˚C; adsorbent size: 75 µm; contact time: 24 hours)

3.3 Effect of Initial Dye Concentration
A series of adsorption study was carried out at various initial dye concentrations such as 10, 30, 50, 100, 150 and 200 mg/L. The percentage of CBB dye removal increased for the three initial dye concentrations 10 to 50 mg/L (96.31% to 98.37%) and started to decrease from 50 mg/L to 200 mg/L (98.37% to 82.01%) (Figure 3). The increase of percentage of removal of CBB dye for three initial concentrations could be due to the availability of large numbers of active sites in the adsorbent and the greater surface area of the adsorbent was still unsaturated [15]. The high initial dye concentration contains more dye molecule that can attach to the active sites of adsorbent that result in the adsorption process occurs more efficiently [16]. However, the percentage of removal of CBB dye decreased with the increase in the initial dye concentration after the optimum concentration may due to the limitation of active sites which has been occupied and large number of dye molecules have to compete with each other to penetrate into the active site on the adsorbent [16]. Therefore, the optimum concentration obtained was observed in the initial dye concentration of 50 mg/L.

![Figure 3](image-url)  
**Figure 3.** Effect of initial dye concentration of CBB dye removal, (volume: 100 mL; temperature: 25°C; adsorbent sizes: 75 μm; adsorbent dosages: 2.3 g; contact time: 24 hours)

### 3.4 Effect of Contact Time.

The effect of contact time was studied at 1, 3, 5, 7, 9, 10, 11 and 12 hours in room temperature. The CBB dye was observed to uptake continuously during the first 9 hours (95.95%) and attained maximum adsorption after 9 hours in which the dye molecules adsorbed was reduced. At the first 9 hours, the strong attractive force was developed between raw oyster shell powder and the CBB dye when the ratio of the surface-active site to the dye molecules is high [17]. The maximum adsorption was observed at 9 hours due to saturation of the active site which stopped the further adsorption to take place [18]. Besides, the initial adsorption of dye molecule occurred on the surface of the raw oyster shell powder due to more vacant active sites were found [19]. However, it became difficult to occupy at the later stage due to the repulsive force was formed between the dye molecules and the oyster shell powder [20]. Thus, when the surface was fully filled, desorption may take place results in a slight decrease of the percentage of removal during the 10 (95.87%), 11 (95.78%) and 12 hours (95.37%) (Table 4).
Figure 4. Effect of contact time of CBB dye removal, (volume: 100 mL; temperature: 25°C; adsorbent sizes: 75 μm; adsorbent dosages: 2.3 g; concentration: 50 mg/L)

3.5 Effect of pH
The effect of pH was studied from the pH 1 to 10. The percentage removal of CBB dye increased slightly from pH 1 to pH 2, which was 99.18% to 99.64%. However, the percentage of removal decreased drastically from pH 2 (99.64%) to pH 10 (72.62%). The efficiency of adsorption increased due to the increased positive charges on the surface of the adsorbent by lowering the pH value which can attract the functional groups of the CBB dye that carries negative charges towards the adsorbent [19]. When the pH decreases, the concentration of positive hydrogen in the solution will increase to enhance the attraction between negatively charged CBB dye and positively charged adsorbent. Thus, the anionic CBB dye which can highly attract to the cationic sites on the surface of the adsorbent that cover with positive charge in order to increase the adsorption efficiency. In contrast, the increase of pH value will reduce the percentage of removal in CBB dye adsorption due to the negatively charged hydroxide ions on the surface site of adsorbent will show electrostatic repulsion with the anionic dye and compete with anionic dye to attach to the surface of the oyster shell powder [13].

Figure 5. Effect of pH of CBB dye removal, (volume: 100 mL; temperature: 25°C; adsorbent sizes: 75 μm; adsorbent dosages: 2.3 g; concentration: 50 mg/L; contact time: 9 hours
Figure 6. The colour differences of dye adsorption before and after treatment at optimum conditions (a) dye solution before adsorption and (b) dye solution after adsorption (Contact time; 9 hours, pH= 2, Initial dye concentration; 50 mg/L; adsorbent size; 75 μm and adsorbent dosage; 2.3 g)

4. Conclusion
The feasibility of raw oyster shell for removal of CBB dye was successfully studied. Five parameters included adsorbent size, adsorbent dosage, initial dye concentration, contact time and pH has been investigated to obtain the optimum parameters in adsorption of CBB dye. The result of the optimum adsorption of CBB dye was 75 μm, 2.3 g, 50 mg/L, 9 hours and pH 2. The efficiency of dye adsorption was achieved at 99.64%. This study provided an economical and environment friendly dye removal process for wastewater treatment.

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