Development of Composite Adsorbent Coating Based Acrylic Polymer/Bentonite for Methylene Blue Removal

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Abstract. The development of composite adsorbent coating based acrylic polymer solution (APS) mixed with bentonite (ben) was investigated. The composite adsorbent coating was prepared and coated to a high surface area substrate, cotton cellulosic fiber (CCF). The APS/ben-CCF was used for a single cationic methylene blue (MB) dye adsorption system. Characterization of composition and structure of materials and coating was carried out by X-ray fluorescence (XRF), scanning electron microscopy (SEM), and UV-spectroscopy (UV-VIS). The adsorption properties of the APS/ben-CCF were investigated as a function of solution pH, initial dye concentration and contact time as well as solution temperature of MB dye. The result revealed that the APS/ben-CCF functioned well in solutions of various pH (acidic to alkaline), achieving 100% removal of MB within 2 hours of adsorption for 50 ppm. Kinetic studies showed that APS/ben-CCF is endothermic in nature since the adsorption capacity increased with increasing solution temperature. These results demonstrate that APS/ben-CCF composite adsorbent coating is an advanced adsorbent with advantages such as easy phase separation and capability to remove cationic dyes in a short time period.

Keywords: *acrylic polymer solution; adsorption; bentonite; composite adsorbent coating; methylene blue.*

1   Introduction

The industrial revolution and daily human activities have influenced the stream and loading of water and value of available fresh water [1]. The textile industry is one of the greatest generators of effluents. High volumes of water consumption are required throughout the manufacturing processes of textiles, starting from the washing of fibers to the bleaching, dyeing and washing of finished products. Ultimately, this amounts in the discharge of large quantities of wastewater containing toxic substances. Serious environmental problems associated with textile industries are typically related to water body pollution caused by the discharge of untreated or partially treated effluents. The effluents generated by these industries are complex and contain a wide variety of chemicals, dyes and other aquatic toxins. The aquatic toxins include dispersants,

acids, bases, salts, detergents, humectants, oxidants, ionic metals and toxic organic chemicals [2,3].

Among the numerous chemicals used and released by the textile industry, persistent substances such as heavy metals and some hazardous organic chemicals should be highlighted. These hazardous chemicals pose long-term threats to human health and the environment. What makes many of these chemicals so dangerous is that they are not only persistent (do not readily break down in the environment) but also bio accumulative (can build up in the food chain and impose serious, long-term effects on organisms that ingest them). Some are able to interfere with hormone systems in people and wildlife, even at very low doses, while others are carcinogenic or reprotoxic. More recent use of persistent and hazardous chemicals poses a greater and often invisible threat to ecosystems and human health [4].

According to a report from the Malaysian Environmental Department, due to the increase in sewage treatment plants and manufacturing industries, the number of cases of water pollution caused by sewage treatment plants increased from 9060 (year 2006) to 10,025 (year 2010), while for the manufacturing industry it increased from 8534 (year 2006) to 9069 (year 2010). In 2009, the textile industry contributed only 0.1% to the industrial sources of solid waste produced in Malaysia. Nevertheless, the solid waste generated by the textile industry increased sharply from 744 tons (2007) to 1559 tons in 2009. On the other hand, textile-finishing wastewater accounts for 22% of the total volume of industrial wastewater generated in Malaysia [5]. The total water consumption by the textile industry can reach up to 3000 m^3/day [6].

Dyes in wastewater can be eliminated by various methods, including physicochemical, chemical and biological methods. Wastewater from a dye house is generally multi-colored. The currently available technologies typically are inadequate for the removal of toxic pollutants such as dyes from textile wastewater [7]. Biological and chemical techniques have not been very successful due to the non-biodegradable nature of most dyes. Besides, the conventional methods of wastewater treatment, such as coagulation and flocculation, sedimentation and floatation, membrane filtration, ozonation, oxidation, precipitation, and disinfection, are either expensive or not very effective. These technologies mostly transform pollutants from one phase to another and do not completely eliminate them [8]. Even though membrane filtration produces high quality water, it has a major limitation in membrane fouling thus adding to the operating cost [9]. Hence, strict rules are compelling industries and scientists to search for novel effective and economical methods for the removal of color from effluent.

Therefore, this paper highlights a new type of adsorbent using a composite adsorbent coating. An adsorbent in the form of a coating has advantages compared to adsorbents in particulate form such as powders, pellets or beads. The aim is easy separation after the adsorption operation (e.g. centrifugation or filtration) as well as improving the surface area to weight ratio of the adsorbent used and minimizing the required quantity of solid adsorbent.

2   Experiment

2.1   Reagents and Materials

Methylene blue (MB) as cationic synthetic textile dye was purchased from Modern Lab Sdn. Bhd., Malaysia and used as received without further purification. The chemical formula of MB is $C_{16}H_{18}CIN_3S.xH_2O$ with 319.85 g/mol of it molecular weight. Bentonite particle as a type of clay was supplied by Modern Lab Sdn. Bhd. Commercial acrylic polymer solution (APS) was purchased from NHA Scientific Resource, Cyberjaya, Malaysia. Both bentonite and APS were the dominant ingredients utilized in the development of the acrylic based adsorbent coating. Distilled water was used to prepare adsorbate and adsorbent. The pH of the MB solution was adjusted by adding either 0.10 M HCl or NaOH. As support for the composite coating, cotton cellulosic fiber (CCF) was used in this experiment. It was purchased from a local fabric shop at Parit Buntar, Malaysia.

2.2   Preparation of Acrylic Based Adsorbent Coating

The composite adsorbent coating of APS/ben-CCF was prepared by dissolving 0.2 g bentonite into 1 g of APS and 3 mL of distilled water as a carrier. Bentonite, APS and distilled water were stirred slowly until a slurry was obtained. The APS/ben slurry was then coated on both sides of 100 cm^2 CCF with a brush. The coated APS/ben-CCF was dried in an oven at 80 °C for 5 hours. The mass of the single composite adsorbent coating (CAC) was measured according to the following Eq. (1):

$$Mass_{CAC} = Mass_{APS/ben-CCF \text{ after drying}} - Mass_{CCF \text{ before coating}} \qquad (1)$$

2.3   Batch Adsorption Experiment

The experimental adsorption of MB onto APS/ben-CCF was performed in a series of 250 mL beakers containing 200 mL of MB solution. The APS/ben-CCF was clipped in the interior part of the beakers, which were then placed on a high-performance multi-position magnetic stirrer with integrated temperature control plate (model RT 10 Power) at 480 rpm and temperature controlled between 30°C and 70°C. The agitation was carried out until the solution

attained equilibrium. The adsorption batches were carried out by varying several experimental variables, such as initial dye concentration (50-200 mg/L), pH (3-11) and temperature (30-70 °C), to determine the optimum uptake conditions for adsorption. At every 30-minute time interval, the concentrations of MB were monitored using a UV-VIS spectrophotometer at the maximum wavelength (λ_{max}) of adsorption at 664.5 nm. The dye adsorption performance was expressed by removal efficiency, R.E (%) of MB, and was calculated using the following Eq.(2):

$$R.E \ (\%) = [(C_0 - C)/C_0] \ x \ 100 = [(A_0-A)/A_0] \ x \ 100 \qquad (2)$$

where C_0 is concentration at time 0, C is initial concentration of MB, A_0 refers to value of absorbance at time 0, A is initial value of absorbance.

2.4   Characterization of Composite Adsorbent Coating

A scanning electron microscope, SEM (model Crest System (M) Sdn. Bhd. Quanta Feg 450) was used to characterize the surface morphologies of the composite adsorbent coating. The analysis of compositional metal was performed using X-ray fluorescence (XRF) (S4 Explorer 7KP103, Brucker, Karlsruhe, Germany). The chemical analyses of bentonite, APS and APS/ben are presented in mass percentage (%).

## 2.5   Physical Properties of Composite Adsorbent Coating

The physical properties of the APS/ben-CCF were observed through its physical appearance in terms of coating condition and structure through photographic images. Coating thickness was obtained from 10 measurements taken at different spots of the APS/ben-CCF using a digital thickness gauge. The average of the measurements was then calculated.

3   Results and Discussion

X-ray fluorescence (XRF) is the technique of analyzing fluorescent X-rays in order to gain information about the elemental composition contained in particular materials. In this research, bentonite, APS and APS/ben were prepared for XRF analysis. Only the major chemical components of all samples are presented in Table 1. High proportions of SiO_2 and Al_2O_3 were found in the bentonite with a chemical composition of 70.8% and 20.9% respectively. The APS had a smaller percentage of SiO_2 (22.14%) and Al_2O_3 (14.57%) compared to bentonite. Another chemical compound present in the APS at quite a high percentage was TiO_2 (20.81%). However, after blending the bentonite with the APS, the percentages of the chemical components changed drastically. This may be due to the balanced mixture of APS and bentonite during the mixing process. The major chemical components of the APS/ben are shown in Table 1.

Table 1 XRF Results of Bentonite, Acrylic Polymer Solution (APS) and APS/ben based on their Chemical Composition (%)

Chemical composition%	Bentonite	APS	APS/ben
SiO_2	70.8	22.14	39.08
CaO	1.2	39.55	27.30
Al_2O_3	20.9	14.57	16.42
TiO_2	0.12	20.81	12.85
Fe_2O_3	3.39	0.37	1.54
MgO	1.43	0.58	1.03
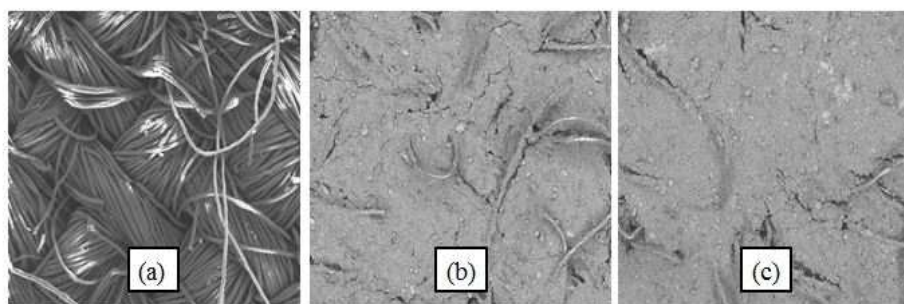
Figure 1 Scanning electron micrographs of (a) CCF, (b) APS/ben-CCF, (c) APS/ben-CCF after adsorption (120x mag.).

The surface morphology of the composite adsorbent coating was evaluated by analyzing the SEM images obtained in Figure 1. The bare CCF can be seen in Figure 1(a). It is composed of a loosely spiral network of cellulosic fibers with a diameter range for every single spiral of around ~10±5 µm. The CCF was selected as adsorbent coating support due to its intra-fibrous pores, which contribute to a high surface area for adsorption to take place, as well as its thinness, low weight, being easy to handle and, most importantly, being reasonably priced. The coated mixture of APS/ben fully covered the CCF surface, as can clearly be seen. The average thickness of the sample was approximately 236 µm ± 3. A very thin layer of APS/ben formed on the CCF surfaces. Besides, there was a change in the surface morphology of the APS/ben-CCF adsorbent coating before (Figure 1(b)) and after adsorption of MB (Figure 1(c)). The surface of APS/ben-CCF was covered with MB particles after the adsorption process was carried out. The presence of MB dye can be clearly observed with the naked eye, as can be seen in Figure 3(c).

In this experiment, CCF was used as a substrate or inert material to support APS/ben adsorbent. Figure 2 exhibits that CCF does not have any effect towards the removal of MB dyes. Its removal efficiency remained 0% until 180

minutes of experiment. Investigation of the bentonite coated CCF showed fluctuations in the result because the bentonite was peeled off from the CCF. The powdery form of bentonite disturbed the adsorption process and created secondary pollution in the treated water. The leaching of bentonite into the dye solution occurred due to its miniature size (20-30 µm). The removal percentage of MB dye using ben-CCF varied from 60% to 70% until the end of the adsorption process. As for APS-CCF, it showed good removal efficiency: 90% removal was achieved within 120 minutes of adsorption. Acrylic polymer is a type of coating material that has good adhesion strength, which contains resin in the matrix of its polymer. Besides that, further experimentation was conducted for mixed APS/ben-CCF with independent APS, bentonite and CCF. From Figure 2 it can be concluded that mixing bentonite with APS and coated onto CCF can give higher adsorption performance for MB dye removal. Almost 100% removal can be achieved within 120 minutes of adsorption.
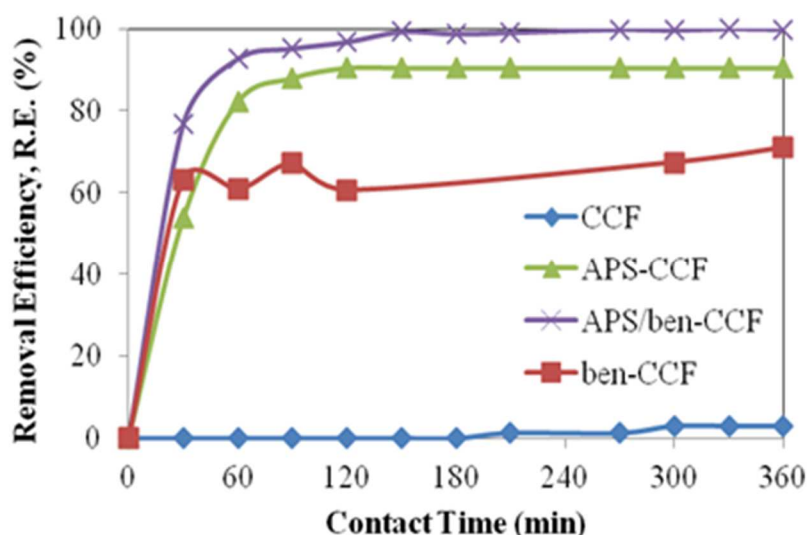

Figure 2 Removal percentage of CCF, ben-CCF, APS-CCF and APS/ben-CCF adsorbents towards MB solution (V = 200 ml, T = 30 °C, stirring speed = 120 rpm, MB concentration = 50 ppm).

Figure 3 shows photographic images of the CCF and the APS/ben-CCF before and after adsorption of MB dye solution. It was observed that all samples had a good mechanical structure as is required for easy separation properties after the adsorption treatment. The APS/ben-CCF maintained its structure and form without the coated APS/ben being torn or peeled off, even after hours of immersion in dye solution.
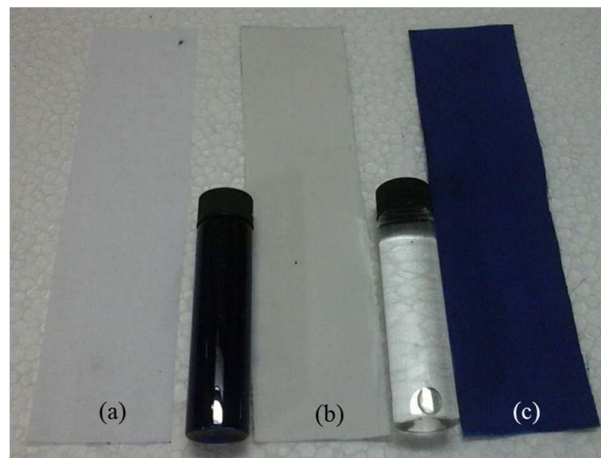
Figure 3 (a) CCF strip, (b) APS/ben-CCF composite adsorbent coating and MB solution in a bottle, (c) APS/ben-CCF coating after adsorption of MB and clear MB solution after adsorption process placed in a bottle.

A proposed illustration of the adsorption process flow, step by step, of the APS/ben-CCF adsorbing MB solution in the system is given in Figure 4. Figure 4a shows the APS/ben-CCF composite adsorbent coating in a schematic image. The mixture of bentonite, APS and distilled water was coated onto the CCF strip and then dried in an oven to harden the composite adsorbent coating on the front side and the back side of the CCF strip. The APS/ben-CCF was immersed in a high-concentration MB solution to carry out the adsorption process (Figure 4(b)). Figure 4(c) shows the changes in MB concentration, which was reduced as the MB particles were adsorbed into the adsorbent coating over time. MB dye particles diffused into the inner part of the APS/ben-CCF and solution become slightly clear (Figure 4(d)). Finally, the MB dye was fully adsorbed into the adsorbent coating, which makes the solution clear (Figure 4(e)). The MB particles penetrate the APS/ben-CCF coating and become blue in color.

The variation in removal percentage of MB dye with contact time at different initial concentrations ranging from 50 to 200 mg/L is presented in Figure 5. The experiment was carried out until 6 hours of operation, i.e. until the process attained equilibrium. After that no significant change in the extent of adsorption was observed. For all initial concentrations tested, 100% MB could be removed using APS/ben-CCF. From the above observation it is evident that for lower initial MB concentrations (50-100 ppm), the adsorption is very fast during the first hour of the process since the MB removal showed 95% efficiency and reduced gradually thereafter. This indicates that the adsorption rate was high. The dye removal percentage took longer to reach equilibrium at higher initial

dye concentrations (150-200 ppm) because of the fact that with an increase in dye concentration there will be increased competition for the active adsorption sites and the adsorption process will slow down increasingly. This explains the longer adsorption contact time for higher dye concentrations [10].
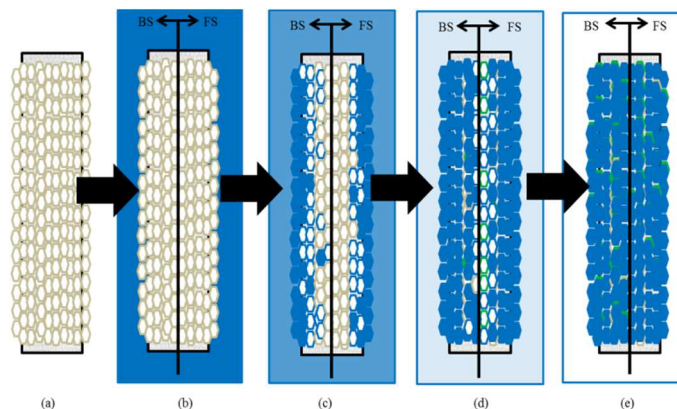

Figure 4 Proposed illustration of adsorption process flow, step by step, of APS/ben-CCF adsorbing MB solution in the system (BF = back side, FS = front side, blue color = MB solution).
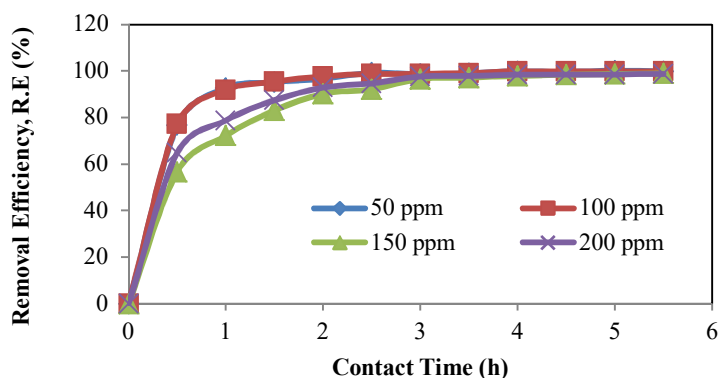

Figure 5 Effect of contact time and initial dye concentration on the adsorption of MB by APS/ben-CCF (V = 200 ml, T = 30 °C, string speed = 120 rpm, mass of APS/ben = 1 g).

An important parameter that affects the adsorption of dye molecules is the pH of the solution. It has effect on the characteristics of the dye with adsorbent surface charge [10]. The study of initial pH was carried out over a pH range from 3.09 to 11.15, as shown in Figure 6. The effect of solution pH on dye adsorption was monitored by keeping the concentration of dye (50 mg/L) and

the amount of APS/ben-CCF constant. As a result, the percentage of MB dye removal attained equilibrium in 2 hours of adsorption. Even at lower or higher pH, the overall results showed 100% removal of MB. A similar trend of dye removal efficiency could be explained by the fact that the APS/ben-CCF stabilizes the MB solution into normal MB pH along the adsorption process. The adsorption sites of the APS/ben-CCF give greater affinity to attract the MB dye compared to the various pH solutions tested.

The abundance of OH^{-1} ions results in strong ionic attraction between the negatively charged surface of the APS/ben-CCF and the cationic dye molecules [10]. Thus it is clear that even at various pH, APS/ben-CCF can function well in adsorbing the pollutant. This will have a benefit in an actual situation of wastewater treatment since the pH may be varied in order for the APS/ben-CCF to be used optimally.
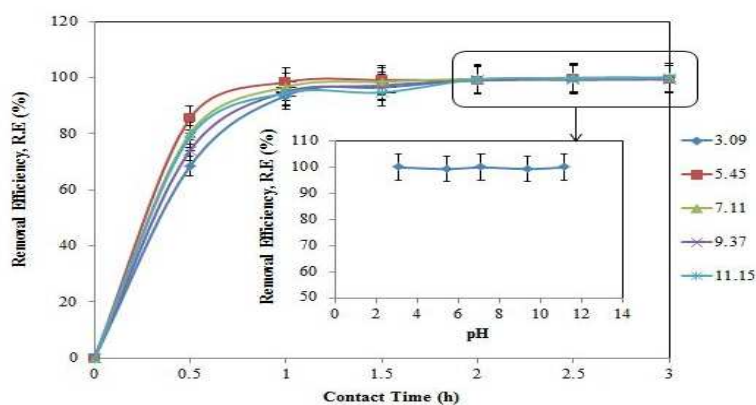

Figure 6 Effect of solution pH on MB removal efficiency (%) ($[MB]_0$ = 50 mg/L, temperature = 30 °C, stirring speed = 120 rpm, contact time = 3 hours).

It is important to study the effect of temperature in the adsorption process since any changes in temperature will cause changes in the adsorption capacity of the dye solution. The effect of temperature on the adsorption of MB studied at 30 °C, 55 °C and 70 °C is shown in Figure 7. The adsorption took shorter time to attain equilibrium at higher MB solution temperature. Within 30 minutes of adsorption operation of the APS/ben-CCF on the MB dye at 70 °C, the removal of MB already approached 100% removal. The shorter time required at higher solution temperature is due to the increase in mobility of dye cations penetrating into the internal structure of the APS/ben-CCF. Besides, the adsorption capacity that increases with the increase in solution temperature indicates the endothermic nature of the adsorption reaction [10].
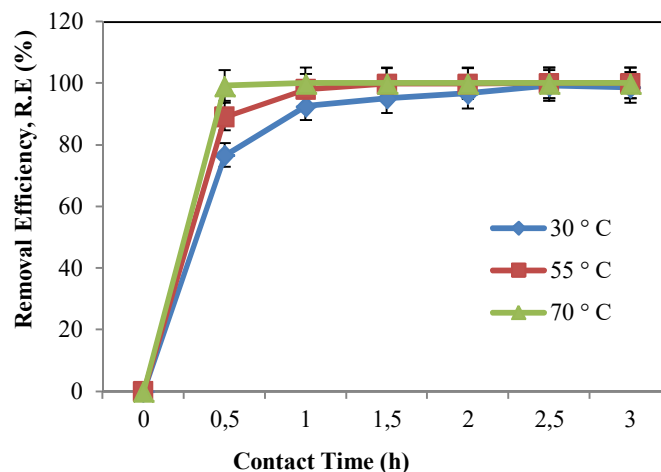
Figure 7 Effect of temperature on equilibrium adsorption capacity of MB solution ($[MB]_0 = 50$ mg/L, temperature = 30 °C, stirring speed = 120 rpm).

4 Conclusion

In this research, an acrylic based composite adsorbent coating was developed, with the aim to eliminate cationic dyes from aqueous solutions and also to assist the solid/liquid separation after adsorption treatment. APS/ben-CCF offered suitable mechanical and textural appearances even after hours of immersing in dye solution. APS/ben-CCF adsorption was favored at lower and higher pH ranges by giving 100% removal of MB dye at every pH tested. Kinetic studies exhibited that the APS/ben-CCF rapidly adsorbed cationic dyes, approaching 100% removal within 30 minutes at higher solution temperature with 36.6 mg/g adsorption capacity. Important potential adsorption sites were identified in APS/ben-CCF, including SiO_2 and Al_2O_3.

Acknowledgements

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