Synthesis of Sodium Alginate Graphene Oxide Thin Film for Adsorption Application

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Abstract. This paper essentially describes the synthesis of sodium alginate graphene oxide silver (SA-(GOAg)) composite thin film for adsorption of methylene blue. The composite thin film is synthesized using simple solvent casting method by varying the amount of GOAg (20 ml, 40 ml, 60ml, 80ml and 100 ml) into SA solution. The thin film then characterized by using UV-Visible absorption spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. The degradation of methylene blue was observed by using UV-Vis and recorded in every 5 minutes for one hour. The results reveal that the combination of SA and 100 ml GOAg shows the highest adsorption rate in one hour compared to other value of SA-GOAg thin films. The SA-GOAg thin film is believed to have a huge potential in adsorption application such as water treatment.

1. Introduction

Water pollution is a never-ending issue especially for developed countries where the industries are springing up like mushrooms after rains. Due to lack of waste management, the industries which is using dyes in their daily operation have caused many environmental problems. One of the unsettling issues is the presence of dyes in water and this has caused water and soil pollution. Some of the dyes are not easily biodegradable which have caused some harmful effect towards human and animal such as diarrhoea, shock, jaundice, increasing a heart rate and worst carcinogenic. Besides, the release of dyes in a high amount into ecosystem also can lead to the disruption of aquatic ecosystem. Therefore, it is crucial to have a solution to remove the dyes that have been release into the ecosystem.

There are several methods that have been studies for the removal of dyes and methylene blue (MB) such as membrane separation, coagulation, ozonation, aerobic and anaerobic treatment and adsorption since 1998 [1]. However, adsorption has been considered as an attractive method to remove MB due to its facileness, unexpansive and insensitive towards other smaller substances [2]. Graphene oxide (GO) has been widely studied for adsorption of dyes or methylene blue apart from activated carbon, carbon nanotubes, graphene, cellulose and others adsorbent. Among the aforementioned
adsorbent, GO is a major MB removal due its large surface area, colloidal stability in solvents and improved biocompatibility [3]. Apart from that, the use of composite GO in nanosized has improved the adsorption rate and capacity which can be used to overcome the environmental pollution. Rather than using GO alone, it has been suggested that the combination between some other material in nanocomposite form can enhance more properties of the material.

Sodium Alginate (SA) is one of the polysaccharides that is naturally found in algal plant. This linear polysaccharide which is made up from mannnuronic acid and guluronic acid which is bound by 1,4 glycosidic linkages possesses unique gelling properties. This unique property has shown the ability to immobilized GO and others adsorbent in order to create a composite which is able to remove heavy metals and dyes from aqueous solution. Besides, the utilization of silver (Ag) into the SA-GO helps to improve the adsorption activity due to the plasmonic properties of Ag which also can be used in colourless organic pollutant [4].

Herein, we employed simple casting techniques for the preparation of SA-GOAg thin film with different ratio of SA and GOAg. The characterization was explored using UV-Visible absorption spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. The degradation of methylene blue (M.B) was observed and recorded in every 5 minutes for 1 hour under UV-light.

2. Experimental Method

2.1. Synthesis of Silver Graphene Oxide nanocomposite

GO Ag was synthesis by using microwave irradiation method by using silver-ammonia complex reaction. Silver ammonia complex was prepared by stirring 10ml of 0.1 M silver nitrate (AgNO₃) solution vigorously and 100 µl of 25 wt% ammonia (NH₃) is added slowly until the cloudy solution of AgNO₃ becomes clear. This indicate the formation of silver ammonia complex solution [Ag(NH₃)₂OH]. Then the solution is mixed with 3ml of 0.5mg/ml GO solution. The solution is then sonicated for 5 minutes in 60°C water bath and microwaved for 2 minutes. The final product is then centrifuge for 15 minutes with 10 000 rpm force and washed by distilled water for several times.

2.2. Synthesis of Sodium Alginate Graphene Oxide Silver Thin film

5 g of SA was stirred with 100 ml of distilled water for one hour until it fully dissolved. The SA solution is added with different amount of GOAg which is 20 ml, 40 ml, 60 ml, 80 ml and 100 ml. The mixture then casted into a petri dish and dried under ambient temperature for 24 hours. The thin film obtained then immersed into 100 ml of calcium chloride (CaCl₂) solution and dried for a few minutes.

2.3. Characterization and adsorption activity

The absorption feature of GO and GOAg and the degradation of MB is observed using UV Visible, Spectroquant Pharro 300 by Merck within the range 190-900 nm. The crystalline structure of the thin films was observed by using XRD machine Bruker d2 phase and the chemical composition of the thin film were observed using FTIR-ATR. The adsorption activity of the thin films was obtained by immersing the thin films into the MB solution. The sample then irradiated under UV-light. The degradation of the methylene blue is observed in every 5 minutes for 1 hour.

3. Results and Discussion
The UV-Vis spectra of GO and GOAg are shown in figure 1. GO shows a strong absorption peak at 230 nm that correspond to the $\pi$-$\pi^*$ transitions of aromatic C-C bonds while the shoulder peak at 300 nm contributes to the n-$\pi^*$ transition of C=O respectively. Meanwhile, for GOAg, a sharp peak at ~ 400 nm contributes to the surface plasmon resonance of silver nanoparticle, AgNPs hence confirms the presence of silver in the GO solution. Meanwhile, the reduction of 230 nm peak in GOAg solution indicates the partial reduction of GO and the reduction of Ag$^+$ to AgNPs [5].

![Figure 1. UV-Vis for GO and GOAg](image)

Figure 1. UV-Vis for GO and GOAg

Figure 2 shows the FTIR-ATR analysis of SA-GOAg thin films. From the results, it can be observed that both GO and SA-GOAg thin film show a broad wide peak between 3000 cm$^{-1}$ to 3500 cm$^{-1}$ which can be attributed to the bending and vibration of hydroxyl group (OH). This spectrum indicate that the samples contain a large number of OH and the spectrum is gradually decreasing as the amount of GOAg increasing. However, the peak in SA-GOAg are more prominent than GO due to the interaction of alginate and GO through intermolecular hydrogen bonds [5]. The characteristic of GO can be observed at 3231 cm$^{-1}$, 3235 cm$^{-1}$, 3239 cm$^{-1}$ and 1589 cm$^{-1}$ which assigned to the OH stretching and C=C stretching [6]. Meanwhile the strong peak that is observed for the thin films at 1080 cm$^{-1}$ is due to the C-O-C stretching of the glyosidic units from SA .
The XRD pattern of GOAg thin films can be observed in figure 3. From the figure, the characteristic peak of GO was focussed at 10.0° assigned to the (0 0 1) impression of GO. However, after addition of SA into GOAg, the characteristic diffraction peak of GO was not observed which indicates that it is dispersed well into the SA matrix [6]. For the thin films, the characteristic peak of GO is shifted to more than 30° suggesting the reduction of GO after the exposure to the microwave irradiation. Furthermore, the diffraction peak that appeared at 38°, 44°, 66° and 82° corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal plane of the face centre cubic (fcc) of metallic silver respectively [7]. The presence of peak indicates the complete formation of AgNPs and GO.

Figure 2. FTIR-ATR Spectra for GO and SA-GOAg thin films
The adsorption activity of MB solution is shown in Figure 4. From the graph, it can be seen that the absorption peak of MB appears between 640nm to 690nm. It can be observed that the absorption peak of MB gradually decreases over time hence proving that the SA-GO films are successfully adsorb the MB after 60 minutes. Other than that, the blue solution of MB is noticed to become colourless after 60 minutes in each of the samples. This changes are due to the collapse of conjugated π system in MB chains [8]. As observed in this figure, the absorption value of MB is increases as the volume of SA-GOAg is increases where the maximum absorption of MB was reached by 100ml of SA-GOAg solution and the minimum absorption of MB was reached by 20ml of SA-GOAg. The higher amount of SA-GOAg is proven to have better adsorption of MB due to the large surface area provided by GO [9] and also due to the hydrogen bonding form between alginate and GO which causes a better adsorption between SA-GOAg and MB [6]. Hence, further studies can be conducted in order to find the maximum limit of GOAg that can be used for MB adsorption.
4. Conclusion

This work has successfully demonstrated a simple technique to create a composite from SA-GOAg film for MB adsorption. This composite thin film has demonstrated its ability to reduce the methylene blue amount in 60 minutes whereas the solution that contains methylene blue becomes clear. It has been discovered that the absorbance of MB is increases as the volume of SA-GOAg in the film increases. From this experiment, 100ml of SA-GOAg in film shows the highest absorption value than other amount of SA-GOAg film. Other than that, the composition and characteristic of the thin films also discovered for future studies. Therefore, the use of sodium alginate incorporated with graphene oxide silver has serve an interesting outcome that indicates the potential of the thin film for adsorption application.

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