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Dispersion of Graphene Using cetyltrimethylammonium bromide (CTAB): Dye Removal and Characterization Studies

Ferda MİNDİVAN¹, Meryem GÖKTAŞ², Ülküye Dudu GÜL³

Abstract

The aim of this study is to determine the usability of cetyltrimethylammonium bromide (CTAB)-reduced graphene oxide (RGO) composites in the removal of methylene blue (MB) from aqueous solutions and to investigate the stability of composites in the aqueous dispersions. And also, we compared the effects of three different CTAB concentrations on the decolorization of MB. The CTAB-RGO composites performed increasing decolorization activity, decreasing average particle size and resulting individual graphene layers with the increasing CTAB concentration. CTAB-RGO with 40 and 80 mg/L composites were unstable, RGO and CTAB-RGO with 120 mg/L had good stability in the aqueous solutions. Effective repulsive forces of CTAB-RGO-120 composite prevented to forming graphene aggregates. The highest decolorization rate of CTAB-RGO-120 composite at neutral pH can result from both the electrostatic interaction and π-π interaction.

Keywords: reduced graphene oxide, cetyltrimethylammonium bromide, decolorization, methylene blue

1. INTRODUCTION

Surfactants are the surface-active agents which are commonly used in industrial applications [1]. Most studies emphasized that surfactants were used in coloring the products to improve color quality [2, 3]. It is known that the effluents of coloring industries include both surfactants and dyes together [4]. The treatment of industrial effluents is an ongoing problem and most of the studies continuously aim to solve this problem. The most concerning issue is the dye-containing
effluents due to their toxic effects on the health of living organisms and also the environment [5]. Recently, inexpensive and environmentally friendly treatment technologies are searched for the treatment of industrial effluents [6]. Some of the studies are shown the positive effect of surfactants on the removal of dyes from aqueous solutions [7, 8]. The recent studies focused on the use of graphene as an adsorbent in the treatment of wastewaters with the adsorption process. Because of the excellent properties of graphene, it has attracted much attention for various applications [9]. Graphene derivatives (Graphene oxide (GO), Reduced graphene oxide (RGO)) were used for in the treatment of Methylene Blue (MB) dye contaminated wastewater [10-14]. However, there is limited study that shows the MB removal properties of CTAB-graphene composites [15-17]. For example, Sankar et al. [17] reported that the chemical reduction of graphene oxide by hydrazine hydrate in the presence of CTAB and was obtained a highly stable aqueous dispersion. Yusuf et al. [16] synthesized GO, reduced to graphene (GN) by ascorbic acid and intercalated with CTAB. Then, prepared GN-CTAB was used for the adsorptive removal of acid red 265 (AR265) and acid orange 7 (AO7) dyes from water. Mahmoodi et al. [15] manufactured rGO/CTAB nanomaterial and characterized in detail. They used the rGO/CTAB to remove anionic dyes (direct red 80 and direct red 23) from wastewater. Therefore, the decolorization of MB with CTAB-RGO composite has never been explored and thus requires investigation.

The objectives of this study are the following: (1) to prepare CTAB-RGO composites with three different CTAB concentrations, to analyses the structures of CTAB-RGO composites and to investigate the stability of composites in the aqueous dispersions, (2) to use the composites as sorbents to remove MB from aqueous solutions and to examine the effects of pH.

2. MATERIALS AND METHOD

2.1. Preparation of Composites

GO was prepared by the modified Hummers method; the details of the process were described by Mindivan [18]. For each experiment, 0.1 g of GO was mixed with 25 ml each of the aqueous solutions of CTAB at different concentrations under ultrasonic agitation. Accordingly, concentrations of 40, 80 and 120 ppm were used for the CTAB aqueous solution. Then, 0.1 g ascorbic acid was added into the mixture. The amount of ascorbic acid was determined according to optimum values obtained from previous reports [19]. Then, the mixture was heated to 98 °C for 12 h. After that, the mixture was centrifuged to remove excess ascorbic acid and CTAB. By changing the various concentrations of CTAB in the resulting composites, a series of CTAB-RGO composites were prepared and coded as CTAB-RGO-40, CTAB-RGO-80, and CTAB-RGO-120. The synthesis process of RGO as a control sample was presented in our previous reports [19].

2.2. Characterization of Composites

X-ray diffraction (XRD) analyses were carried out by an X-ray diffractometer in the range of 20 = 5° to 40° (PAN analytical Empyrean). The zeta-potential and particle size of dispersions were measured by a Zetasizer Nano ZS (Malvern Instruments, Malvern, UK). The surface morphology of CTAB-RGO-120 composite was examined by a field emission scanning electron microscopy (FESEM, Supra 40VP, Zeiss).
2.3. Preparation of Dye Solution

MB, which was a cationic dye, used in this study. The stock dye solution was prepared by dissolving in distilled water at a concentration of 2% (w/v). Experiments were carried out with the desired amounts of these stock solutions.

2.4. Decolorization Experiments

Decolorization experiments were done via the batch technique using 50 ml flasks contained solutions with MB. The experimental flasks were continuously agitated on a shaker with a constant shaking rate of 100 rpm for 24 hours. To examine the effect of adsorbent type on MB adsorption, the different types of graphene-based composites (Dry weight: 1 g/L) were added into flasks contained 50 ml distilled water with 50 mg/L MB at pH 7.05 for 0 to 1440 minutes. The 50 ml distilled water flask containing only MB without adsorbent was used as a control. The experiments were repeated four times and the averages were used and also, the standard deviations were calculated.

2.5. Decolorization Analysis

The 1 ml samples were taken at certain times and centrifuged at 10000 rpm for 7 minutes. The supernatants were analyzed with a spectrophotometer (Thermo scientific, Genesys 150) at 665 nm. The control group contained only distilled water was used in the spectrophotometric method. Equation 1 was used to calculate the percentage of decolorization;

Equation 1: \[ D(\%) = \frac{(C_o - C_f)}{C_o} \times 100 \] (1)

Equation 2 was used to calculate the dye uptake capacity of adsorbent;

Equation 2: \[ q_m=(C_o - C_f) / X_m \] (2)

In these equations; \( D(\%) \) is the percentage of dye removal rate, \( q_m \) is the maximum specific dye uptake (mg/g), \( X_m \) is the maximum dried cell mass (g/L), \( C_o \) is the initial dye concentration (mg/L), \( C_f \) is the final dye concentration (mg/L).

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

The diffraction patterns of RGO and CTAB-RGO composites were shown in Figure 1. As shown in Figure 1, the typical diffraction peak of RGO appeared at about \( 2\theta = 25.31^\circ \). This broad peak indicated that the successful synthesis of RGO by ascorbic acid [20]. The location of the diffraction peaks of CTAB-RGO composites was the same as that of the RGO sample. But the increase in the interlayer distance from 3.52 Å to 3.90 Å was due to CTAB intercalated for CTAB-RGO-120 composite compared to RGO. At the same time, the diffraction peak of the composite shifted leftward. Hu et al. [21] found similar results and reported that interlayer \( \pi-\pi \) van der Waals bond was broken after the intercalation of surfactants.

![Figure 1 The diffraction patterns of RGO and CTAB-RGO composites](image)

3.2. ZP Analysis

The zeta potential values of the RGO and CTAB-RGO composites are presented in Figure 2a. The zeta potential exhibits surface charges of colloidal particles and the colloidal stability of the solution. Particles with zeta potentials between \([ -31 \text{ mV} ] - 40 \text{ mV} \) and \([ -41 \text{ mV} ] - 50 \text{ mV} \) are known that they exhibited moderate stability (no agglomeration) and good stability, respectively [22]. Zeta
potential in Figure 2a was -41.0 mV for RGO due to oxygen-containing functional groups and had good stable dispersion. As the CTAB concentrations were increased, the surface charge became more positive, the highest value of zeta potential (42.4 mV) was shown for the CTAB-RGO-120 composite, which was the most stable composite [23]. Particles with zeta potential between [-41] mV and [-50] mV were considered to form good stable dispersion due to electrostatic repulsion between the charged particles. While the CTAB-RGO-40 and CTAB-RGO-80 remaining composites showed the absolute value of zeta potential less than 30 mV. These ZP values of CTAB-RGO-40 and CTAB-RGO-80 composites could be caused unstable aggregations of graphene in the aqueous solutions because lower repulsive forces did not overcome the attractive van der Waals forces [24]. As a result, the highest CTAB concentration played a role better than the other two CTAB concentrations and RGO, due to high surface coverage of CTAB-RGO-120 could be enough for an effective dispersion process [24]. Figure 2b showed the average particle sizes of RGO and CTAB-RGO composites. It could be seen that the average particle size of composites decreased by increasing the CTAB concentration. Increasing the concentration from 40 ppm to 120 ppm resulted in an average particle size decrement from 2028 nm to 554.0 nm. And also, RGO resulted in large particle size in the range of 2468 nm. Sarsam et al. [23] reported that low average particle size indicates high stability of the colloidal suspension. Average particle size results confirmed with the ZP values because zeta potential value linked directly to the stability of a colloidal suspension.
3.3. FESEM Analysis

Figure 3 displayed the FESEM images of three different magnification of the highest stability composite (CTAB-RGO-120) that were prepared in this study. It could be seen that the CTAB-RGO-120 exhibited smooth structures and the individual graphene layers showing the effect of concentration of CTAB (Figure 3(a)). These layers were seen more obvious in enlarging the FESEM images (Figure 3. (b) and (c)). These images are compatible with the literature. For example; Wu et al. [25] reported that the graphene layers were become thinner and more obvious by the CTAB and this situation was increased the adsorption surface area. Nazari et al. [24] reported that the aggregation of graphene flakes was seen before adding CTAB but the image of the sample with CTAB showed that graphene flakes were stacked flat on top of each other.

Figure 2 The zeta potential values (a) and average particle sizes (b) of the RGO and CTAB-RGO composites

Figure 3 FESEM images of three different magnification of the highest stability composite (CTAB-RGO-120)
3.4. Decolorization Experiments

Decolorization of MB dye by RGO and CTAB-RGO composites such as were examined in this study. As seen in Figure 4, the composites performed increasing decolorization activity with the increasing CTAB concentration. Previously, most of the studies reported that surfactants could enhance the decolorization capacity of some adsorbents such as fungal biosorbent [26], active carbon [27] and gold graphene composite [28]. A similar pattern was observed in this study and the maximum decolorization rate was occurred by using the CTAB-RGO-120 composite. The electrostatic interaction between the positively charged headgroup of CTAB and the negatively charged surface of RGO was the highest at CTAB-RGO-120 composite. At the same composite, the excellent intercalation of CTAB succeeded in reducing the Van der Waals forces between the graphene layers. Effective dispersion forces between the charged particles due to good stable dispersion of composite prevented graphene aggregates. As a result, the dominant mechanism in CTAB-RGO-40 and CTAB-RGO-80 composites were Van der Walls forces, but the effective mechanism in CTAB-RGO-120 composite was electrostatic interactions.

The effect of pH on decolorization was also tested and the results were given in Figure 5. The initial pH of the solution affected the decolorization rate by RGO and the decolorization rates were 4.98% and 53.76% at pH 5 and 7, respectively. It was reported that the carboxyl groups found on the surface of RGO were protonated at low pH values [29]. The dye used in this study MB was also a cationic dye with a positively charged. So, it was expected that the affinity of dye molecules to the adsorbent surface was reduced at acidic conditions such as pH 5. The maximum decolorization rate was reached at pH 7 for CTAB-RGO adsorbents in this study (Figure 5). Maximum dye uptake by CTAB-RGO-120 was calculated as 4.33 mg/g. MB was not favorable under acidic conditions as the CTAB-RGO surface was highly protonated. As pH increased above 5, the deprotonation of the CTAB-RGO surface resulted in electrostatic forces between CTAB-RGO surface and cationic dyes, meaning an increase of decolorization rate. CTAB-RGO-120 exhibited a much higher decolorization rate rather than RGO and other composites. This high decolorization rate was due to π-π interactions between the aromatic rings of MB dyes and delocalized π electrons of CTAB-RGO-120 [16]. Three forces such as electrostatic interaction, π-π stacking interaction and Van der Waals forces are very important at the adsorption of dyes onto graphene-based materials [30, 31]. The highest decolorization rate of CTAB-RGO-120 composite at neutral pH may have resulted from both the electrostatic interaction and π-π interaction. The driving forces were Van der Walls forces and π-π interaction for CTAB-RGO-40 and CTAB-RGO-80 composites. The Schematic representation for the interactions between of RGO-CTAB and RGO-MB were shown in Figure 6.
CONCLUSION

In this study, the effect of CTAB concentration ability to produce optimal dispersion of graphene and on the decolorization of methylene blue (MB) dye was also examined. We determined that the optimal concentration of CTAB was 120 ppm. According to ZP analysis results were found that CTAB-RGO-120 composite was both the most stable composite and average particle size was the lowest. The individual graphene layers of the composite were seen thin and obvious at SEM images and it exhibited maximum decolorization rate. Unstable aggregations of graphene in the aqueous solutions of CTAB-RGO-40 and CTAB-RGO-80 composites had lower repulsive forces and they did not overcome the attractive van der Waals forces. In CTAB-RGO-120 composite, a good stable dispersion was created; compared to the other composites and an effective dispersion forces prevented to forming graphene aggregates. CTAB-RGO-120 exhibited the highest decolorization rate at pH 7 due to π-π interactions between the aromatic rings of MB dyes and delocalized π electrons of it.

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The Declaration of Conflict of Interest/ Common Interest

The authors declare that they have no conflict of interest.

The Declaration of Ethics Committee Approval

This study does not require ethics committee approval or any special permission.

Authors’ Contribution

The authors contributed equally to the study.

The Declaration of Research and Publication Ethics

The authors of this study followed the scientific, ethical and quotation rules of Sakarya University.
Journal of Science in all processes of the paper and that they did not make any falsification on the collected data. The authors declare that Sakarya University Journal of Science and its editorial board have no responsibility for all ethical violations. All responsibility belongs to the responsible author and this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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