Synthesis and Application of Graphene Oxide (GO) for Removal of Cationic Dyes from Tannery Effluents

Md. Israil HOSSAIN[1], Amal Kanti DEB[1], Md. Zakir SULTAN[2]*, A. A. SHAIKH[1], Manjushree CHOWDHURY[1]*, Md. Rayhan SARKER[1]

[1]Institute of Leather Engineering and Technology, University of Dhaka, Dhaka-1209, Bangladesh
[2]Centre for Advanced Research in Sciences (CARS), University of Dhaka, Dhaka-1000, Bangladesh
* zakir.sultan@du.ac.bd; israil.rafi.du@gmail.com

Original scientific article
UDC 675.088:628.31
DOI: 10.31881/TLR.2020.12
Received 10 Jul 2020; Accepted 26 Aug 2020; Published Online 30 Aug 2020

ABSTRACT

The increasing demands for dye in tanning industries have resulted in unconstrained throwing away of dyes into water bodies causing enormous environmental pollution. The removal of these dyes from effluents is mandatory and needs the recommendation of the latest technology and less expensive processes in this regard. Graphene oxide (GO) was prepared, characterized, and applied in the process of removal of cationic dye. GO was characterized by FTIR, X-RD, SEM, and TGA and the following functional groups were found: –COOH, OH, -C=O, and C-O-C. Basic Blue 3 (BB 3) was used as a model synthetic cationic dye. The dye adsorption studies were carried out in terms of the adsorbent dose, the pH, initial dye concentrations, and contact time. The removal efficiency for BB 3 was found to be 100% dye concentration up to 600 ppm at pH 7 with 10 mg (0.1g/L) of the adsorbent, GO, within 6 minutes. In the case of real tannery effluents, the eradication efficiency was found to be 91.2%. The results revealed that GO was a suitable adsorbent for the removal of cationic dyes from tannery effluents.

KEYWORDS

Graphene oxide, adsorption, effluent, tannery, environment

INTRODUCTION

With the speedy progress of various industries like leather, textiles, paper, and printing the consumption of dyes has increased and at the same time effluents containing industrial dyes discharged into the water environment were increasing day by day. These discharged effluents are causing serious water pollution and posing a dramatically life-threatening complication for the environment. Due to their strong colour and visual pollution, dyes have the potency to tone down the environment. Many dyes used in leather-dyeing processes can biologically transform into toxic species and cause interference in the natural photosynthesis process [1-2]. It is quantified that more than 10,000 tons of dyes are utilized in different industries and around 100 tons is relieved into water reservoirs annually. Their concentration in effluents usually varies from 10 to 200 mg L^{-1} [5]. The untreated dye effluents are the key sources of poor surface-water quality and this creates new forms of diseases because of the ecological imbalance. Wastewater treatment is the key global environmental concern because water problems are becoming increasingly significant worldwide. Different types of synthetic dyes have been used in various industries which leads to the contamination of the environment due to harmfulness to the human body, toxicity, and non-biodegradability [2-4]. Leather dyes are considered the most dangerous hazard for the water environment among various types of water pollution. Dyes are a common waste of leather processing, even a low concentration (1 ppm) of dye in water bodies is visible and makes it awful for use. The photosynthetic activities in the ecosystem cannot perform smoothly because of colouring agents in the water surface; these dyes have complex aromatic formations that make them fatal, carcinogenic, and non-biodegradable. There are many treatment processes, including adsorption [6-7] physical and chemical coagulation [8], photocatalytic degradation [9], advanced oxidation processes [10] and biodegradation [11], which are applied for the removal of colour dyes from industrial wastewater. Among them, adsorption is the most widely used, suitable, and inexpensive method to remove heavy metals and organic pollutants including dyes. Moreover, it is cost-effective and has high efficiency.

Graphene oxide (GO) is the most known graphene composite material which is an oxidized product of graphite. It is a highly oxidized form of graphite which consists of different types of oxygen functionalities. GO is a compound which has a hexagonal carbon lattice bonded to oxygen-containing groups such as carboxyl (-COOH), carbonyl (-C=O), epoxy (C-O-C) and hydroxyl (-OH). Graphene oxide (GO) has been considered widely as a prominent precursor and a starting material for the synthesis of different processable materials [12-13]. In the treatment of the dye laden wastewater the chemical groups containing oxygen play a significant role as they have large surface area. Many researchers have proclaimed that graphene oxide (GO) can be utilized as an adsorbent for the decontamination of dye molecules, and heavy metal ions [14-15]. Li et al. have established that fluoride can be eliminated by using graphene oxide [16] and graphene sponges have been tested by the hydrothermal analysis of graphene [17]. Graphene-based composites as nano-adsorbents have tendered prospective advantages for the treatment of various pollutants; for example, the adsorption capacity of graphene sponges was found to be 184 mg g^{-1}, 72.5 mg g^{-1}, and 11.5 mg g^{-1} for methylene blue, rhodamine B, and methyl orange respectively [18-19]. Basic Blue is a cationic dye, green and light blue in colour with the molecular formula $C_{20}H_{26}ClN_3O$, M.W: 359.89 g, and CAS Number 4444-00-3.

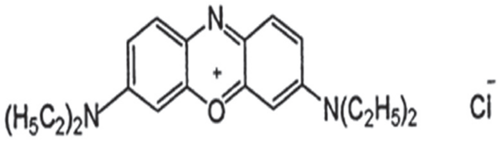

Figure 1. Molecular structure of cationic dye, Basic Blue 3 [20]

In this study, we have prepared graphene oxide (GO) and it was synthesized from graphite powder by the oxidation method. Graphene oxide was characterized by FTIR, SEM, X-RD, UV-visible spectroscopy, and TGA analysis. The adsorption capability of synthesized GO was assessed in the degradation of a synthetic model of the cationic dye Basic Blue 3 (BB 3) and also real tannery effluents. The adsorption processes were investigated in terms of the adsorbent dose, the pH, initial dye concentrations, and contact time.

MATERIALS AND METHODS

Chemicals and reagents

Analytical grade chemicals and reagents were used for all experimental purposes and without any further purification. The principal raw materials were graphite powder (98% extra pure) which was bought from Loba Chemie Pvt Ltd. and the cationic dye (Basic Blue 3, CAS number 4444-00-3, linear formula $C_{20}H_{26}ClN_3O$, M.W.: 359.89 g) was collected from Stahl India Pvt Ltd. The other important chemicals and reagents for the production of graphene oxide are sodium nitrite ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid 98% (H_2SO_4), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2).

Instruments and accessories

Graphene oxide was synthesized and analysed using the following instruments and accessories: a digital scale (XB 220A, Precisa), a hotplate with magnetic digital stirrer (PA 1180, LK LAB Korea), a pH meter, (HANNA instruments), a Fourier transform infrared spectrophotometer (FTIR) (Model IRPrestige21, Shimadzu Corporation, Kyoto Japan), a thermogravimetric analyser (TGA-50, Shimadzu), a UV-visible spectrophotometer (Model Spectro UV-Vis duel beam, uvs-2700, Labomed, Inc.), X-ray diffraction (Ultima IV, X-ray Diffractometer), scanning electron microscopy (SEM, JSM-6490LA, JEOL). A filter paper (102 qualitative, medium speed, pore 20-30μm) and a petri dish were used to prepare graphene oxide.

Synthesis of graphene oxide (GO)

Graphene oxide was synthesized from natural raw materials - graphite fine powder (98% extra pure) - by following the Hummer's method [21]. In detail, 3 g of graphite powder and 2 g of $NaNO_3$ were added in 100 ml of sulfuric acid (H_2SO_4). The mixture was continuously stirred (60 rpm) for 2 hours. Then the mixture was cooled in an ice bath (below 20 ˚C) and an oxidizing agent, $KMnO_4$, was slowly added (6 g) while stirring for 1.3 hours. After the reaction was completed, 100 ml of distilled water was added to the above mixture with continuous stirring and the temperature around 98 ˚C for 1.3 hours. After that the heater was turned off and 200 ml of distilled water was added and stirred for an hour. 10 ml of hydrogen peroxide (H_2O_2) (30%) was added to the mixture to remove the extra potassium per magnetite. In the end, the mixture was cleaned with HCl (5%) to diverge metal ions and rinsed with distilled water many times. The obtained solid composites were dried in a vacuum oven at 70 ˚C. Finally, the powder form of graphene oxide (GO) samples were used for the experimental purpose. The physical appearance of the synthesized graphene oxide is shown in fig. 2.

Figure 2. Optical image of prepared graphene oxide (GO)

Adsorption studies of cationic dye

Preparation of stock solution

Basic Blue 3 (molecular formula: $C_{20}H_{26}ClN_3O$; molecular weight: 359.89g; CAS: 4444-00-3; Stahl India Private Limited) was used to prepare a stock solution of analytical grade. 1 g of BB 3 was dissolved in 1000 ml of distilled water to make 1000 mg L^{-1} / 1000 ppm stock solution. Various concentrations of dyes were prepared by diluting the appropriate amount of the stock solution using the formula $V_1S_1= V_2S_2$, where S_1 is the stock solution's concentration, V_1 is the volume of stock solution being diluted, S_2 is the dilute solution's concentration, and V_2 is the volume of the dilute solution. Millimetres (ml) is the unit of volume and milligrams per litre (mg/L) or ppm is the unit of concentration.

Calibration curve for Basic Blue 3 (BB 3)

The molar absorption coefficient of the BB 3 dye solutions was determined from the calibration curve (absorbance vs. concentration) by using Beer-Lambert law. Seven different concentrations of 20, 50, 80, 110, 140, 170, and 200 ppm BB 3 solutions were prepared and their absorbance values were determined. UV-vis spectrophotometer (Model Spectro UV-Vis duel beam, UVS-2700, Labomed, Inc.) was used for the spectrophotometric determination. It gives distinct characteristics spectra for BB 3 at 654 nm (Fig. 3)

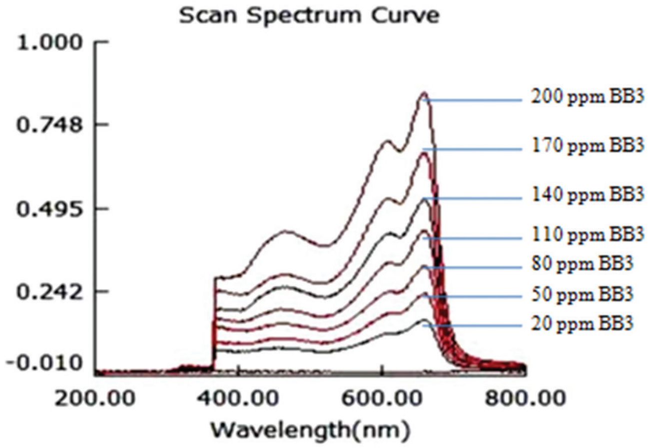

Figure 3. Absorbance spectrum of Basic Blue 3 at 654 nm for seven different concentrations

Adsorption studies of BB 3

The adsorption of dye (BB 3) onto the synthesized GO was studied at room temperature. A fixed volume (100 mL) of 200 ppm (200 mg L^{-1}) of dye was taken in a beaker to perform the experimental studies. The following four parameters: the adsorbent dose, the initial adsorbate concentration, the pH, and contact time have been investigated in order to explore the adsorption capacity of dye onto the synthesized graphene oxide. 0.1M NaOH or 0.1M HCl solutions were used to calibrate the pH. The percentages of removal efficiency of BB 3 dye solutions were calculated by using the following equation: $\%R = \frac{A_0 - A_t}{A_0} \times 100\%$, where A_0 is the initial absorbance (at λ_{max}) and A_t is the final absorbance at time t in the dye solution respectively [2].

RESULTS AND DISCUSSION

Characterization of synthesis graphene oxide (GO)

FTIR analysis

The FTIR spectra were applied to measure wavelength and intensity which are characteristic for specific types of molecular vibration and stretching that are used to identify functional groups of GO. The FTIR spectrum of GO is illustrated in fig. 4.

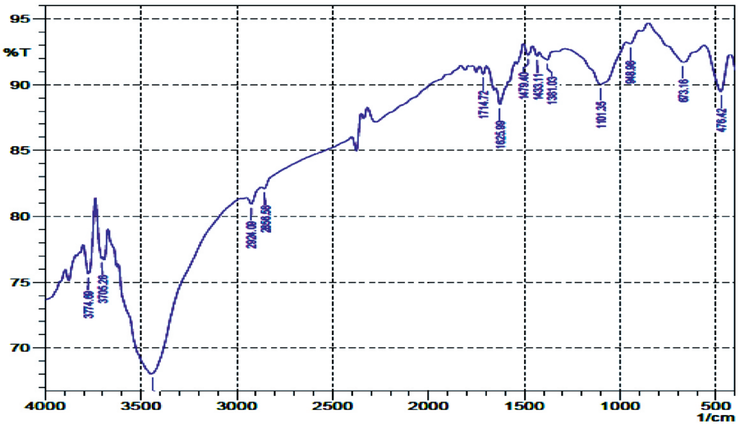

Figure 4. FTIR spectrum of GO

The FTIR spectra of GO indicated the presence of various oxygen-containing functional groups on its surface, assuring its formation. The strong broad peak centred at 3442 cm^{-1} of stretching vibration of O–H bond referred to alcohol and carboxylic acid groups as well as adsorbed water molecules [22]. The functional groups such as hydroxyl, epoxy group, and carboxyl are introduced as characteristic for GO. The peak at 1714 cm^{-1} confirmed the carbonyl group (C=O) present in GO. The peak centred at 1625 cm^{-1} is mainly from stretching vibration of C=C bond indicating the presence of sp^2 hybridized carbon along with a contribution from bending vibration of O-H bond resulting in higher intensity [23]. The peak found at 1000 to 1300 cm^{-1} of stretching vibration of the C-O bond referred to the presence of the epoxy group [24]. Therefore, all the peaks shown in the above figure satisfied the theoretical characteristic peak values of graphene oxide.

XRD analysis

X-ray diffraction (XRD) is the most useful technique for the characterization of general crystalline materials. The XRD pattern of the synthesized graphene oxide (GO) is shown in fig. 5. The figure exhibits three major 2θ at 26.52, 43.58, and 54.84 angles. The characteristic peak at 26.52 is the major peak. The diffraction peak at around 2θ=26^0 confirmed the modification of graphite to graphene oxide [25]. Moreover, the characteristic of the XRD pattern also confirms that the synthesized GO is in crystalline form.

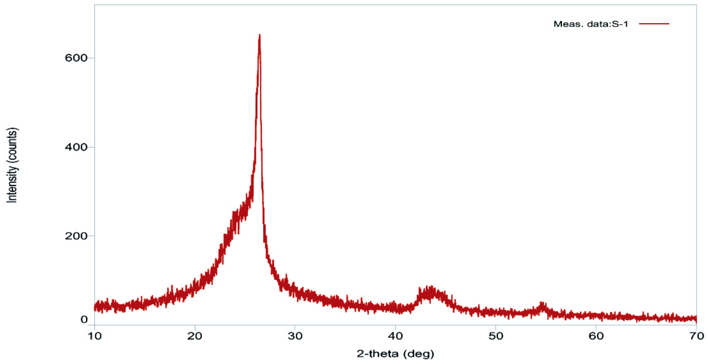

Figure 5. XRD pattern of GO

SEM analysis

The surface of the graphene oxide was investigated by scanning electron microscopy. SEM was used to examine the morphological structures and surface of the analysed samples. Fig. 6 depicts the SEM image of at low (left) and high magnification (right) of the GO sample. At low magnification, as shown in the first picture, the surface appeared agglomerate. Additionally, the sample was taken at high magnification to observe the surface and the observed particles appeared to have clear edges.

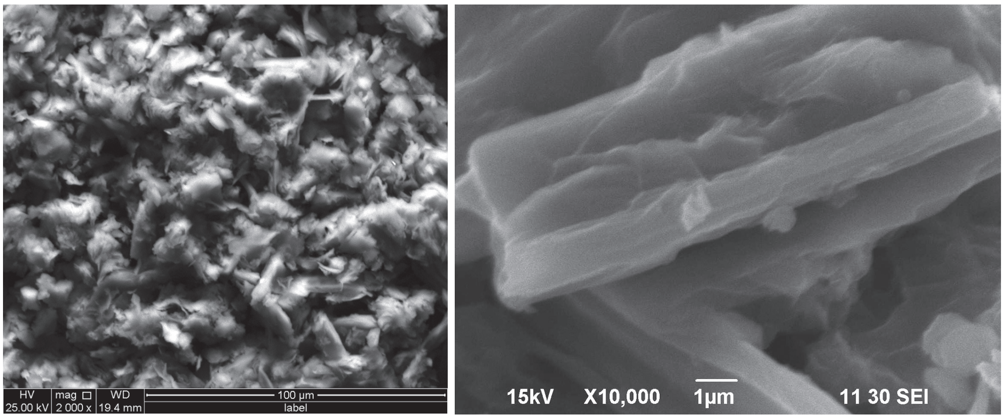

Figure 6. SEM images of graphene oxide (GO)

TGA analysis

The percentages of weight loss with the increase in the temperature of GO has been investigated by thermal gravity analysis. The graph shows 18.27% weight loss within 24 to 483 ˚C due to the removal of surface moisture and the interlayer of absorbed water. By increasing the temperature, a large amount of weight loss occurred and it's about 74.93% weight loss within 483 to 726 ˚C due to the decomposition of O_2, CO, carboxylic, and CO_2 gas. Eventually, it reaches 99.19 % weight at 800 ^{0}C.

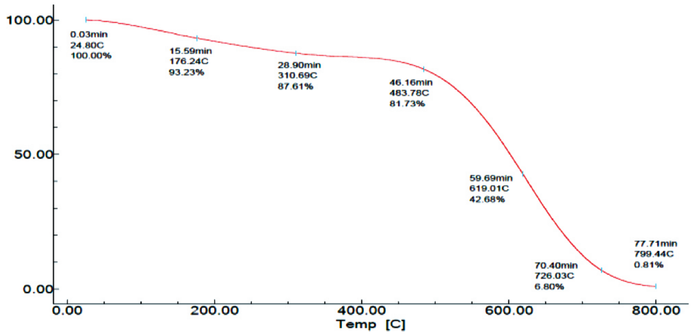

Figure 7. TGA diagram of GO

UV- visible absorption analysis

The UV-visible spectroscopy of graphene oxide (GO) is given in fig. 8. From the figure, it is noticed that the absorption peak of GO appeared near 280 nm, which represents the π-π^* transition in the aromatic C-C bonds. Moreover, another significant peak was near 320 nm which is assigned to the transitions n-π^* [26] of C=O bonds.

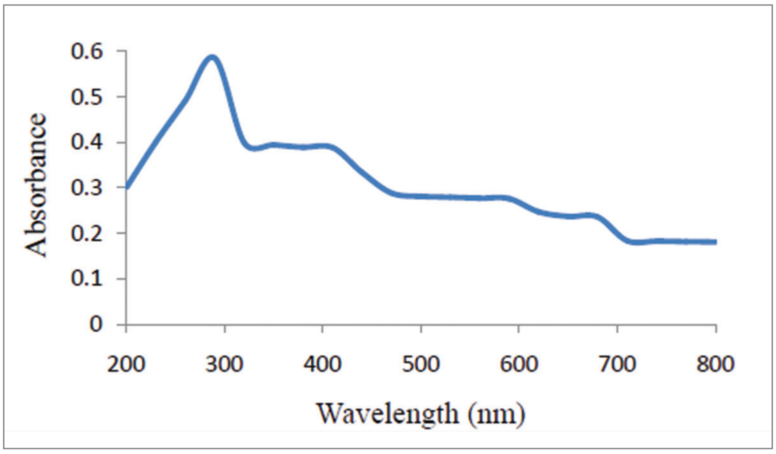

Figure 8. UV-visible absorption spectroscopy for GO

Adsorption study of Basic Blue 3 (BB 3) on GO

Molar absorption coefficient

The molar absorption coefficient was determined by using the Beer-Lambert law from the slope of the plot of absorbance vs. concentration for Basic Blue 3 (BB 3) solutions at seven different concentrations: 20, 50, 80, 110, 140, 170 and 200 ppm. According to the Beer-Lambert law (A=εcl), it was found that the molar absorption coefficient of BB 3, $\varepsilon=2.072\times10^3$ L $mol^{-1}cm^{-1}$.

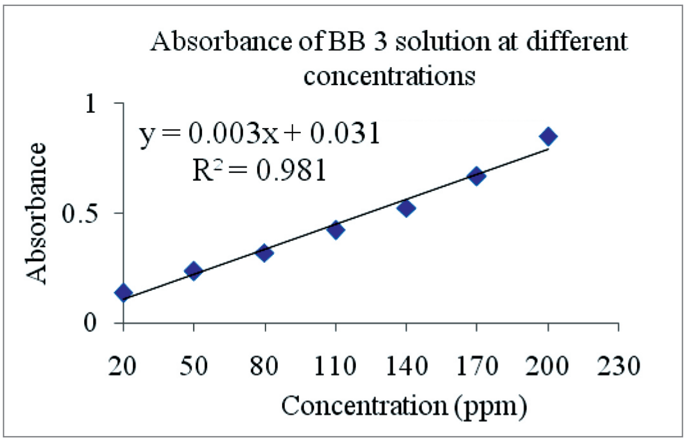

Figure 9. Absorbance of BB 3 solution's at different concentrations

Effect of adsorbents dose

The effect of dissimilar adsorbent doses on the adsorption of BB 3 in aqueous solution was carried out by varying the adsorbent dose from 5 to 12 mg as shown in fig. 10. The doses are added to a series of 100 mL BB 3 dye solution of 200 ppm concentration at pH 7 and room temperature and stirred for 10 minutes at 120 rpm to get the optimum dose of the adsorbent. From the graph, it is visible that the adsorption efficiency increases with the increase in the adsorbent dose due to the higher number of available active binding sites for cations in the dye solution. In the beginning, the adsorption efficiency is 68.1% for a very low amount of the adsorbent dose (5 mg) and 88.58% for 9 mg of the adsorbent dose and then it increases up to 100% for the adsorbent dose of 10 mg. Therefore, the optimum dose for the removal of BB 3 was considered to be 10 mg of GO and used for further adsorption studies.

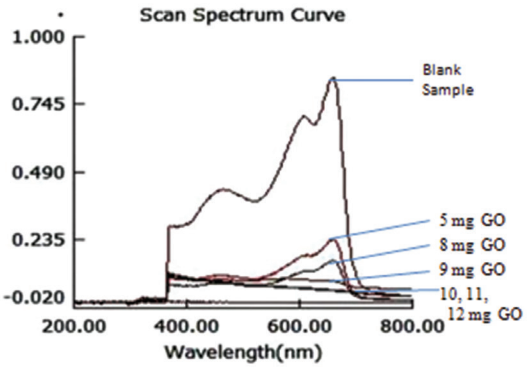

Figure 10a. Absorption spectrum of six different adsorbent doses of GO for BB 3

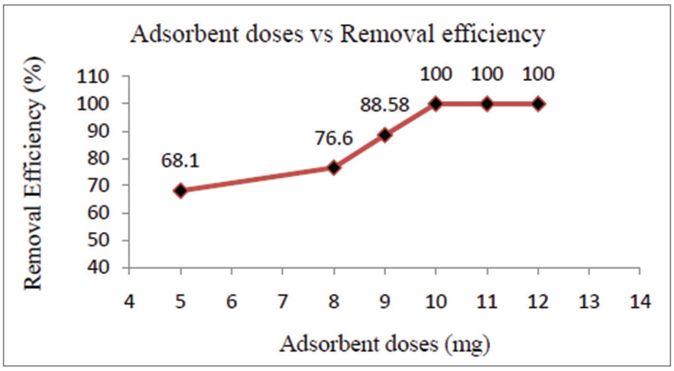

Figure 10b. The effect of adsorbent doses vs. removal efficiency (%) of BB 3 on GO with an initial dye concentration of 200 ppm at room temperature and pH7

Effect of pH

The effect of pH on adsorption was studied at room temperature by varying the pH from 2 to 12 to get both acidic and basic conditions in the initial BB 3 dye solution concentration of 200 ppm and the 10 mg adsorbent dose. The pH plays an important role in a solution containing ions as it affects the electrostatic interaction between the adsorbent and the adsorbate. From fig. 11, it is noticeable that the increase in the pH leads to the increase in removal efficiency. It is also manifested that cationic dyes completely were removed at the pH range 6 to 12 but at pH 2 the removal was only up to 75.83% and at pH 4 it was up to 86.44%. The lower pH values lead to protonation of the adsorbent surface; therefore, adsorption efficiency is low due to the electrostatic repulsion of the cationic dye molecules with the adsorbent surface [27]. The negative charges escalated when the pH raised and slowly de-protonation occurred in the surface of GO; therefore, the electrostatic correspondence increases with the cationic dye. The optimum pH value for the adsorption of BB 3 was found at pH 6 to 12; therefore, we considered pH 7 for adsorption studies.

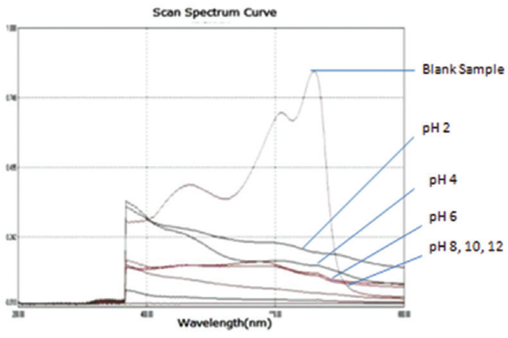

Figure 11a. Absorption spectrum of different pH ranges of GO for the removal of BB 3

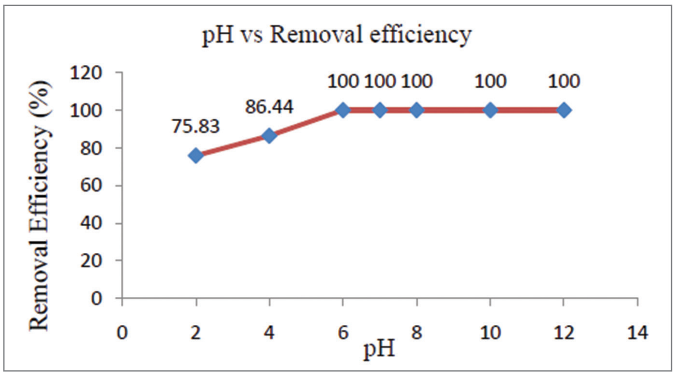

Figure 11b. The effect of pH vs removal efficiency (%) of BB 3 on GO with an initial dye concentration of 200 ppm and 10 mg adsorbent dose (0.1 g/l) at room temperature

Effect of contact time

The effect of contact time on the removal of BB 3 with GO was observed by using 100 mL of 200 ppm dye solution, 10 mg adsorbent dose at pH 7 and at room temperature by varying the contact times. Firstly, the mixture was stirred for 5 minutes at 120 rpm and then the supernatant was collected in one-minute intervals. Fig. 12 shows that the removal efficiency increased rapidly with contact time for cationic dye BB 3 and it was found that after 5 minutes of stirring it removed almost 91% of impurities. It was discovered that, initially, the rate of binding is high because of a higher number of open active sites which get saturated with the increase in the stirring time. After 6 minutes, the removal efficiency reached 100%.

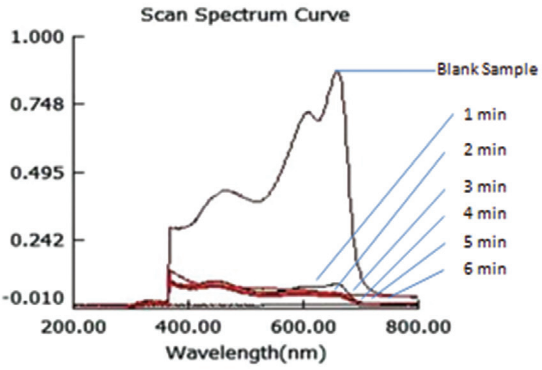

Figure 12a. Absorption spectrum of different time intervals (0-6 minutes) of GO for BB 3

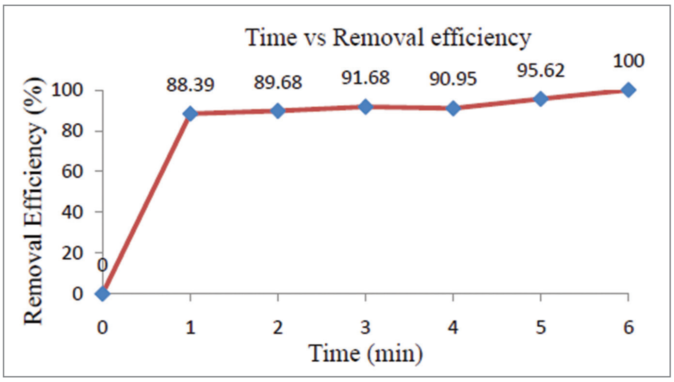

Figure 12b. The effect of contact time vs. removal efficiency (%) of BB 3 on GO with an initial dye concentration of 200 ppm, adsorbent dose 10 mg (0.1 g/l) at room temperature and neutral pH; under 5 minutes stirring

Effect of initial dye concentration

The experiments were performed to manifest the effect of initial BB 3 dye concentration on adsorption onto adsorbent GO. For this experiment, the initial concentration of dye was varied from 200 ppm to 1000 ppm with optimum adsorption dose, time, and pH. It is noticeable from the result that the adsorption efficiency of BB 3 remained constant up to 600 ppm of dye concentration. Therefore, from fig. 13, it is observed that the removal efficiency decreased from 100% to 62.02%; this is due to the lack of receivable active binding sites needed for the high concentration of BB 3 dye solutions. The results also indicated that the higher uptake of dye at a low concentration of adsorbent may be attributed to the presence of more active binding sites on the surface of adsorbent GO for a small number of adsorbate species.

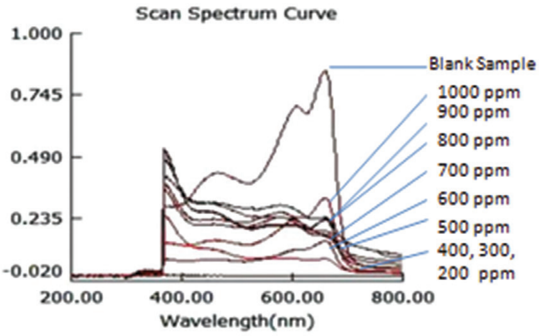

Figure 13a. Absorption spectrum of varying concentration (200-1000 ppm) of BB 3 adsorbed by GO

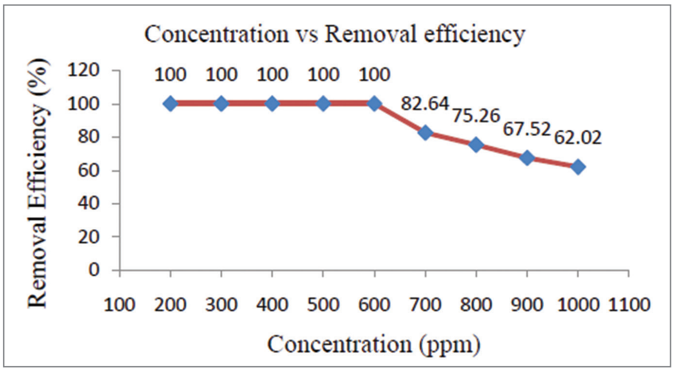

Figure 13b. The effect of initial concentrations of BB 3 vs. removal efficiency (%) by GO with an adsorbent dose 10 mg (0.1 g/l) at room temperature, neutral pH and time 6 minutes after 5 minutes stirring

Adsorption studies of GO for real tannery effluents containing dyes

The real tannery effluents containing dyes were collected in October 2018 from a tannery estate located in Savar, Bangladesh. The adsorption tests of tannery effluents were carried out before and after treatment. 50 mL of tannery effluent was taken in a beaker and 10 mg of GO was added. Then the sample was stirred for 20 minutes at 300 rpm. The visible colours of the effluent were reduced and the adsorption test was carried out using a UV-visible spectrometer. It was found that the removal efficiency was 91.2%.

Mella et al. (2018) [28] found that in the treatment of leather-dyeing effluents with the associated process of coagulation-flocculation/adsorption/ozonation, the removal efficiency of colour was only 61.13%. Harrelkas et al. (2009) [29] studied the treatment of textile effluents by various combinations of physicochemical methods by adjoining coagulation/flocculation (CF) with adsorption on activated carbon (AC), and found that colour reduction was only 50%. These results indicate that the treatment of real tannery dye effluents by using GO as the adsorbent may be a feasible alternative and even applicable on a large scale.

CONCLUSION

The studies exhibited that GO can be utilized as an efficient adsorbent for the removal of cationic dyes from tannery effluents. The adsorption performance of GO on the cationic dye BB 3 was found to be 100% by using only a 10 mg adsorbent dose (0.1g/l) at pH 7, within 6 minutes, with the dye concentration up to 600 ppm. In the case of real tannery effluents, the removal efficiency was found to be 91.2%. The adsorption result was showed very fast and this may be due to the electrostatic interaction of oppositely charged molecules of the cationic dye and GO as the adsorbent along with their π-π interaction and the available binding sites on the surface of the adsorbent. The results from the experiments specified that GO as an adsorbent might be the best alternative when it comes to removing the cationic dyes from tannery effluents.

Acknowledgement

The authors wish to acknowledge the Ministry of Science and Technology (MOST) the government of Bangladesh for financial support through M.S. NST Fellowship Program 2018-2019, ID: 795 and government order no: 3900.0000.012.002.03.18.22

REFERENCES

[1] Filipowicz N, Momotko M, Boczkaj G, Pawlikowski T, Wanarska M, Cieśliński H. Isolation and Characterization of Phenol-Degrading Psychrotolerant Yeasts. Water, Air, and Soil Pollution. 2017; 228(6):210. Doi: 10.1007/s11270-017-3391-8

[2] Deb AK, Shaikh MAA, Sultan MZ, Hossain MI. Application of lac dye in shoe upper leather dyeing upper leather dyeing. Leather and Footwear Journal. 2017; 17(2):97-106. Doi: 10.24264/lfj.17.2.4

[3] Chatterjee S, Gupta A, Mohanta T, Mitra R, Samanta Mandal BA, Majumder M, Rawat R, Singha, NR. Scalable Synthesis of Hide Substance–Chitosan–Hydroxyapatite: Novel Biocomposite from Industrial Wastes and Its Efficiency in Dye Removal. ACS Omega. 2018; 3(9):11486-11496. Doi: 10.1021/acsomega.8b00650

[4] Singha NR, Dutta A, Mahapatra M, Roy JSD, Mitra M, Deb M, Chattopadhyay P. In Situ Attachment of Acrylamido Sulfonic Acid-Based Monomer in Terpolymer Hydrogel Optimized by Response Surface Methodology for Individual and/or Simultaneous Removal(s) of M(III) and Cationic Dyes. ACS Omega. 2019; 4(1):1763–1780. Doi: 10.1021/acsomega.8b02545

[5] Ianoş R, Muntean SG, Muntean E, Păcurariu C, Nistor MA, Todea A. Removal of Colored Organic Pollutants from Wastewaters by Magnetite/Carbon Nanocomposites: Single and Binary Systems. Journal of Chemistry. 2018; 1–16. Doi: 10.1155/2018/6249821

[6] Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y, Yang Z. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere. 2015; 125:70–85. Doi: 10.1016/j.chemosphere.2014.12.058

[7] Wang L, Mao C, Sui N, Liu M, Yu WW. Graphene oxide/ferroferric oxide/polyethylenimine nanocomposites for Congo red adsorption from water. Environmental Technology. 2017; 38(9):996–1004. Doi: 10.1080/09593330.2016.1215352

[8] Sadrnourmohamadi M, Gorczyca B. Removal of dissolved organic carbon (DOC) from high DOC and hardness water by chemical coagulation – relative importance of monomeric, polymeric and colloidal aluminum species. Separation Sceince and Technology. 2015; 50(13). Doi: 10.1080/01496395.2015.1014494

[9] Li S, Lin Q, Liu X, Yang L, Ding J, Dong F, Li Y, Irfan M, Zhang P. Fast photocatalytic degradation of dyes using low-power laser-fabricated Cu_2O–Cu nanocomposites. RSC Advances. 2018; 8(36):20277–20286. Doi: 10.1039/C8RA03117G

[10] Bethi B, Sonawane SH, Bhanvase BA, Gumfekar SP. Nanomaterials-based advanced oxidation processes for wastewater treatment: A review. Chemical Engineering and Processing - Process Intensification. 2016; 109:178–189. Doi: 10.1016/j.cep.2016.08.016

[11] Chen J, Xiaohui W, Hao W, Gao Y, Yang B, Wang Q. Biodegradation and Decolorization of Dye Wastewater: A Review Related content Bioremediation of coractive blue dye by using Pseudomonas spp. isolated from the textile dye wastewater. IOP Conferences Series: Earth and Environmental Science. 2018; 178:12013.

[12] Singh V, Joung D, Zhai L, Das S, Khondaker SI, Seal S. Graphene based materials: Past, present and future. Progress in Material Science. 2011; 56(8):1178–1271. Doi: 10.1016/j.pmatsci.2011.03.003

[13] Ivanovskii AL. Graphynes and graphdyines. Progress in Solid State Chemistry. 2013; 41(1–2):1-19. Doi: 10.1016/j.progsolidstchem.2012.12.001

[14] Vilela D, Parmar J, Zeng Y, Zhao Y, Sánchez S. Graphene-Based Microbots for Toxic Heavy Metal Removal and Recovery from Water. Nano Letters. 2016; 16(4):2860–2866. Doi: 10.1021/acs.nanolett.6b00768

[15] Pavagadhi S, Tang ALL, Sathishkumar M, Loh KP, Balasubramanian R. Removal of microcystin-LR and microcystin-RR by graphene oxide: Adsorption and kinetic experiments Water Research. 2013; 47(13):4621–4629. Doi: 10.1016/j.watres.2013.04.033

[16] Li Y, et al. Adsorption of fluoride from aqueous solution by graphene. Journal of Colloid Interface Science. 2011; 363(1):348–354. Doi: 10.1016/j.jcis.2011.07.032

[17] Zhao J, Ren W, Cheng HM. Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations. Journal of Materials Chemistry. 2012; 22(38):20197. Doi: 10.1039/C2JM34128J

[18] Liu T, et al. Adsorption of methylene blue from aqueous solution by graphene. Colloids and Surfaces B: Biointerfaces. 2012; 90(1):197–203. Doi: 10.1016/j.colsurfb.2011.10.019

[19] Zhao J, Ren W, Cheng HM. Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations. Journal of Materials Chemistry. 2012; 22(38):20197. Doi: 10.1039/C2JM34128J

[20] Dye/World dye variety. Archive for the Basic Dyes Category [Internet]. 2018; Available from: http://www.worlddyevariety.com/category/basic-dyes

[21] Hummers WS, Offeman RE. Preparation of Graphitic Oxide. Journal of American Chemical Society. 1958; 80(6):1339–1339. Doi: 10.1021/ja01539a017

[22] Abdolhosseinzadeh S, Asgharzadeh H, Kim HS. Fast and fully-scalable synthesis of reduced graphene oxide. Scientific Reports. 2015; 5:10160. Available from: https://www.nature.com/articles/srep10160

[23] Gharib A, Fard LV, Pesyan NN, Roshani M. A New Application of Nano - Graphene Oxide (NGO) as a Heterogeneous Catalyst in Oxidation of Alcohols Types. Chemistry Journal. 2015; 1(4):151–158.

[24] Hossain MI, Deb AK, Chowdhury M, El-naggar M, Sarker MR. Removal of Dye Basic Black 7(BB7) from Tannery Wastewater Using Convenient Modified Graphene Oxide (MGO). Global Scientific Journal. 2019; 9(7):427-432.

[25] Paulchamy B, Arthi G, Lignesh BD. A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial. Journal of Nanomedicine and Nanotechnology. 2015; 6(1).

[26] Pavia DL. Introduction to spectroscopy, 5th ed. Washington: Cengage Learning; 2017.

[27] Badhai P. Graphene oxide-magnetite hybrid nanoadsorbents for toxin removal in aqueous system [dissertation on the Internet]. Odisha: Department of Ceramic EngineeringNational Institute of Technology: 2016. p79. Available from: https://pdfs.semanticscholar.org/2243/089c26a2388ce9f48e9d2fa89cd6670a3740.pdf

[28] Mella B, Carvalho Barcellos BS, Silva Costa DE, Gutterres, M. Treatment of Leather Dyeing Wastewater with Associated Process of Coagulation-Flocculation/Adsorption/Ozonation. Ozone: Science and Engineering. 2018; 40(2):133–140. Doi: 10.1080/01919512.2017.1346464

[29] Harrelkas F, Azizi A, Yaacoubi A, Benhammou A, Pons MN. Treatment of textile dye effluents using coagulation–flocculation coupled with membrane processes or adsorption on powdered activated carbon. Desalination. 2009; 235(1–3):330–339. Doi: 10.1016/j.desal.2008.02.012