A BREAKTHROUGH APPROACH WITH COLLAGEN-GRAPHENE OXIDE NANOCOMPOSITE: SUSTAINABLE SOLUTION FOR DYE WASTEWATER

SHAZNEEN CHOWDHURY, SABBIR ISLAM SHOWROV, HASIBUR RAHAMAN SANTO, AND MD. ELIAS UDDIN*

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna 9203, Bangladesh, e-mail: chowdhury2219555@stud.kuet.ac.bd, e-mail: sabsabbir01@gmail.com, e-mail: santohasib79@gmail.com , e-mail: eliasuddin@le.kuet.ac.bd

***Corresponding author**

ABSTRACT

Rapid industrialization has resulted in immense deterioration of water bodies, primarily from the deposition of anthropogenic organic contaminants into water sources. As it prevents light from penetrating the water body, turbid tannery effluent is a serious environmental problem because it interferes with photosynthesis in aquatic habitats. Recently, it has become common practice to use nanotechnology to focus on removing colors and phenolic pollutants from wastewater before it is discharged. This literature describes the creation and application of a remarkable collagen-graphene oxide nanocomposite for lowering dyes in tannery effluent that has improved surface area, biocompatibility, cheap cost, and high affinity to organic molecules. In order to create nanocomposites, a straightforward solution casting method was used. Additionally, UV-Vis spectroscopy, FT-IR, and SEM analyses were used to examine the dispersibility, chemical bonding, and morphology of the nanocomposites, respectively. Process optimization has also been studied in relation to the contact time, pH, and adsorbent dosage of nanocomposite materials. However, 99.3% dye reduction at pH 5 was seen utilizing $2gL^{-1}$ of adsorbent after only 15 minutes of contact time. Finally, the experimental findings were used to evaluate the isotherm model and adsorption kinetics. Evidently, the pseudo-second-order kinetics and Freundlich isotherm were successfully aligned to the chemisorption with multilayer adsorption, which finally contributed to the reduction of turbidity in tannery effluent due to electrostatic interaction between the adsorbent and adsorbate.

Keywords: Graphene Oxide, Nanocomposite, Wastewater, Adsorption, Tannery Effluent.

1. INTRODUCTION

Bangladesh's leather industry has been deemed a high-priority sector due to its potential for growth and economic impact. Unfortunately, the environmental contamination keeps these sectors from meeting the criterion (Zhang et al., 2020). To produce leather with the suitable final quality, a number of batch processes involving copious amounts of water and chemical treatments are needed. Maintaining the discharge limit is becoming increasingly difficult due to the handling of the large amount of tannery influent (20-30 m^3/ton rawhide processing) (Angelucci et al., 2017). Due to the presence of various pollutants, such as fine organic particles from raw hides or skins, excess chemical residue, and reagents from waste liquors, the tannery influent is essentially very turbid (Aboubaraka et al., 2017). The leather production industry is known for adding a large number of dyes to the wet finishing process in order to get particular chemical and quality characteristics. However, a significant portion of these dyes is lost during the dye washing process, which can range from 10% to 50%. Many of these pigments resist removal by traditional wastewater treatment techniques, meaning they stay in the environment (Piccin et al., 2016). These stubborn dyes can cause hemolysis, hypertension, jaundice, organ damage, tissue necrosis, and respiratory problems in people, among other health hazards. Then again, the direct discharge of such turbid influent prevents light penetration, reducing photosynthesis in aquatic ecosystems, and ultimately driving aquatic species towards extinction by upsetting the food chain, decreasing productivity, and impairing gill function (Solak et al., 2009; Amosa et al., 2016). Therefore, in order to address this anthropogenic digester and maintain environmental sustainability, it is imperative to guarantee a workable wastewater treatment system. Ion exchange, coagulation flocculation, membrane process, chemical precipitation, and flotation are some of the well-liked technologies that have been developed recently to address this issue (Yusuf and Song, 2020). Nevertheless, putting these strategies into practice in poorer nations is difficult. Adsorption is currently being investigated extensively for its decontamination of environmental toxins as a practical, affordable, and alluring treatment (Payam and Arash, 2020). At this stage, using nanocomposite adsorption might be seen as a sustainable water treatment method that gets beyond all of the limitations that are in place. Because of its higher specific surface area (2630 m^2g-1), graphene oxide (GO) is a very promising material for nanocomposite applications (Gao et al., 2014). In addition to GO, other biomaterials including collagen, keratin, and its derivatives are also employed to filter out many kinds of organic pollutants from water, including heavy metals, oil, fat, and organic and inorganic detritus. To improve adsorption efficiency, the morphological structure of these biopolymers is also chemically modified. Collagen is a cheap, safe, pH-dependent, and highly biodegradable protein material. Although, chemical modification is therefore required to get the physicochemical properties and stability to making it suitable for use in practice. Considering this, collagen can be used to create an adsorbent that might extract pollutants such as charged metal ions from aquatic media. Previously, One promising coagulant has been developed for treating synthetic wastewater which is GO-CS (Graphene oxide-Chitosan) to eliminate turbidity as well as other impurities (Eman et al. 2016).

The objective of this study is to synthesize GO-Co an adsorbent utilizing leather waste derived collagen combined with GO, with the potential to reduce dye and other organic pollutants in tannery effluent. This is the first study to try to remove turbidity from tannery wastewater using materials such as GO-Co nanocomposite. The nanocomposite exhibits exceptional efficacy in combating dye wastewater and holds significant potential for industrial implementation. Not just tannery effluent, but all industrial wastewater types would benefit greatly from the use of nanocomposites for turbid dye removal.

METHODOLOGY

2.1 MATERIALS

Acetic acid, Sulfuric acid, Salt, potassium permanganate, and hydrogen peroxide were acquired for the oxidation of the crystalline graphite flakes, which were then utilized to prepare GO. Reagents employed in this investigation were laboratory standard chemicals e.g., hydrochloric acid sodium

hydroxide, aluminium sulphate, sodium thiosulfate; potassium dichromate, starch and ferrous ammonium sulphate, Ethanol, Tetrahydrofuran.

2.2 PRETREATMENT OF WASTEWATER

Plastic containers were employed to collect wastewater (sample) from leather dyeing operation of the SAF Leather Industries Ltd., Jashore, Bangladesh. In this experiment, dye removal was the prime concern by adsorption process with nanocomposites. Furthermore, some other physicochemical parameters such as pH, Turbidity, TDS, TSS, salinity, EC, BOD, COD, etc. of the treated wastewater were compared with the standard discharged level (ECR, 1997).

2.3 PREPARATION OF GO-Co NANOCOMPOSITE

According to modified Hummers method, GO was synthesized by the oxidation of natural graphite flake (Uddin, Kuila et al. 2013). Collagen was exacted through acid hydrolysis process then precipitated using salt and collected after dialysis (Liu. et al. 2016). According to T. Tanabe et al. (2002) collagen was dissolved in glacial acetic acid (dilute) at 80º c and agitated for three hours at room temperature, and the solution had been blended uniformly by ultrasonication. GO-Co nanocomposites were created utilizing the simple solution mixing approach (G. Feng et al. 2020). The first step of the synthesis involved dispersing prepared graphene oxide (1g) in deionized water using ultrasonication for 1hr. To create a suitable, homogenous solution, prepared collagen solution was then combined dropwise and sonicated for 15 minutes. The mixture was then transferred to a conical flask and allowed to reflux (24 hours at 55ºC) at room temperature and cooled down. To get rid of unreacted components, the residue was then collected and rinsed with de-ionized water to get rid of unreacted components. The resultant slurry was then heated once again for 72 hours at 50 °C in an oven to dry under vacuum. Finally, the residuals material was prepared as powdered form adsorbent (GO-Co nanocomposite) for further use of experimentation.

2.4 CHARACTERIZATION OF GO-Co NANOCOMPOSITE

GO-Co dispersibility in water at ambient temperature was investigated by UV-Vis spectroscopy (model: UVS-2100 SCINCO). Fourier-transform infrared spectroscopy (FTIR) (model: NICOLET 6700, Perkin Elemer, USA) was used in the 400–4000 cm^-1 frequency range to determine the various functional groups involved in the chemical bonding of the GO-Co nanocomposite. Thermally activated adsorbents' surface morphology was assessed using a SEM (JEOL JSM-6490, USA).

2.5 BATCH ADSORPTION ANALYSIS

In order to investigate the adsorption efficiency and the impact of operating parameters, batch adsorption studies on the elimination of turbidity by GO-Co nanocomposite were carried out. Throughout the entire data evaluation process, the removal efficiency verified the nanocomposite's strength and uniqueness. The turbidity (measured in absorbance) of the treated samples was then assessed at a wavelength of 550 nm using a UV-Vis spectrophotometer in order to determine the efficiency of the adsorbent. Every experiment was run three times, and the standard deviation and mean value were used.

Table 1: Experimental framework for batch analysis

Parameters	Range of value	Unit
pH(maintained by using 0.1 M HCl & 0.1M NaOH)	4,5,6,7,8,9	-
Dosage of nanocomposite	0.5, 1, 1.5, 2.0, 2.5, 3.5,4	g
Contact time	2,5,8,12,15,18,22,25,28	min
Settling time	1	hr

3. RESLUTS AND DISCUSSION

3.1 UV-VIS SPECTROSCOPY ANALYSIS OF NANOCOMPOSITE

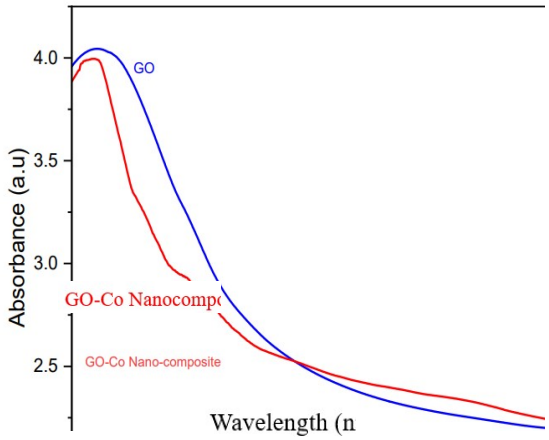


Figure 1. UV-Vis spectroscopy of pure GO and GO-Co Nanocomposite.

Figure 1. exhibits the UV-Vis adsorption spectra of GO-Co and nanocomposite.In the case of GO, an intense peak appeared at 230 nm, which attributed the π-π* transition of C=C (Lai et al., 2012). The change between intense peak highlights the presence of available functional group and conjugated bond of individual substance.The π-π* transition peak shifts in the case of the nanocomposite from GO and a small band appears at around 300 nm corresponded to the n-π* transition of C=O, indicating the restoration of conjugated structures that could be related to the complex formation of GO and collagen (Dhayal et al., 2020).

3.2 FT-IR ANALYSIS OF NANOCOMPOSITE

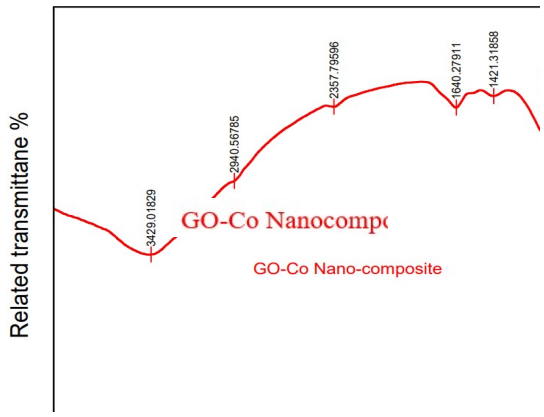
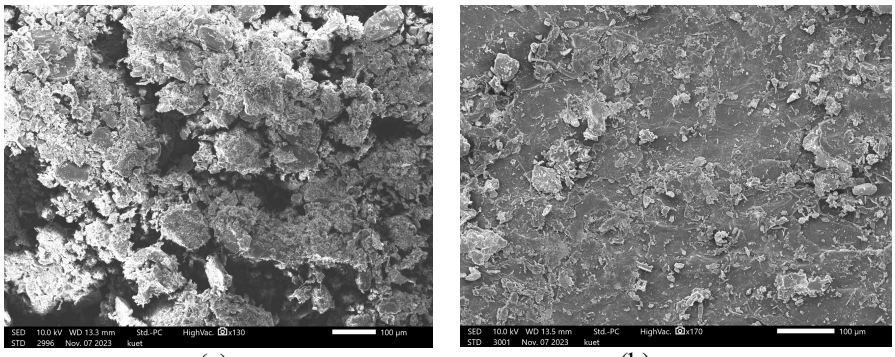


Figure 2. FT-IR Spectra of the GO-Co nanocomposite

The nanocomposite was found in spectrum at ~3429, ~2940, ~2358 , ~1640, ~1421 and ~1123 cm^{-1} due to the presence of N-H stretching, C-H stretching, O=C=O stretching, C=N stretching, O-H bending and C-O stretching in composite materials respectively(Fig. 2). Thus, aforementioned peaks are clearly indicating the availability of functional groups and amide linkage in nanocomposite from GO and collagen, and proving the formation of appropriate bonding. The FT-IR data depicts the presence of functional groups, especially –OH, N-H, –CO in the adsorbent, which are significant for adsorption. The –OH, –NH, –CO groups might help in bonding with the targeted materials and might

be responsible for the increase the adsorbent surface area during the adsorption, As a result, Adsorption capacity is influenced by the adsorbent surface porosity and functional groups.

3.3 SEM ANALYSIS OF NANOCOMPOSITE



(a) (b)

Figure 3. SEM analysis of Nanocomposites (a) before and (b) after adsorption)

To better understand the surface morphology and structural changes brought on by the adsorption process, Figure 1 (a-b) shows SEM images of the GO-Co nanocomposite before and after adsorption, respectively. Figure 1 (a), It displays a smooth, multilayered surface made of materials that resemble clouds. The adsorbent surface shape transforms to a more porous surface, which increases its specific surface area and facilitates the deposition of Collagen fibers. Collagen fibers interwined with the GO matrix in 1(b), GO was able to confirm its integral structure without any agglomeration (Sun et al., 2020). Through the adsorption process, in which the dye molecules were adsorbed on the adsorbent, the differences in pore size and surface texture consistency are also discernible.

3.4 ADSORPTION PARAMETERS

Table 2: Optimized Adsorption parameters for GO-Co nanocomposite

Parameters	Unit	Optimum value	Removal Efficiency(%)
pH	-	5	98.63
Dosage of nanocomposite	g	2.0	98.89
Contact time	min	15	99.32

3.5 ADSORPTION KINETICES

The reaction rate dependence on adsorption process was explored by adsorption kinetices . Pseudo 1 st order (PFO) and Pseudo 2nd order (PSO) kinetic models were employed to analyze and explain the adsorption kinetics. The physisorption and chemisorption are indicated in case of the fitness of adsorption process with this two model individually (Mahdavinia et al., 2016; Bai et al., 2018).The linear equation for PFO and PSO kinetic models are represented using the following equations respectively:

$$\ln(qe\text{-}qt) = \ln qe - K_1 t$$

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} t$$

Where: while qe and qt both are the values of adsorbed mass per unit adsorbent mass (mg/g) at equilibrium state and at specific time (mg/g), respectively 'K_1' (min^{-1}), 'K_2' ($gmg^{-1}min^{-1}$), 'are the rate constant of PF order, PS order, kinetic model, respectively; To evaluate the kinetics parameters, the value of log (qe–qt) vs. time (t), t/qt vs. time (t), were plotted linearly for the PFO and PSO kinetic model, respectively. The rationality of the adsorption process is determined through the calculation of coefficient value (R^2).

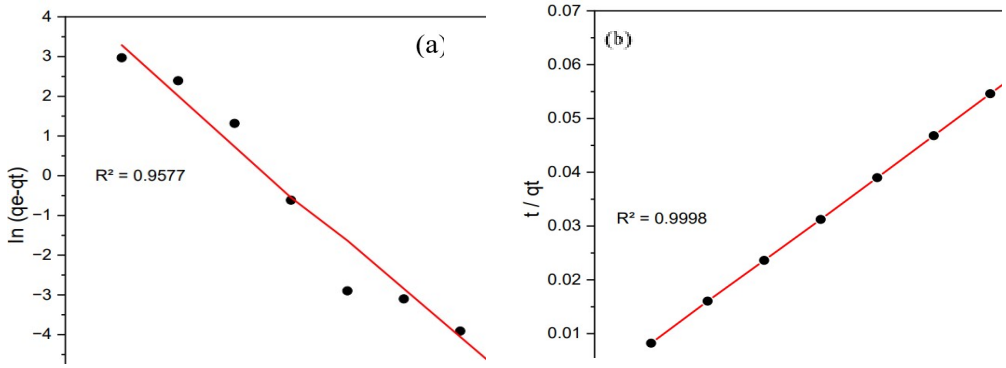


Figure 4. linear Plot of (a) pseudo-first-order and (b) second-order kinetic

Figure 4. (a), (b) represent pseudo-first-order and pseudo-second-order kinetics models respectively. It is observed that, coefficient value (R^2) of the second-order kinetics is 0.999, which is higher than the coefficient value (0.958) of first-order kinetics. The accessible functional groups led to the conclusion that the adsorption mechanism was chemisorption, and there was irreversible adsorption between the contaminants and the GO-Co nanocomposites.

3.6 ADSORPTION ISOTHERM

Adsorption isotherm analysis is essential to determine how interactively adsorbent and adsorbate behave in order to evaluate adsorption performance. The Langmuir and Freundlich models were executed to explain the adsorption isotherm. Langmuir theory represents the partition mechanism of the adsorbate in solid and liquid phase following the linear isotherm model (Guo et al., 2019). To represent the multilayered adsorption theory, one of the most popular isotherms, the Freundlich model is exploited. The linear equation for Langmuir and Freundlich isotherm models are represented using the following equations respectively:

$$\frac{Ce}{qe} = \frac{1}{qmKL} + \frac{Ce}{qe}$$

$$\log qe = \log KF + \frac{1}{n} \log Ce$$

Where, qe is the amount of adsorbed suspended solids (mg/g) at equilibrium, Ce is the concentration of aqueous solution at equilibrium state (mg/L), 'KL' (L/mg) and 'KF' (L/mg) are the constants of Langmuir and Freundlich adsorption isotherm, respectively; 'qm' (mgg^{-1}) denotes the capacity of maximum adsorption; 'n' stands for the parameter of Freundlich isotherm.

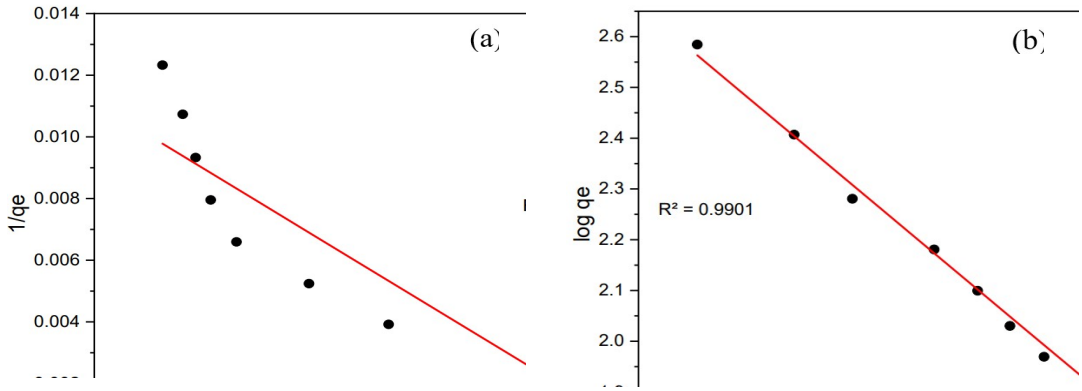


Figure 5. linear Plot of (a) Langmuir isotherm, (b) Freundlich isotherm

Figure 5. shows the correlation coefficient value of the isotherms (R^2) in this study. Therefore, the sorption process fit the Freundlich model R^2=0.9901 better than the Langmuir isotherm R^2=0.8695, confirming multilayer adsorption into the active binding layers of GO-Co nanocomposites. It is important to note that the previously mentioned experiments were not conducted in tannery wastewater and the present study is centered on the idea of removing dye from tannery wastewater through the use of GO-Co nanocomposite.

Table 3: Comparison of different parameters between before and after treatment

Parameters	Unit	Raw sample	Treated sample	Standard Value (ECR 97)
pH	-	3.9	6.5	6.0-9.0
COD	mg/L	4123	373	200-400
BOD	mg/L	2015	225	30-250
Turbidity	(absorbance at 550 nm)	1.449	0.01	-
TDS	mg/L	9147	863	2100

4. CONCLUSIONS

This study investigated the synthesis and application of GO-Co nanocomposite as an adsorbent for dynamic adsorption of dyes from tannery effluents. Ultraviolet-Visible spectroscopy (UV-Vis), FTIR, and SEM examination were used to determine the nanocomposite's priority. The process of characterisation aids in the verification of the dispersibility, morphological examination, and chemical bonding between functional groups. 99.3% of the turbidity lowered from the tannery effluent could be controlled, according to adsorption efficiency analysis, utilizing a 2g/L GO-Co based adsorbent at 5 pH for 15 minutes. Nonetheless, a variety of factors are crucial in eliminating turbidity because they hinder adsorbent precipitation and prolonged response times, overdose aggregation, etc. The GO-Co nanocomposite additionally validates the decreases in salinity, TSS, BOD, and COD. However, further research should be done to streamline manufacturing processes, validate affordable production of the nanocomposite, sustainable disposal after use, and establish financial sustainability.

ACKNOWLEDGEMENTS

"We extend our sincere gratitude to the collaborative efforts of the Common Lab, Testing Lab, and Manufacturing Lab Center of Excellence at KUET. Their invaluable support and resources have significantly contributed to the success of this research paper.

REFERENCES

Aboelfetoh, E. F., Aboubaraka, A. E., & Ebeid, E.-Z. M., 2021. Binary coagulation system (graphene oxide/chitosan) for polluted surface water treatment. Journal of Environmental Management, 288, 112481.

Ali, I., Basheer, A. A., Mbianda, X. Y., Burakov, A., Galunin, E., Burakova, I., Mkrtchyan, E., Tkachev, A., & Grachev, V., 2019. Graphene based adsorbents for remediation of noxious pollutants from wastewater. Environment International, 127, 160-180.

Amosa, M. K., Jami, M. S., Alkhatib, M. a. F. R., Tajari, T., Jimat, D. N., & Owolabi, R. U., 2016. Turbidity and suspended solids removal from high-strength wastewater using high surface area adsorbent: Mechanistic pathway and statistical analysis. Cogent Engineering, 3(1), 1162384

Bai, R., Zhang, Y., Zhao, Z., Liao, Q., Chen, P., Zhao, P., Guo, W., Yang, F., & Li, L., 2018. Rapid and highly selective removal of lead in simulated wastewater of rare-earth industry using diglycolamic-acid functionalized magnetic chitosan adsorbents. Journal of Industrial and Engineering Chemistry, 59, 416-424.

Dhayal, V., Hashmi, S.Z., Kumar, U., Choudhary, B.L., Kuznetsov, A.E., Dalela, S., Kumar, S., Kaya, S., Dolia, S.N. and Alvi, P.A., 2020. Spectroscopic studies, molecular structure optimization and investigation of structural and electrical properties of novel and biodegradable Chitosan-GO polymer nanocomposites. Journal of Materials Science, 55, 14829-14847.

Gao, F., Qu, J., Zhao, Z., Zhou, Q., Li, B. and Qiu, J., 2014. A green strategy for the synthesis of graphene supported Mn_3O_4 nanocomposites from graphitized coal and their supercapacitor application. Carbon, 80, 640-650.

Lai, Q., Zhu, S., Luo, X., Zou, M., Huang, S., 2012. Ultraviolet-visible spectroscopy of graphene oxides. AIP Adv. 2(3), 032146.

Liu, X.; Dan, N.; Dan, W. Preparation and characterization of an advanced collagen aggregate from porcine acellular dermal matrix. Int. J. Biol. Macromol. 2016, 88, 179–188.

Mahdavinia, G.R., Hasanpour, S., Behrouzi, L. and Sheykhloie, H., 2016. Study on adsorption of Cu (II) on magnetic starch-g-polyamidoxime/montmorillonite/Fe3O4 nanocomposites as novel chelating ligands. Starch-Stärke, 68(3-4), 188-199.

Mosca Angelucci, D., Stazi, V. and Tomei, M.C., 2023. Sustainable approach for removal of Remazol Red using absorptive polymers: optimization of process performance and sorbent regeneration. International Journal of Environmental Science and Technology, 1-12

Sun, B., Zhang, Y., Li, R., Wang, K., Xiao, B., Yang, Y., Wang, J. and Zhu, L., 2021. New insights into the colloidal stability of graphene oxide in aquatic environment: Interplays of photoaging and proteins. Water Research, 200, 117213.

Uddin, M.E., Kuila, T., Nayak, G.C., Kim, N.H., Ku, B.C. and Lee, J.H., 2013. Effects of various surfactants on the dispersion stability and electrical conductivity of surface modified graphene. Journal of Alloys and Compounds, 562, 134-142.

Yusuf, M., Song, K., Geng, S. and Fazhi, X., 2020. Adsorptive removal of anionic dyes by graphene impregnated with MnO_2 from aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 595,124667.

Zhang, C., Lin, J., Jia, X., & Peng, B. (2016). A salt-free and chromium discharge minimizing tanning technology: the novel cleaner integrated chrome tanning process. Journal of cleaner production, 112, 1055-1063.