

REMOVAL OF SAFRANIN FROM THE ENVIRONMENT BY USING GRAPHENE OXIDE PAPER

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To create interspace-enlarged and sites-exposed graphene-based adsorbents for pollutant management, two-dimensional macrostructures were facilely constructed via self-assembly of two-dimensional graphene oxide nanosheets (2D GO). The flexible, free-standing GO paper was prepared by vacuum filtration of GO dispersion. GO composite paper was characterized by using Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. GO paper was used as adsorbents for safranin. After the adsorption of safranin on GO paper, it has been observed that the surface structure is very compact. Moreover, it was determined that with the penetration of safranin between the GO layers, the distances between the plates increased. The FTIR spectrum obtained after safranin is adsorbed on the GO, in addition to the vibration peaks of GO, the peaks corresponding to the C=N vibration in the phenazine ring occurred new peaks at around 1900 cm^{-1} . XPS spectrum of the GO paper before safranin adsorption revealed C (1s) and O (1s) peaks, while that after adsorption exhibited the N (1s) peak beside the C (1s) and O (1s) peaks. Raman measurements were also performed to determine the microstructure of GO paper before and after safranin adsorption. GO paper displays two peaks at 1345 and 1650 cm^{-1} , corresponding to the well-documented D and G bands, respectively. The intensity ratios of the D and G bands (I_D/I_G) are calculated to determine the surface defects of graphene-based paper I_D/I_G for the safranin absorbed GO paper (0.75) decreases in comparison with that of the GO paper (0.92), confirming the adsorption of safranin species to disordered regions of GO surface. This composite paper exhibited superior adsorption capabilities for safranin (8.1 mg cm^{-2}). The adsorption capacity of GO paper for safranin is higher than other two-dimensional conventional adsorbents reported; this can be attributed to electrostatic attraction and π - π interactions between GO and safranin. We propose a super graphene-based adsorbent that is competitive and scalable for water purification.



INTRODUCTION

Water pollution is threatening all living organisms in the world. The main source of this problem is the indifference of companies that have factories contributing to the dye sector. Since they need to use dyes for coloring, they are polluting rivers, oceans, and lakes with their wastewaters. The effluents from textile plants contain portions of dyes, which are deeply colored, multicomponent,

and low biodegradable, and have become one of the most serious pollutants in water.¹ For example, most dyes have high tinctorial values, and less than 1 ppm of the dye produces an obvious coloration in water. Many methods have been developed for the removal of dyes, including adsorption, chemical coagulation, photodegradation, biodegradation, active sludge, etc.² Among them, adsorption on carbon-based materials is one of the most efficient processes for dye removal and decoloration,

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because of large specific surface areas, chemical inertness, and good mechanical stability of carbon.³ There has been an increasingly large amount of literature devoted to the study of adsorption for the removal of aqueous-organic species using graphene oxide (GO) layers.⁴ Paper-like GO-based materials usually emerged as adsorbents, are widely used in the preparation of composite materials with different structural and functional properties.⁵ Compared to other paper-like materials, the most common features of GO papers are their superior flexibility, high mechanical performance, and high adsorption capacity due to hydrophilic GO layers. These flexible materials provide the convenience of utilization in many applications due to possessing shapeable, cuttable, and rollable features.^{6,7} One of the most dangerous dyes is safranin. Safranin is a red dye matter, and its formula is $C_{20}H_{19}N_4Cl$. Safranin is used in the textile, cosmetic, and paper industries. It affects the structure of bacteria, so it may disrupt beneficial bacteria, too. Thus, it causes sustainability problems for the environment.^{8,9}

In this study, GO was synthesized by the modified Hummers method and its aqueous dispersion was prepared. GO dispersion was then vacuum filtered through the membrane. A free-standing GO paper was obtained and investigated through various spectroscopic techniques. The as-prepared composite paper was further used for the removal of safranin basic dye from aqueous solutions by adsorption. The results revealed that GO paper exhibits excellent adsorption toward safranin, which should be a promising candidate for efficient adsorbents in water purification.

MATERIAL AND METHOD

1. Synthesis of GO

GO was synthesized from natural graphite powder by the modified Hummers method.^{10,11} 12.5 mL of concentrated H_2SO_4 was first heated to $90^\circ C$. 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5 were added with stirring over hot concentrated acid and allowed to dissolve at $80^\circ C$. 3 g of graphite powder (325 mesh) was slowly added to this mixture. After the resulting bubble product precipitated, the mixture was left at $80^\circ C$ for 5 hours. The mixture was cooled to room temperature and diluted to 500 mL with water and left overnight. Then, the mixture was filtered and

rinsed several times with water to remove the residual chemicals. The product was dried at room temperature overnight. The product obtained after the pre-oxidation treatment was added to 115 mL of concentrated H_2SO_4 solution at $0^\circ C$. Then, 15 g $KMnO_4$ was gradually added to the mixture under stirring and cooling in an ice bath. The mixture was stirred at $35^\circ C$ for 2 h, and then it was diluted with 250 mL of water. The addition of water was carried out in an ice bath to keep the temperature below $50^\circ C$. Then 250 mL of water was added to the final mixture. The color of the mixture changed from dark brown to yellow with the addition of 20 mL H_2O_2 and it was left overnight at room temperature. The mixture was filtered and washed with 1:10 aqueous HCl solution. The resulting product was dried under atmospheric conditions and dialyzed for 3 weeks to remove any metal ions. The dispersion was filtrated after dialysis and 500 mg of solid graphite oxide was dispersed in 500 mL of ultra-pure water with ultrasonication treatment for 5 h. This homogeneous GO aqueous dispersion (1.0 mg mL^{-1}) was stable for several months.

2. Preparation of GO paper

80 mL GO (1.0 mg mL^{-1}). Flexible GO paper was fabricated by vacuum filtration of 80 mL GO (1.0 mg mL^{-1}) suspension through a nuclepore polycarbonate membrane (Whatman; $\varnothing = 47 \text{ mm}$; pore size, $0.2 \mu\text{m}$) using an ultrafiltration vacuum cell (EZ-Stream). After washing with distilled water several times, air-drying, and peeling it from the membrane, obtained free-standing and flexible GO paper.

3. Chemicals

All the chemicals were of analytical reagent grade, purchased from Sigma-Aldrich, and used without any further purification. Double distilled water was used throughout the experiments.

4. Apparatus

Raman spectra were tested by a micro-Raman spectrometer (WITech alpha 300R) at room temperature. Powder X-Ray diffraction (XRD) was carried out using a Rigaku TTR III X-ray diffractometer equipped with monochromatized $Cu \text{ K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). X-ray photoelectron

spectroscopy (XPS) measurements were performed on a Spect-Flex spectrometer with a standard Al X-ray source. UV-Vis absorption spectra were recorded using a Shimadzu 3101PC UV-Vis-NIR spectrophotometer. The morphology of the GO paper was analyzed by using a scanning electron microscope (SEM, ZEISS SIGMA 300).

5. Dye Adsorption Experiments

Safranin was used to explore the adsorption performance of the obtained GO paper. Safranin was dissolved in deionized water to prepare solutions with the initial concentration of 5×10^{-5} M. GO paper was then added into the aqueous dye solution (20 mL), followed on hold at room temperature until achieving the adsorption equilibrium. The concentration of the dye solution was measured by UV-Vis spectrometry at the maximum absorbance of the dye. The removed quantity of dye (Q_{ep} , mg cm^{-2}) was calculated with the following equation:¹²

$$Q_{ep} = \frac{(C_0 - C_{eq}) \times V}{A}$$

where C_0 (mg L^{-1}) and C_{eq} (mg L^{-1}) is the initial and final (at adsorption equilibrium) concentration of dye solution, respectively. V (L) is the volume of dye solution. A (cm^2) is the cross-sectional area of GO composite paper after drying.

RESULT AND DISCUSSION

The flexible, free-standing GO paper was prepared by vacuum filtration of GO dispersion, which is schematically shown in Figure 1. In addition, it is shown in Figure 1 that GO paper is highly flexible and durable. The chemical structure of safranin, a phenazine derivative cationic dye, and its aqueous solution are shown in Figure 1. In addition, when the chemical structure of saffron is examined, it is seen that it has a π - π conjugate system. The adsorption of safranin by GO paper was applied using a simple absorption technique. GO paper and safranin (5×10^{-5} M) were put in a beaker. GO paper was kept in the safranin solution for 3 days. Eventually, safranin was absorbed by GO paper. Consequently, the color of safranin solution lightened after the applied process as seen

in Figure 1. It has been reported that safranin can adsorb to the surface of GO layers by both π - π interactions and electrostatic interactions.^{13,14}

The photographs of GO paper before and after the adsorption of safranin are presented in Figure 1. When Figure 1 was examined, it was observed that the structure of GO paper, which was quite stable before adsorption, was deformed and ruptured after kept in safranin solution for 3 days. In addition, it was observed that the black color of GO paper changed after the adsorption process and its flexibility decreased and became brittle. Thus, it was concluded that the absorbent prepared was not durable for long-term use.

SEM technique was used for the morphological characterization of GO paper and GO-safranin papers. The GO paper displays the characteristic wrinkle feature that is visible on its surface as shown in Figure 2.¹⁵ In the cross-section view, it is shown that the GO paper structure is formed as a result of the regular stacking of the GO plates (Figure 2).¹⁶ After the adsorption of safranin on GO paper, it has been observed that the surface structure is very compact. Moreover, it was determined that with the penetration of safranin between the GO layers, the distances between the plates increased.

XRD technique is one of the most prevalently used spectroscopic methods for crystal structure analysis. In Figure 3.a, the XRD spectra of GO paper and GO-safranin composite paper are given. The peak at 10.4° with broadband between 20 and 35° , corresponding to the characteristic crystal diffraction of the graphene structure (002) was observed in the XRD spectrum of GO paper (JCPDS card no 4-0783).¹⁷ In XRD data of the GO-safranin paper formed after the application of the adsorption process, the broadband disappeared, proving the attachment of safranin molecules onto GO. However, safranin doesn't have a diffraction peak because it has an amorphous structure.

XPS was performed for the structural characterization of GO paper before and after safranin adsorption (Figure 3.b). XPS spectrum of the GO paper before safranin adsorption revealed C (1s) and O (1s) peaks, while that after adsorption exhibited the N (1s) peak beside the C (1s) and O (1s) peaks. Therefore, it was determined that safranin was successfully added to the paper electrode structure after absorption.

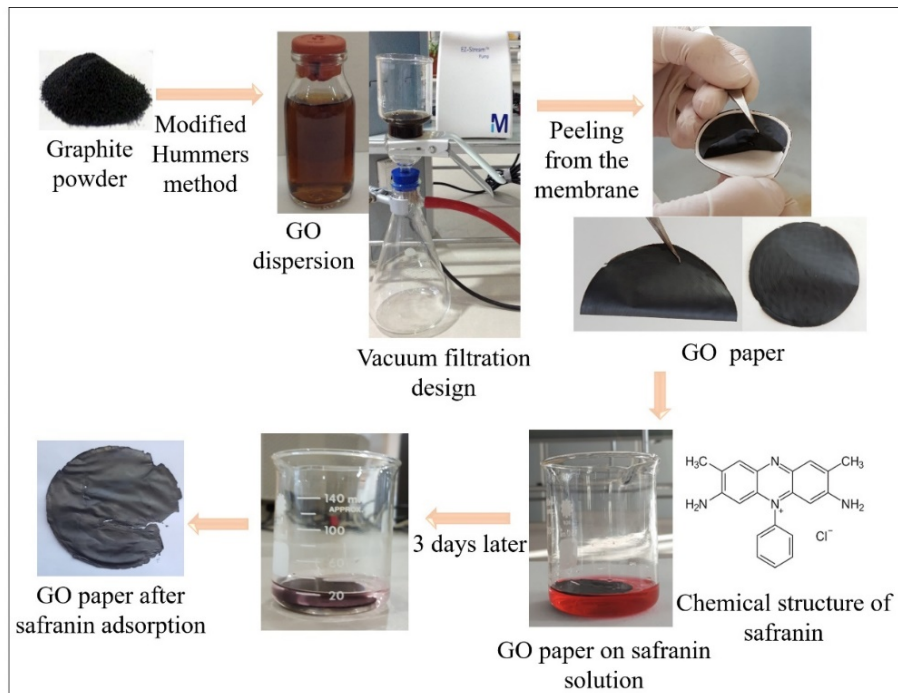


Fig. 1 – Schematic fabrication procedure of the GO paper and adsorption of safranin by GO paper.

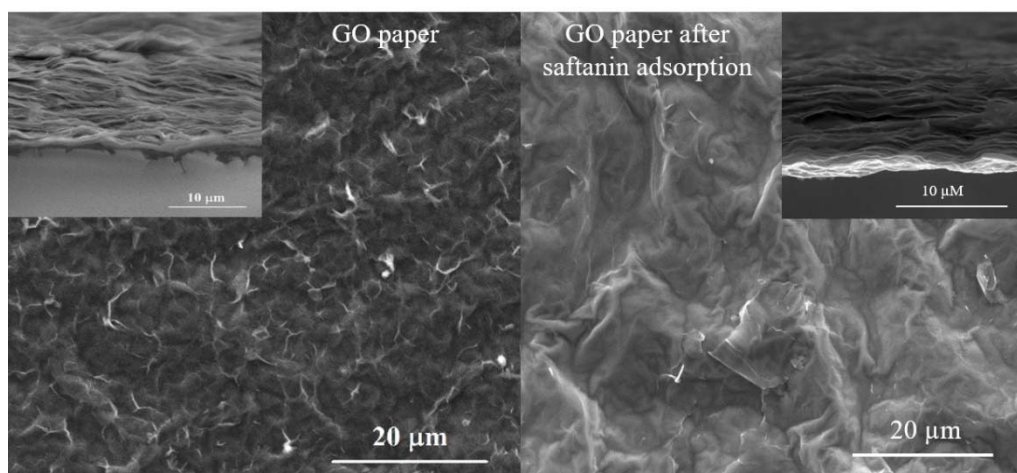


Fig. 2 – Top-view cross-sectional SEM images of GO paper before and after safranin adsorption.

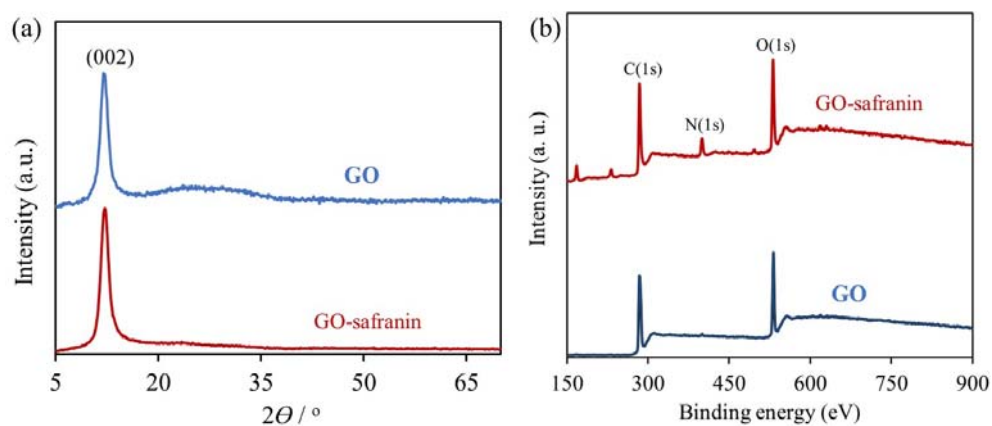


Fig. 3 – (a) XRD, (b) XPS spectra of the GO paper and GO-safranin paper.

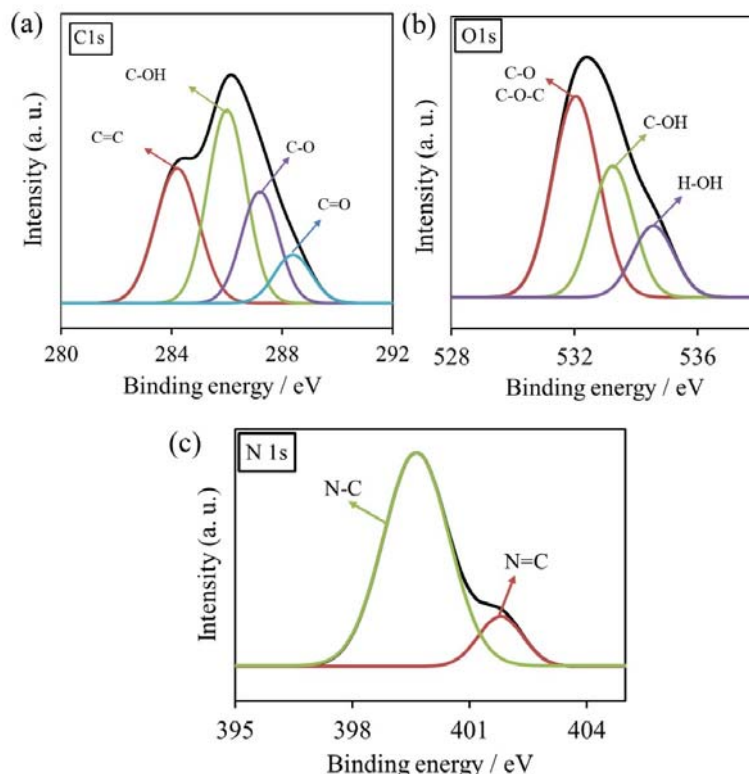


Fig. 4 – XPS spectra of GO-safranin paper, (a) C 1s, (b) O 1s, and (c) N 1s.

The C 1s spectrum of GO-safranin could be deconvoluted into four main peaks with binding energies of 283.7, 286.7, 287.6, and 288.7 eV, which were assigned to C=C, C-OH, C-O, and C=O, respectively (Figure 4.a). In Figure 4.b, O 1s spectrum could be fitted into three peaks at 531.9, 533.2, and 535.3 eV, which could be attributed to C-O-C, C-OH, and H-OH. Figure 4c presents two peaks of N centered at 399.8 eV for the N-C and 401.8 eV for N=C.¹⁸ These results demonstrated that the composite sponge structure was successfully prepared.

Raman measurements (Figure 5.a) were also performed to determine the microstructure of GO paper before and after safranin adsorption. The G band is assigned to the in-plane vibration of sp^2 carbon atoms in a 2D hexagonal lattice, and the D band is related to the vibrations of sp^3 carbon atoms of disordered graphite.¹⁹ GO paper displays two peaks at 1345 and 1650 cm^{-1} , corresponding to the well-documented D and G bands, respectively. For safranin-adsorbed GO paper, these two peaks remain at the same position. The intensity ratios of the D and G bands (I_D/I_G) are calculated to determine the surface defects of graphene-based paper.²⁰ I_D/I_G for the safranin adsorbed GO paper (0.75) decreases in comparison with that of the GO paper (0.92), confirming the adsorption of safranin

species to disordered regions of the GO surface. These results evinced that safranin was successfully adsorbed on GO paper.

The structure of the GO paper was further characterized by FTIR spectroscopy, as shown in Figure 5.b. From the FTIR spectrum of GO paper, it was examined that peaks corresponding to O-H, C=O, C=C, and C-C stretching vibrations occurred at 3500, 1713, 1620, and 1219 cm^{-1} , respectively.²¹ The FTIR spectrum obtained after safranin is adsorbed on the GO, in addition to the vibration peaks of GO, the peaks corresponding to the C=N vibration in the phenazine ring occurred new peaks at around 1900 cm^{-1} .²² Thus, it was identified that a composite structure was formed after absorption.

The UV-vis absorption spectra were obtained depending on the holding time of GO paper in the solution of safranin (20 mL, 5×10^{-5} M). As the holding time increased, it was seen that the intensity of the absorption peak of safranin at 518 nm wavelength decreased. The adsorption capacity of the safranin dye of GO paper (with a surface area of 36 cm^2) within 24 hours was calculated as 8.2 $mg\ cm^{-2}$. UV-visible absorption spectra were used to determine the rate of adsorption of safranin on the surface of GO paper within 3 days. Firstly, the UV-visible absorption spectra obtained for different concentrations of safranin solutions are shown in

Figure 6.a. It was figured out that the peak intensity at 518 nm decreased depending on the reduction in concentration. The calibration curve obtained from absorption spectra is presented in Figure 6.b. To calculate the non-adsorbed amount of safranin, a spectrum of safranin solution after a 3-day treatment with GO paper was also formed and compared with standard solutions to calculate the adsorbed amount

of safranin onto GO paper. (The value obtained from Figure 6.b was subtracted from 5.0×10^{-5} M (starting concentration of safranin solution)). Prepared 36 cm^2 of graphene oxide paper adsorbed 90.28% of safranin from water. Hence, this method can be offered as a beneficial approach for environmental protection against dye factory pollutants.

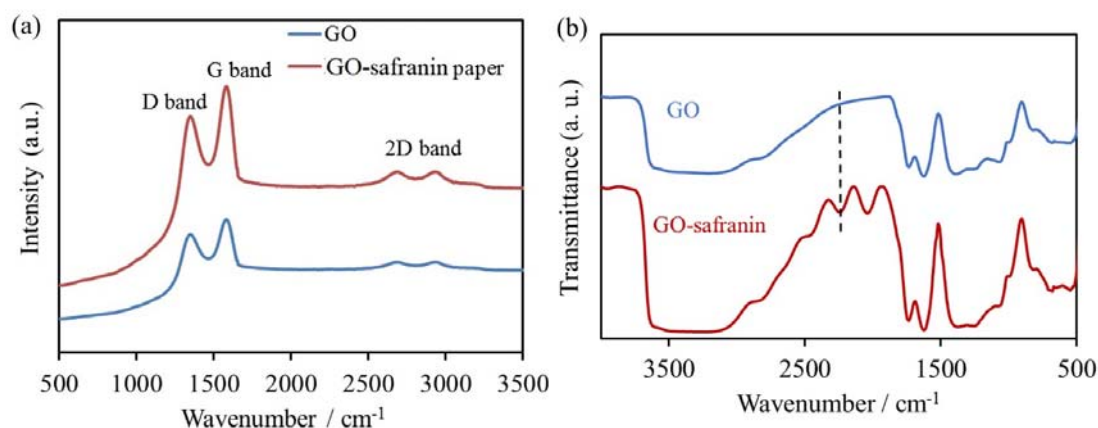


Fig. 5 – (a) Raman, (b) IR spectrum of the GO paper and GO-safranin paper.

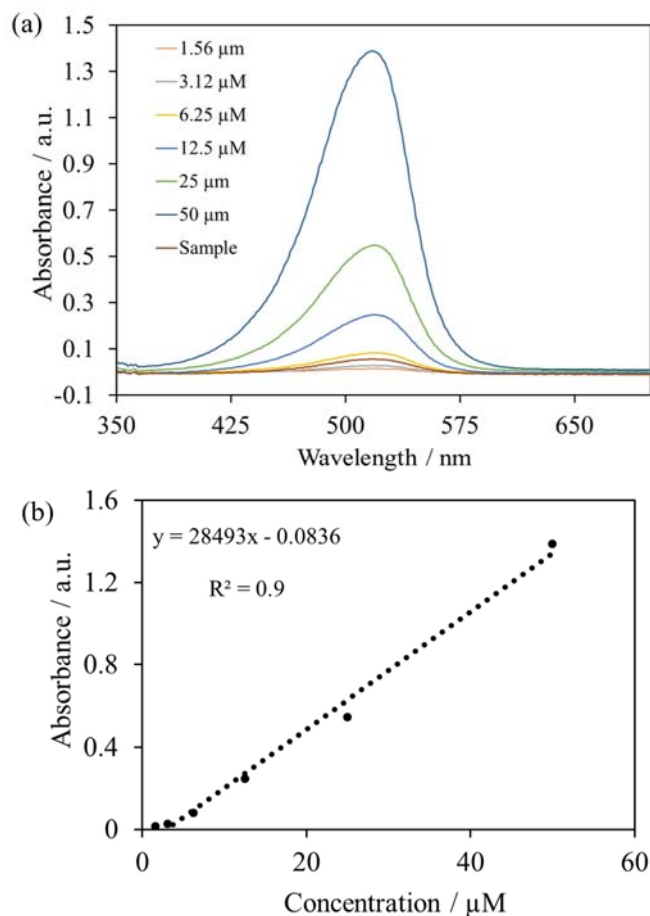


Fig. 6 – UV-visible absorption spectra of standard safranin solution after adsorption process. Inset: Calibration curve of standard safranin solutions.

CONCLUSION

In this paper, flexible free-standing GO paper was fabricated through vacuum filtration. GO paper was used as adsorbents for safranin. The chemical and morphological characterization of the GO and GO-safranin papers were investigated by using various spectroscopic techniques. GO paper exhibited superior adsorption capabilities to emerging pollutants such as safranin (8.1 mg cm^{-2}). In the adsorption of safranin on the GO paper surface, it is determined to be effective due to both electrostatic and π - π interactions. It was observed that the absorption capacity of the GO paper was not very high when compared to previous studies. However, the fact that the GO paper in this study, which is used as an adsorbent, has a block structure that can be easily removed from the solution and does not leave any impurities in the solution, whereas similar studies in literature use nanoparticles like graphene powder which requires an additional effort for disposing the adsorbent from the dye solution. Consequently, the block structure of the GO paper in this study is considered to be the greatest advantage of this method.

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