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Preparation and Characterization of graphene-based keratin nanocomposite as an adsorbent for removal of anionic dye from tannery wastewater

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ABSTRACT

Usable water in the environment is one of the most important natural resources, and anthropogenic contaminants from various sources endanger this usable water. Consequently, extreme tannery dye wastewater is a significant environmental problem due to severe disturbance of aquatic habitat photosynthesis by hampering light penetration into the waterbody. The aim of this study is to fabricate the graphene-keratin nanocomposites for the removal of dye from tannery wastewater. Nanocomposite was prepared using a facile solution casting method and characterized by UV-Vis spectroscopy, and material interactions. The pH effects, adsorbent dosage, and contact time of composite has been studied for process optimization. At pH 8, about 96.3 % dye removal was obtained with $6gL^{-1}$ nanocomposite adsorbent within 240 minutes. Prepared nanocomposite treats tannery wastewater utilizing a tannery solid waste as the keratin powder was prepared using waste hair from tannery. It could have industrial application as a cost-effective adsorbent with an easy preparation process for dye removal from tannery wastewater.

Keywords: Graphene, Nanocomposites, Absorbent, Turbidity, Environment pollution.

1. Introduction

Water pollution has become a severe problem now a days. Many types of pollution exist in the water environment involving organics, microorganisms, metal ions, and others [1]. The tannery industry is one of the most polluting industrial sectors. Tannery effluents carry heavy pollution loads due to a massive presence of highly colored compounds, sodium chloride and sulphate, various organic and inorganic substances, toxic metallic compounds, different types of tanning materials, which are biologically oxidizable, and large quantities of putrefying suspended matter [2]. Among the different types of water pollutants, dye represents a major polluting group. Every year, leather manufacturing industries consume a massive volume of water and generate an equally alarming quantity of dye-rich effluents. In dye washing baths, approximately 10-50% of the dyes used in the dyeing process are lost. Most of them escape conventional wastewater treatment processes and persist in the environment. Dyes are primarily stable due to their complex molecular structure. They do not biodegrade readily and are usually toxic, carcinogenic, mutagenic and stable to temperature, light, and microbial attacks [3]. The presence of dyes, inhibits the aquatic life growth, which is required for self-purification, acute and chronic toxicities and complications in treatment of water by biological methods, on top of that, the azo-structure, can be reduced to aromatic amines that are carcinogenic [4]. Dyes are difficult to treat by the traditionally physicochemical and biological processes. Though several processes are available for dye removal from wastewater, adsorption is popular its simple operation process, high efficiency and cost-effectiveness. Adsorption is used as a top-quality treatment procedure to remove dissolved organic pollutants like dyes from industrial wastewater [5].

Carbon-based materials are widely being used for the dye removal process. Graphene or graphene oxide materials can be used as promising adsorbent materials for the removal of the dye molecule from the wastewater. Graphene is made of a single layer of carbon atoms which are closely packed into honeycomb two-dimensional (2D) lattice [6]. Graphene has emerged as a useful nano-adsorbent for environmental applications because of its high theoretical surface area (~2620 m^2g^{-1}) [7]. Another adsorption mechanism between graphene and dye molecules is the pi–pi interaction. The pi–pi interaction happens between aromatic rings of dyes and graphene structure. [8]. Apart from the conventional mechanisms, hydrophobic interaction is another important contribution to the adsorption of pollutants on graphene adsorbents. It is driven by the entropic effect, originating from excluding the ordered water molecules from non-polar surface (basic or nucleophilic). Hydrophobic interaction is a widely existing interaction between the hydrophobic chains and graphene structure. The hydrophilic pollutants and other hydrophobic pollutants would adsorb into graphene via hydrophobic interaction. Even for the hydrophilic pollutants, if they contain hydrophobic parts, the hydrophobic interaction would happen between the hydrophobic parts and graphene structure, contributing to the whole adsorption interaction. Dye removal is mostly achieved by electrostatic interactions between positively charged amino groups of dye molecules and the negatively charged surface of the adsorbate due to oxygen containing groups, van der Waals forces and pi interactions [9-11].

Large amounts of solid wastes are produced in beam house operations, such as bovine hair, raw trimmings, wet-blue shavings, trimmings, and sludge. Some of the solid wastes such as hair can be used as byproducts or as inputs for other industries. There are two hair removal processes: one with hair destruction and another with total or partial hair preservation. The main problem related to the hair destruction process using high amount of lime and sodium sulphide is the toxicity of these elements and it implies a much higher organic pollution of the wastewater. Environmental damage caused by effluent containing these chemicals includes increased

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pH, BOD, COD, and the generation of the toxic hydrogen sulphide gas. An effective way to reduce the generation of organic waste is to employ hair-saving unhairing technology accompanied by hair recovery as conventional hair-burning process the hair is destroyed and cannot be removed by filtration. The recovery of hair takes place by filtration of the liming wastewater and provides the opportunity for using recovered hair for other purposes [12]. In this work, a nanocomposite was prepared using hair (a leather solid waste) and graphene. In addition, it was investigated for its removal capacity of dye from dye wastewater (containing Orange 2GL, Red GS, Orange II) in aqueous solution. The composite was characterized by FTIR and influences of dose, pH, dilution and reuse on its adsorption capacity were also investigated.

2. Materials and Methods

2.1 Reagents & Chemicals

Commercial sodium sulphide (Na_2S), Sulphuric acid (H_2SO_4), Ethanol, Industrial dye wastewater, Graphene sheet.

2.2 Keratin powder preparation

Hair waste was collected from the leather manufacturing workshop, Department of Leather Engineering, KUET, Bangladesh during the unhairing and liming process. The collected hair sample was washed with distilled water and disrupted with dilute sulfuric acid. Then the disrupted hair sample was washed with excess water and filtered. The hair residue was dried at 105^0C and then grinded into powder form.

2.3 Nanocomposites with respect to weight ratio of graphene and hair

Four composites with four different ratios of graphene and hair powder were prepared. This way we were able to deduct which composite would work more efficiently and moreover less time consuming. Before adding them with ethanol solution we fixed the amount of hair powder and varied the amount of graphene to be used in preparing the nanocomposites. The mixture ratios adopted to develop the nanocomposite are tabulated below:

Table 1 Composite with respect to weight ratio of graphene and hair.

Sample composite (g)	Amount of Graphene oxide (g)	Amount of hair powder (g)	Volume of ethanol (ml)
GH_1	0.05	1	50
GH_2	0.10	1	50
GH_3	0.15	1	50
GH_4	0.00	1	50

2.4 Graphene-hair nanocomposite preparation

Four samples of the desired composite were developed in accordance with the proposed sample ratios. Graphene was first shredded with a spatula into very small pieces and put into beaker and added 50ml ethanol. Then it was put under ultrasonication for 10 minutes. 1g previously grinded hair powder was added to the ethanol solution and ultrasonicated for another 10 minutes. The mixture was then filtered and dried at 105°C. Thus, the composite was made.

(a) (b)

Fig.1 (a) Graphene sheet and (b) Final Graphene-hair (GH) nanocomposite.

2.5 Treatment process of dye removal with prepared nanocomposites

Dye wastewater from SAF, Noapara, Jessore was collected for the experimentation. The dye was obtained after the top dyeing process. The dye was then diluted 10 times for the treatment process. The dye wastewater obtained from SAF was a mixture of three anionic dyes i.e., Orange 2GL, Red GS and Orange II. Initially the dye was diluted 10 times,

Absorbance of diluted dye at 650nm = 0.054 ads

Fig.2 10 times diluted dye wastewater

Four dye solutions that were previously diluted in accordance with the compatibility of the UV-Vis spectrophotometer were mixed with the four different GH nanocomposites. The mixture was stirred for 30 minutes and let sit for 4 hours where absorbance was checked every hour with UV-Vis Spectroscopy.

The removal percentage was calculated using the data obtained from the UV-Vis spectroscopy. By comparing the percent removal, the optimum dose for the composite and required time was found. The following formula was used for calculating the removal percentage of dye.

Percentage of dye removal:

$$R = \frac{\alpha - \beta}{\alpha} \times 100\%$$

Here,

R = Percentage of dye removal (unit= %)
α = Initial absorbance of treated wastewater
β = Final absorbance of untreated wastewater
The chosen composite with optimum graphene and hair ratio was then investigated for the effect of pH, dose, dilution and reuse.

3. Results and Discussion

3.1 Composite with optimum graphene & hair ratio determination

GH1, GH2, GH3, GH4 composites were compared based on % removal of dye from the solutions and GH_1 composite showed most promising results among all within 4 hours.

Table 2 % Removal with time Using GH_1 sample

Sample	Time (hours)	Absorbance	%Removal
GH_1	1	0.036	33.33
	2	0.011	81.48
	3	0.003	94.44
	4	0.002	96.30

Table 3 % Removal with time Using GH_2 sample

Sample	Time (hours)	Absorbance	%Removal
GH_2	1	0.018	66.67
	2	0.011	79.63
	3	0.009	83.33
	4	0.009	83.33

Table 4 % Removal with time Using GH_3 sample

Sample	Time (hours)	Absorbance	%Removal
GH_3	1	0.015	72.22
	2	0.015	72.22
	3	0.009	83.33
	4	0.004	92.59

Table 5 % Removal with time Using GH_4 sample

Sample	Time (hours)	Absorbance	%Removal
GH_4	1	0.032	40.74
	2	0.021	62.96
	3	0.014	74.07
	4	0.009	83.33

As sample GH_1 showed extraordinary results in turbidity removal it was used for further experimentations.

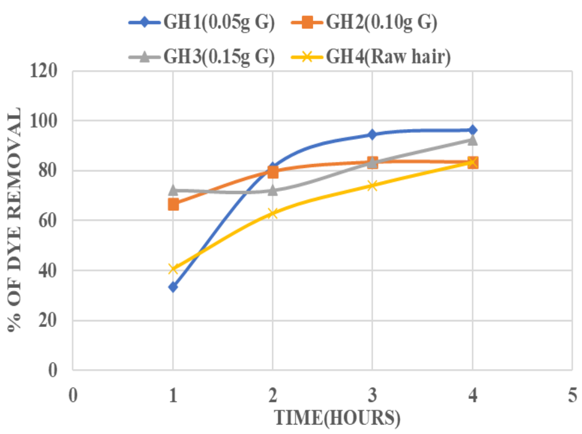

Fig.3 Effect of composite with respect to weight ratio of graphene and hair on dye removal.

3.2 FTIR analysis of the composite

In Fig 3.2.1, form the FTIR spectra it was evident that, the peaks in the graphs for keratin powder and GH_1 composites are very different and around the range of 1800-1785 cm^{-1} and 995-985 cm^{-1} there is similarity in peaks in both graphs. Here the peak at 1800-1730 cm^{-1} represents C=O moiety of –COOH groups and 995-985 represents strong C=C bond bending.

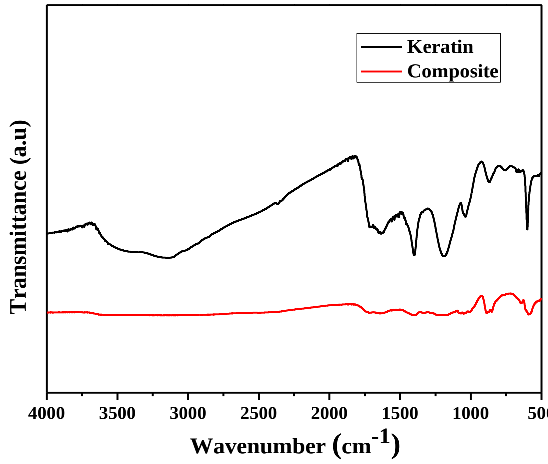

Fig.4 FTIR analysis of Keratin powder and Graphene based goat hair composite.

3.3 Effect of pH on dye removal

The initial pH of diluted dye wastewater was 4.7 and the absorbance measured was 0.054. To determine the optimum pH for the composite to remove dye four different pH 5,6,7,8 dye samples (10 times diluted) were prepared. The pH was adjusted using 1N NaOH solution and dilute HCl solution. Then 0.5g GH_1 composite was mixed to each breaker containing 100 ml dye solution. The solutions were stirred for 30 minutes. Then checked the absorbance every 60 minutes interval for 4 hours. And at pH 8 the absorbance was the most.

Table 6 Effect of pH on dye removal

pH	Absorbance at 650nm	% Removal
5	0.006	88.89
6	0.018	66.67
7	0.012	77.78
8	0.002	96.30

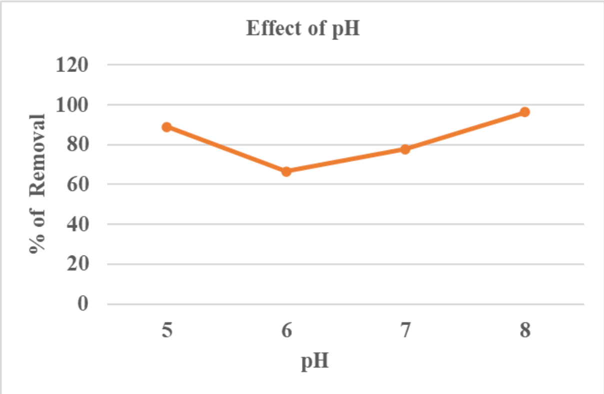

Fig.5 Effect of pH on dye removal

3.4 Effect of Dose on dye removal

After the pH of the waste water was adjusted to previously found optimum 8 by adding 1N NaOH. For this experiment 50ml 10 times diluted dye with an absorbency of 0.054 abs was taken in 4 beakers. After that 0.2, 0.3, 0.4, 0.5g GH_1 sample was added to the 4 beakers and stirred continuously for 30 minutes and let it rest for an hour. Then it was filtered and put through UV-Vis spectroscopy to check absorbency. 0.3g for 50ml dye waste water showed the best results.

Table 7 Effect of GH_1 dose on dye removal

Dose	Absorbance at 650nm	% Removal
0.2	0.008	85.19
0.3	0.004	92.59
0.4	0.009	83.33
0.5	0.018	66.67

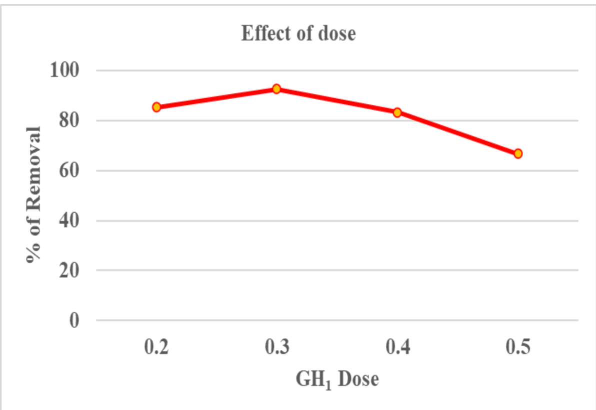

Fig.6 Effect of dose on dye removal

3.5 Effect of dilution on removal of dye

Among the 4 different dilutions of 0 times,5 times,10 times, 20 times were taken for experiment. 10 times and 20 times dilution showed the best results. Although 20 times diluted sample showed a bit better result than 10 times diluted dye waste water sample, 10 times diluted dye had more dye in it and to conserve more water 10 times dilution was taken as optimum.

Table 8 Effect of dilution on dye removal

Dilution	Absorbance at 650nm	% Removal
0	0.055	20.29
5	0.031	49.18
10	0.007	87.04
20	0.005	88.37

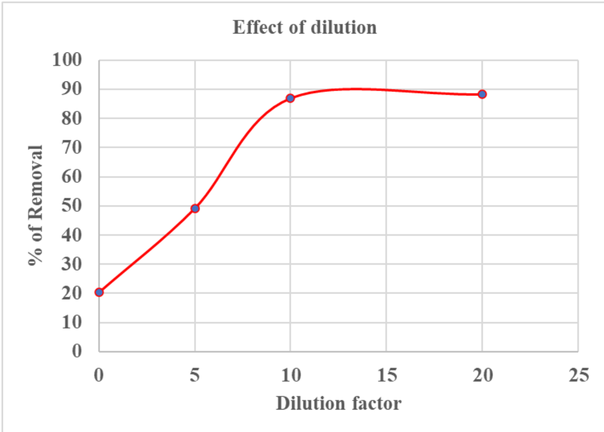

Fig.7 Effect of dilution on dye removal

3.6 Reuse of GH_1 sample

The GH_1 sample already used to treat was collected after treatment and dried to reuse. Then the used GH_1 sample was checked for its reuse ability. Initial absorbance of 10 times diluted dye before treatment was 0.054 and final absorbance after treatment with used GH_1 was 0.012. So, percentage of dye removal was 77.78%.

4. Conclusion

This graphene-based nanocomposite showed far reached performance in terms of treating anionic dye waste liquor. The nanocomposite GH_1 performed best within 4 hours at pH 8 in dose $6gL^{-1}$ and eventually removed 96.3% dye from the wastewater. This adsorbent might have the potential to become the future of wastewater treatment technology. It has successful proven to satisfy two major grounds. Firstly, the utilization of hair as a system of waste management. Secondly, the treatment of direct industrial dye wastewater as an innovation for environmental science. Graphene-hair nanocomposite showed promising results as an adsorbent and we believe it might open up an entire new and wide spectrum of researches in the field of material science and other domains of engineering.

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NOMENCLATURE

BOD : Biological Oxygen Demand
COD : Chemical Oxygen Demand
GH : Graphene-Hair
pH : Potential of hydrogen
FTIR: Fourier -transform infrared spectroscopy