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Understanding the adsorption property of graphene-oxide with different degrees of oxidation levels

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ABSTRACT

In this paper, we report the systematic removal of synthetic dye compound from aqueous solution using graphene-oxide (GO) nanostructures as an adsorbent. The various levels of oxidized GO were used in this study and their results were systematically compared. Highly oxidized GO revealed superior adsorption capacity than the GO with lower degree of oxidization. In highly oxidized GO, the presence of more hydrophilic (sp^3 hybridization) functional groups enhanced the dye adsorption. At ambient atmospheric condition, the adsorption rates were increased with respect to the oxidation rate of GO which is due to its increase in negative charge molecules in the hydrophilic functional groups. The adsorption property of GO was investigated by gradually varying the pH of solution, temperature and reaction time. Thermodynamic parameters were also calculated using Van't Hoff plot. The value of Gibbs free energy was found to be negative as the adsorption reaction was spontaneous. The positive value of ΔH indicates that the adsorption process of all GO samples is purely based on an endothermic process. The adsorbent was characterized by using XRD and the functional groups in GO were characterized by using an FTIR spectrometer. Our results show a very simple and cost effective procedure for removing the toxic and carcinogenic dyes from the waste water and their applications.

1. Introduction

Synthetic dye stuff wastage has been highly harmful and toxic for humans as well as the environment [1]. Every year synthetic dye stuff usage has been rapidly increasing in the industry. More than 20% of dye effluent has been released to rivers or land, resulting in more number of problems [2]. The synthetic dyes were produced from harmful chemicals which encompass non-biodegradable aromatic functional groups [3]. Hence a cost effective and short time process is highly required to handle this problem. Ozonation, electrochemical oxidation, photo-Fenton, semiconductor photocatalysis, chlorination, reverse osmosis, anaerobic process and nano-filtration are some of the processes reported until now [4–7]. Hence out of these methods, adsorption is one of the simple and cost effective methods for removing dye wastage from waste water [8].

Carbon family materials are known for their tremendous adsorption capacity due to their high porosity and their electrostatic interaction with adsorbate. Universally activated carbon has been extensively used for adsorption purpose. This carbon family not only eliminates harmful dye, in addition it takes away antibiotics and non-biodegradable chemical compounds similar to phenol [9]. A. Yu et al. reported that graphene-oxide (GO) can successfully remove the radioactive ravage from water [10]. In recent days, carbon nanotubes (CNT), graphene oxide and reduced graphene-oxide (rGO) were used progressively for dye removal processes. Among all, GO has incredible adsorption property attributed to its high surface area and functional groups compared to others.

Graphene and graphene-oxide are used in a bunch of applications since the discovery of graphene. Graphene oxide, a single layer of graphene nanosheets functionalized by several oxygen-containing groups has been synthesized via oxidation of graphite into graphitic oxide followed by exfoliation [11]. GO is the intermediate product and graphene is the final product. A limited number of papers have been reported on GO adsorption by using different structures of GO such as pure GO, exfoliated GO, functionalized GO, GO composites, layered GO, rGO-based hydrogels, rGO and graphene [12–14]. GO has the ability to adsorb non-biodegradable dye compounds like methylene green, methylene violet, orange G, rhodamine B, tetracycline (antibiotics), chromium, Cu^{2+}, bis-phenol and acridine orange [15–20]. Excellent adsorption was observed in GO from all of the above reports. This remarkable adsorption was achieved owing to its high surface area and π–π interaction on the surface of GO. The toxic biphenyl compound was removed due to the hydrogen bonding of graphene [21]. Compared to graphene, GO has some striking properties such as hydrophilic nature, negative charge molecule and so on.

Synthesis of bulk amount of activated carbon is very costly; moreover sometimes activated carbon shows minimum adsorption property.

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In CNT, the adsorption equilibrium was achieved within 1 h; on contrary in GO the equilibrium was reached spontaneously owing to π–π stacking. S.T. Yang et al. reported about the needs of systematic kinetic data and it is highly necessary in order to improve the efficacy of dye removal [15]. Still some issues are unresolved pertaining to GO adsorption process. Therefore, we attempted to understand the adsorption of GO by varying the degree of oxidization gradually while preparing GO. Consequently the effect of functional groups in the adsorption of dye was studied using GO with various oxidation levels. So in this vision the binding site between GO and dye molecules was studied using MB as model dye with different pH and temperature. Kinetic data are also given in this report.

2. Experimental

2.1. Materials and methods

Expandable graphite powder of size lesser than 25 μm, MB and 30% of H_2O_2 were procured from Rankem Chemicals (India). All reactions were carried out using double distilled deionized (DD) water. Structural characterization of the prepared adsorbate was performed with powder X-ray Diffractometer system (X-6000 Shimadzu). The functional groups in GO were analyzed by an FTIR spectrometer [model Nicolet-6700]. The UV–vis spectroscopy measurements were done using a spectrophotometer (JASCO V-60). Adsorption activity was carried out by using the model dye MB ($C_{14}H_{14}N_3SO_3Na$).

2.2. Synthesis of graphene oxide with different degrees of oxidation level

The different degrees of oxidized GO were synthesized by using modified Hummers method [22,23]. Expandable graphite powder (2 g) was used as starting material. The same was stirred in 50 ml of concentrated hydrochloric acid in a 500 ml beaker for 30 min and 2 g of $KMnO_4$. The solution was then stirred for another 5 to 8 h and 90 ml of DD water was added to it. Then the reaction was terminated by the addition of 5 ml of H_2O_2 (30%) solution. The obtained GO was washed using 5% HCl aqueous solution and was followed by repeated washing with deionized water until the pH of the solution reaches neutral. After that 160 ml of DD water was added which results in the formation of precipitate. A uniform suspension of GO was obtained after sonication. Similar process was followed for GO with different degrees of oxidation by adding 2 g, 4 g, 6 g and 8 g of $KMnO_4$ and the samples were depicted as G1, G2, G3 and G4 respectively.

Table 1
XRD parameters of GO samples with different degrees of oxidation.

Sample name	Peak position	'*d*' value	FWHM	Intensity
Graphite	26.66	3.34	2.520	108
G1	25.32	4.02	1.983	536
G2	12.92	7.6	1.605	1936
G3	11.64	8.3	1.081	2230
G4	10.41	8.48	1.007	3623

2.3. Adsorption experiment

MB adsorption experiment was carried out in magnetic stirrer at constant rate (500 rpm). 0.5 ml of known concentration of methylene blue (MB) dye solution was taken and mixed with a particular amount of GO. At a regular time interval, 3 ml of dye was taken out from the solution and centrifuged for 5 min at 3500 rpm. Supernatant free

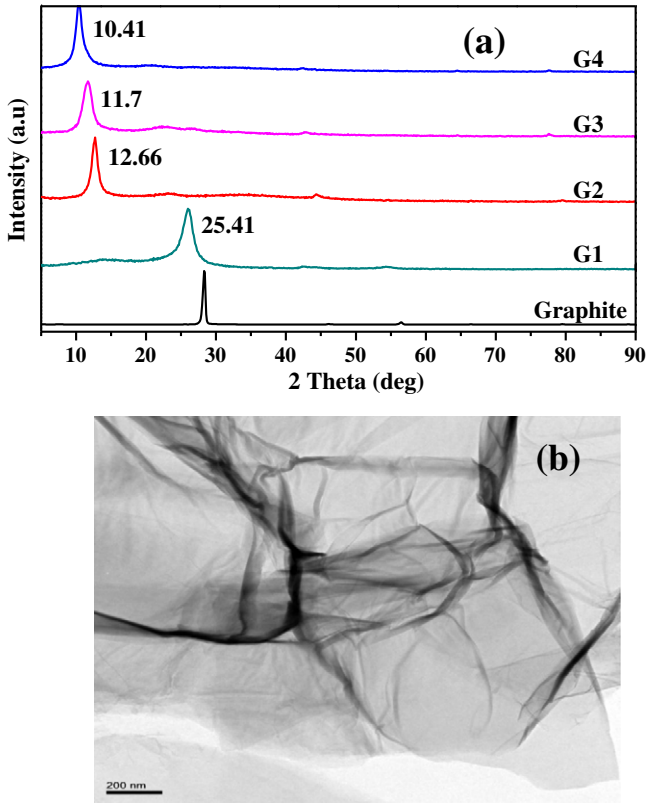

Fig. 1. (a) Powder X-ray diffraction patterns for pristine graphite and GO samples with different degrees of oxidation levels (G1–G4). (b) Transmission electron microscopy image of GO (G4).

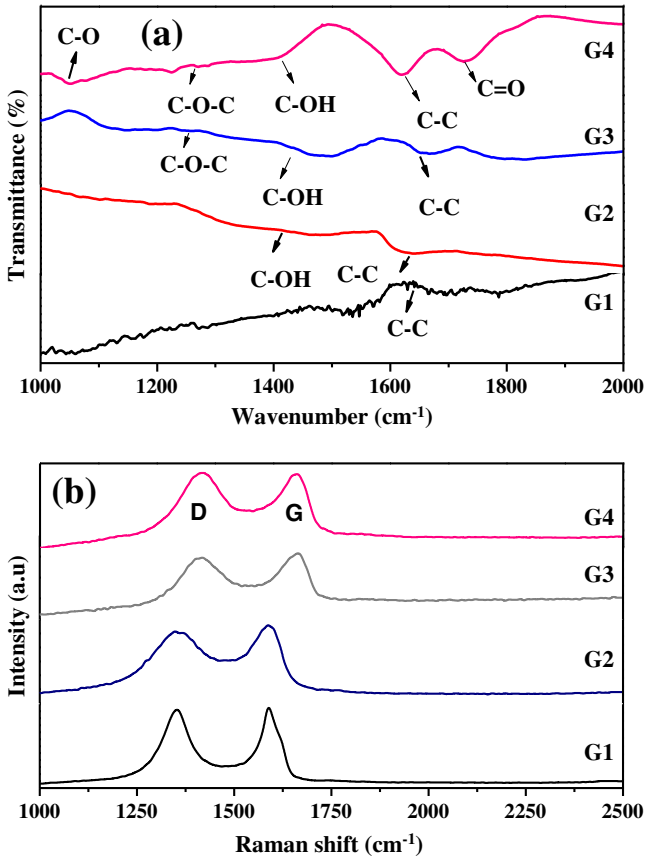

Fig. 2. (a) Fourier transform infrared spectra. (b) Raman spectra of GO samples with different degrees of oxidation levels.