Adsorption of Cr(VI) from aqueous solution on graphene oxide (GO) prepared from graphite: equilibrium, kinetic and thermodynamic studies

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Abstract

The present work demonstrated the removal of hexavalent chromium from aqueous solutions on synthesized graphene oxide (GO) from graphite. The prepared GO was characterized by various analytical techniques such as X-ray diffraction, scanning electron micrograph, Fourier transformed infrared and zero point change. The entire metal adsorption study was conducted through batch mode with keeping constant stirring rate (150 rpm). The operating variables such as pH (2–8), contact time (1–60 min), adsorbent dose (0.005 g–0.01 g L⁻¹) and initial concentration (5–80 µg L⁻¹) were considered, and optimized variables were fixed at maximum percentage of removal. The studied results ascertained that the maximum removal (92.8%) was achieved at acidic pH(4). The equilibrium of Cr(VI) adsorption data was nicely fitted with Langmuir model with maximum adsorption capacity (q_m) 1.222 µg g⁻¹. The sorption kinetics was nicely explained with pseudo-first-order and intraparticle diffusion mechanism. Thermodynamics of Cr(VI) adsorption revealed that the adsorption was spontaneous, endothermic and entropy-driven process. Therefore, it is concluded that graphene oxide could be an effective and efficient alternative toward removal of Cr(VI) from aqueous solution.

Keywords Graphene · Hexavalent chromium · Adsorption · Sorption kinetics · Thermodynamics · Regeneration

Introduction

Rapid growth of industrial development leads to excessive heavy metal load in the environment (Bhattacharya et al. 2019). Many industries including tannery, electroplating, metal extraction, paints and pigments, chrome industries, etc., serve as the excellent source of heavy metals. Among the different toxic metals, chromium is considered as a potent toxic metal. It exists mainly in hexavalent [Cr(VI)] and trivalent [Cr(III)] states in the aquatic body. Hexavalent chromium is almost 1000 times greater toxic than trivalent chromium (Karthik and Meenakshi 2014). However,

different forms of chromium in aquatic medium mainly depend on the pH of the aquatic body. Under acidic pH, chromium exists as negative species such as Cr₂O₄, HCrO₄⁻, Cr₂O₇²⁻, HCr₂O₇⁻. (Khan et al. 2017). In aquatic medium, the chemistry of chromium also revealed that hexavalent chromium Cr(VI) is thermodynamically more stable than trivalent chromium Cr(III) (Dhal et al. 2013) and also Cr(VI) is dynamic and migrated easily from soil to water or vice versa (Zhang et al. 2018), whereas Cr(III) does not show such mobility.

When aquatic body is contaminated with Cr(VI), it causes many health problems such as irritation, dermatitis, vomiting, nausea. Toxicological study revealed that hexavalent chromium may cause mutagenic, carcinogenic and teratogenic effects (Duranoğlu et al. 2012; Alemayehu et al. 2011). Chromium mainly enters in the human body through food, water and even through respiratory system, and it is mainly present as trivalent state [Cr(III)] in the blood and maintains the blood metabolism (Ali et al. 2016). The tolerable limit of Cr(VI) is 50 µg L⁻¹ in potable water; however, 100 µg L⁻¹ is for the inland surface water (Khan et al. 2017). The recommended dose of daily dietary intake (DDI) of chromium is

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50–200 $\mu\text{g day}^{-1}$ (Ali et al. 2016). However, World Health Organization (WHO) stipulated the discharge standard of Cr(VI) into inland is 0.2 mg L^{-1} and drinking water must be below 0.05 mg L^{-1} (Duranoğlu et al. 2012) and as per USEPA, it should be 0.1 mg L^{-1} (Lyu et al. 2017). Therefore, it is imperative that the level of Cr(VI) from contaminated water should be reduced below permissible limit. There are numerous methods available through which Cr(VI) can be removed such as reverse osmosis, electrodialysis, precipitation, ion-exchange, ultrafiltration (Owlad et al. 2009). However, above-mentioned methods have many limitations such as generation of excessive sludge formation and high operational cost. However, the above problems can be overcome by introducing adsorption technique which is very easy to operate, sludge free environment and low cost (Samiey et al. 2014).

Previous studies (Mondal and Nayek 2019; Mondal et al. 2019a) highlighted that many such easily available biosorbents like rice bran, fly ash, spent activated clay, activated rice husk carbon, saw dust, floating macrophytes and magnolia leaf, etc., have been used for removal of Cr(VI) from aqueous medium. However, none of the adsorbent shows excellent performance toward significant Cr(VI) removal efficiency as well as adsorption capacity. Very recently, Mondal et al. (2019b, c; Mondal and Basu 2019) reported that Cr(VI) can be removed by using mosambi peel, chicken feather and human hair. Therefore, more new materials should be developed so that effective Cr(VI) removal can be achieved. Carbon atoms arranged in a systematic hexagonal layer form as when such layer arranged one by one to form graphite and force behind the binding between two layers is Van der Waals force. This special form of carbon is called graphite. It is an allotropic form of carbon. When a single hexagonal layer is separated from graphite, it is known as graphene. Graphite can be converted to graphene oxide which is the functionalized form of graphene. Recently, it is highlighted that graphene and graphene oxide can act as an excellent absorbent for removal of dye (Li et al. 2011a, b) arsenic (Chandra et al. 2010) and fluoride (Li et al. 2011a, b), heavy metals (Deng et al. 2010), from aqueous solutions. Keeping in mind the above fact, the present research is formulated in such a way that graphene oxide can be formed from graphite and the same is used for removal of Cr(VI) from laboratory made solution through batch study with varying initial concentration absorbent dose, contact time, pH and temperature.

Materials and methods

Preparation of Graphene Oxide (GO)

Modified Hummers and Offeman's (1958) method was used for synthesis of GO. Initially, 2.0 g of graphite flakes along with 2.0 g of NaNO_3 and 90 mL concentrated H_2SO_4 were

mixed and kept in ice bath and stirring for 1 h. Then, very slowly 12.0 g KMnO_4 was added an again stirring for next 3.0 h. The entire reaction chamber was kept at less than 15 °C. The mixture was then diluted by adding cold water and temperature maintained at 35 °C with continuous stirring. Then, the mixture was transfer to a reflux system at 98 °C for 10–15 min. After that the temperature was changed to 30°C which resulted in a brown colored solution. Finally, the mixture was treated with H_2O_2 which transformed the color to bright yellow. The brown color solution was added to a beaker containing 200 mL of water and stirred for 1 h. After stirring, the mixture was kept undisturbed for 3–4 h for complete settling. The settled material was repeatedly washed and centrifugation with 10% HCl followed by deionized water until a gel-like substance was obtained. Finally, the material was vacuum dried at 60 °C for 7 h and powders GO was stored in a dry container.

Determination of pHzpc

Zero point charge is a very important parameter for predicting the exact mechanism of adsorption by varying pH of the reaction mixture. In this study, zero point charge was determined by the solid addition method (Mondal 2010). 0.1 M KNO_3 solution was taken in different conical flasks, and pH of the flask was adjusted from 1.0 to 10.0 by using 0.5 N HNO_3 or 0.1 N KOH. Then, 0.5 g of GO was added to each flask which was securely capped immediately and stirred for 48 h. The pH values of the supernatant liquid were noted after 48 h.

Batch experiments

After varying all the operating variables, final solution was treated with 1–5 diphenyl carbazide and purple color was measured by UV-Spectrophotometer. The percentage of removal was calculated by following equation (Eq. 1)

$$\text{Removal(\%)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (1)$$

where C_{initial} and C_{final} are the concentrations of Cr(VI) at the initial and at the end of the adsorption process.

XRD, FTIR and SEM study

Different analytical instruments were used such as scanning electron microscope (SEM) (HITACHI-S-530), Fourier transform infrared spectroscopy (FTIR) (BRUKER, Tensor 27) and X-ray diffraction (XRD) (D500 Siemens (Germany)).

Isotherms, kinetics and thermodynamic study

Equilibrium of Cr(VI) adsorption data fitted with Freundlich, Langmuir and D-R isotherms model. Equilibrium data were analyzed by fitting the data in the linear equations, and constants of different isotherm equations were evaluated. Kinetics of Cr(VI) adsorption onto GO was evaluated by applying linear form of pseudo-first-order, pseudo-second-order and intraparticle diffusions. The thermodynamics of Cr(VI) adsorption was studied through entropy, enthalpy and free energy calculation.

Results and discussion

Characterization of graphene oxide

UV–vis spectroscopy study

After synthesis of GO from graphite, the optical absorption measurements were carried out by UV–visible spectrometric

signature (Fig. 1) that clearly demonstrated the formation of GO which agrees with the literature value (Choi et al. 2010). Figure 1 clearly highlighted that there is a sharp peak at 237 nm which is the results of π – π^* transition of the atomic C–C bond. However, there is a small peak at 300 nm which is perhaps due to π – π^* transition of aromatic carbon–carbon bond as reported by previous researcher (Xu et al. 2013).

Scanning electron microscopy (SEM)

The scanning electron micrograph (Fig. 2a) of graphene oxide indicates a very rough and heterogamous surface structure. However, originally graphene has a layer structure. On fictionalization, GO exhibits a three-dimensional network of randomly oriented sheet-like structures with a wrinkled texture and hierarchical pores with a wide size distribution which may be the preferable sites for heavy metal binding (Liu et al. 2019). After chromium removal, SEM structure of GO showed a more smooth surface (Fig. 2b) which may be due to chromium adsorption on the surface GO. Almost similar reason has been expressed by the earlier

Fig. 1 UV–vis spectrophotometer of GO nanoparticle

Fig. 2 **a** SEM before Cr(VI) adsorption **b** SEM after Cr(VI) adsorption

researcher (Li et al. 2013). Very recently, Janik et al. (2018) reported almost similar type of TEM structure of graphene oxide modified with amino silanes.

X-ray diffraction (XRD) study

The XRD pattern of graphite and graphene oxide is presented in Fig. 3a and b, respectively. The XRD pattern GO was dominated by single broad peak at $2\theta = 25.1$, which correspond to an interlayer distance of 0.84 nm. Almost similar observation was reported by the earlier researchers (Gohel et al. 2017).

Fourier transform infrared spectroscopy (FTIR) study

The intense band at 3296 cm^{-1} attributed the O-H stretching vibration and the bands at 1705 cm^{-1} attributed C=N stretching vibration and the bands at 1043 cm^{-1} signify the skeletal vibrations from unoxidized graphitic domains (Fig. 4a). The band at 1037 cm^{-1} indicates C–O

stretching vibrations. Moreover, other characteristics peaks at 1570 cm^{-1} correspond to the carbon–carbon double bond vibration spectrum of porphyring and the peak at 1043 cm^{-1} possibly due to C–O stretching frequency. On the other hand, another sharp peak was recorded at 1705 cm^{-1} which is corroborated with the C=N stretching frequency of porphyring ring. The disappearance of the peak at 463 cm^{-1} clearly indicates that in graphene oxide C–O functional groups may completely be involved toward binding of chromium (Fig. 4b). Kumar et al. (2013) demonstrated almost similar findings in their research.

Zero point charge (pH_{zpc})

From Figure S1, it was clear that the zero point charge of GO is 2.134. This indicate that at this particular pH, the surface of GO has no net charge. However, above this pH surface of GO behaves as negative surface and below this pH surface behaves as positive surface (Nayak et al. 2017).

Fig. 3 a XRD of graphite b XRD for GO

Fig. 4 a FTIR of GO before Cr(VI) removal b FTIR of GO after Cr(VI) removal

Effect of initial concentration

Adsorption experiments were conducted by varying the initial concentration 5, 10, 20, 40 and 80 mg L⁻¹ to investigate the influence of initial concentration with keeping other conditions constant (Fig. 4). As can be revealed from Figures S2, the removal efficiency decreased with increasing initial concentrations of Cr(VI). This is probably due to quick saturation of limited available adsorbent sites at higher concentration (Dehghani et al. 2015). At lower concentration, the removal of Cr(VI) is maximum due to the ratio of the available surface area of adsorbent to the initial number of moles of Cr(VI) ions that is large (Goharshadi and Moghaddam 2015).

Effect of adsorbent dose

The influence of graphene oxide dose on removal of Cr(VI) at 30 °C is presented in Figure S3. Study results highlight that when adsorbent dose increases from 0.005 to 0.01 g, the removal of Cr(VI) increased from 31.56 to 92.8% (figure S3). However, further increase in adsorbent dose does not favor the Cr(VI) removal. Initially, removal increase with increasing adsorbent dose is probably due to availability of higher adsorption sites (Kan et al. 2017). But further increase in adsorbent dose, covered the available adsorption sites which reduced the effective adsorption (Esposito et al. 2001). Almost similar observation was reported by Dehghani et al. (2015), for removal of Cr(VI) by single- and multi-walled carbon nanotube. They explained that initial increment of Cr(VI) removal is due to the large number of vacant adsorption sites and the greater surface area hence favoring more Cr(VI) ion adsorption.

Effect of pH

pH plays a remarkable role to maintain the overall acidity or alkalinity of the aqueous solution during removal of metal ions through adsorption mechanism (Dehghani et al. 2015). The present investigation was conducted by varying the pH of the solution from pH 2 to 8 (Fig. S4). Study results indicate that at lower pH(4), maximum (92.8%) removal occurred. However, at higher pH(8), percentage of Cr(VI) removal drastically reduced to 18.38% (Fig. S4). This is quite possible, because the surface of graphene oxide is generally covered with functional groups containing oxygen-like epoxy and hydroxyl groups (Samuel et al. 2018). With the increasing pH, the availability of OH⁻ ions concentration increases which competes with Cr(VI) ions (Zhu et al. 2011; Zhang et al. 2013). Therefore, percentage of Cr(VI) removal decreases at higher pH (Parlayici et al. 2015). On the other hand, in highly acidic medium, Cr(VI) exists as oxo-anionic form (Barrera-Díaz et al. 2012; Albadarin et al. 2012). Very recently, Samuel et al. (2019)

reported that hexavalent chromium can be removed at pH 2 by using chitosan-grafted graphene oxide nanocomposite. Cr(VI) ion is mainly available in the form of HCrO₄⁻ at the pH range from 1 to 4 (Liu et al. 2019). However, purely oxo-anion, CrO₄²⁻ will be available in the pH range 4–7 (Yang et al. 2014; Dehghani et al. 2015). On the other hand, the species CrO₄²⁻ that is the main form of Cr(VI) will exist at pH > 7, at that time it is associated with small and tiny concentration of HCrO₄⁻ and H₂CrO₄, respectively (Argum et al. 2007).

Effect of contact time

The present research was conducted for removal of Cr(VI) on graphene oxide as a function of contact time (1–60 min) at a constant temperature 40 °C (Fig. S5). From the figure S5, it is clear that removal efficiency of Cr(VI) ions from aqueous solution increases rapidly up to 40 min. The higher adsorption of initial stages is perhaps due to higher availability of adsorption sites which saturates with progress of adsorption reaction (Goharshadi and Moghaddam 2015).

Effect of temperature

Temperature is one of most crucial factors which directly influence the mobility and transfer of metal ions in aqueous medium (Wang et al. 2019a, b). The effect of temperature was conducted by varying the temperature from 25 to 70 °C (Fig S6). Figure S6 shows that the percentage of Cr(VI) removal increased with increasing temperature. The higher rate of removal at higher temperature may be due to the lower kinetic energy of Cr₂O₇²⁻ at lower temperature. Therefore, the contact between Cr₂O₇²⁻ and active sites of graphene is very weak at low temperature leading to lower removal efficiency. Conversely, at higher temperature, the kinetic energy of the active species Cr₂O₇²⁻ overcomes the attraction potential energy between Cr₂O₇²⁻ and active sites available on graphene (Goharshadi and Moghaddam 2015).

Equilibrium modeling

The equilibrium data of Cr(VI) adsorption on graphene oxide were fitted on various isotherm models. In the present study, three isotherms were used such as Freundlich, Langmuir and D-R models. The linearized form of Langmuir, Freundlich and D-R isotherm equations is expressed in Eqs. 2–4:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$\ln q_e = \ln q_{\max} - \frac{1}{2E^2} * \left[RT \ln \left(1 + \frac{1}{C_e} \right)^2 \right] \quad (4)$$

where q_m is the maximum uptake (mg g^{-1}), q_e the uptake capacity at equilibrium (mg g^{-1}), C_e the equilibrium solution concentration (mg L^{-1}), K_L and K_F are the Langmuir (L mg^{-1}) and Freundlich ($\text{mg g}^{-1}(\text{L mg}^{-1})^{1/n}$) constant, respectively, and ' n ' is the adsorption intensity.

Table 1 depicts the Cr(VI) adsorption by graphene oxide at constant temperature. The output of Langmuir constant (q_m and b) and correlation coefficient (R^2) is presented in Table 1. As can be seen from Table 1, the adsorption isotherm of Cr(VI) exhibited Langmuir behavior, which indicates a monolayer adsorption. The adsorption of Cr(VI) by graphene oxide is well fitted with both Freundlich and Langmuir models; therefore, the Langmuir–Freundlich equation was also applied to test the entire data sets.

Adsorption kinetics

To predict the kinetics of Cr(VI) adsorption by graphene oxide, pseudo-first-order, pseudo-second-order (HO and McKay 1999) and intraparticle diffusion kinetics models were used to check the fittings of the equilibrium data (Table 2). In Table 2, it is clearly revealed that the experimental data nicely fitted with pseudo-first-order kinetic model with R^2 value 0.863. These information highlighted that the adsorption of Cr(VI) on to GO is favorable, and the same is endorsed by the pseudo-second-order equation (Hubbe et al. 2019; Aksu 2001). On the other hand, pseudo-first-order and intraparticle diffusion model are moderately fitted with the experimental data (Table 2). Almost similar observation was reported by Jiang et al. (2011).

Thermodynamics of Cr(VI) adsorption

The sorption of Cr(VI) on the GO was evaluated by the calculation of different thermodynamic parameters such as standard enthalpy (ΔH^0), standard entropy (ΔS^0) and standard free energy (ΔG^0), and these are evaluated by following equations:

Table 2 Summary of parameters for various kinetic models of Cr(VI) adsorption by GO

Kinetic model	Parameters (unit)	Values	R^2
Pseudo-first-order	q_e (mg g^{-1})	12.389	0.863
	K_1 (min^{-1})	3.376×10^{-2}	
Pseudo-second-order	Q_{cal} (mg g^{-1})	0.692	0.780
	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	26.954×10^{-2}	
Intraparticles	K_1 ($\text{min}^{-1/2}$)	3.344	0.812
	C	0.812	

$$\Delta G^0 = -RT \ln K_c \quad (5)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where K_c is obtained from the ratio of the concentration of Cr(VI) in the solid and liquid phases. R is the gas constant, and T is the temperature. Results revealed that initially adsorption of Cr(VI) decreases with increasing temperature which is again reflected from the variation of initial free energy change (Table 3). However, at intermediate temperature (333 K), free energy change is maximum ($\Delta G = -3586.05 \text{ kJ mol}^{-1}$) that means the adsorption is thermodynamically favorable at this temperature. Mondal et al. (2017) also reported such temperature dependence Cr(VI) adsorption by *Aspergillus niger* biomass. Very recently, Arslan et al. (2019) highlighted that magnetic particle-loaded micro-sized chitinous egg shells can remove Cr(VI) from aqueous solution.

Comparison of GO with other adsorbents for Cr(VI) adsorption

Hexavalent chromium adsorption capacity is usually determined by Langmuir and Freundlich adsorption isotherms, and it is normally reported as mg g^{-1} . It is noted that Cr(VI) adsorbed onto other materials has been reported in the literature. Previous literature demonstrated that various materials such as modified groundnut hull (Oswalude and Tella 2016);

Table 1 Isotherm data for adsorption of Cr(VI) by GO

Adsorption isotherm	Parameters (unit)	Values	R^2
Langmuir isotherm	$q_{\max}$ (mg g^{-1})	1.222	0.981
	K_L (L mg^{-1})	1.305	
Freundlich isotherm	K_F ($\text{mg g}^{-1}(\text{L mg}^{-1})^{1/n}$)	3.625	0.899
	n	12.195	
D-R isotherm	$q_{\max}$	244.04	0.794
	E (kJ mol^{-1})		

Table 3 Thermodynamic parameters for adsorption of Cr(VI) adsorption by GO

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})
298	− 771.407	+ 172.32	+ 57.44
303	− 284.504		
323	− 968.688		
333	− 3586.05		
343	− 1198.432		

carbon from mango kernel (Rai et al. 2016); chitosan micro-/nano-particles (Dima et al. 2015); osage orange (Pehlivan et al. 2012) have been used for removal of Cr(VI) from aqueous solution. In this study, a comparison of adsorption capacity of different adsorbents with GO is presented in Table 4. From Table 4, it is clear that very high adsorption capacity was recorded for GO, whereas adsorbents like fly ash, bentonite clay, calcined bauxite, etc., show moderate and clarified sludge, TiO₂, biochar, etc., (Rajapaksha et al. 2018) exhibited low level of adsorption capacity. The present adsorbent (GO) shows low level of adsorption capacity, and it is better than fly ash and bentonite clay adsorbents.

Regeneration study

The performance of exhausted adsorbent and their subsequent use can be done through regeneration process (Wang et al. 2019a, b). The regeneration experiment was conducted by 0.1 (N) NaOH solutions. Experimental results revealed that desorption of Cr(VI) from the surface of the exhausted adsorbents is very difficult. The regeneration experimental results revealed that maximum 56.20% desorption was achieved (Figure not provided). However, the above results are one cycle regeneration with very short span of time (30 min). Almost similar regeneration status of graphene oxide/polyamidoamine dendrimers by using 0.5 M NaOH was reported by Liu et al. (2019) after one cycle. Therefore, it is strongly recommended that for achieving higher level

of regeneration both duration and multi-cycling regeneration should be done. Previous research (Han et al. 2019) highlighted that GO-related adsorbent can be regenerated by using 0.5 M NaOH or HCl solution also.

Conclusion

From the present study, it can be concluded that stable graphene oxide (GO) can be prepared from graphite under laboratory condition which again proved from spectroscopic study. Study outcome also demonstrated that GO has enough potentiality toward capture of Cr(VI) from aqueous medium. Isotherm study revealed that the adsorption Cr(VI) onto GO is dominated by monolayer adsorption with adsorption capacity 1.222 mg g⁻¹ under acidic condition (pH 4). In addition, the kinetics of Cr(VI) adsorption clearly revealed that the pseudo-second-order kinetic model accurately described the kinetic adsorption process. The kinetics of hexavalent chromium adsorption is followed pseudo-first-order kinetics and intraparticle diffusion mechanism. The thermodynamic study suggests the adsorption reaction is endothermic and entry-driven process. Therefore, conversion of graphite to graphene oxide provides a new strategy for the removal of hexavalent chromium from aqueous solutions. However, more research is needed for complete unfolding the versatility of GO and also try to enhance the adsorption capacity.

Table 4 Adsorption capacity of various adsorbents

Name of product	Sorption capacity [$\{(\text{mg g}^{-1})(\text{a})\}$ or $\{(\text{mmol g}^{-1})(\text{c})\}$]	References
Activated alumina	25.57(a)	Bhattacharya et al. (2008)
Aniline–formaldehyde condensate coated silica gel	20.7(a)	Kumar et al. (2007)
Acid-activated clay	83(a)	Arfaoui et al. (2008)
Bentonite clay	0.572(a)	Khan et al. (1995)
Clarified sludge	26.31(a)	Bhattacharya et al. (2008)
Calcined bauxite	2.021(a)	Baral et al. (2007)
Crystalline hydrous titanium oxide	20.00 (a)	Debnath and Ghose (2008)
Chitosan	153.850(a)	Baran et al. (2006)
Fuller's earth	23.58(a)	Bhattacharya et al. (2008)
Fly ash	23.86(a)	Bhattacharya et al. (2008)
Fly ash	0.0005(a)	Rao et al. (2002)
Humic acid	2.75(a)	Ying et al. (2008)
Modified hectorite clays	14.01(c)	Guerra et al. (2009)
Graphene oxide (GO)	106.3(a)	Zhao et al. (2011)
GO	246(a)	Wang et al. (2013)
GO aerogel	29.59(a)	Mi et al. (2012)
Chicken feather	90.91	Mondal et al. (2019c)
Human hair	9.852	Mondal and Basu (2019)
GO	1.222(a)	Present study

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Compliance with ethical standards

Conflict of interest The authors declared that they have no conflict of interest.

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