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Removal of Cadmium Ion from Waste Water Using Carboxylated Nanoporous Graphene (G-COOH)

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ABSTRACT

Carboxylated nanoporous graphene (G-COOH), an excellent adsorbent, were successfully synthesized by an in chemical vapor deposition method and used for the removal of Cd (II) ion from aqueous solution. The synthesized G-COOH were characterized by SEM, XRD and FT-IR techniques. Various operational parameters such as pH, initial Cd (II) ion concentration and contact time in batch systems were investigated on the use of G-COOH. Equilibrium data obtained have been fitted to the Langmuir and Freundlich adsorption isotherms. Langmuir isotherm best fits the experimental results. The sorption kinetics exhibited the best fit to the pseudo-second order equation and the equilibrium followed Langmuir isotherm model. The maximum sorption capacity q_{max} in Langmuir isotherm of Cd (II) ion 3.37 mg/g showed onto G-COOH, Isotherms had also been used to obtain the thermodynamic parameters such ΔG^0 indicates the feasibility and spontaneity of the adsorption process. The positive ΔH^0 suggests the endothermal nature of the adsorption. The positive values of ΔS^0 reflects the affinity of G-COOH towards Cd (II) ion. The results indicated that Cd (II) ion adsorption onto G-COOH composite might be a physical adsorption.

Keywords: ultrasonic assisted removal, Cd (II) ion, carboxylated nanoporous graphene (G-COOH), isotherm, kinetic, thermodynamic

INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders [1, 2]. Long-term effects of Cd (II) in humans such as hypertension, renal dysfunction, lung damage and hepatic injury, diarrhoea, and being teratogenic and short term effects such as vomiting, nausea, and cramps have been reported [3-5]. The maximum permissible concentration of Cd (II) in drinking water is 5 ppb according to the World Health Organization (WHO) [6].

Cadmium is widely used and extremely toxic in relatively low dosages [7]. The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms. The treatment of cadmium contaminated water is similar to that of many metal contaminated effluents. There are several methods to treat the metal contaminated effluent such as precipitation, ion-exchange, adsorption. But the selection of the treatment method is based on the concentration of waste and the cost of treatment [8-11]. In the last few years, application of adsorption is emerged from advantages including simplicity, low cost, high efficiency, adsorption has been shown to be an economically feasible alternative method for removing trace metal from wastewater and water supplies [12, 13].

Recently, magnetic materials are being used because of their fast separation efficiency for investigating decomposition or deformation in chemical processes such as separation, purification [14-16]. Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation. Recently ultrasonic assisted adsorption process has been developed to favor the kinetic of the mass-transfer process of the adsorbate to the adsorbent and to reduce the time required for adsorption [17]. The nature and properties of the adsorbent are of prime importance in this method. In practice, the main requirements for a solid sorbent are: (a) the fast and

quantitative sorption and elution, (b) a high surface area and high capacity, and (c) high dispersibility in liquid samples.

Graphene has recently emerged as an attractive nanosorbent for removal of heavy metal ion owing to its outstanding properties like large surface area, high adsorption capacity, and good chemical and thermal stability. Graphene is a two-dimensional, one atom thick sheet of sp^2 hybridized carbon atoms arranged in a hexagonal lattice. Unlike carbon nanotubes, both sides of the planar sheets of graphene are available for molecule adsorption [18]. Herein, the development of functionalized graphene is recommended. Functionalization may further enhance the selectivity of adsorbent. Recently, nanoporous graphene has been synthesized by chemical vapor deposition (CVD) method and successfully been applied for the sorption of crude oil and hydrocarbons from water with respect to its large specific surface area (410 m^2 g^{-1}), high pore volume (1.17 cm^3g^{-1}), and small pore size [19]. This report studied the adsorption properties of commercially-available carboxylated nanoporous graphene for ultrasonic assisted removal of Cd (II) ion from aqueous samples. All main factors affecting the batch adsorption process were investigated and optimized. From this point of view, it was decided to evaluate the potential usage of carboxylated nanoporous graphene as renewable, inexpensive, green and environmental-friendly absorbent for the competitive and removals of Cd (II) ion. Firstly, the G-COOH was characterized by SEM, XRD and FT-IR. Then the effects of important experimental parameters including effect of aqueous solution pH, contact time, adsorbent concentration and initial dyes concentration were studied and optimized. The carboxylated nanoporous graphene is applicable for the removal of high amount of Cd (II) ion in a very short contact time. The adsorption mechanism was followed by investigation of the kinetics and equilibrium data by different conventional models.

EXPERIMENTAL PROCEDURE

Materials and Instrumentation

The chemical compounds and reagents used in this work were of analytical grade and purchased from Merck (Darmstadt, Germany). The stock solution of Cd (II) were prepared in Cd (II) ion in deionized water. For treatment experiments, the desired concentration of the metal ion were prepared by successive dilution of their stock solution in deionized water. A Shimadzu 6800 Atomic Absorption Spectrophotometer The FTIR spectra were recorded on a Shimadzu FTIR 8000 spectrometer. A Metrohm 780 pH meter was used for monitoring the pH of the solution.

Synthesis and Carboxylation of Nanoporous Graphene

Nanoporous graphene was prepared by special CVD (chemical vapor deposition) method in a catalytic basis [19]. The reaction was carried out at 900–1100 °C for 5–30 min using methane as the carbon source and hydrogen as the carrier gas in a ratio of 4:1. The product was then stirred in 18% HCl solution and washed repeatedly with deionized water until the solution became neutral. The treated product was finally dried in oven at 100°C. For carboxylation process, 1 g of the as-prepared nanoporous grapheme was mixed with a 100 mL mixture of concentrated H2SO4 and HNO3 (3:1 v/v) for 3 h at 60°C in an ultrasonic bath (40 kHz and 100 W). After cooling to room temperature, the reaction mixture was diluted with 500 ml of deionized water and then vacuum-filtered through a filter paper (0.22 μm porosity). This washing operation is repeated until the pH of the filtrate solution became the same as deionized water pH. Finally, the G-COOH was dried in oven at 60°C.

Batch Sorption Study

Batch adsorption experiments were carried out to determine the Cd (II) ion adsorption isotherm onto G-COOH composite and its thermodynamic properties: 100 mL solution having 100 mg/L concentration of Cd (II) ion was prepared and Initial pH of the solution was adjusted with the help of 0.01N HCl / 0.01N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 50 mL solution were taken in ten 250 mL flasks containing fixed adsorbent dose of 10 mg. One of the sample flasks was withdrawn from orbital shaker after fixed time intervals (10 to 240 min) and analyzed for remaining metal ion present in the adsorbate solution. G-COOH was separated from aqueous solution by filtration through Whatman No. 42 filter paper. The concentration of the Cd (II) ion in solution samples were analyzed by using a "Shimadzu 6800 Atomic Absorption Spectrophotometer" equipped with an air-acetylene flame. The metal removal (%A) or removal efficiency of metal ion is evaluated by using the equation:

$$\%A = C_0 - C_t/C0*100 \tag{1}$$

where C_0 and C_e are the initial and final concentration of Cd (II) ion in solution (mg/L), respectively. The amount (mg/g) of Cd (II) ion adsorbed at equilibrium was calculated by using the following equation:
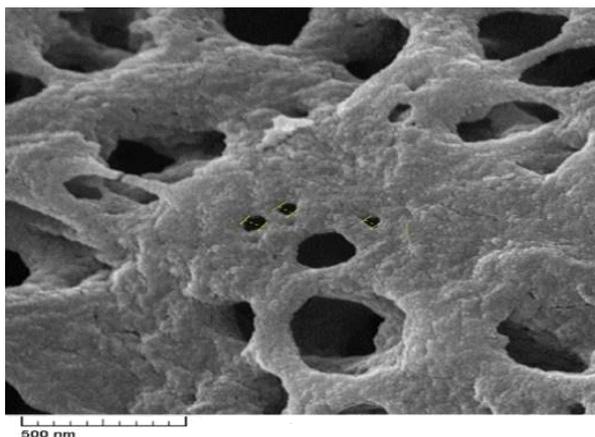
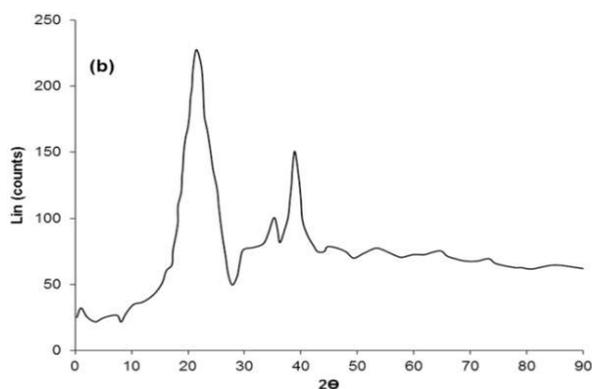**Figure 1.** SEM image of the prepared carboxylated nanoporous graphene (G-COOH)

Figure 2. XRD pattern of the prepared carboxylated nanoporous graphene (G-COOH)
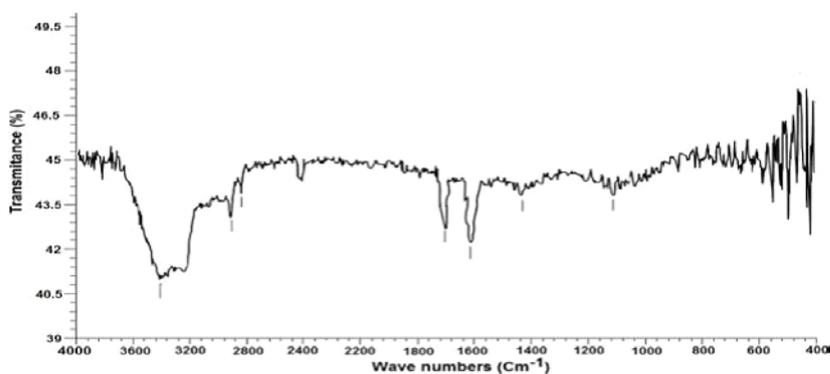

Figure 3. FT-IR transmittance spectrum of the prepared carboxylated nanoporous graphene (G-COOH)

To evaluate the thermodynamic properties of the adsorption process, 10 mg/L of G-COOH composite was added into 100 mL initial Cd (II) ion concentration ranging from 2 to 25 ppm in each experiment. Each solution was shaken continuously for 50 min at 25°C. After the solution reached equilibrium, the Cd (II) ion concentration were measured, and the desorption results were then obtained. Each experiment was carried out in triplicate and the average results are presented in this study.

RESULTS AND DISCUSSION

Characterization of G-COOH

The SEM image of G-COOH (**Figure 1**) illustrates the highly porous structure of this material with pore sizes from 45 to 63 nm. The XRD pattern of the sample is shown in **Figure 2**. G-COOH shows a strong and sharp (002) peak at 2θ=24.26° (corresponding to a d-spacing of 0.35 nm), which is the characteristic peak of graphene [19]. The
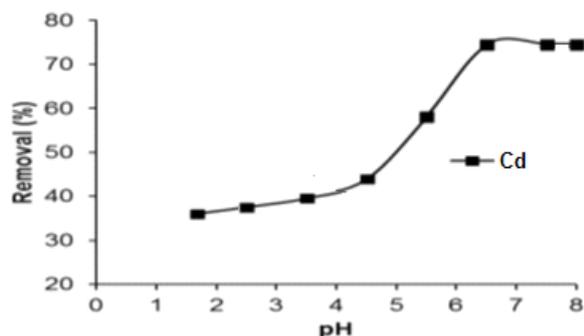
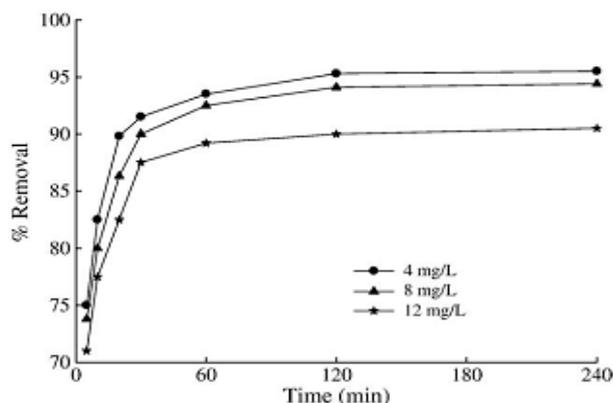**Figure 4.** Effect of solution pH on adsorption of Cd(II) ion onto G-COOH M sorbent 0.1 g; t=30 min; T=293±2 K)

Figure 5. Effects of initial concentration and time on Cd(II) ion adsorption onto G-COOH (G-COOH dose=0.1 g; pH=6.5; T=293±2 K)

further proofs about the functional groups are offered by the following FT-IR analysis (**Figure 3**). The HNO3-H2SO4 treatment produced carboxyl groups on the surface of nanoporous graphene because of oxidation, as indicated by the presence of characteristic peaks at 3430 cm^{-1} and 1725 cm^{-1} for stretching vibration of O–H and C=O of the carboxyl groups, respectively. Also, the peak at 1123 cm^{-1} is corresponded to C–O stretching vibration of the carboxyl/or ether groups. A band at around 1630 cm^{-1} belongs to the stretching mode of the aromatic C=C double bond that forms the skeletal of the graphene sheets.

Effect of pH

The pH of the dye solution plays an important role in the adsorption process because it can alter the surface properties of the adsorbent as well as the degree of ionization of the metal ion. In this study, the influence of pH on adsorption of Cd (II) ion onto the G-COOH surfaces was assessed for pHs of 1.5 to 8.0 and the results are shown in **Figure 4**. As illustrated in **Figure 4**, removal percentage of Cd (II) ion increased as the pH increased from 2 to 6 and then remained constant up to pH=8.0. At low pH values (pH< pHPZC~4.5), solution is strongly acidic and the surface of the sorbent is surrounded by hydrogen ion and due to the competition of protons with metal ion, the removal percentages were low. At higher pH values (pH> pHPZC~4.5), the sorbent surface becomes negatively charged (G-COOH) due to the deprotonation reaction so, the increased removal of Cd (II) ion is due to the strong electrostatic attraction between the sorbent surface and metal ion. Accordingly, pH=6.5 was chosen as the optimal pH for all further studies.

Effects of Initial Concentration and Time

Figure 5 shows the effect of contact time on cadmium adsorption onto G-COOH. One can see that the adsorption is rapid in the initial 30 min of the contact time. Sixty minutes is almost enough to attain equilibrium for the three concentration of Cadmium used in this study. The initial steep adsorption curve suggests that the adsorption occurs rapidly on the surface of G-COOH. The adsorption becomes slow subsequently because of the longer diffusion into the inner cavities in exiguous solution.

Such slow diffusion will cadmium to a slow increase in the adsorption curve at later stages. At low concentration, sufficient adsorption sites are available for adsorption of the Cd (II) ion. Therefore, the fractional
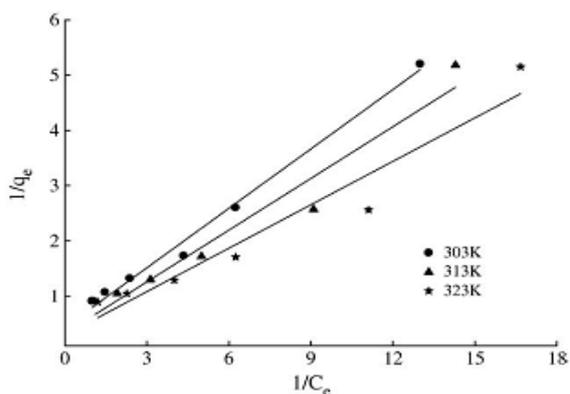
Figure 6. Fitting lines of the Langmuir adsorption isotherms of Cd (II) onto G-COOH at various temperatures (G-COOH dose=0.1 g; pH=6.5)
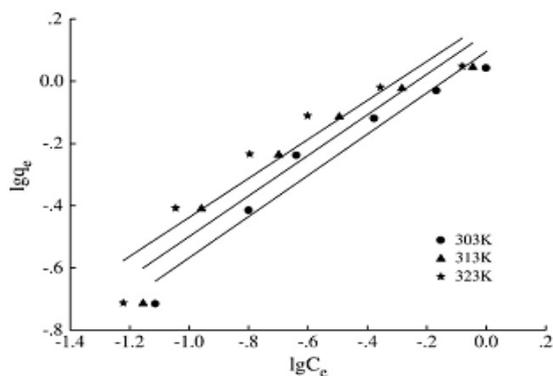

Figure 7. Fitting lines of the Freundlich adsorption isotherms of Cd (II) onto G-COOH at various temperatures (G-COOH dose=0.1 g; pH=6.5)

adsorption was observed to be independent of initial metal ion concentration. However, at higher concentration the numbers of heavy metal ion are relatively higher compared to availability of adsorption sites. Hence the percentage removal of Cd (II) ion depends on the initial metal ion concentration and decreases with an increase in initial metal ion concentration. According to the above results, the shaking time was fixed for 120 min for the rest of the batch experiments to make sure that equilibrium was reached.

3.4. Effect of Biosorbent Dose

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cd (II) ion as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 0.1 g. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction, whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. The maximum biosorption was attained at biosorbent dosage, 0.1 g. Therefore, the optimum biosorbent dosage was taken as 10 g for further experiments. This can be explained by when the biosorbent ratio is small, the active sites for binding metal ion on the surface of G-COOH is less, so the biosorption efficiency is low. As the biosorbent dose increased, more active sites to bind Cd (II) ion, thus it results an increase in the biosorption efficiency until saturation.

Adsorption Isotherms

The equilibrium data obtained for the adsorption of Cd (II) onto G-COOH were fitted to linear Langmuir equation. Linear plot of $1/q_e$ versus $1/C_e$ (**Figure 6**) was examined to determine b and a values. The experimental data were fitted to the Langmuir equation (**Table 1**), and the parameter ($0<R_L> 1$) indicates that the G-COOH is a suitable adsorbent for the adsorption of Cd (II) from aqueous solution. The equilibrium data were fitted to linear Freundlich equation for the adsorption of Cd (II) onto > (**Figure 7**). A fairly satisfactory empirical isotherm can be used for nonideal adsorption because the coefficient of determination (R^2) was 0.9002–0.9546 (**Table 1**). From the linear plot of Freundlich isotherm, K_0 and $1/n$ were found as 1.244–1.546 and 0.6267–0.6621, respectively. The

Table 1. Parameters of Langmuir and Freundlich models

Cd(II) Ion	Langmuir isotherm			Freundlich isotherm		
	a	b	R^2	K^0	1/n	D
303	1.22	2.28	0.9914	1.244	0. 6621	0.9546
313	1.04	3.08	0.9535	1.423	0. 6522	0.9234
323	1.13	3.37	0.9369	1.546	0. 6267	0.9002

Table 2. Parameters calculated using the pseudo-first-order and the pseudo-second-order models for the adsorption of Cd (II) ion on G-COOH

concentration	Pseudo first - order kinetic				Pseudo second-order kinetic			
	qe(exp)	qe(cal)	K_1	R^2	V_0	qe(cal)	K_2	R^2
4 mg/L	0.288	0.069	0.0387	0.9743	0.240	0.386	1.612	1.0000
8 mg/L	0.62	0.149	0.0368	0.9817	0.412	0.762	0.706	1.0000
12 mg/L	0.14	0.169	0.0309	0.8934	0.669	1. 096	0.557	1.0000

values of 0.1<1/n<1 show favorable adsorption of cadmium ion onto G-COOH. The correlation coefficients show that the Langmuir model is better fitted than the Frendlich.

Adsorption Kinetics

To describe the adsorption behavior and rate, the data obtained from adsorption kinetic experiments were evaluated using pseudo-first- and pseudo-second-order reaction rate models. The pseudo-first-order Lagergren equation is given by [20]:

$$(qe-qt)= \log qe - K1t/2.303 \qquad (2)$$

where k1 is the pseudo-first-order rate constant (min-1), *qe* and *qt* are the amount of dye adsorbed (mg g^{-1}) at equilibrium at time *t* (in min), respectively. The pseudo second-order model can be expressed as [21]:

$$t/q_t = t/qe + 1/k_2 q_e^2 \qquad (3)$$

where *k2* (g mg^{-1} min^{-1}) is the rate constant of pseudo second-order adsorption. The rate constants k1 and k2, metal ion adsorbed at equilibrium (qe) and regression coefficient (R^2) obtained from the plots of pseudo-first and second-order rate equation for the adsorption Cd (II) ion onto G-COOH given in **Table 2**. The regression coefficient (R^2) from pseudo second order rate equation for adsorbent are higher when compared to the pseudo first order equation. These results revealed that the kinetics of Cd (II) ion of adsorbent exhibited best fit to the pseudo-second order equation for Cd(II) ion by G-COOH. The linear plots obtained for the pseudo-second order rate equation for Cd(II) ion are given in **Figure 8** and **9**. This means that the rate of the surface adsorption depends on the rate of the chemical adsorption process as the rate-determining step.

Thermodynamic Studies

The thermodynamic parameters, the values of enthalpy, ΔH^0, and entropy, ΔS^0, and Gibbs free energy, ΔG^0, of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic, and spontaneity of the adsorption process. The parameters can be calculated from the binding, ab, obtained from the Langmuir's equation, using the following equation [22]:

$$\Delta G^0 = -RT \ln ab \qquad (5)$$

The ΔH^0 values are calculated from the slopes of the linear variation of lnab versus 1/T (in **Figure 10**):

$$\ln ab = -\frac{\Delta H^0}{RT} + constant \qquad (6)$$

The values of ΔS^0 were calculated from:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \qquad (7)$$

where R (8.3145 Jmol^{-1} K^{-1}) is the ideal gas constant, and T (K) is the temperature. Relevant data calculated from Eqs. (5)–(7) are tabulated in **Table 3**. The adsorption of Cd (II) increases with the increase of temperature and the value of ΔH^0 is positive. The positive ΔH^0 value confirms that the absorption process is endothermic for Cd (II), which is an indication of the existence of a strong interaction between G-COOH and Cd (II). The ΔG^0 for the adsorption process was obtained as −2.58, −3.03 and −3.59 kJ/mol at 303, 313 and 323 K, respectively. The negative ΔG^0 values at different temperatures were due to the fact that the adsorption process is spontaneous. The value of
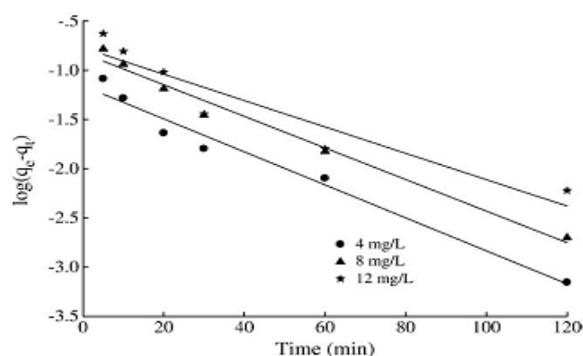
Figure 8. Pseudo-first-order kinetics for adsorption of cadmium onto G-COOH (G-COOH dose=0.1 g; pH=6.5; T=293±2 K)
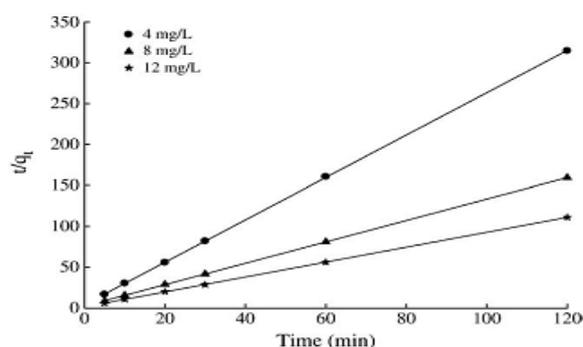

Figure 9. Pseudo-second-order kinetics for adsorption of Cd(II) ion onto G-COOH (G-COOH dose=0.1 g; pH=6.5; T=293±2 K)
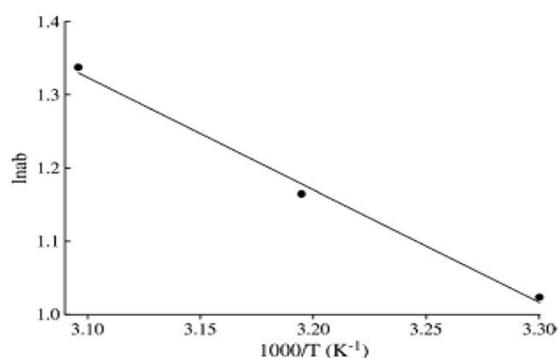

Figure 10. Plot of ln ab vs. 1/T(K) for Cd(II) adsorption onto G-COOH (G-COOH dose=0.1 g; pH=6.5; T=293±2 K)

ΔG^0 decreased with an increase in temperature, indicated that the spontaneous nature of the adsorption of Cd (II) is inversely proportional to the temperature. Generally, the absolute magnitude of the change in free energy for adsorption is between 0 and −20 kJ/mol. Adsorption type can be explained as physisorption [23, 24]. The positive values of ΔS^0 reflect the affinity of adsorbent material towards Cd (II).

Desorption of Cd (II) ion from G-COOH

A desorption study is also important because it is useful in the recycling of the adsorbent and recovery of heavy metals. The results (**Table 4**) show that the percentage adsorption of Cd (II) onto G-COOH decreases with the increase of initial Cd (II) concentration in the solution, with a decrease slightly in Cd (II) ion loading and keeps high. These results indicate that Cd (II) ion adsorption is reversible and can be desorbed easily by adjusting the pH. Thus the G-COOH can be employed repeatedly in the heavy metal adsorption.

Table 3. Thermodynamic parameters for Cd(II) ion adsorption onto G-COOH

ΔH^0 (kJ mol^{-1})	12.9
ΔS^0 (kJ mol^{-1}K^{-1})	0.034
$-\Delta G^0$(kJ mol^{-1}K^{-1})	-
303	2.58
313	3.03
323	3.59

Table 4. Desorption of Cd (II) ion from loaded G-COOH

C$_0$ Cd(II) (mg/L)	% Adsorption	After dsorption (mg/L)	% Desorption
4	**95.5**	3.76	98.4
8	94.4	7.33	97.1
12	90.5	10.32	95.0

Table 5. Comparison of the adsorption capacities of various adsorbents for Cd(II) ion removal by batch method

Metal Ion	Adsorbent	Adsorption dosage (g/L)	Adsorption capacity (mg g^{-1})	References
Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III)	tannic acid immobilized activated carbon	2.0	1.73	[25]
Cd(II)	Rice Husk	1.0	21.28	[26]
Ni (II), Cd(II), Co (II)	Eucalyptus leaves ash	2.0	25.40	[27]
Cd (II)	Graphene oxide (GO)nano	1.0	49.60	[28]
Pb (II) and Cd (II)	Organic wastes	0.5	19.92	[29]
Cd(II)	graphene carboxylated (G-OOH) nano	0.1	3.37	This Work

Comparison of G-COOH Batch Adsorption Method with Other Methods

A comparison of the maximum adsorption capacities of different adsorbents for removal of Cd (II) ion was also reported in **Table 5**. The variation in q$_{max}$ values between the adsorbents can be related to the type and density of active sites responsible for adsorption of metal ion from the solution. It is clear from this table that the adsorption capacity of G-COOH used in the present study is significant high. This may be attributed to the effect of particle size and distribution, morphology, and surface structure of the adsorbent.

CONCLUSION

Carboxylated nanoporous graphene (G-COOH) was synthesized via CVD method and successfully functionalized with carboxyl groups. It was observed that the carboxylated nano porous graphene is an efficient adsorbent for the removal of Cd (II) ion. The maximum removal percentage of the studied metal ion (R=99%) was obtained at optimum condition: pH of 6.5, 0.1 g of sorbent, 30 min ultrasonication time, and 293±2 K.

In the light of the finding of this work, the following main conclusion can be stressed:

(1) The Cd (II) ion uptake at equilibrium by G-COOH could be described by both the Langmuir and the Freundlich adsorption isotherms. The correlation coefficients show that the Langmuir model is better fitted than the Frendlich.
(2) The adsorption process follows a pseudo-second-order kinetics.
(3) The negative value of ΔG^0 indicates the feasibility and spontaneity of the adsorption process. The positive ΔH^0 suggests the endothermal nature of the adsorption. The positive values of ΔS^0 reflects the affinity of G-COOH towards Cd (II) ion.

The G-COOH proposed sorbent is useful for quantitative adsorption of Cd (II) ion with high sorption capacities in short time.

ACKNOWLEDGEMENTS

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