Punica granatum (pomegranate) carpellary membrane and its modified form used as adsorbent for removal of cadmium (II) ions from aqueous solution

Suman Saini, Rajeev Kumar, Jyoti Chawla and Inderpreet Kaur

ABSTRACT

Punica granatum carpellary membrane (PGCM) has been chemically modified with 2,4-dinitrophenylhydrazine by one step reaction process. Pristine PGCM and modified *Punica granatum* carpellary membrane (MPGCM) have been employed as adsorbents for removal of cadmium (II) ions from aqueous solution. Modification on the surface of PGCM was characterized by Fourier transform infrared, scanning electron microscope, energy dispersive X-ray spectroscopy and X-ray diffraction techniques. Removal of Cd (II) ions was carried out at various optimized conditions, i.e. adsorbent dose (20 mg/l), pH (7), contact time (2 h), and temperature (303 K). The Langmuir isotherm model was the best fit with a high value of regression coefficient ($R^2 = 0.991–0.999$) compared with the Freundlich and Temkin models. Langmuir maximum adsorption capacity for cadmium was found to be 111.11 mg/g for PGCM and 142.85 mg/g for MPGCM. Kinetics of adsorption of cadmium onto MPGCM was best described by pseudo-second-order kinetics model compared with pseudo-first-order. The negative value of free energy change showed that adsorption was highly spontaneous and favorable. Also the positive value of entropy and enthalpy showed that the process of adsorption was associated with increased randomness and endothermic in nature. Mechanism of removal of cadmium ions from water by MPGCM has also been explicated.

Key words | 2,4-dinitrophenylhydrazine, adsorption, cadmium (II) ions, Langmuir isotherm, *Punica granatum* carpellary membrane, thermodynamic parameters

Suman Saini
Rajeev Kumar (corresponding author)
Jyoti Chawla
Department of Chemistry,
Manav Rachna International University
(Faculty of Engineering & Technology),
Sector-43, Delhi-Surajkund Road, Aravali Hills,
Faridabad, Haryana 121004,
India
E-mail: *rajeevkumar.fet@mriu.edu.in*

Inderpreet Kaur
Department of Chemistry, Centre of Advanced
   Study,
Guru Nanak Dev University,
Amritsar,
India

INTRODUCTION

Elements such as lead, mercury, cadmium and arsenic have many environmental implications and cause major human health problems in different parts of the world. The World Health Organization (WHO) has identified ten chemicals of major public health concern that include cadmium, arsenic, lead and mercury (WHO 2017) which when present at higher concentrations than permissible limits pose adverse effects on various biological systems. It was strongly recommended that there should be a multi-sectoral action plan to protect the environment and human health from the harmful effects of chemicals. Some of the greatest threats to human health come from contaminated water.

Discharges of water from industries and households are the main sources of water pollution. Heavy metals such as lead, arsenic, cadmium and chromium are the main constituents of various industrial processes (Chowdhury *et al.* 2016). Cadmium metal is most widely used in pigments, smelting, metal plating, cadmium nickel batteries, alloy industries and phosphate fertilizers (Kumar & Chawla 2014; Kumar *et al.* 2015). The presence of cadmium in water is a very serious issue because cadmium is non-biodegradable in nature and has a tendency to bio-accumulate in the biological systems which may lead to serious acute or chronic diseases (Kumar & Chawla 2014). Therefore it is

necessary to develop some methods and techniques for the removal of cadmium from industrial effluents before their discharge into water bodies.

Many techniques have been developed for removal of heavy metal ions from water. Conventional methods used for the removal of cadmium and other heavy metal ions from water are chemical oxidation and reduction method, ion-exchange, filtration, chemical precipitation, electrochemical treatment, membrane technologies, reverse osmosis, coagulation-sedimentation, reverse osmosis, and adsorption (Chawla *et al.* 2015; Ihsanullah *et al.* 2016; Kaur *et al.* 2016; Kyzas *et al.* 2016; Wang *et al.* 2016; Zhao *et al.* 2016). However, some methods are quite expensive, complicated to handle and less efficient for water treatment at large scale. Among these techniques, adsorption is one of the preferred methods for removal of heavy metal ions from water/wastewater because of its low cost, and because it is easy to operate and highly efficient. Various synthetic materials such as nano-materials are used as adsorbent for removal of cadmium from water but these are expensive and also pose certain environmental implications (Mahmoud *et al.* 2016; Zhao *et al.* 2016). A low cost material with high efficiency to remove cadmium from water is still a challenge and more efforts are required in this direction. Many plant waste materials and peels have also been used as natural adsorbents worldwide for the treatment of wastewater contaminated with heavy metals. Availability of natural adsorbents is another important aspect as some of the adsorbents showing high adsorption capacity are not available everywhere. Pomegranate is one of the easily available commercial fruits in India. Moreover, in some parts of India, especially in central and southern India, it is available throughout the year. Pomegranate belong to the genus *Punica*, order *Myrtales* and family *Lythraceae*. Few researchers have used only the pomegranate peel for the removal of heavy metals such as chromium (Najim & Yassin 2009), iron (Moghadam *et al.* 2013), lead (Alam *et al.* 2012), cadmium (Kumar & Kumar 2015), lead and copper (El-Ashtoukhy *et al.* 2008) from water or wastewater using the adsorption method.

The pomegranate fruit has several anatomical parts such as peel, carpellary membrane, seeds and arils. Half of the total fruit weight corresponds to the peel. The carpellary membrane, which separates the seeds within the fruit, acts as a protective membrane and contains poly-phenols including gallic acid (trihydroxy benzoic acid), ellagic acid (EA) (hexahydroxydiphenic acid), gallagic acid condensed tannins, catechins, gallocatechins and prodelphinidins, flavonoids (luteolin, quercetin, kaempferol, gallagic, EA glycosides, EA, punicalagin, punicalin, peduncalagin), proanthocyanidin, ellagitannin compounds, minerals and complex polysaccharides (Kulkarni *et al.* 2004; Mohammad & Kashani 2012). The aim of this study is to use *Punica granatum* carpellary membrane (PGCM) in its pristine form and chemically modified PGCM with 2,4-dinitrophenylhydrazine (MPGCM) for the removal of cadmium metal ions from water and wastewater. In this study, PGCM and MPGCM were used as new adsorbents to investigate the effect of the various physiochemical parameters such as pH, contact time, adsorbent dose, temperature, etc., on adsorption of cadmium ions. Different techniques were employed for characterization of both adsorbents, i.e. pristine PGCM and modified MPGCM, before and after the adsorption process.

MATERIALS AND METHODS

Experimental

Reagent grade 2,4-dinitrophenylhydrazine (2,4-DNP) from E. Merck Ltd, India, was used for the modification of PGCM. AR/GR grade cadmium nitrate [$Cd(NO_3)_2$] was received from E. Merck Ltd, India and was used without further purification. The stock solution of cadmium nitrate of 1,000 mg/l was prepared in double distilled water. The solutions of various concentrations (20 to 100 mg/l) were prepared by dilution of the stock solution. 0.1 N HNO_3 and 0.1 N NaOH were obtained from LOBA Chemie, India and used for adjusting pH while carrying out pH experiments. The surface area, pore diameter and pore volume of the adsorbents were determined by the Brunauer–Emmett–Teller (BET) method. Regeneration of adsorbents was carried out by 20% H_2SO_4. Thermodynamic studies were carried out at 297 K to 333 K at optimized conditions. All used apparatus was firstly washed with aqua regia then with double distilled water.

Modification of adsorbent

PGCM was carefully separated from the pomegranate fruit collected from Gurgaon, India and washed with double distilled water several times. Initially, it was sun dried followed by drying in an oven at 373 K. The dried sample was finally crushed, ground properly and sieved to get the fine particle size of the adsorbent. The fine powdered sample was stored in closed glass bottles for further use. PGCM was modified by 2,4-DNP. For surface modification: 2.5 g of 2,4-DNP was mixed in 50 ml of ethanol with 1–2 drops of sulfuric acid and filtered to obtain a clear solution of 2,4-DNP (Figure 1(a)). This solution was mixed with PGCM powder and stirred on a magnetic stirrer for 8 to 10 hours at 323–333 K. After stirring, the solution was filtered and washed several times with ethanol and dried in the oven for further use.
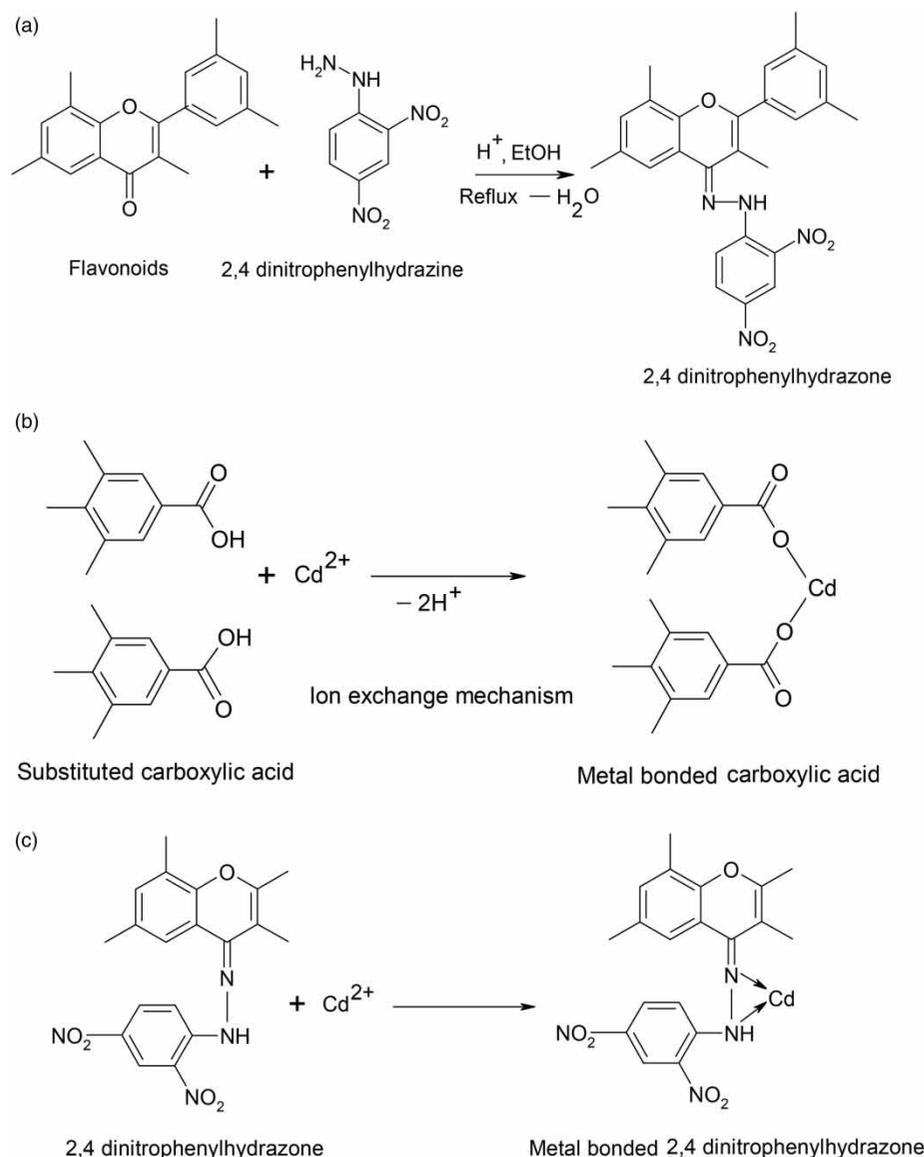

Figure 1 | Schematic diagram (a) modification of PGCM by 2,4-dinitrophenylhydrazine, (b) removal of cadmium (II) ions by ion exchange mechanism with MPGCM and (c) removal of cadmium (II) ions by coordination mechanism with MPGCM.

Characterization and adsorption studies

The Fourier transform infrared (FTIR) spectrum was recorded by FTIR spectrophotometer in the range of 500–4,000 cm^{-1} (Shimadzu). X-ray diffraction (XRD) analysis (RIGAKU) of the adsorbent and scanning electron microscope (SEM) analysis (JEOL JSM-6100) was carried out to study the morphology of the adsorbent.

Adsorption of cadmium (II) ions on PGCM and MPGCM were studied using the batch mode adsorption method by shaking a known amount of PGCM and MPGCM adsorbent with cadmium (II) ion solution in 50 ml reagent bottles or glass vials. The adsorption study was carried out systematically in terms of various parameters such as initial cadmium ion concentration (20–100 mg/l), different pH (1–8), different time intervals (20 min to 180 min), various adsorbent doses (0.1 g/l to 0.5 g/l) and various temperatures (297–333 K) at 150 rpm. After proper shaking of the contents in the reagent bottles, adsorbent powder was filtered from the solution using Whatman filter paper no 41. The residual cadmium ions concentration in aqueous solution before and after equilibrium was determined by atomic absorption spectrophotometer (AA-6200, Shimadzu). The equilibrium data obtained in the batch adsorption experiments was used to calculate the amount of cadmium (II) ions adsorbed per unit mass of PGCM and MPGCM (q_e in mg/g) using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o is initial concentration of cadmium (II) ions in aqueous solution (mg/l), C_e is final concentration of cadmium (II) ions in aqueous solution (mg/l), q_e is amount of cadmium (II) ions adsorbed per unit mass of PGCM or MPGCM (mg/g), V is volume of aqueous solution of cadmium (II) ions in liters and m is mass of PGCM or MPGCM powder in grams.

The adsorption rate was evaluated by fitting the experimental data into kinetic models such as pseudo-first-order and pseudo-second-order kinetic model (Lagergren 1898; Demirbas *et al.* 2002). From the experiments, pseudo-first-order rate constant (k$_1$), pseudo-second-order rate constant (k$_2$) and equilibrium uptake capacity (q$_e$) were calculated.

RESULTS AND DISCUSSION

Characterization studies of PGCM and MPGCM

The characterization of modified PGCM and adsorption of cadmium (II) ions on PGCM and MPGCM were investigated by different techniques and the results obtained are discussed in the following sections.

SEM analysis

SEM delivers images with information about the topography of samples by scanning the surface of the sample with a focused electron beam. Figure 2 shows SEM images of PGCM (Figure 2(a) and 2b)) and MPGCM (Figure 2(c) and 2(d)). before and after adsorption of cadmium (II) ions, respectively. Figure 2(a) and 2(c) show sample PGCM and MPGCM at 1000X magnification, respectively. It can be seen clearly that there are number of vacant sites available. However, in Figure 2(b) and 2(d), these sites are occupied or covered by the cadmium (II) ions due to adsorption.

XRD analysis

XRD analysis is used to explore the degree of crystallinity in the materials. In this technique, a beam of X-rays falls on the sample and the scattered beam is analyzed. The X-rays scattered by the atoms of the material constructively interfere with each other to determine various characteristics of the crystalline materials. XRD spectra of PGCM and MPGCM adsorbents were recorded and are shown in Figure 3(a) and 3(b). It can be seen in both spectra that there are two peaks at 2θ of 0.18, 0.68 for PGCM and 0.19, 0.73 for MPGCM. The broadening of diffraction peaks and the absence of other diffraction peaks in higher regions indicates the amorphous nature of the material.

FTIR spectroscopy analysis

Surface modification of PGCM was confirmed by FTIR analysis. The IR spectra of the PGCM and MPGCM were recorded on Fourier transform spectrometer in the mid-infrared region (4,000–650 cm^{-1}). Many functional groups
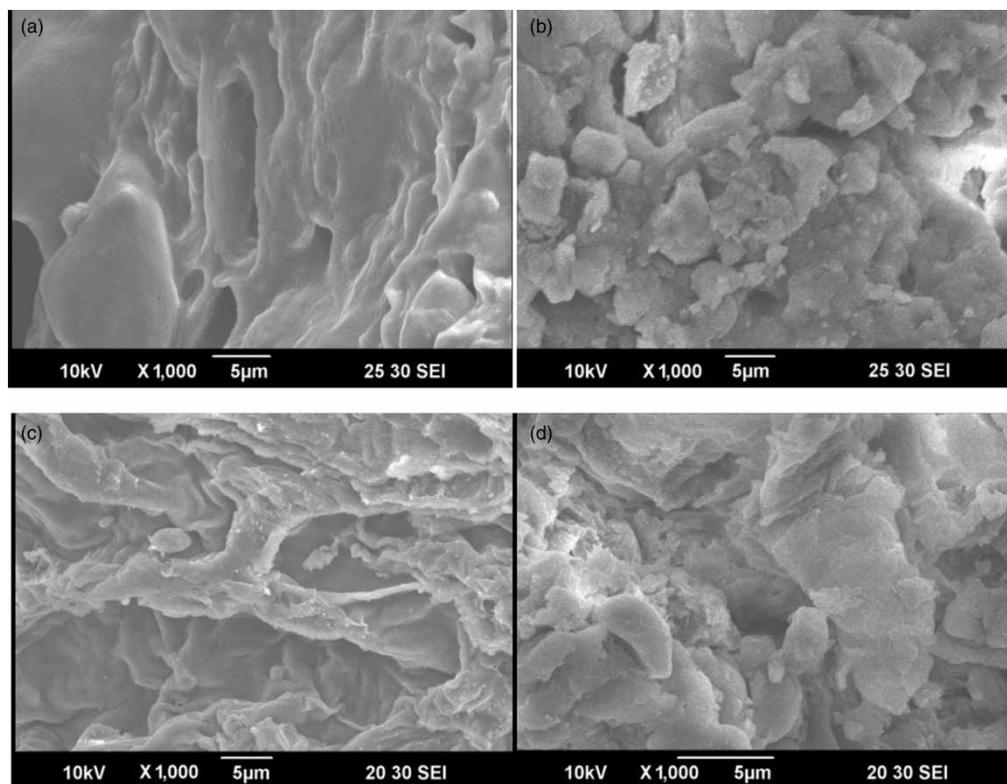
Figure 2 | SEM images of (a) PGCM, (b) PGCM-Cd(II), (c) MPGCM, (d) MPGCM-Cd(II).
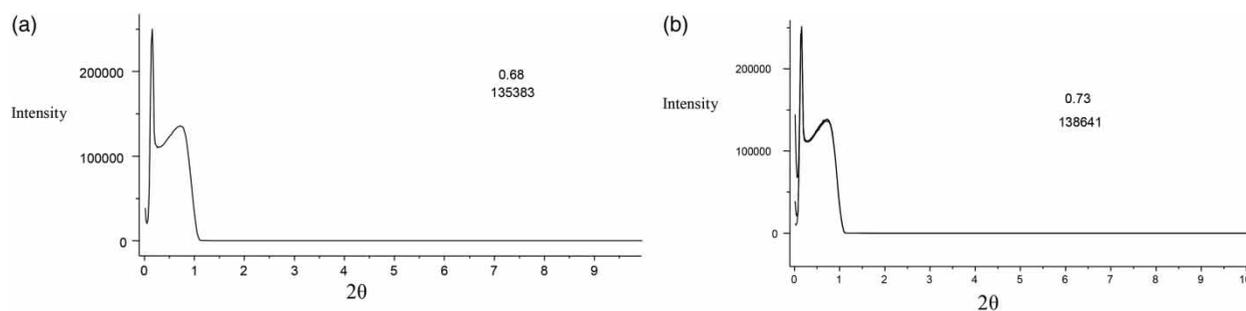

Figure 3 | XRD analysis of (a) PGCM and (b) MPGCM.

give characteristic absorption peaks in the specific range. However, signals corresponding to functional groups may vary over a wide range due to the complex interaction between the coordinating atoms of the modifying reagent, i.e. 2,4-DNP, with other functional groups on the surface of adsorbent and cadmium ions. The FTIR spectra of the PGCM and MPGCM are shown in Figure 4(a) and 4(b) before adsorption of cadmium (II) ions and Figure 4(c) and 4(d) after adsorption of cadmium (II) ions.

FTIR spectrum of PGCM exhibited characteristic bands of carbonyl stretching ($1,729 \, \text{cm}^{-1}$) and –OH stretching ($3,169 \, \text{cm}^{-1}$) of poly phenols on the surface of the adsorbent. However, the FTIR spectrum of MPGCM exhibited all the characteristic bands of PGCM with additional bands at $3,174 \, \text{cm}^{-1}$, $3,348 \, \text{cm}^{-1}$ (stretching of Ar–NH, –NH, =NH), $1,521 \, \text{cm}^{-1}$ (asymmetric stretching of Ar–NO$_2$), $1,223 \, \text{cm}^{-1}$ (stretching vibration of C–N) and $923 \, \text{cm}^{-1}$ (twisting, bending of –NH, =NH) (Mohammad & Kashani 2016). Intensity
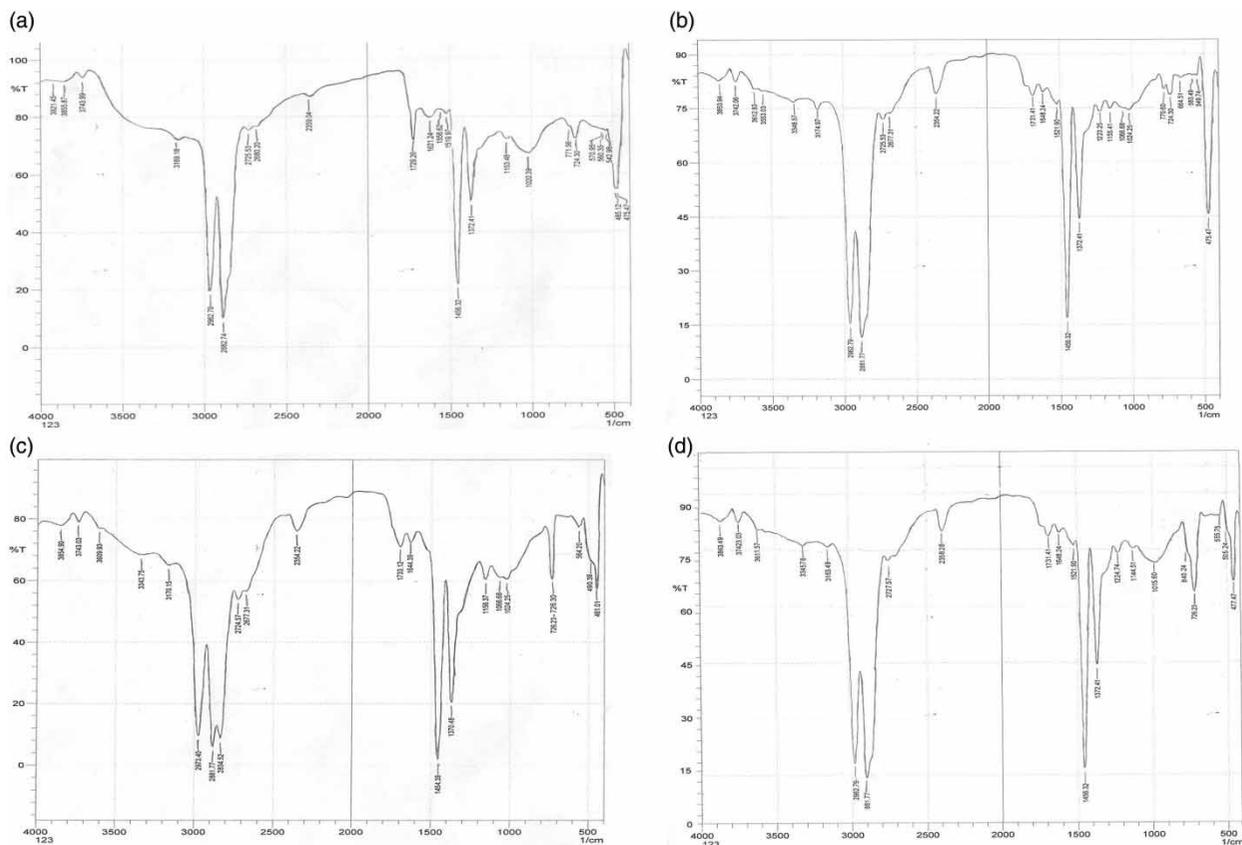
Figure 4 | FTIR spectra of (a) PGCM, (b) MPGCM, (c) PGCM-Cd(II), and (d) MPGCM-Cd(II).

of carbonyl stretching $(1{,}729 \, \text{cm}^{-1})$ peaks of PGCM was observed to be decreased which confirmed the modification of PGCM due to reaction of the carbonyl group with 2,4-dinitrophenylhydrazine. The IR spectra of PGCM and MPGCM adsorbents were slightly different after adsorption of cadmium (II) ions. Intensity of carbonyl stretching $(1{,}729 \, \text{cm}^{-1})$ peaks of PGCM was further slightly decreased with higher wave numbers $(1{,}733 \, \text{cm}^{-1})$ which can be attributed to the interaction of cadmium ions with carbonyl group. Also a new band was observed at $726.23 \, \text{cm}^{-1}$ due to Cd–O stretching which confirms the bonding of cadmium ions on the surface of PGCM adsorbent with additional characteristics of a weak band of CdO at 564 and $490 \, \text{cm}^{-1}$ (Abd El-Salaam & Hassan 1982; Aldwayyan *et al.* 2013). On other hand, a new broad band at $840 \, \text{cm}^{-1}$ due to Cd–N stretching was observed in the IR spectrum of cadmium loaded MPGCM which could be bonding of cadmium ions with the nitrogen of dinitrophenylhydrazine.

EDX analysis

The energy dispersive X-ray spectroscopy (EDX) detects X-rays emitted from the sample during bombardment by an electron beam to characterize its elemental composition. The EDX detector measures the relative abundance of emitted X-rays versus their energy and the spectrum of X-ray energy versus counts so obtained allow the determination of elemental composition of the sample. EDX spectra of PGCM and MPGCM before and after adsorption are shown in Figure 5(a)–5(d). EDX spectrum of PGCM and MPGCM did not exhibit any characteristic peak for cadmium (II). However, both PGCM and MPGCM after adsorption of cadmium (II) exhibited an additional peak of cadmium (II) ions at 3.1 keV in the spectrum, which confirmed the adsorption of Cd(II) on the surface of PGCM and MPGCM (Table 1).
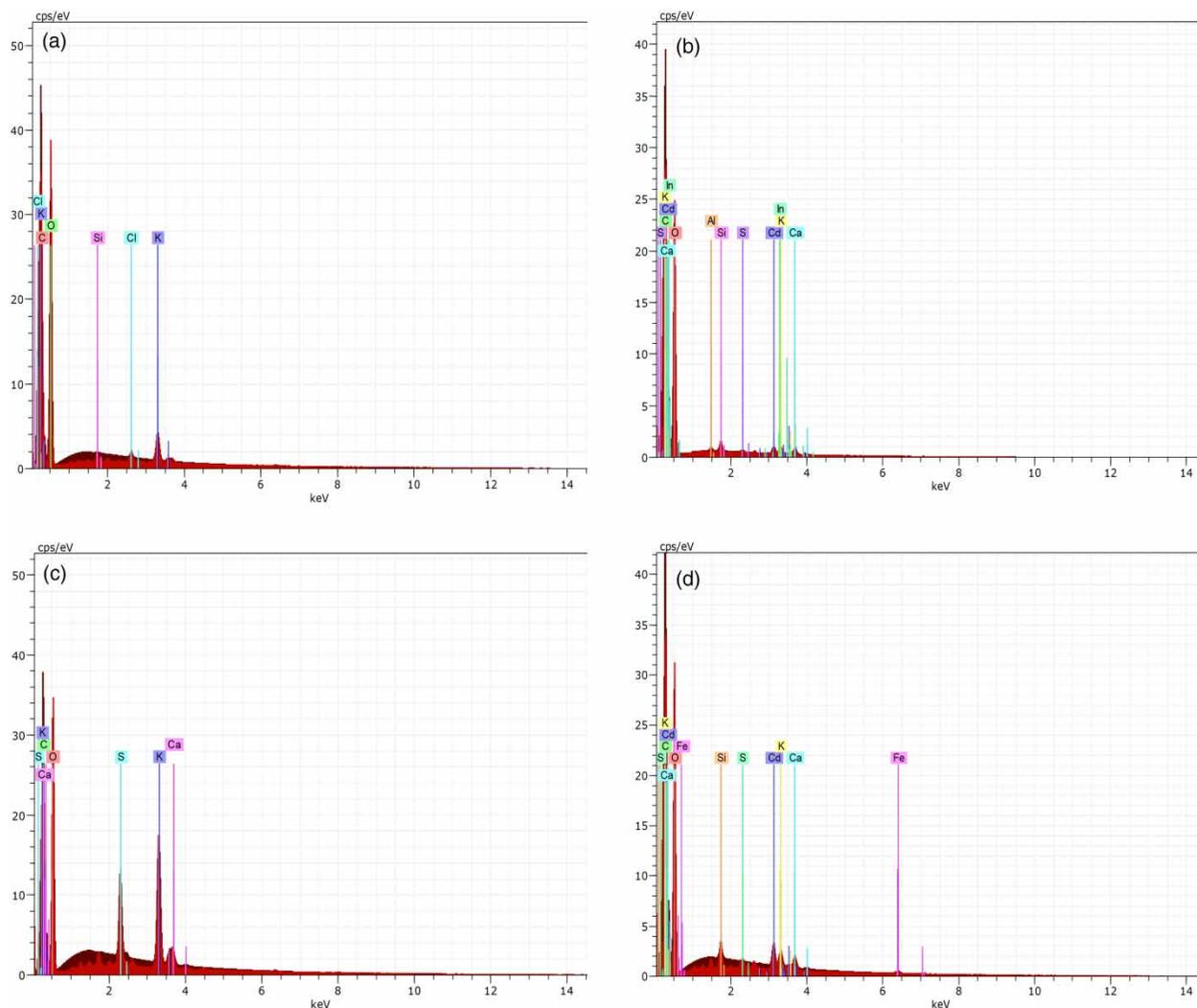
Figure 5 │ EDX spectra of (a) PGCM, (b) PGCM-Cd(II), (c) MPGCM and (d) MPGCM-Cd(II).

BET surface area analysis

The BET method is used to determine the total surface area of adsorbents (Brunauer *et al.* 1938). Barrett–Joyner–Halenda (BJH) adsorption-desorption analysis helps in understanding the proportion of pore area and pore volume (Villarroel-Rocha *et al.* 2014). Surface area of PGCM and MPGCM was analyzed by the BET method. It was observed that the surface area decreased from 10.85 m²/g for PGCM to 5.058 m²/g for MPGCM. The corresponding pore sizes were 71 Å and 52.81 Å and pore volumes were 3.262×10^{-3} and 2.786×10^{-3} cc/g, respectively, for PGCM and MPGCM. The decrease

in all the surface parameters supports the surface modification of adsorbent which may be attributed to the occupation of pores of adsorbent PGCM by molecules of 2,4-DNP via a condensation reaction between functional groups on the surface and 2,4-DNP. A similar observation was reported by Sayari & Hamoudi (2001).

Adsorption studies of cadmium (II) ions on adsorbent

Adsorption experiments were carried out systematically in order to optimize the set of parameters to achieve the

Table 1 | Elemental composition of PGCM and MPGCM before and after cadmium (II) ions adsorption

	PGCM			**MPGCM**		
S. no.	Element	Wt.% before adsorption	Wt.% after adsorption	Element	Wt.% before adsorption	Wt.% after adsorption
1	Carbon	22.93	36.81	Carbon	13.53	32.7
2	Potassium	1.18	0.01	Oxygen	79.81	64.77
3	Oxygen	75.76	59.71	Potassium	3.64	0.12
4	Silicon	0.01	0.42	Sulfur	1.38	0.02
5	Chlorine	0.12	0.02	Copper	1.27	0.1
6	Cadmium	–	2.28	Calcium	0.37	0.01
7	–	–	–	Cadmium	–	3.03
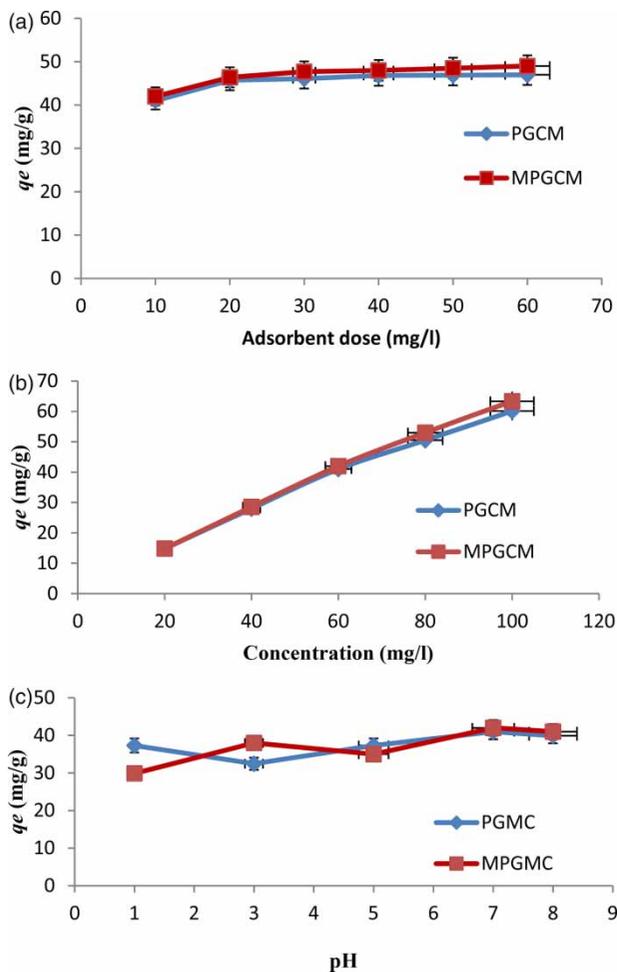
Figure 6 | Effect of (a) adsorbent dosage, (b) initial cadmium (II) ions concentration and (c) pH for adsorption of cadmium on PGCM and MPGCM.

best performance of the adsorbents, PGCM and MPGCM, and the results obtained are discussed in the following sections.

Effect of adsorbent dose

It is important to study the effect of adsorbent dose on adsorption in order to optimize the adsorption conditions. From Figure 6(a) it can be seen that the amount of cadmium (II) ions adsorbed per unit mass (q_e) initially increases with adsorbent dosage as availability of adsorption sites increases with increasing dose. The effect of adsorbent dose for removal of cadmium (II) ions was examined by varying the dose between 10 mg/l and 60 mg/l for 60 ppm cadmium (II) ions solution and contact time up to 2 h. It was observed that the adsorption did not change significantly beyond the adsorbent dose of 20 mg/l for both PGCM and MPGCM due to reduction in concentration gradient (Kumar *et al.* 2011). However, the value of q_e remained constant when the adsorbent dose increased to 60 mg/l for both adsorbents. The increase in adsorption with increasing MPGCM adsorbent dose is due to the increase in availability of adsorption sites with functional groups of the modifying reagent. Moreover, further increase in the MPGCM adsorbent dose hardly increases the adsorption because of overlapping of the modified adsorption groups as a result of overloading on the surface of adsorbent particles (Kumar & Gayothri 2009). Therefore, adsorbent dose of 20 mg/l was considered as the optimum dose for all adsorption studies.

Effect of initial cadmium (II) ions concentration

The adsorption capacity of adsorbent was also affected by the initial concentration of cadmium (II) ions. The effect of initial cadmium (II) ions concentration on adsorption

was studied by taking the various concentrations of cadmium (II) ions solution ranging from 20 mg/l to 100 mg/l with optimum adsorbent dose of 20 mg/l and contact time of 2 h (Figure 6(b)). When the concentration of metal is lower, the adsorption was observed to be quite significant because of availability of more active sites on the surface of the adsorbent.

Effect of contact time

Contact time plays a crucial role in optimizing the adsorption condition of cadmium (II) ions on the surface of the adsorbent. In this study, the effect of contact time on both of the adsorbents was investigated at constant adsorbent dose (20 mg/l) for 60 mg/l cadmium (II) solution from 20 minutes to 180 minutes. The adsorption increased rapidly with increase in time and became constant at 120 minutes for both of the adsorbents. The adsorption increases in the beginning because of availability of more adsorption sites on the surface of the adsorbent. After 120 minutes, the adsorption becomes constant because most of the sites were occupied by cadmium (II) ions from solution.

Effect of pH

pH of the solution is the main parameter which affects the removal of any heavy metal ions from solution. The adsorption study was carried out with initial pH varying from 1 to 8 at other constant parameters (adsorbent dose = 20 mg/l, contact time = 120 min, C_o = 60 mg/l and T = 303 K). The solution pH was adjusted by the addition of 0.1N HNO_3 for acidic solution and 0.1N NaOH for alkaline solution. The maximum adsorption of cadmium (II) ions was found at pH 7 using both adsorbents as shown in Figure 6(c). The adsorption capacity of both adsorbents was found to increase with increasing pH of solution up to pH 7. However, at lower pH, hydrogen ions compete with the cadmium ions for adsorption sites which makes the adsorbent surface positive and at pH higher than 8, precipitation of cadmium ions as hydroxide decreases the adsorption of cadmium (II) ions. It is important to mention that the pH of solution after equilibrium decreased very little

(>0.32) and it was as a result of replacement of H^+ ions on functional groups on the adsorbent by cadmium ions.

Effect of temperature

Temperature has significant effect on adsorption of cadmium (II) ions on the adsorbent surface. The temperature study was carried out within the temperature range of 297 K to 333 K at other constant parameters (adsorbent mass = 20 mg/l, contact time = 120 min, initial concentration = 60 mg/l and pH = 7). It was observed that adsorption of cadmium (II) ions increases with the increase in temperature. This is due to the combined effect of mobility of the ions and activity of the sites which increases with increase in temperature.

Adsorption isotherms

Adsorption capacity of the adsorbent is determined by applying various isotherms such as Langmuir isotherm, Freundlich isotherm and Temkin isotherm. These isotherms are quite helpful to evaluate the equilibrium relationship between the metal ions in solution and outer surface of the adsorbent.

The Langmuir isotherm

The standard linear form of Langmuir isotherm may be described as follows (Kaur *et al.* 2016):

$$\frac{C_e}{q_e} = \frac{1}{(q_{max}.K_L)} + \frac{C_e}{q_{max}} \tag{2}$$

where C_e is equilibrium concentration of cadmium (II) ions, q_e is amount of cadmium (II) ions adsorbed at equilibrium (mg/g), q_{max} is maximum adsorption capacity on the monolayer surface (mg/g), and K_L is equilibrium constant related to energy of adsorption. Langmuir constant (K_L) is the essential characteristic of Langmuir isotherms and used to determine the dimensionless separation factor (R_L). Dimensionless separation factor R_L can be calculated as follows:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{3}$$

where C_o is the initial concentration of cadmium ions (mg/l) and K_L is Langmuir constant or equilibrium constant. The value of dimensionless separation factor (R_L) indicates the favorability of the isotherm whether irreversible, favorable, linear or unfavorable. If $R_L = 0$ isotherm will be irreversible; if $R_L = 1$, isotherm will be linear; if $0 < R_L < 1$, isotherm will be favorable and if $R_L > 1$ isotherm will be unfavorable. The R_L values for cadmium (II) ion adsorption by PGCM and MPGCM were found to be less than one but greater than zero for all experiments, indicating favorability of the isotherm (Table 2). Maximum adsorption capacity (q_{max} in mg/g) and Langmuir constant (K_L in l/g) can be evaluated from the slope and intercept of the linear plot of C_e versus C_e/q_e (Figure 7(a)).

Freundlich isotherm

The standard linear form of Freundlich isotherm can be described as follows (Kaur *et al.* 2016):

$$ln\, q_e = ln\, K + 1/n\, ln\, C_e \tag{4}$$

where K (mg/g) is Freundlich constant related to the adsorption capacity, q_e is amount of cadmium ions adsorbed at equilibrium (mg/g), C_e is concentration of cadmium (II) ions at equilibrium concentration, $1/n$ is heterogeneity factor of adsorption, n is related to adsorption intensity and measure of the deviation from linearity of adsorption. Freundlich constant K (mg/g) and q_e (mg/g) can be evaluated from slope and intercept of the linear plot of $ln\, C_e$ and $ln\, q_e$ (Figure 7(b)). Heterogeneity factor n may be varied from 1 to 10 for classification of favorable adsorption (Chantawong *et al.* 2003). The value of $1/n$ if lower than one indicates a normal adsorption whereas the value $1/n$ if greater than one indicates adsorption is much more favorable and known as cooperative adsorption. The Freundlich

isotherm is found to be linear with slope $1/n$ and intercept $ln\, K_F$ (Figure 7(b)) for adsorption of cadmium (II) ions on the surface of PGCM and MPGCM. The results are summarized in Table 2. From the data it can be seen that the value of $1/n$ is lower than one which indicates a normal adsorption. Apart from the homogeneous surface on PGCM, the Freundlich equation is also suitable for a highly heterogeneous surface on MPGCM which can be seen by the smaller values of $1/n$ indicating greater heterogeneity.

Temkin isotherm

The adsorption potential of adsorbent/adsorbate interactions can be evaluated by the Temkin isotherm which explicitly takes into account the interactions of adsorbate ions of the solution and the surface of the adsorbent (Kaur *et al.* 2016). The standard linear form of the Temkin isotherm can be described as follows:

$$q_e = B\, ln\, A + B\, ln\, C_e \tag{5}$$

where A is the equilibrium binding constant, B is also a constant that can be calculated by $B = RT/b$, b is the Temkin constant which is related to heat of sorption (J/mol), T is the temperature (K) and R is the ideal gas constant (8.314 J/mol/K), C_e is concentration of the adsorbate at equilibrium (mg/l), q_e is the amount of adsorbate adsorbed at equilibrium (mg/g). Constants A (l/min) related to the maximum binding energy and B related to heat of adsorption can be evaluated from slope and intercept of the linear plot of q_e versus $ln\, C_e$. The Temkin isotherm was found to be linear with slope B and intercept $B\, ln\, C_e$ for adsorption of cadmium (II) ions on the surface of PGCM and MPGCM (Figure 7(c)). The results are summarized in Table 2. From Table 2, it can be seen that the value of B is 22.21 J/mol for PGCM and 24.85 J/mol for MPGCM indicating the process

Table 2 | Parameters of isotherm models for adsorption of cadmium (II) ions on PGCM and MPGCM

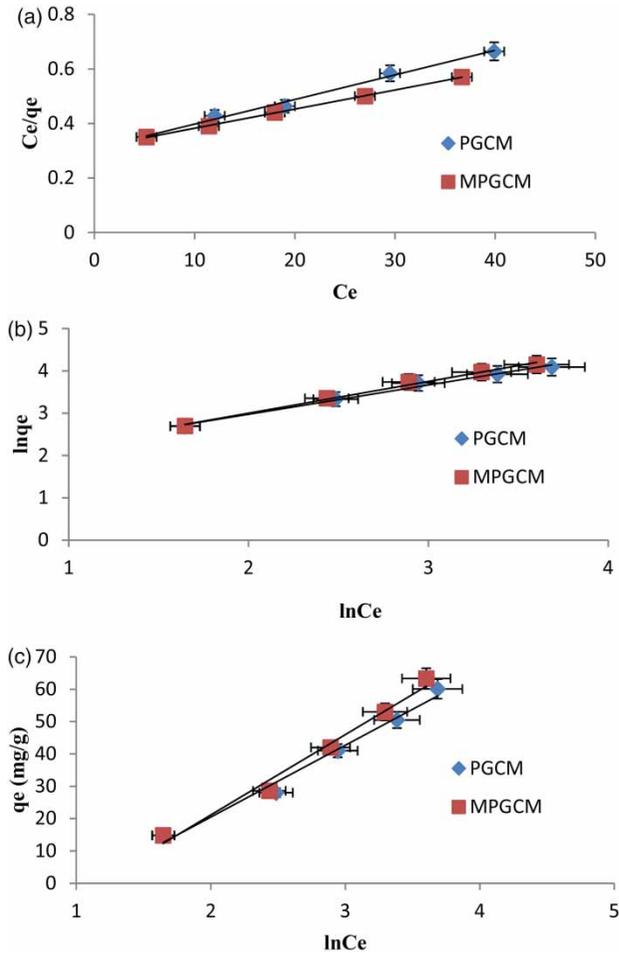| | Isotherm model | | | | | | | | |
| | Langmuir | | | Freundlich | | | Temkin | | |
Adsorbent	q_{max} (mg/g)	K_L (l/g)	R^2	n	K	R^2	B	A	R^2
PGCM	111.11	0.029	0.991	1.44	4.89	0.990	22.21	0.34	0.984
MPGCM	142.85	0.022	0.999	1.33	4.47	0.992	24.85	0.31	0.983

Figure 7 │ Isotherm models, (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm, for adsorption of cadmium on PGCM and MPGCM.

of physical adsorption. Low values of B in this study indicate a weak interaction between adsorbent and adsorbate supporting a mechanism of ion exchange.

From the comparative analysis of results, specifically regression correlation coefficients, it can be concluded that the Langmuir model was best fitted for cadmium (II) ions on the surface of PGCM and MPGCM compared with Freundlich and Temkin models. The regression correlation coefficient of the Langmuir equation is more close to unity compared with the other two isotherms studied. The maximum adsorption capacity (q_{max}) and Langmuir constant (K_L) determined from the slope and intercept of the Langmuir plot are found to be 111.11 mg/g and 0.0293 l/mg for PGCM and 142.85 mg/g and 0.02243 l/mg for MPGCM, respectively.

Kinetics of adsorption

The adsorption rate can be evaluated by fitting the experimental data into different kinetic models and predicting information about the physiosorption or chemisorption of the adsorbate. The distinctive nature of equilibrium kinetic profiles was studied to determine the rate-limiting steps involved in the process of adsorption of cadmium (II) ions. Different models, pseudo-first-order and pseudo-second-order kinetic models (Lagergren 1898; Demirbas *et al.* 2002), were applied to determine the rate constant for adsorption.

Pseudo-first-order kinetic model

The pseudo-first-order kinetic model to determine the rate constant for adsorption can be expressed as (Lagergren 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where q_e and q_t refer to amount of cadmium (II) ions adsorbed (mg/g) at equilibrium and at any time t, respectively and k_1 (L/mg/min) is equilibrium rate constant of pseudo-first-order. The standard linear form of the first-order kinetic equation is

$$ln\,(q_e - q_t) = ln\,(q_e) - k_1 t \tag{7}$$

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model to determine the rate constant for adsorption can be expressed as (Demirbas *et al.* 2002):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where q_e and q_t refer to amount of cadmium (II) ions adsorbed (mg/g) at equilibrium and at any time, t, respectively and k_2 (g/mg/min) is equilibrium rate constant of pseudo-second-order. The standard linear form of pseudo-second-order kinetic equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

The value of q_e and k_1 were calculated from the slope and intercept of the linear plot of $ln\ (q_e - q_t)$ versus time (Figure 8(a)). However, the values of q_e and k_2 for pseudo-second-order kinetics were calculated from the slope and intercept of the linear plot of t/q_t versus time (Figure 8(b)). The results so obtained are summarized in Table 3.

Results showed that the value of the regression correlation coefficient (R^2) for pseudo-second-order reaction kinetics was found to be very close to that of the pseudo-first-order rate kinetic equation (Table 3). The q_e values calculated using pseudo-second-order kinetics were found to be in good agreement with the experimental q_e values which also proved that the

kinetics of adsorption of cadmium onto PGCM and MPGCM followed the pseudo-second-order model.

Thermodynamics study

Thermodynamic studies have been carried out to evaluate spontaneity and feasibility of adsorption. Effect of temperature on the adsorption of cadmium (II) ions using PGCM and MPGCM has been investigated in terms of thermodynamic parameters, such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) which were calculated according to the following equations:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

$$K_D = \frac{q_e}{C_e} \tag{11}$$

where q_e is amount of cadmium (II) ions absorbed per unit mass of adsorbent (mg/g), C_e is concentration of cadmium (II) ions in the solution at equilibrium (mg/l), K_D is the thermodynamic constant for the adsorption reaction at equilibrium, R is universal gas constant (8.314 J/mol/K), and T is absolute temperature (Kelvin).

Gibbs free energy change (ΔG^0) of adsorption was calculated using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

Change in the enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from the slope and intercept of a linear plot of $ln\ K_D$ versus $1/T$ (Figure 8(c)).

The thermodynamic parameters are summarized in Table 4. From the data analysis, it was found that the values of enthalpy (ΔH^0) and the entropy changes (ΔS^0) are positive which indicated that adsorption of cadmium (II) ions on PGCM and MPGCM is endothermic in nature and associated with an increase in randomness associated with the adsorption phenomenon. The positive value of ΔS^0 reflected the high affinity of the adsorbents PGCM and MPGCM towards cadmium (II) ions and is also attributed to the addition of water molecules previously adsorbed on the surface of adsorbent and displaced by cadmium (II)
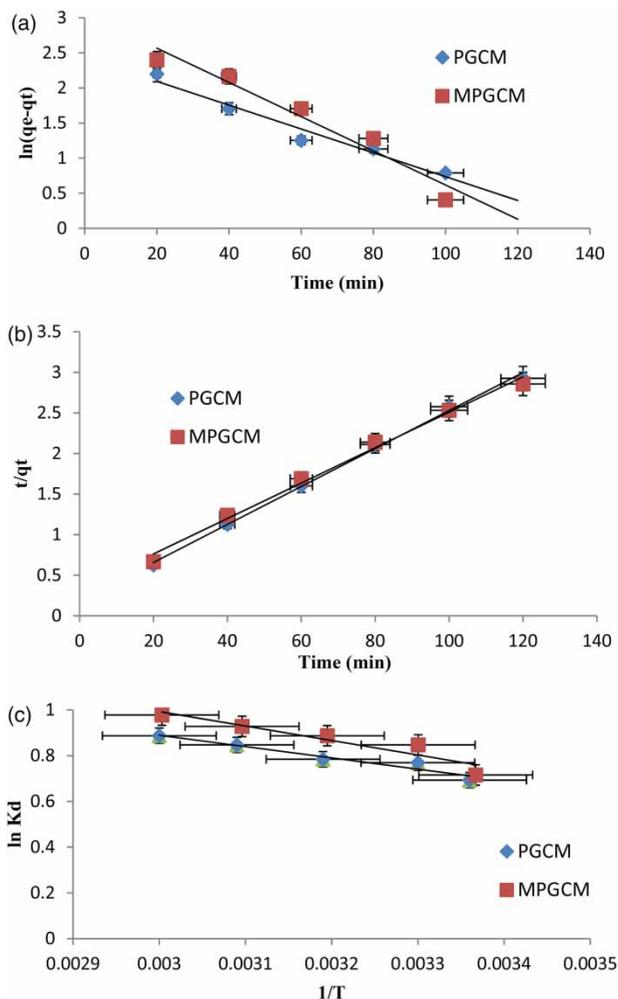

Figure 8 │ Kinetic models (a) pseudo-first-order kinetic model, (b) pseudo-second-order kinetic model, (c) Van't hoff equation, for adsorption of cadmium on PGCM and MPGCM adsorbents.

Table 3 | Parameters of adsorption kinetics of cadmium (II) ions on PGCM and MPGCM

Adsorbent	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
	q_e	k_1	R^2	q_e	k_2	R^2	q_e, exp. (mg/g)
PGCM	15.08	0.019	0.965	43.47	0.0027	0.997	41.0
MPGCM	11.38	0.017	0.950	47.60	0.0023	0.992	42.0

Table 4 | Thermodynamic parameters for adsorption of cadmium (II) ions on PGCM and MPGCM

Adsorbent	Thermodynamic parameters						
	ΔG^0 (kJ/mol)					ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol/K)
Temp (K)	297	303	313	323	333	–	–
PGCM	−1.55	−1.66	−1.85	−2.04	−2.23	4.09	0.019
MPGCM	−1.57	−1.70	−1.93	−2.16	−2.39	5.26	0.023

during adsorption. Also, the negative values of ΔG^0 at various temperatures indicated the spontaneous nature of the adsorption process.

Mechanism

Carpellary membrane, which separates the seeds within the fruit acting as a protective membrane, contains flavonoids such as Luteolin, quercetin, kaempferol, gallagic acid, EA glycosides, EA, punicalagin, punicalin, and pedunculagin (Kulkarni *et al.* 2004; Mohammad & Kashani 2012). In the present study, the functional groups of flavonoids on the surface of the carpellary membrane were used for surface modification. 2,4-dinitrophenylhydrazine was used as surface modifying reagent which reacted with the carbonyl functional groups of flavonoids to form 2,4-dinitrophenylhydrazone, resulting in red color compounds (Figure 1 (a)) on the surface of the adsorbent. The surface modified adsorbent, MPGCM, was then applied for the removal of cadmium (II) ions from aqueous solution.

The rate of removal of cadmium ions from water depends on availability of binding sites and ion exchange capacity of the adsorbent. Ion exchange capacity of poly-phenols depends on the electron withdrawing atom attached to the carbon atom to facilitate the ease of breaking of the O–H bond and this explains the very low ion exchange capacity of poly-phenols (Ibezim-Ezeani *et al.* 2010). Removal of cadmium by PGCM was facilitated either by adsorption or by ion exchange mechanism by the existing carboxylic group (Figure 1(b)). However, modification on the surface of PGCM by 2,4-dinitrophenylhydrazine facilitates the adsorption of cadmium ions from water on to its surface through ion exchange as well as coordination mechanism (Figure 1(b) and 1(c)).

Regeneration of the adsorbents

Sometimes it is more economical to discard the adsorbent rather than regenerate it especially when the cost of adsorbent is very low. However, such disposal of used adsorbents would be hazardous for the environment as well as human beings. In the present work, although the cost of raw adsorbent and its surface modification is very low, the regeneration was carried out in recognition of the need for environmental safety. Regeneration of PGCM and MPGCM was carried out by using a desorbing agent, H_2SO_4 (Cant & Walker 1977). It was found that as the concentration of H_2SO_4 was increased initially, there was also an increase in efficiency of the desorption process up to a certain concentration (20% H_2SO_4). It was also observed that high concentration of H_2SO_4 may deteriorate the adsorbent. In two cycles of treatment with desorbing agent 20% H_2SO_4, desorption of cadmium (II) from used adsorbent was achieved after 10 to 15 minutes with ~90% efficiency. After chemical interaction with H_2SO_4, adsorbents were

washed with de-ionized water and dried at 100 °C for 24 hours, and stored in a dry place for reapplication.

Comparison of PGCM and MPGCM adsorbent with other natural adsorbents

Finally, a comparison of PGCM and MPGCM with natural and surface modified adsorbents, previously reported in the literature was made and is shown in Figure 9. On analyzing the figure, maximum adsorption capacities (q_{max}) for removal of cadmium ions from water by PGCM and other natural adsorbents under a given set of conditions follow the following order:

PGCM (111.11) > medlar peel (98.14) > orange rind (peel) (83.33) > black gram husk (49.74) > *Tamarix articulata* wastes (41.6) > cactus cladodes (30.42) > grape stalk
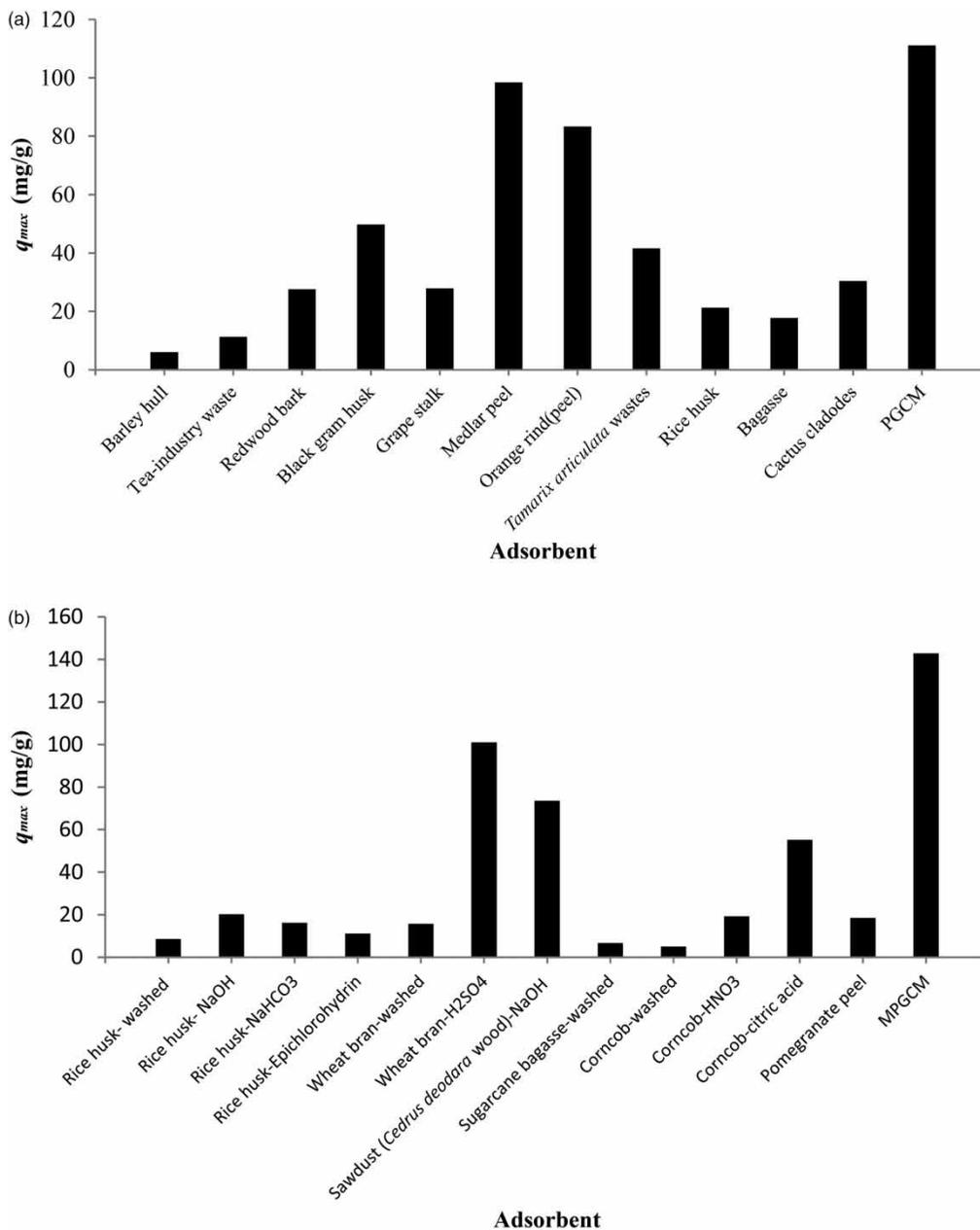

Figure 9 | Comparison of maximum adsorption capacity of (a) PGCM with other natural adsorbents and (b) MPGCM with other surface modified adsorbents.

(27.88) > redwood bark (27.6) > rice husk (21.28) > bagasse (17.73) > tea industry waste (11.29) > barley hull (6.06) for unmodified natural adsorbents.

Similarly, the performance of MPGCM and previously reported surface modified natural adsorbents can also be arranged in the following order:

MPGCM (142.85) > wheat bran-sulfuric acid (101) > saw-dust (*Cedrus deodara* wood)-NaOH (73.62) > corncob-citric acid (55.2) > rice husk-NaOH (20.24) > corncob-HNO$_3$ (19.3) > pomegranate peel-HCHO (18.5) > rice husk-NaHCO$_3$ (16.18) > wheat bran-water washed (15.71) > rice husk-epichlorohydrin (11.12) > rice husk-washed (8.58) > sugarcane bagasse-water washed (6.79) > corncob-washed (5.09) for modified natural adsorbents.

From Figure 9 it can be seen that the maximum adsorption capacity of peel of the natural adsorbent is very high compared with other outer parts of the natural adsorbents. This may be due to the presence of more active functional groups in the peel of the products to interact with heavy metal ions in water (Babel & Kurniawan 2003). It is practically quite difficult to compare or correlate the result of one adsorbent with another adsorbent because of varying experimental conditions. However, the data gives the general idea about the nature of adsorbents at normal or ambient conditions. Adsorption capacity of modified forms of natural adsorbents was also found to be higher than the unmodified form because of the presence of additional functional or other groups on the surface of the adsorbent (Ngah & Hanafiah 2008). The adsorption capacities of PGCM and MPGCM adsorbents are found to be better than other commercially available or modified natural adsorbents.

CONCLUSION

The surface modification of PGCM with 2,4-dinitrophenyl-hydrazine by one-step reaction process was successfully carried out to prepare MPGCM. Both adsorbents were applied for the removal of cadmium (II) ions from aqueous solution. Different isotherm models such as Langmuir isotherm, Freundlich and Temkin isotherm models have been applied for adsorption studies. Langmuir isotherm model was the best fitted model with high value of regression coefficient. The Langmuir maximum adsorption capacity for cadmium ions on PGCM and MPGCM was 111.11 mg/g and 142.85 mg/g, respectively. Pseudo-second-order kinetic model was the best fitted for the adsorption of cadmium ions on both the adsorbents. The adsorption process was endothermic and spontaneous in nature. This study demonstrates that natural PGCM and MPGCM can be used cost-effectively for removal of cadmium ions from water. Further studies can be elaborated for the removal of other contaminants present in water. The performance of both adsorbents was found to be comparable with and superior in many respects to other adsorbents already reported in the literature.

REFERENCES

Abd El-Salaam, K. M. & Hassan, E. A. 1982 Active surface centres in a heterogeneous CdO catalyst for ethanol decomposition. *Surface Technology* **16** (2), 121–128.

Alam, M., Nadeem, R. & Jilani, M. I. 2012 Pb(II) removal from wastewater using pomegranate waste biomass. *International Journal of Chemical and Biochemical Sciences* **1**, 24–29.

Aldwayyan, A. S., Al-Jekhedab, F. M., Al-Noaimi, M., Hammouti, B., Hadda, T. B., Suleiman, M. & Warad, I. 2013 Synthesis and characterization of CdO nanoparticles starting from organometallic Dmphen-CdI$_2$ complex. *International Journal of Electrochemical Science* **8**, 10506–10514.

Babel, S. & Kurniawan, T. A. 2003 Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Material* **97** (1–3), 219–243.

Brunauer, S., Emmett, P. H. & Teller, E. 1938 Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* **60** (2), 309–319.

Cant, P. A. E. & Walker, N. J. 1977 Regeneration of monocarbonyls from their 2, 4-dinitro-phenylhydrazone derivatives. *Journal of Chromatography A* **130**, 267–273.

Chantawong, V., Harvey, N. W. & Bashkin, V. N. 2003 Comparison of heavy metal adsorptions by Thai kaolin and ball clay. *Water, Air & Soil Pollution* **148**, 111–125.

Chawla, J., Kumar, R. & Kaur, I. 2015 Carbon nanotubes and graphenes as adsorbents for adsorption of lead ions from water: a review. *Journal of Water and Supply: Research and Technology-Aqua* **64**, 641–659.

Chowdhury, S., Mazumder, M. A. J., Al-Attas, O. & Husain, T. 2016 Heavy metals in drinking water: occurrences, implications and future needs in developing countries. *Science of the Total Environment* **569–570**, 476–488.

Demirbas, E., Kobya, M., Oncel, S. & Sencan, S. 2002 Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. *Bioresource Technology* **84** (3), 291–293.

El-Ashtoukhy, E. S. Z., Amin, N. K. & Abdelwahab, O. 2008 Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination* **223**, 162–173.

Ibezim-Ezeani, M. U., Okoye, F. A. & Akaranta, O. 2010 Studies on the ion exchange properties of modified and unmodified orange mesocarp extract in aqueous solution. *International Archive of Applied Sciences and Technology* **1** (1), 33–40.

Ihsanullah, Abbas, A., Al-Amer, A. M., Laoui, T., Al-Marri, M. J., Nasser, M. S., Khraisheh, M. & Atieh, M. A. 2016 Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. *Separation and Purification Technology* **157**, 141–161.

Kaur, I., Mandiyal, D., Singh, B. P., Kumar, R. & Chawla, J. 2016 Amino-functionalized mesoporous MCM-41: an efficient adsorbent for the removal of chromium (III) ions from aqueous solution. *Journal of Water Supply: Research and Technology-Aqua* **65** (6), 480–493.

Kulkarni, A. P., Aradhya, S. M. & Divakar, S. 2004 Isolation and identification of a radical scavenging antioxidant: punicalagin from pith and carpellary membrane of pomegranate fruit. *Food Chemistry* **87** (4), 551–557.

Kumar, S. & Gayothri, R. 2009 Adsorption of Pb^{2+} ions from aqueous solutions onto bael tree leaf powder: isotherms, kinetics and thermodynamics study. *Journal of Engineering Science and Technology* **4** (4), 381–399.

Kumar, R. & Chawla, J. 2014 Removal of cadmium metal from water/wastewater by nano-metal oxide: a review. *Water Quality, Exposure and Health* **5**, 215–226.

Kumar, A. & Kumar, V. 2015 Kinetic, equilibrium isotherm and thermodynamic study for removal of cadmium from wastewater by using modified pomegranate peel. *Journal of Chemical and Pharmaceutical Research* **7** (1), 685–697.

Kumar, P. S., Ramalingam, S., Kirupha, S. D., Murugesan, A., Vidhyadevi, T. & Sivanesan, S. 2011 Adsorption behavior of nickel(II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design. *Chemical Engineering Journal* **167** (1), 122–131.

Kumar, R., Chawla, J. & Kaur, I. 2015 Removal of cadmium metal from water by carbon based nanosorbents: a review. *Journal of Water and Health* **13** (1), 18–33.

Kyzas, G. Z., Deliyanni, E. A. & Matis, K. A. 2016 Activated carbons produced by pyrolysis of waste potato peels: cobalt ions removal by adsorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **490**, 74–83.

Lagergren, S. 1898 About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* **24** (4), 1–39.

Mahmoud, M. E., Fekry, N. A. & El-Latif, M. M. A. 2016 Nanocomposites of nanosilica-immobilized-nanopolyaniline and crosslinked nanopolyaniline for removal of heavy metals. *Chemical Engineering Journal* **304**, 679–691.

Moghadam, M. R., Nasirizadeh, N., Dashti, Z. & Babanezhad, E. 2013 Removal of Fe(II) from aqueous solution using pomegranate peel carbon: equilibrium and kinetic studies. *International Journal of Industrial Chemistry* **4** (19), 1–6.

Mohammad, M. S. & Kashani, H. H. 2012 Chemical composition of the plant *Punica granatum* L. (pomegranate) and its effect on heart and cancer. *Journal of Medicinal Plants Research* **6** (40), 5306–5310.

Najim, T. S. & Yassin, S. A. 2009 Removal of chromium from aqueous solution using modified pomegranate peel: mechanistic and thermodynamic studies. *E-journal of Chemistry* **6** (S1), S153–S158.

Ngah, W. S. W. & Hanafiah, M. A. K. M. 2008 Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology* **99** (10), 3935–3948.

Sayari, A. & Hamoudi, S. 2001 Periodic mesoporous silica-based organic inorganic nanocomposite materials. *Chemistry of Materials* **13** (10), 3151–3168.

Villarroel-Rocha, J., Barrera, D. & Sapag, K. 2014 Introducing a self-consistent test and the corresponding modification in the Barrett, Joyner and Halenda method for pore-size determination. *Microporous and Mesoporous Materials* **200**, 68–78.

Wang, F., Lu, X. & Li, X. 2016 Selective removals of heavy metals (Pb^{2+}, Cu^{2+} and Cd^{2+}) from wastewater by gelation with alginate for effective metal recovery. *Journal of Hazardous Materials* **308**, 75–83.

World Health Organization (WHO) 2017 Ten chemicals of major public health concern. Available online: http://www.who.int/ipcs/assessment/public_health/chemicals_phc/en (accessed 19 October 2017).

Zhao, J., Liu, J., Li, N., Wang, W., Nan, J., Zhao, Z. & Cui, F. 2016 Highly efficient removal of bivalent heavy metals from aqueous systems by magnetic porous fe_3o_4-mno_2: adsorption behavior and process study. *Chemical Engineering Journal* **304**, 737–746.