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Mesoporous Carbon Xerogels Adsorbents for Adsorption of Cadmium and p-Nitrophenol Pollutants: Kinetic and Equilibrium Studies

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Abstract

Mesoporous carbon xerogels were prepared by carbonization of resorcinol-formaldehyde xerogel in presence of tannic acid as a soft-template at 700ºC for 30, 60 and 90 min, respectively. Morphology, textural, surface functional surface groups and thermal analyses were measured. Their efficiency in liquid-adsorption of cadmium ions and p-nitrophenol (PNP) in a batch mode was carried out. Effect of some key factors such as pH, carbon dose, and contact time of cadmium ions and PNP as well as kinetic adsorption studies were performed. It was found that the obtained carbon xerogels of mesoporous structure have a moderate total surface area reached to 268 m^2/g with various surface functional groups are effective sites for adsorbing cadmium ions and PNP from aqueous solutions. The adsorption behavior of both adsorbates on the prepared carbon samples was best described by the pseudo-second-order kinetic and Langmuir adsorption models. The maximum adsorption capacities of cadmium ions and PNP were 99 and 133 mg/g, respectively; onto the prepared carbon xerogel at 700ºC and 60 min. As a result of these observations, the produced mesoporous carbon samples are very effective adsorbents for extracting considerable amounts of cadmium ions and PNP from aqueous solutions.

Keywords: Carbon xerogels; adsorption; cadmium ions; para-nitrophenol; equilibrium studies

1. Introduction

In order to enhance the performance of carbon materials as adsorbents, catalysts or catalyst supports, many researchers accommodated between the porous structure and chemical surface properties of them, which in turn, control the strength of the interactions between the surface of carbon material and the corresponding target molecule [1-5]. One of the main advantages of carbon xerogels is their versatility in both porous structure and physicochemical properties that can be easily modified to one specific application. The most common synthesis of such materials is via the polycondensation of resorcinol with formaldehyde in water as solvent and a basic or acid catalyst followed by drying in a conventional dryer and then carbonization at elevated temperatures [2, 3, 5].

For environmental tasks, activated carbons (ACs); among various adsorbents, is still by far the most important one in current use in the environmental pollution. This is mainly attributed to its large surface area, high adsorption capacity to a limit extent, microporous structure and selective adsorption [4, 6, 7]. However, the dominance of micropores (<2 nm) in ACs limits the transport of metal ions, hydrated metal ions and large molecules through the surface of ACs into inside pores. Thus, it is essential to produce mesoporous carbon adsorbents with both accessible pores and surface active sites [8, 9] which would improve the adsorption rate and efficiency [10]. Accordingly, the remediation of several pollutants such as heavy metals and organics introduced into surface water during discharging wastewater of many industries is a target of many researchers nowadays. Increasing the accumulative dose of heavy metals (such as lead, mercury, copper, zinc and cadmium) in water which do not degrade biologically like some organics can be caused major concerns because they can affair poisoning, cancer and nervous system damages. [8, 11-15]. In particular, the accumulation of cadmium in drinking water can affair some diseases such as lung

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insufficiency, muscular cramps, cancer, diarrhea, nausea and renal degradation [14, 15]. Many techniques have been used in the literature to reduce the dosage of these metals in water, such as chemical oxidation, reduction, precipitation, membrane filtration, ion exchange, and adsorption [8, 11-15]. Adsorption has been reported to be a promising technique for the removal of metal ions from wastewater sources due to its simplicity, economics, and appropriateness during removal operations, and it can pave the way to discover innovative and high-efficiency adsorbents.

On the other hand, organic chemicals such as phenolic derivatives are disposed very frequently in wastewater from heavy chemical, petrochemical, and oil refining industries [16-19]. Therefore, removal to less noxious structures of phenolic compounds is essential for purification of wastewaters as well as raw water. In particular, para-nitrophenol (PNP) is mostly applied as a model of phenolic contaminant [18, 19].

In this paper, carbon xerogels were prepared by carbonization of resorcinol-formaldehyde xerogel in presence of tannic acid as a soft-template at 700ºC for 30, 60 and 90 min, respectively. The removal of cadmium ions and PNP over prepared mesoporous carbon xerogels was carried out. The batch mode adsorption was selected due to its simplicity. The influence of some key factors such as pH, carbon dose, and contact time of metal ions and PNP were investigated. Kinetic adsorption studies were performed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models to determine the mechanism of adsorption. The adsorption isotherm studies of cadmium and PNP species were determined by a batch operation at pH of 5 and room temperature of 25ºC. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherms to specify the type of adsorption process on the surface of adsorbents.

2. Materials and methods

2.1. Materials

As carbon xerogel source, resorcinol (R, $C_6H_4(OH)_2$, Panreac, 99%) was polymerized with formaldehyde (HCHO, 37%, Aldrich), methanol (CH_3OH, Aldrich, 99%), and sodium carbonate (Na_2CO_3, Lab Rasayan, 99%) as catalyst. Tannic acid (TA, $C_{76}H_{52}O_{46}$, SDFCL, 99%) was used as a soft template to avoid shrinkage during drying and carbonization process. Ammonia solution (NH_4OH, Adwic, 25–28%) and nitric acid (HNO_3, Alpha Chemika, 60–63%) were applied for adjusting pH. Acetone (CH_3COCH_3, Adwic, 96%) was used for solvent exchange during the drying process.

2.2. Synthesis of mesoporous carbon xerogels

The preparation method includes two steps; the first is sol-gel step and second one is the carbonization of prepared gel at 700ºC within different times. Typically, about 4.24 g of R and 7.99 g of TA were dissolved in a 20 ml of methanol as a solvent at 25ºC, followed by slow addition of F (14.8 mL). Then, NH_4OH (0.5 mmol L^{-1}) was added into R/TA/F solution under vigorous stirring to pH 10. After that, low amount of dissolved Na_2CO_3 in distilled H_2O was added as catalyst. A dark brown homogenous sol was observed and started to form the alcogel after 20 min through raising temperature from 25 to 80ºC. The formed alcogel was immersed in acetone solution for exchanging with methanol and water to avoid shrinkage during the conventional drying step. After pulling gel from acetone, the gel was dried in air-oven at 90ºC for 4 h and overnight at 110ºC. Then, some portions of the dried gel were carbonized at 700ºC under N_2 gas flow for 30, 60 and 90 min. The symbols of prepared carbon xerogels were labelled as CX-700-30, CX-700-60 and CX-700-90.

2.3. Characterization tools

Scanning electron microscopy of JEOL JXA-840A and transmission electron microscopy (JEOL model, TEM-1230 Electron analyzer) were used to visualize the surface morphology of selected carbon xerogel. Before scanning run, the sample was coated with gold using quick auto-coaters (JFC-I500, JEOL). Thermogravimetric analysis (TGA) was performed under N_2 atmosphere with heating rate of 10º/min using TGAQ500V20.10 Build (universalV3.9A, TA instruments). The sample was put in silica crucible and subject to pyrolysis program starting from room temperature to 800ºC. Fourier transform infrared spectroscopy (FTIR) was recorded within the wavenumber range 4000–400 cm^{-1} using a spectrophotometer of FTIR-2000 Perkin Elmer (USA), employing pressed KBr-pellets with a mass ratio of 0.002 sample/0.998 KBr (g/g) and then scanned. Moreover, the porous properties of the prepared samples were evaluated using N_2 adsorption analysis at -196ºC (BEL-Sorp, Microtrac Bel Crop, Japan) as listed in Table 1.

2.4. Adsorption experiments

The main objective of this study was to assess the feasibility of mesoporous carbon xerogels in

adsorption of Cd (II) and p-nitrophenol (PNP) from their aqueous solutions. Stock solutions of each Cd (II) and PNP with initial concentration of 500 mg/L were prepared. The effect of the following parameters on the kinetic removal of both pollutants was studied: *(i)* pH variable (2-8) (ii) carbon dose (0.01 – 0.1 g) and (iii) agitation time (0–180 min) at a temperature (25ºC). In each batch adsorption round, about 100 mg of dried powder carbon adsorbent was added into a 100 mL of Cd (II) ions and PNP solutions, separately; with those initial concentrations in a 250mL stopper conical flasks under shaking at 150 rpm for the desired time at 25ºC. Initial concentrations of Cd (II) ions and PNP pollutants with initial concentrations (20-200 mg/L) and (100-500 mg/L), respectively, were conducted to study the isotherm and mechanism of adsorption. At the end of the adsorption period, the solution sample (2ml) was taken and filtered using filter paper of Whatman No.45. The residual concentrations of Cd (II) ions in aqueous solutions were measured by atomic absorption spectrophotometer (AAS, a Perkin –Elmer model 2380) at wavelength equal 485nm. For determination PNP residual concentration, its absorbance value was taken at wavelength of 317 nm by using a UV–Vis spectrophotometer (Shimadzu-2401PC).

2.5. Kinetic and equilibrium studies

The amount of adsorbate adsorbed onto the prepared adsorbents at equilibrium (q_e, mg/g) or at time t (q_t, mg/g) was calculated according to the following equations:

$$q_e = \frac{(C_0 - C_e)}{\mathrm{m}} V \qquad \textbf{(1)}$$

$$q_t = \frac{(C_0 - C_t)}{\mathrm{m}} V \qquad \textbf{(2)}$$

where C_0, C_e, and C_t are initial, equilibrium and time concentrations (mg/L) of adsorbate, respectively. V is the volume of solution (mL) and m is the mass of adsorbent (mg). The effect of the contact time (0-180 min) was carried out to investigate the kinetic models such as:

Lagergren-first-order kinetic model which can be described by the equation [20]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad \textbf{(3)}$$

While pseudo-second-order kinetic model which **is** expressed by the equation [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad \textbf{(4)}$$

where q_e and q_t are the adsorbed amounts of adsorbate (mg/g) at equilibrium and time t (min), respectively; k_1 is the rate constant of the Lagergren-first-order kinetic model (min^{-1}). The values of k_1 were calculated from the plots of log (q_e–q_t) versus *t*. In equation (4), k_2 is the rate constant (g/mg min) of pseudo-second-order kinetic model of adsorption. The slope and intercept of the linear plots t/q_t against *t* yield the values of $1/q_e$ and $1/k_2q_e^2$.

The intra-particle diffusion model as proposed by Weber and Morris [22] is described by the equation:

$$\boldsymbol{q_t = k_{id}\, t^{1/2} + C} \qquad \textbf{(5)}$$

where C (mg/g) is the intercept and k_{id} is the intra-particle diffusion rate constant (mg/g $min^{1/2}$), which can be calculated from the slope of the linear plots of q_t *versus* $t^{1/2}$. All the calculated kinetic parameters are summarized in Table 2.

To examine the equilibrium adsorption of adsorbates onto the prepared adsorbents, thus the adsorption data were analyzed in terms of Langmuir and Freundlich isotherms. The linear form of the Langmuir isotherm [23] is expressed as the following equation:

$$C_e / q_e = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \qquad \textbf{(6)}$$

where C_e is the equilibrium concentration of adsorbate (mg/ L), q_e the amount of adsorbate adsorbed at equilibrium (mg/g), and Q_m is the monolayer adsorption capacity (mg/ g) and K_L (L /mg) is the Langmuir adsorption equilibrium constant. The free energy of adsorption, ΔG (kJ/mol) can also be evaluated from the parameter K_L according to the expression:

$$\boldsymbol{\Delta G = -RT \ln K_L} \qquad \textbf{(7)}$$

In addition Langmuir adsorption isotherm can be given in expression of a dimensionless constant called a "separation factor" and noted as (R_L):

$$R_L = \frac{1}{1 + K_L C_0} \qquad \textbf{(8)}$$

The equation representing linear form of Freundlich adsorption [24] can be given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \textbf{(9)}$$

where K_F (mg/g (L/mg)$^{1/n}$) is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. Freundlich constants K_F and *1/n* can be calculated from the intercept and slope of the linear plot with *log* q_e against *log* C_e. To justify the applicability of each isotherm, the correlation coefficient (R^2) was calculated.

3. Results and discussion

3.1. Surface characteristics of adsorbents

It is essential to elucidate the morphology of adsorbent to investigate the surface properties of adsorbent. Fig. 1 (a and b) shows both SEM and TEM images of selected sample (CX-700-60). It can be deduced that the carbonization of resorcinol and formaldehyde gels in presence of tannic acid as soft template produced semi-spherical carbon particles appearing as interconnected nodules. The size of developed carbon particles is ranged between 50 and 120 nm as calculated from TEM. Otherwise, carbon xerogels formulated from only resorcinol-formaldehyde organic gels had spherical carbons with lower sizes than 50 nm; however, their porous structures companied with large shrinkage during drying and carbonization as reported in elsewhere [9, 10, 25-28]. In the TEM image (Fig. 1b) it can be seen formation of intercluster voids confirming the generation of the mesopores into CX network.

Fig. 2 displays FTIR spectra of the carbonized samples at 700ºC for 30, 60 and 90 min, respectively. The surface functional groups in all samples are similar; however, a considerable reduction in their intensities is observed with increasing in the carbonization time. Moreover, the samples are enriched in oxygen functional groups such as –OH, COO–, C=O and C−O [3, 9, 10]. For example, the boarder band at 3420 cm^{-1} is associated to H-bonded water molecules, to hydroxyl groups from carbonyls, phenols or alcohols. A shoulder band at 1712 cm^{-1} is assigned to C=O stretching vibration in ketenes, aldehydes, lactones or carboxylic groups which disappeared in CX-700-90. At 1620 cm^{-1}, sharper band is assigned to C=C aromatic skeletal stretching or conjugated C=O stretching vibration in aromatic system [3, 9, 10]. Bands between 1300 and 900 cm^{-1} in all spectra are currently assigned to C−O stretching in acids, alcohols, phenols, ethers, and esters.

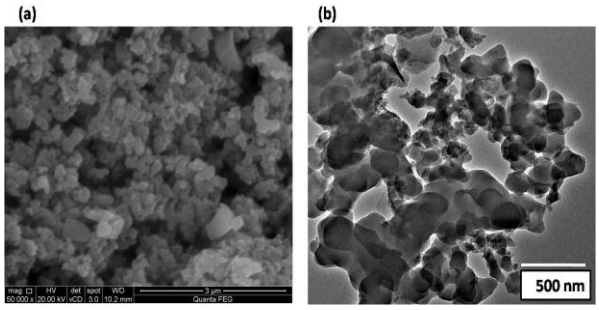

Fig. 1: (a) SEM and (b) TEM images of CX-700-60 adsorbent.

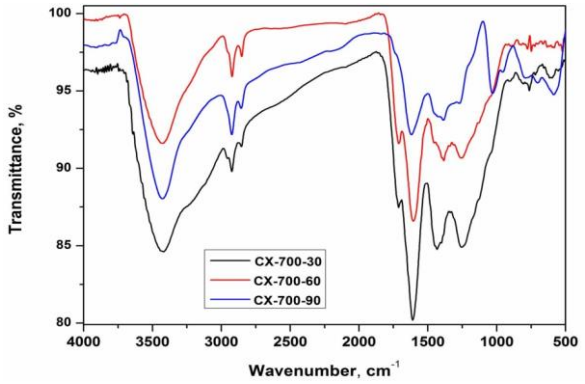

Fig. 2: FTIR spectra of the investigated samples.

In order to follow the changes in the thermal behavior of prepared carbon xerogels, CX-700-60 was selected as shown in Fig. 3. This sample was subjected to the thermo-analytical measurements up to 800ºC under flowing N_2 gas. The dramatic thermal decomposition in TGA of CX-700-60 is occurred after 350ºC (88% weight is fixed) till 800ºC (17% weight is fixed). About 6% of sample is decomposed till 100ºC due to the release of water and solvents, followed by further 6% of weight loss is happened up to 350ºC which is resulted from decomposition of light organics to CO_2 and CH_4 gases. After this temperature, larger organics in carbon network are decomposed gradually with formation CO gases at higher temperatures confirming that gasification process of carbon sample is high [3]. This could be ascribed to the high O-content of the surface which enhances the self gasification reaction [3, 28]. From these findings, the prepared samples exhibited superb thermal stability.

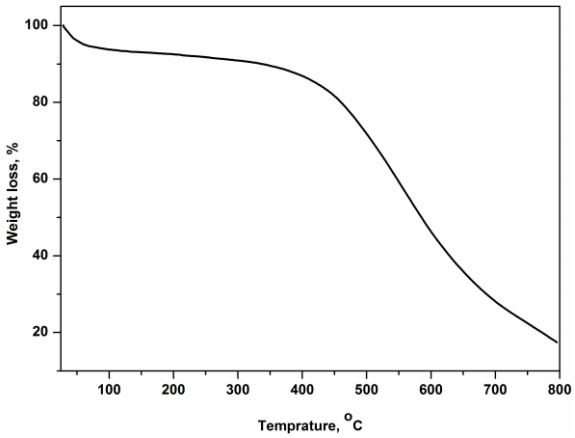

Fig. 3: TGA profile of the prepared CX-700-60 sample.

3.2. Textural properties of samples

Evaluation of the microporosity and mesoporosity development in the prepared samples was employed with regarding to the following parameters: the BET surface area (S_{BET}, m^2/g), total pore volume at relative pressure P/P_0= 0.97 (V_P, cm^3/g), mean pore radius (W_P, Å) was calculated from $(2V_P/S_{BET}) \times 10^4$, micropore volume ($V_{micro}$, cm^3/g) and micropore surface area (S_{micro}, m^2/g) were calculated from the t-plot theory and mesopore volume (V_{meso}, cm^3/g) from the difference between V_p and V_{micro} as listed in Table 1.

When the organic gel exposed to thermal carbonization at 700ºC during different times, it was found that increasing time from 30 to 60 min developed well-porosity with high total surface area in CX-700-60. Whereas the higher time of carbonization could be inhibited the total porosity as shown in CX-700-90. Also, CX-700-60 sample has high total surface area and mesoporosity reached to 64.7% which could enhance the adsorption of heavy metals and organics from aqueous solution. Therefore, good quality adsorbent carbons can be obtained by heat treatment at 700ºC for 60 min. Overall, mesoporous carbon xerogels are synthesized successfully using tannic acid as template through sol-gel process of resorcinol with formaldehyde followed by drying and then pyrolysis at 700ºC with different times.

3.3. Adsorption studies of cadmium (II) ions by the samples

In order to find the suitable pH working and carbon dose in removal of cadmium ions by the prepared carbons. Cadmium solutions (C_0= 50 mg/L) with different pH values (2, 4, 5, 7 and 8) were performed with 0.04 g of each sample as shown in Fig. 4a. The maximum Cd(II) removal occurred in the pH range 5–8 while removal of cadmium was very slightly at pH 2 [14, 29, 30]. At pH 8, the removal of cadmium was completely occurred onto CX-700-60. It has been reported that at pH 8.0, the species distribution is approximately 90% Cd^{2+} and 10% $Cd(OH)^+$ [30]. The maximum removal was occurred at pH of 5.

Table 1: Porosity parameters developed in the investigated carbon xerogels.

Sample notation	S_{BET} (m^2/g)	V_P (cm^3/g)	W_P (Å)	S_{micro} (t- plot) (m^2/g)	V_{micro} (t-plot) (cm^3/g)	V_{meso} (cm^3/g)	% V_{meso}
CX-700-30	136	0.114	16.8	70	0.042	0.072	63.2
CX700-60	268	0.244	18.2	141	0.086	0.158	64.7
CX700-90	225	0.188	16.7	115	0.074	0.114	60.6

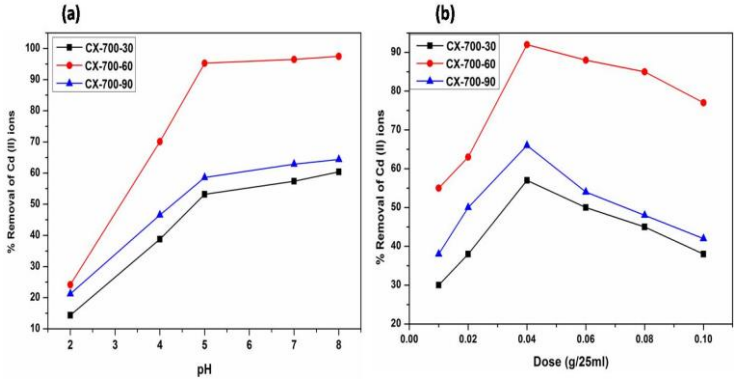

Fig. 4: Effects of (a) pH variable (C_0= 50 mg/L, m = 0.04 g, V = 25 ml, time = 2 h and T =25ºC) and (b) carbon dose on the removal of Cd (II) ions from aqueous solutions (C_0= 50 mg/L, V = 25 ml, time = 2 h and T = 25ºC).

Carbon dose effect within different values (0.01 to 0.1 g/25 mL) with initial concentration of Cd (II) ions equal to 50mg/L was tested as shown in Fig. 4b. The highest removal of Cd (II) ions was discovered at 0.04 g of all samples, after which there was reduction in removal efficiency. Accordingly, over the optimum carbon dose (0.04 g); an aggregation phenomenon is happened and led to a decrease in the available surface area followed by a decrease in adsorption efficiency [14, 29].

At initial concentration of 100 mg/L in 100 mL aqueous solution conducted with 0.1 g of sample, effect of contact time is studied as depicted in Fig. 5. Adsorption of Cd (II) is increased frequently with an increasing in the contact time. The equilibrium time is started at 30 min over the surface of tested adsorbents. The highest sample of total surface area and mesopores (CX-700-60) exhibited superior adsorption of cadmium at 5 min (75mg/g) which reached to 98 mg/g at 180 min.

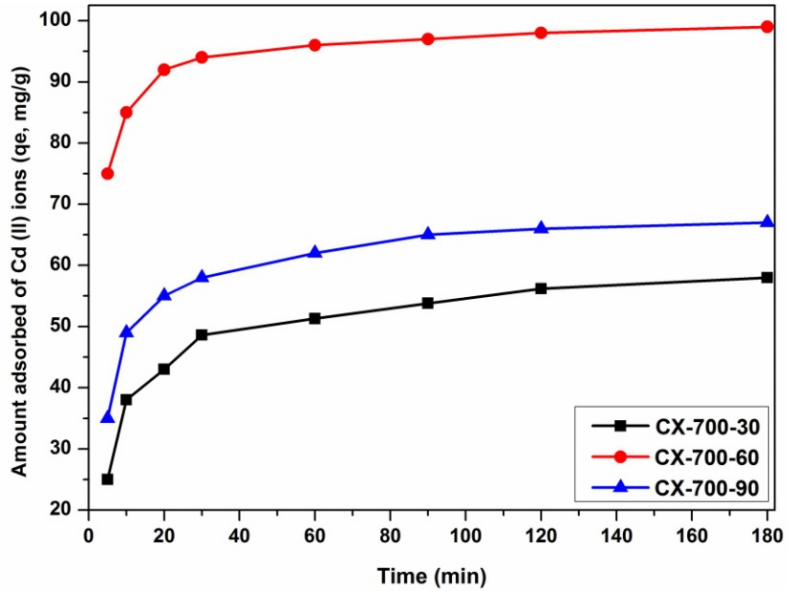

Fig. 5: Effect of contact time on the amount adsorbed of Cd (II) ions onto carbon samples as a function of C_0 = 100 mg/L, m = 0.1 g, V = 100 ml, pH= 5 and T=25ºC.

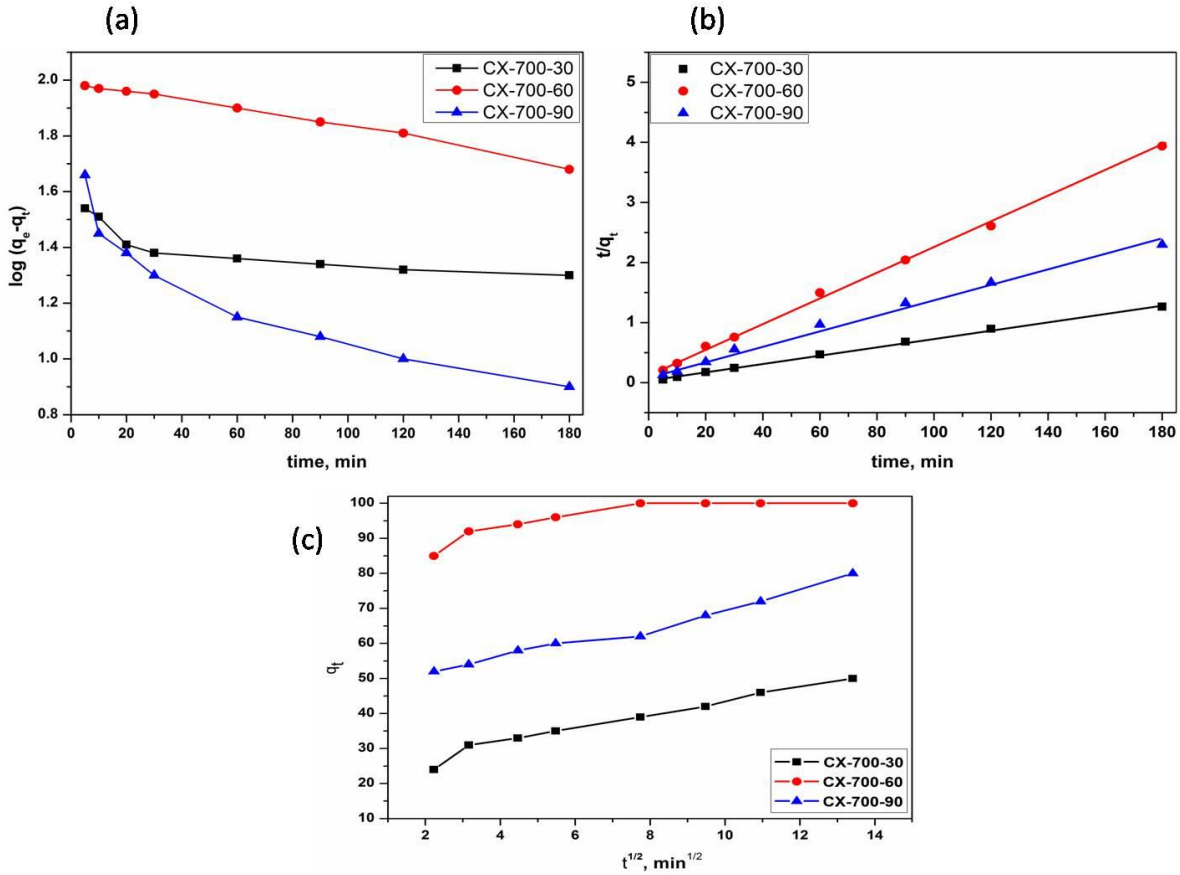

Fig. 6: Plots of (a) pseudo-first order kinetic (b) pseudo-second order kinetic and (c) Intraparticle diffusion models (C_0 = 100 mg/L, m = 0.04 g, V = 100 ml, pH= 5 and T=25ºC).

Kinetic studies of Cd (II) adsorption by using three kinetic models are estimated and drawn in Fig. 6. The calculated constants of those models are listed in Table 2. Correlation coefficients (r^2) of pseudo-first order and pseudo-second order kinetic models are summarized in Table 2. The straight lines in plot of linear pseudo-second order equation showed good agreement of experimental data given higher correlation coefficients closed to unity as compared to pseudo-first order kinetic model. This affirms that the adsorption of Cd (II) onto prepared carbons is most suitably represented by a pseudo-second order rate process. Moreover, the intraparticle diffusion plots showed two stages of adsorption as seen in Fig 6c. The first linear portion refers to the boundary layer diffusion (film diffusion) and the latter portion is owing to the intraparticle diffusion [14, 29]. This result indicates that the adsorption process proceeds by surface adsorption and intraparticle diffusion.

Equilibrium adsorption is also analyzed using two-known models such as Langmuir and Freundlich isotherms. Table 3 lists the values deduced from both isotherms as well as their correlation coefficients (r^2). The cadmium adsorption capacity (Q_m, mg/g) by the obtained carbon adsorbents was found to be in the decreasing order as follows: CX-700-60 > CX700-90 > CX-700-30. The Langmuir equation fitted the data better than the Freundlich equation by describing the data over the entire concentration range (100-500 mg/L) due to they have higher r^2 values. Table 4 shows comparison adsorption capacity of different adsorbents toward adsorption of cadmium. It can be indicated that the prepared carbons exhibited superior adsorption capacity as compared to other reported carbon adsorbents such as activated carbons and carbon nanotubes. This finding may be attributed to their morphology and mesopores in their porous structure which are proper for uptaking cadmium ions.

Table 2: Adsorption kinetic constants for adsorption of Cd (II) ions by the investigated carbon xerogels (carbon weight = 0.1 g, volume =100 mL, pH= 5 and temperature= 25ºC).

Samples	C_0 (mg/L)	*First order kinetic*			*Second order kinetic*				*Intraparticle diffusion*	
		q_{e1} (mg/g)	k_1 (min^{-1})	r^2	q_{e2} (mg/g)	k_2 (g/mg min)	h (mg/ g min)	q_{e2} (mg/g)	K_{id} ($mg/g\ min^{0.5}$)	q_{e1} (mg/g)
CX-700-30	**100**	28.6	0.010	0.887	28.7	3.01×10^{-4}	0.248	0.999	1.03	15.0
CX-700-60	**100**	55.9	0.016	0.977	97.3	9.03×10^{-5}	0.238	0.995	1.84	23.9
CX-700-90	**100**	42.2	0.002	0.940	67.1	1.10×10^{-4}	0.495	0.996	3.28	11.3

Table 3: Langmuir and Freundlich constants for the adsorption of Cd (II) ions.

Sample Notation	Langmuir parameters					Freundlich parameters		
	Q_m mg/g	K_L L/g	R_L	ΔG^o kJ/mol	r^2	K_F	1/n	r^2
CX700-30	57	0.0345	0.168	- 18.6	0.998	3.6	0.632	0.911
CX700-60	99	0.0737	0.127	- 19.7	0.998	11.1	0.420	0.922
CX700-90	74	0.0418	0.145	- 19.3	0.999	9.5	0.449	0.915

Table 4: Comparison of adsorption capacities of Cd (II) ions onto different carbon adsorbents

Adsorbents	S_{BET} (m^2/g)	Amount adsorbed (mg/g)	Refs
Activated carbons-common reed	**1193**	**83.4**	[14]
Activated carbon- cotton stalks	**253**	**31.6**	[29]
Activated carbons	**130.4-234.4**	**40.9-48.1**	[31]
Carbon nanotubes	**60**	**~ 17.9**	[32]
Carbon xerogels	**136-268**	**57-99**	This work

3.4. Adsorption studies of p-nitrophenol by the samples

Fig. 7 (a) depicts the effect of pH variation between values of 2 and 8 on the removal of PNP onto the prepared carbons with initial concentration 100mg/L, carbon dose of 0.04g and volume 25 mL at 25ºC. At pH range of 2 to 5, all samples showed increase in removal percentage as pH increased from 2 to 5, and the maximum removal (37, 66 and 55 % by CX700-30, CX-700-60 and CX-700-90, respectively) occurred at pH of 5 where molecular PNP existed in the solution.

By increasing pH to 6 and 8, the removal percentage decreased due to the electrostatic repulsions between the negatively charged surface of samples and anionic forms of PNP [33]. Thus the highest removal occurred at pH of 5 which be used in next adsorption experiments.

Fig. 7b describes the effect of carbon dose (0.01 to 0.1 g/25 mL) with 50mg/L of PNP at 25ºC. As cadmium adsorption, the optimum carbon dose occurred at 0.04 g/25mL. Over this dose, the adsorption of PNP decreased because of the active sites in the samples become saturated and undergo aggregation, thereby reducing their adsorption capacities [34].

Fig. 7c illustrates the results obtained from effect of contact time on the amount adsorbed of PNP when an initial concentration of 100 mg/L in 100 mL aqueous solution conducted with 0.1 g of sample. Fast PNP adsorption is observed with increasing the contact time and CX-700-60 showed the better adsorption than other tested samples. Table 5 lists the kinetic constants derived pseudo-first order, pseudo-second order kinetic and intraparticle diffusion models with their correlation coefficients (r^2) to explore the possible mechanism of p-nitrophenol adsorption on the samples. Results indicate that pseudo-second order kinetic can satisfactorily fit the kinetic data based on the high r^2 (0.959–0.991). This finding means that the adsorption process is controlled by chemisorption on the surface on adsorbent.

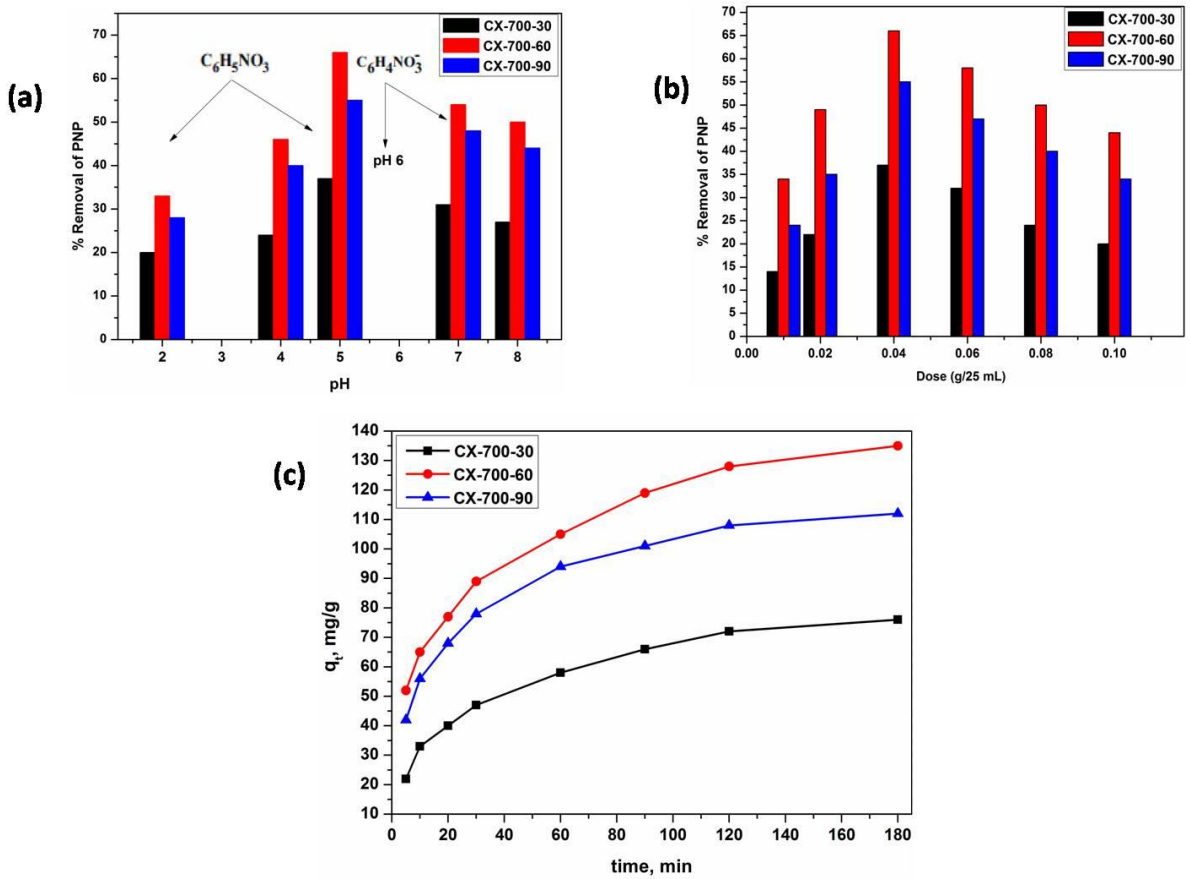

Fig. 7: Effects of (a) pH variable (C_0= 50 mg/L, m = 0.04 g, V = 25 ml, time = 2 h and T =25ºC); (b) carbon dose (C_0= 50 mg/L, V = 25 ml, time = 2 h and T = 25ºC) and (c) contact time on the removal of PNP from aqueous solutions (C_0= 100 mg/L, V= 100 mL, pH= 5 and T = 25ºC).

Adsorption isotherms are provided for the adsorption of PNP on CX-700-30, CX-700-60 and CX-700-90 samples as shown in Fig. 8. The results indicated that the adsorption of PNP is described well with L-type (Langmuir) isotherm confirming that monolayer adsorption took place on the surface with a range of p-nitrophenol concentrations (100, 150, 200, 300, 400 and 500 mg/L). It was found that Langmuir isotherm displayed high values of r^2 (0.997-0.999) and is a more suitable model to explain the adsorption behavior of PNP. The maximum adsorption quantity (Q_m) of PNP onto CX-700-30, CX-700-60 and CX-700-90 samples was found to 69, 133 and 103 mg/g, respectively. In a particular, CX-700-60 showed the highest adsorption capacity. Also, the calculated Langmuir characteristics parameter (or separation factor, R_L) strongly indicate that the adsorption process of PNP is a favorable, where the values of R_L are much less than 1.0.

The negative value of ΔG^o means that the adsorption of PNP is a spontaneous and physisorption process as a result of interaction of π-electron region of the aromatic structures of carbon surface with the electron acceptor on the aromatic ring of p-nitrophenol *via* π–π interactions [18, 19, 32]. In a conclusion, good adsorbing mesoporous carbons are obtained by carbonization of resorcinol-formaldehyde templated on tannic acid, as observed by the uptake of p-nitrophenol from aqueous solutions.

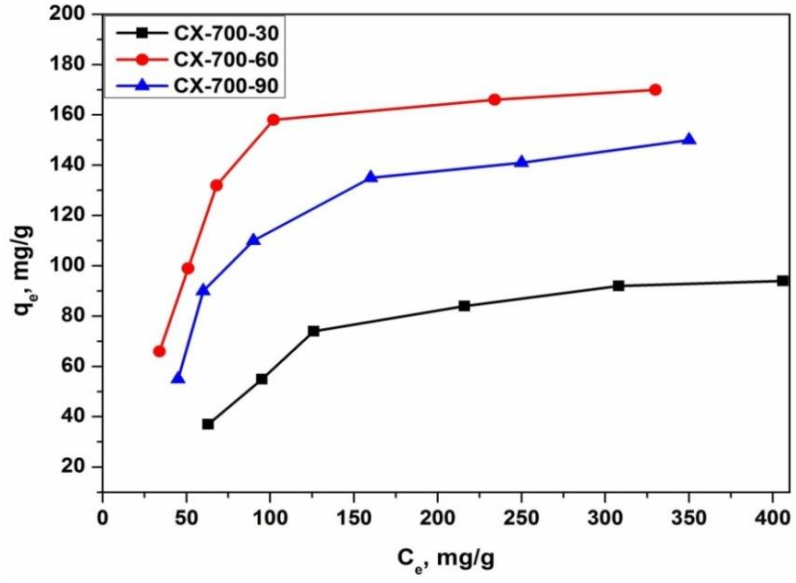

Fig. 8: Adsorption isotherms of PNP onto the prepared samples (pH= 5 and T = 25°C

Table 6: Langmuir and Freundlich constants for the adsorption of PNP.

	Langmuir parameters					Freundlich parameters		
Sample Notation	**Q_m mg/g**	**K_L L/g**	**R_L**	**ΔG^o kJ/mol**	**r^2**	**K_F**	**1/n**	**r^2**
CX700-30	69	0.154	0.047	- 19.6	0.997	3.6	0.632	0.911
CX700-60	133	0.277	0.107	- 22.7	0.999	11.1	0.420	0.942
CX700-90	103	0.168	0.075	- 21.3	0.999	9.5	0.449	0.925

Table 7: Comparison of adsorption capacities of PNP onto various carbon adsorbents.

Adsorbents	Amount adsorbed (mg/g)	Refs
Activated carbons	**116-212**	[18]
Carbon fibers	**155-258**	[19]
Sawdust biochars	**~ 29- 117**	[33]
Microalgal biochar	**~ 205**	[34]
Nanographite oxide	**~269**	[35]
Oxidized graphite	**333**	[36]
Carbon xerogels	**69-133**	This work

In addition, Table 7 summarizes the adsorption capacity of PNP onto different carbon materials with our prepared carbon xerogels samples [18, 19, 33-36]. It can be disclosed that the capacity of PNP onto carbon xerogels prepared in this study is comparable or less than those reported by other carbon materials. Moreover, the adsorption rate using carbon xerogels is faster throughout their mesoporous structure as compared to these adsorbents in literature.

4. Conclusions

The carbonization of resorcinol-formaldehyde templated on tannic acid for 60 min at 700°C yielded good mesoporous carbon material to be used as adsorbent. Results of liquid-phase adsorption toward cadmium and p-nitrophenol confirmed the high performance of these materials. Maximum adsorption capacity of both cadmium ions and PNP onto the greatest carbon adsorbent (CX-700-60) sample was 99 and 133 mg/g, respectively.

Overall, the final characteristics of the prepared adsorbents; such as high total surface area, degree of mesoporosity as well as the active sites of surface functional groups are the most effective factors in the adsorption of cadmium and p-nitrophenol onto the prepared samples.

Conflict of interest

Authors declare that there is no conflict of interest

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