Removal of Chlorophenols Compounds Using Treated Jatropha Seed Shells Adsorbents: Characterization and Thermodynamic

Ammar Alkhawlani[1] · Saad M. Howladar[2]

Abstract

In this study, Jatropha seed shells from Yemeni plant have been tested for studying adsorption of treated seeds shells to remove chlorophenol compounds. The resulting adsorbents were designated as JAT1, JAT2 and JAT3. Most of the acidic groups on the surface were found to be phenolic in nature (37.5% in the case of JAT1 and 60% in the case of JAT). The adsorption of chlorophenol on JAT1, JAT2 and JAT3 was investigated in the temperature range 35–70 °C for initial chlorophenols concentrations ranging from 20 to 100 ppm. JAT2 was thereby found to be the best with respect to its capability to remove chlorophenols from solution indicating that thermal treatment at 500 °C is suitable to produce a good adsorbent. JAT3 is the worst in removing DCP even at high temperatures. It was also found that the removal efficiencies were in general enhanced at lower pH for all three adsorbents and for the two chlorophenols. For DCP, the corresponding heats of adsorption were found to be $+5.3$, -10.75 and -14.4 kJ/mol. The small values for the heat of adsorption indicate that the interaction of chlorophenols with the adsorbent surface does not differ significantly from its interaction with water molecules in solution.

1 Introduction

Most of the organic compounds released into nature may cause many problems to the environmental and human health because of their high toxicity even at low concentrations. They may dissolve in water, react with other compounds or evaporate to ambient air. A famous group of organic pollutants is chlorophenols which have in virtue of their low solubility in water toxic effects related to interference with the lipid cell membranes of organisms [1]. Chlorophenols are released to the water bodies through industrial waste discharge and leaching of chlorophenols from landfills [2]. Other sources include sewage treatment plants and drinking water treatment, which can result in the chlorination of phenol. In the manufacture of some industrial products such as photographic chemicals, paints, oils, textiles, glues, cellulosic wood fillers, rubber, protein-based products and shampoos and industrial cooling and process waters in mills, chlorophenols are deliberately added to prevent growth of microorganisms [3].

Chlorophenols and their derivatives were major sources of dioxins [4, 5]. Chlorophenols can be introduced into our bodies by direct contact with skin because they can be rapidly absorbed through skin. Some of the chlorophenols can be bound to wood dust which is deposited mainly in the rose [6, 7]. Since chlorophenols are considered pollutant to the ecosystems and toxic to human health, various treatment methods have been developed for the removal of chlorophenols from wastewater and drinking water. Such treatment methods include adsorption, steam distillation, extraction, ion exchange, combined electrochemical reduction and oxidation, immobilization by enzymes, biodegradation, stripping and other technologies [8–11]. A variety of adsorbents have been proposed for the removal of chlorophenols from aqueous solutions including activated carbons (ACs), zeolites, bentonite, polymers, silica gel, clays, graphite and others [12, 13]. In virtue of activated carbons are large surface area per unit weight, fast adsorption rate, wide pore size distribution, high adsorption capacity and easy availability, activated carbon has been found to be effective for removing a wide range of organic pollutants from water. It has been recommended by the Environmental

✉ Ammar Alkhawlani
  ammarpostdoc@gmail.com

1 Department of Chemistry, College of Sciences, University of Mysore, Mysore, India

2 Department of Biology, College of Sciences, University of Jeddah, Jeddah, Saudi Arabia

Protection Agency (EPA) as one of the best available technologies for the removal of chlorophenols compound [14, 15].

Water is a very significant part of the earth's environment and an important component of life. Due to the continuous addition of undesirable chemicals, the consistency of our water supplies is declining day by day [16, 17]. The residues of drugs and pharmaceuticals (new emerging pollutants) in water are harmful to different water pollutants [18, 19]. The world is now in danger of being poisoned by pollutants [20–22]. Of great concern is water contamination due to agricultural and horticultural activities [23–25]. Adsorption process is simple, easy to handle, no need for reagent addition, low cost and has stable operation [26–28]. The adsorption is easy to operate, cost-effective and to a greater degree affect the toxicity and transport biological availability of inorganic and organic species in aqueous media [29–31].

Chlorophenol (CPs) are among the most widespread pollutants of wastewater and natural waters [32, 33]. Chlorophenol causes serious environmental problems, due to their high toxicity, strong odor emission, persistence in the environment and carcinogenic properties [34]. Thus, it is important to prevent their release into the environment and to study methods for their removal from contaminated sites [35]. Several methods are available for the removal of chlorinated phenols from water. Among them, biodegradation [36], oxidation by advanced oxidation processes [37] and adsorption [38] are the most widely used.

Although activated carbon is still the most widely used adsorbent, the high initial cost and the difficulty of regeneration of commercial coal-based activated carbon which stimulated the search for using lower cost and locally available adsorbents. Many successful attempts have been made to develop activated carbons from various agricultural solid wastes such as: ash, husk, peat, stone shells, palm shells, rice husk, olive mill waste, apricot stone shells, sunflower, rubber seed coat and other agricultural by-products [39–41]. Jatropha seed shell is a non-edible and freshly harvested Jatropha dried fruit coating about 35–40% shell and 60–65% seed (by weight) and Jatropha one of the trees grows normally in different types of soil. In this study, the aim was to investigate how the removal of chlorophenols compounds using treated Jatropha seed shells adsorbents: characterization, effect of pH and thermodynamic studies.

2 Materials and Methods

2.1 Preparation of Carbonaceous Adsorbents Jatropha Seed Shells (JSS)

Jatropha seed shells (JSS) were initially boiled in distilled water. The water is frequently replaced with fresh water until no color or turbidity changes to the boiling water are

observed. Then, the (JSS) was dried, grounded, and sieved. The dried material was then subjected to thermal activation under helium or He/O$_2$ atmosphere in a tabular glass reactor surrounded by an electrical. The type of thermal and chemical treatments and designation of resulting material are summarized in Table 1. The treated (JSS) were kept in sealed bottles.

The chemical treatment procedure was performed in the following method: After performing the thermal treatment, the resulting carbonaceous material was immersed in 1 M H$_3$PO$_4$ (1 g carbon in 50 ml H$_3$PO$_4$), shaken well for 1 h and left overnight in a tightly closed flask, next day the adsorbent was filtered and dried at 100 °C overnight.

2.2 Infrared Spectroscopy

Transmission FTIR measurements for all three adsorbents were performed on a Bruker Tensor-27 spectrometer. The samples were dried for 24 h at temperature of 110 °C before being pressed with potassium bromide (KBr).

2.3 Boehm Titration

Boehm titration is a chemical method to identify the acidic oxygen surface functional groups on carbonaceous materials. The technique is based on titrating the acidic surface groups using bases of different base strengths. It was accomplished according to the following procedure:

- For each adsorbent, three 1.5 g samples are dried at 120 °C.
- Each sample was placed into 50-ml volumetric flask. To the first volumetric flask 20 ml of 0.05 M NaOH was added, to the second 20 ml of 0.05 M Na$_2$CO$_3$ and the third 20 ml of 0.05 M NaHCO$_3$
- The previous mixtures were agitated for 24 h and then filtered to remove the carbon using 0.2 μm nylon-membrane syringe microfilter.
- 10-ml aliquots were taken by pipette from the filtered solutions.

Table 1 Type of treatment and designation of the resulting carbon material which prepared from JSS

Designation	Type of Treatment
JAT1	Thermal treatment at 400 °C for 4 h under He followed by one hour under an O$_2$/He mixture (96%He, 4% O$_2$)
JAT2	Thermal treatment at 500 °C for 5 h under He
JAT3	Thermal treatment at 400 °C for 5 h under He followed by chemical treatment using (H$_3$PO$_4$)

- The aliquots of the reaction base Na_2CO_3 were acidified by the addition of 20 ml of 0.05 M HCl to ensure complete neutralization of the base, which require two protons (diprotic), versus addition of 10 ml of 0.05 M HCl which one proton required by NaOH and $NaHCO_3$.
- The acidified solutions were then back titrated against phenolphthalein with 0.05 M NaOH, the tutor base, under continuous degassing with argon to remove CO_2 from solution (degassing starts two hours before the titration is performed).
- All reaction bases were standardized using potassium hydrogen phthalate (KHP) for NaOH, standard NaOH and standard HCl for Na_2CO_3 and $NaHCO_3$ [42, 43].

2.4 Calibration Curves

Stock solution of 4-CP and DCP was prepared by dissolving 0.200 g of analytical grade chemicals in water in 1000-ml volumetric flasks. For each chlorophenol, the stock solution was diluted to the desired initial concentration: 20, 40, 60, 80 and 100 mg/L (ppm), then 20 ml of each one was taken and diluted to 100 ml, and then, the samples were analyzed spectrophotometrically at 500 nm according to the standard 4-amino antipyrine colorimetric method using Shimadzu UV-1800 instrument to construct calibration curves which are linear suggested by Lambert–Beer Law.

2.5 Adsorption Experiment

The stock solution was diluted to desired initial concentration: 20, 40, 60, 80 and 100 mg/L (ppm) for each chlorophenol. 0.25 g adsorbent was placed into each of five volumetric flasks filled with the chlorophenol solution of various but known initial concentration (Ci). The volumetric flasks were covered with plastic screw caps and placed inside a water bath incubator shaker previously adjusted to the desired temperature. The flasks were shaken for 24 h to allow reaching equilibrium. One of the flasks contained only water and adsorbent, without any chlorophenol, to be used as a blank.

- Samples from solution mixture were then with drawn (2 ml) and filtered using the 0.2 μm nylon-membrane syringe microfilter to minimize interference of the carbon fines with the analysis. To reduce the possibility of chlorophenol adsorption on the filter, the microfilter was first saturated with the corresponding chlorophenol solution and washed thoroughly with distilled water.
- The samples of clear filtrate were analyzed spectrophotometrically at 500 nm according to the standard 4-amino antipyrine colorimetric method using a Shimadzu UV-1800 instrument to determine the residual 4-CP and DCP concentration (Ce).

2.6 Standard 4-Amino antipyrine Colorimetric Method

To each sample, 2.5 ml of 0.5 M NH_4OH solution was added and the pH was adjusted to 7,9 by using the phosphate buffer. 1 ml of 4-aminoantipyrine solution (2 g/100 ml) and 1 ml of potassium ferricyanide solution (8 g/100 ml) were added, respectively, and mixed well after each addition. After 30 min, the time required for reproducible color development, the absorbance of sample was recorded against blank at 500 nm (Fig. 1). Standard solution of 20, 40, 60, 80 and 100 ppm concentrations was used to build up a calibration curve for chlorophenol determination [44].

3 Results and Discussion

3.1 Spectrophotometric Determination and caLibration Curve of 4-CP in a Set of Standard Solution

3.1.1 Characterization of Adsorbents

3.1.1.1 Boehm Titration The surface of activated carbon adsorbents is rich with oxygen-containing functional groups such as carboxylic, phenolic and laconic group. Figure 2 is a schematic representation of such a surface with possible functional groups [45]. Boehm titration let us determine the acidic and basic surface groups qualitative and quantitative under the assumption that sodium hydroxide (NaOH) is the strongest base generally, used, and is assumed to neutralize all Bronsted acids (including phenols, laconic groups and carboxylic acids), while sodium carbonate (Na_2CO_3) neutralizes carboxylic and laconic groups (e.g., lactone and lacteal rings) and sodium bicarbonate ($NaHCO_3$) neutralizes carboxylic acids [9, 10]. Practically, a known mass of activated carbon adsorbent is soaked in each volume of standard solution of one of the above-mentioned bases. The amount of base that reacts with the surface acidic groups is evaluated volumetrically by determining the amount of base that reacts with the surface acidic groups is evaluated volumetrically by determining the amount of base remaining in the solution.

There are two different techniques to perform the titration: direct titration and back titration. But the most common is the back-titration technique based on mixing the resulting base solution with an excess of acid solution and titrating with base. In the case of direct titration, the resulting base solution is titrated directly with an acid [42]. The equation used to determine the quantity of surface groups depends on the titration method. For back titration, the amounts of

Fig. 1 **a** Spectrophotometric determination of 4-CP in a set of standards solution, **b** calibration curve for 4-CP Spectrophotometric determination
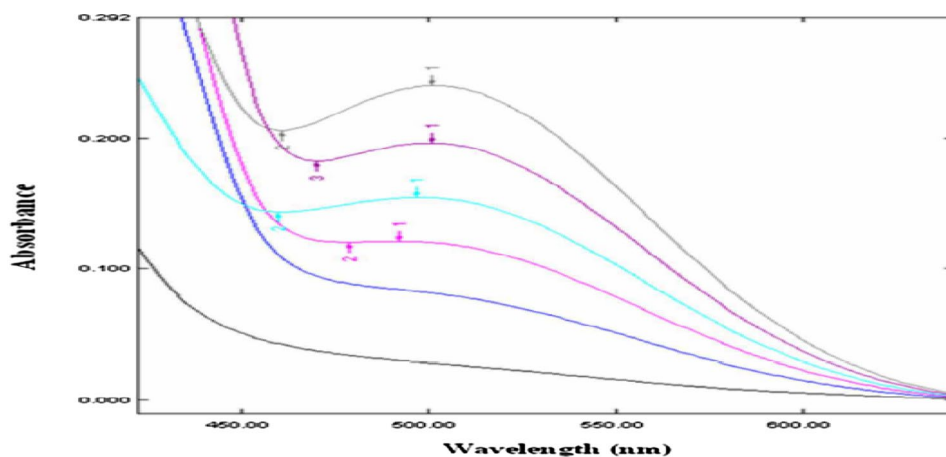

(a) Spectrophotometric determination of 4-CP in a set of standards solution
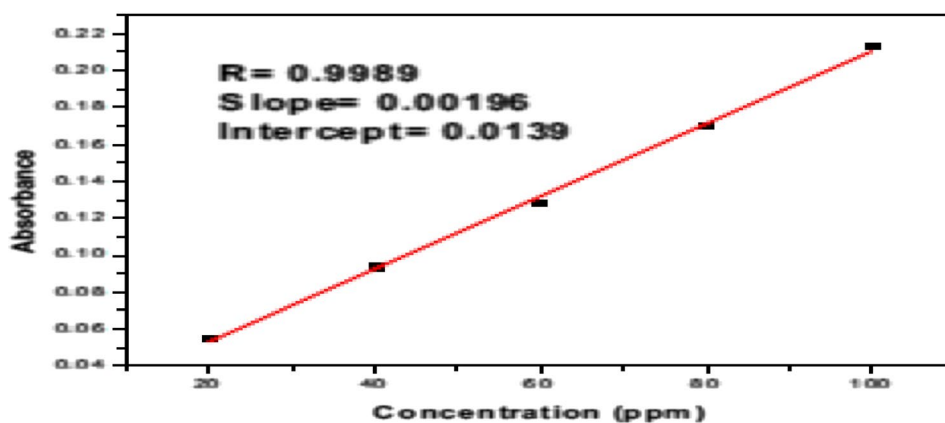
(b) Calibration curve for 4-CP Spectrophotometric determination

Fig. 2 IR- active functional groups on carbon surfaces: **a** aromatic C=C stretching; **b** and **c** carboxyl-carbonates; **d** carboxylic acid; **e** lactone (4-membered ring; **f** lactone (5-membered ring); **g** ether bridge; **h** cyclic ether; **i** cyclic anhydride (6-membered ring); **j** cyclic anhydride (5-membered ring); **k** quinine; **l** phenol; **m** alcohol; and **n** Ketene (Radovic et el.)
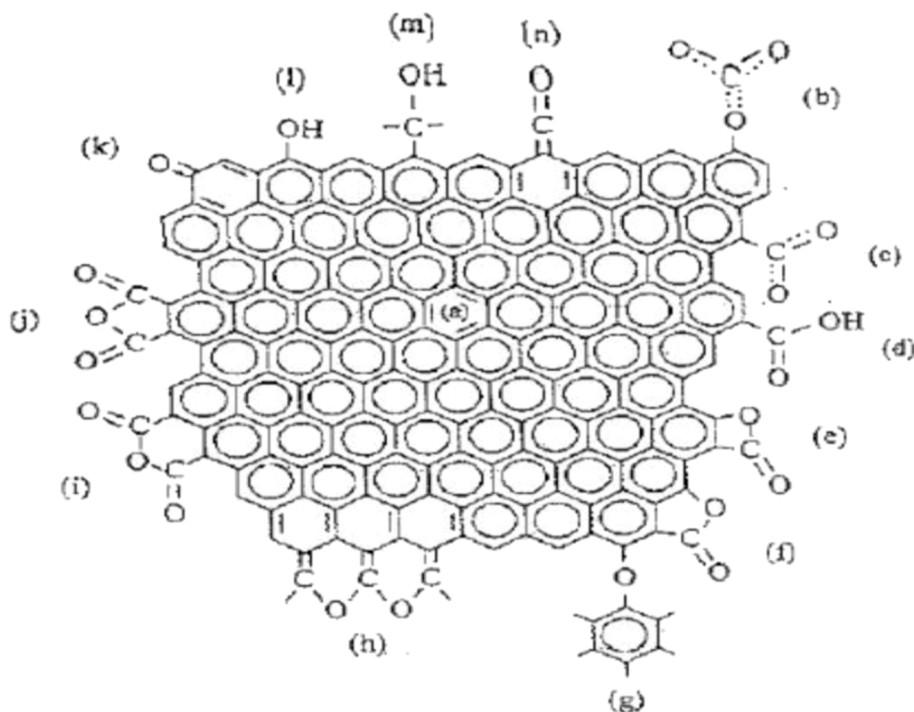
the acidic groups on the carbon surface are determined by Eq. (1) [42]:

$$n_s = \frac{n\text{Hcl}}{n_B}[B]V_B - \left([\text{Hcl}]V_{\text{Hcl}} - [\text{NaOH}]V_{\text{NaoH}}\right)\frac{V_B}{V_a} \quad (1)$$

[B] concentration of the reaction base, V_B volume of the reaction base, ns: moles of the carbon surface functional groups that reacted with the base during the mixing step, V_a: volume of the aliquot taken from the base solution after filtering out the carbon adsorbents, [HCl]: concentration of the acid added to the aliquot taken from the original sample, nHCl\n$_B$: stoichiometric ratio of HCl–to–base, V_{HCl}: volume of the acid added to the aliquot taken from the original sample, [NaOH]: concentration of NaOH used as titrant and V_{NaOH}: volume of NaOH consumed in the titration.

The term [HCl] VHCl gives the number of moles of acid added to the aliquot and available for reaction with remaining reaction base. Then, the remaining moles of acid are determined through the titration with NaOH, [NaOH] and V_{NaOH} is the concentration and the volume of the titrant in the back titration. The calculated n$_s$ of JAT1 and JAT2, in addition to charcoal, are listed in Table 2.

The quantity of the different possible surface groups: phenol, laconic and carboxyl groups can be evaluated from the difference in the n$_s$ values determined to have reacted with each base. NaHCO$_3$ reacts only with carboxylic groups so the number of carboxylic acid groups is directly given from the n$_s$ value for NaHCO$_3$. Na$_2$CO$_3$ reacts with carboxyl and laconic groups then the difference between the ns value for Na$_2$CO$_3$ and NaHCO$_3$ represents the number of laconic groups. NaOH reacts with all groups: carboxylic acids, lactones and phenols so, the difference between the ns value determined with NaOH and the n$_s$ value determined with Na$_2$CO$_3$ will denote the number of phenols on the surface.

The calculated results of Jatropha carbon surface different functionalities are listed in Table 2.

From Table 2, it can be recognized that JAT1 has as twice acidic groups as JAT2. The shares of phenolic, laconic and carboxylic groups in the surface acidity of JAT2 are almost equal. On the other hands, JAT2 has only phenolic and carboxylic group with a little bit higher contribution of the former to the surface acidity of JAT2.

JAT3 has not being titrated because it was immersed with acid (H$_3$PO$_4$) so the acidity acquired by this procedure will over mask the acidity of the carbon–oxygen functionalities.

3.1.1.2 Infrared Spectroscopy
Figure 3 represents the IR spectra of JAT1, JAT2 and JAT3. The JAT1 and JAT2 spectra are very similar and JAT3 is different, they are characterized by the presence of:

1. Broad absorption band centered around 3400 cm^{-1} corresponding to the stretching vibration of the hydroxyl group (O–H) in adsorbed water and OH containing functional group such as phenol, alcohol and carboxylic acid.
2. Small but distinct absorption features just below 3000 cm^{-1} corresponding to the-H stretching vibration (C–H in CH$_3$- 2872 cm^{-1} sym 2962 cm^{-1} Asym, C–H in CH$_2$- 2853 cm^{-1}sym, 2926 cm^{-1} Asym).
3. An overlapping of bands around 1600 cm^{-1} corresponding to aromatic C=C and C=O stretching vibration.
4. Bands around 1430 cm^{-1} which can be attributed to the bending mode of O–H in carboxylic acids. It is also expected to be superimposed with bending mode of C–H.
5. A strong band around 600 cm^{-1} only in the case of JAT3. This band is believed to correspond to the OH bend in phenolic surface group and its presence with such large intensity.

3.1.1.3 Effect of Adsorption Temperature
From the temperature dependence of the adsorption equilibrium constants which are determined from adsorption isotherms, it is possible to determine several thermodynamic parameters of the adsorption process. The equilibrium constant (K_c) represents the ability of the adsorbent to retain the adsorbate and it is related to the free Gibbs energy of reaction by, Eq. (2):

Table 2 Amounts of surface acid groups determined in Boehm titration and functionalities determined by Boehm titration

n_s (μmole/g)	NaOH	NaHCO$_3$	Na$_2$CO$_3$
Charcoal	653	622	634
JAT$_1$	501	158	313
JAT$_2$	250	110	83
n_s (μmole/g)	Phenolic	Laconic	Carboxylic
Charcoal	19	12	622
JAT$_1$	188	155	158
JAT$_2$	167	− 27	110

Fig. 3 FTIR spectra of JAT1, JAT2 and JAT3
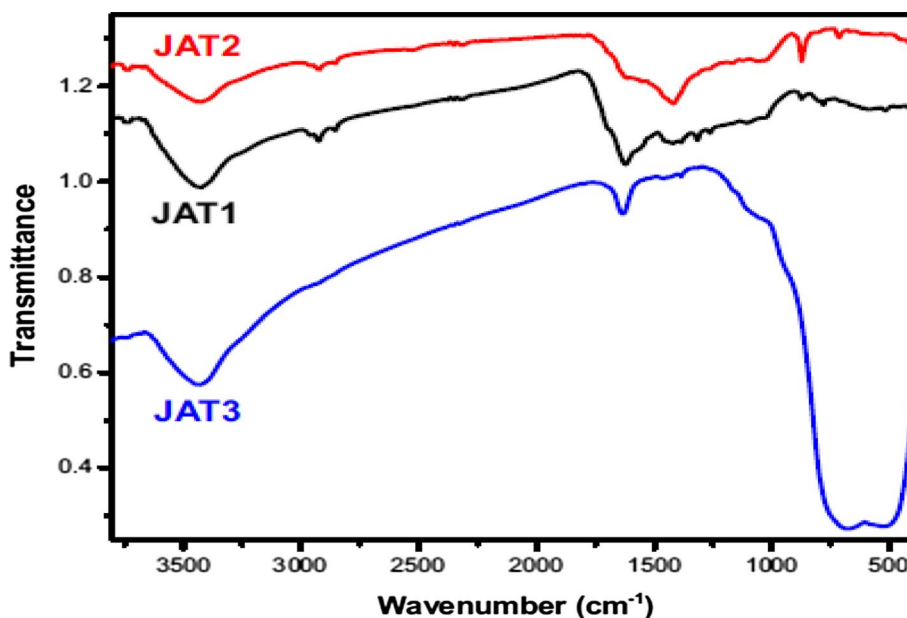
$$\ln k_c = -\frac{\Delta G^\circ}{RT} \tag{2}$$

Substituting $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$ gives Eq. 3:

$$\ln k_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

Equation (3) assumes a linear relation between the logarithm of the equilibrium constant (ln K_c) versus the reciprocal of temperature (1/T). The heat of adsorption (ΔH°) and the entropy of adsorption (ΔS°) are thereby assumed to be temperature independent. Figures 2 and 3 are plots of the logarithm of the adsorption equilibrium constant versus the reciprocal of the temperature for the adsorption of 4-CP and DCP for all three adsorbents. The adsorption equilibrium constants plotted are those determined by modeling the adsorption data according to Langmuir-1, Langmuir-2, Freundlich and Temkin.

Figure 4 is separated into two plots for the purpose of clarity. From the slopes and intercepts of the linear fitting of ln k versus 1/T, the enthalpy of adsorption and the entropy of adsorption for the two compounds have been determined and are tabulated in Table 3.

The values of ΔH° and ΔS° are briefly discussed in the following: in the case of 4-CP on JAT3, all three models (Langmuir-1, Freundlich and Temkin) give close values for ΔH° and ΔS°. There is a large gain in entropy upon adsorption exceeding 200 J/mol. K which indicates that the order in solution was much greater than that achieved on the surface. ΔH° is positive (in the range 80–100 kJ/ mol) reflecting the endothermic nature of the process, meaning that the interaction forces with water molecules in solution are also greater that those with the surface of

the adsorbent. This means also that adsorption is enhanced by increasing the temperature. For JAT2, ΔH° and ΔS° are only slightly positive suggesting that both order and attraction forces in the two states (adsorbed vs. 1/T) for JAT2 and JAT3 makes them intersect in the temperature range 45–55 °C (Fig. 4), which means that below 45 °C JAT2 is, in general, a better adsorbent, while above 55 °C JAT3 is better. For JAT1, the situation is more complicated. Freundlich and Temkin models give similar results (slightly negative ΔH° values in the range 15–30 kJ/mol and negative ΔS° values in the range 60–90 kJ/mol). Langmuir-1 and Langmuir-2 give, however, results in the opposite direction (rather strongly positive ΔH° and ΔS° values). The results of Freundlich and Temkin modeling are trustier because they show a better correlation factor for the Hoff's plot (R- 0.9) compared to R- 0.5 obtained in the case of Langmuir-1 and Langmuir-2 constants.

In the case of adsorbing DCP, JAT2 and JAT3 show comparable values for ΔH° and ΔS°. Both values are negative indicating higher order as the DCP molecule gets adsorbed as well as higher attraction forces to the adsorbent surface than these to water in solution. However, ΔH° is only slightly negative. From Fig. 5, it can also be recognized that the adsorption of DCP on JAT2 is proceeds effectively than on JAT3 and that at all temperatures.

Figure 6 represents the modeling of temperature dependence of the adsorption on JAT2 according to Temkin isotherm for the two chlorophenols. Obviously, the adsorption on JAT2 is slightly exothermic for DCP and endothermic for 4-CP as discussed above. And it shows that the adsorption of DCP proceeds in general more efficiently than 4-DCP at all temperatures below 70 °C. The removal efficiencies for the two chlorophenol become equal at 70 °C.

Fig. 4 Temperature dependence of the adsorption constants of 4-chlorophenol
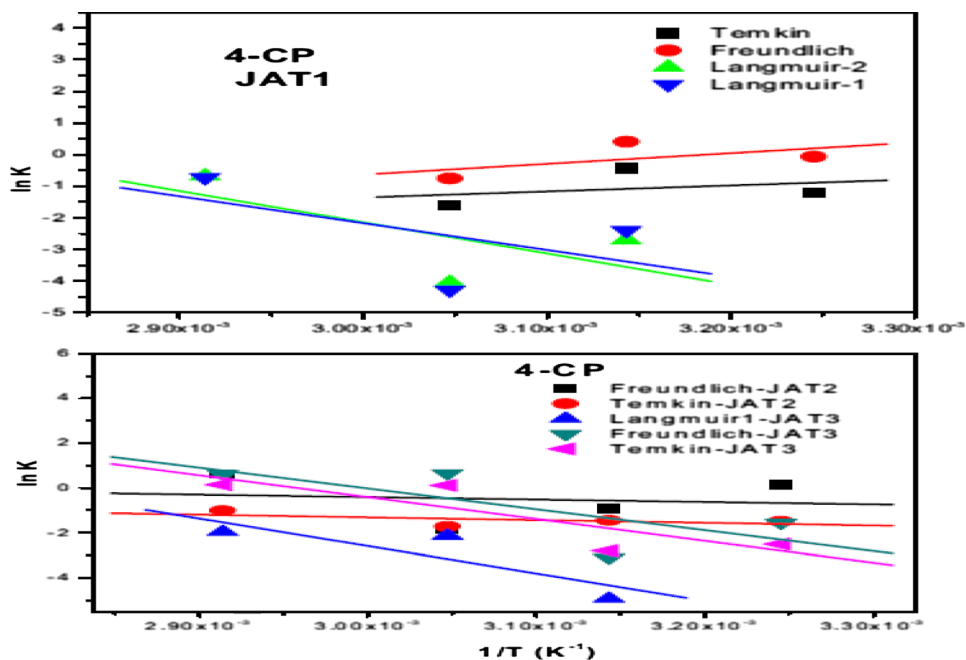

Table 3 Thermodynamic parameters for 4-chlorophenol adsorption from aqueous(4-CP) and thermodynamic parameters for 2,4-dichlorophenol adsorption from aqueous solutions (DCP)

	Intercept	Slope	$\Delta S°$ J/mol K	$\Delta H°$ KJ/mol
4-CP				
L1-JAT1	23.33	− 8499	+ 194	+ 70.66
L2-JAT1	27.53	− 9890	+ 229	+ 82.23
F-JAT1	− 10.8	3386	− 90	− 28.15
T-JAT1	− 7.07	1903	− 59	− 15.82
F-JAT2	2.86	− 1089	+ 24	+ 9.05
T-JAT2	2.28	− 1197	+ 19	+ 9.95
L1-JAT3	34.1	− 12,225	+ 284	+ 101.64
F-JAT3	27.8	− 9283	+ 231	+ 77.18
T-JAT3	28.8	− 9737	+ 240	+ 80.96
DCP				
T-JAT1	− 0.056	− 634	− 0.47	+ 5.27
T-JAT2	− 4.85	1293	− 40	− 10.75
F-JAT2	− 12.76	4180	− 106	− 34.75
T-JAT3	− 6.87	1731	− 57	− 14.39
F-JAT3	− 7.99	2336	− 66	− 19.42

Table 4 represents some of the literature data for the heat of adsorption and entropy of adsorption for selected carbonaceous adsorbents.

3.1.1.4 Effect of pH on the Adsorption Before presenting the effect of pH on the adsorption process of Chlorophenol, it is important to define the removal efficiency, Eq. (4), [40]:

$$\text{Phenol Removal\%} = \frac{[\text{Phenol}]_o - [\text{Phenol}]_e}{[\text{Phenol}]_o} \times 100 \quad (4)$$

It represents the percentage of chlorophenol initially present in solution that has been removed from solution by adsorption.

Figures 7 and 8 show the removal efficiencies of JAT1 and JAT2 for the two chlorophenol under different pH values at 27 °C and constant initial concentration of 80 ppm. It is obvious that the adsorption process is favored at lower pH values and a rather strong decrease in the removal efficiency is observed for the two chlorophenol as the pH is increased. Under the experimental conditions described above, it is also clear that the removal efficiency of JAT1 is higher for DCP than 4-CP at all investigated pH values except for pH = 2 where almost equal values (100%) were obtained. The removal efficiency of JAT2 is in general (for the above-described experimental conditions) lower than that of JAT1 and a strong decrease in the removal efficiency for especially for DCP can be observed to take place with increased pH values.

Enhanced adsorption at low pH suggests that the adsorption of the undissociated phenol proceeds more efficiency than the corresponding phenolate anion. Low pH values are also apparently necessary to hydroxylate the functional groups at the surface making them better adsorbents.

3.1.1.5 Comparison of the Removal Efficiency of Jatropha Shell Derived Adsorbents with that of Commercial Activated Charcoal (CAC) Figures 9 and 10 show the removal efficiencies of JAT1, JAT2, JAT3 and CAC at 35 °C for

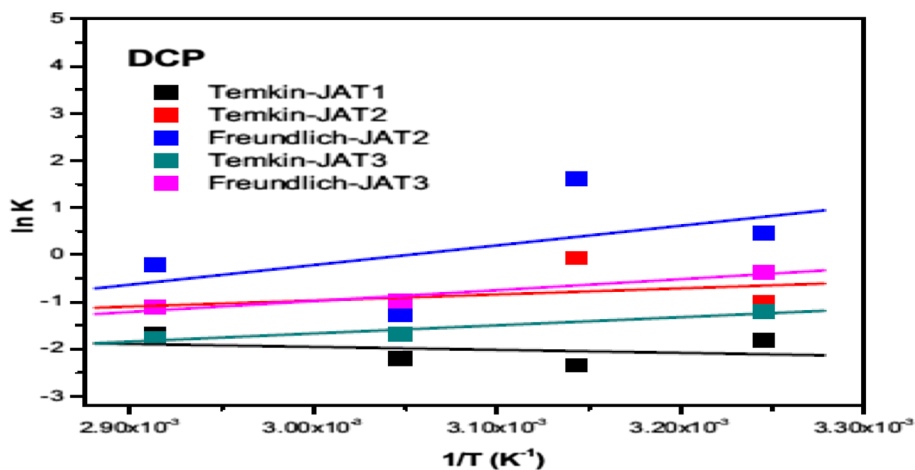**Fig. 5** Temperature dependence of the adsorption constant of 2,4-dichlorophenol

Fig. 6 Temperature dependence of the adsorption constants for 4-chlorophenol and 2,4-dichlorophenol on JAT2
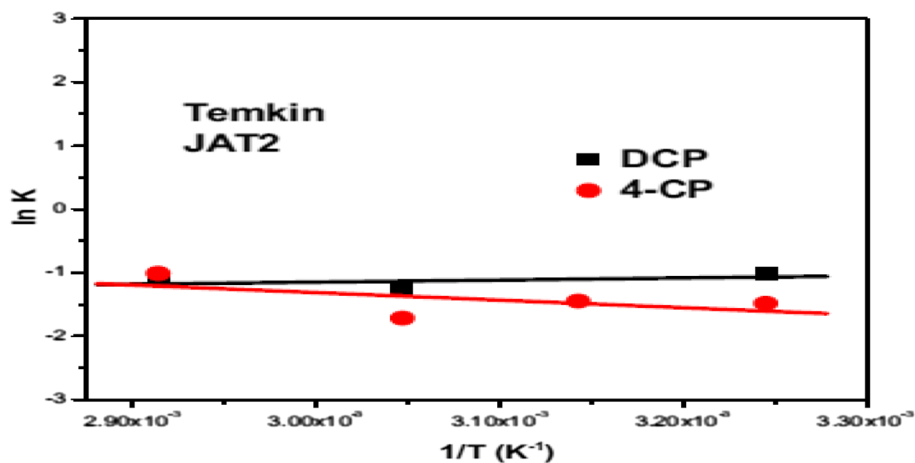

Table 4 The selected literature values for $\Delta H°$ and $\Delta S°$ of 4-chlorophenol and 2,4-dichlorophenol adsorption from aqueous solutions

Adsorbent	4-chlorophenol		2,4-dichlorophenol		
	$\Delta H°$ KJ/mol	$\Delta S°$ J/mol K	$\Delta H°$ KJ/mol	$\Delta S°$ J/mol K	References
Activated carbon fibers	− 13.38	+ 52.53	− 12.04	+ 60.54	[33]
Red mud	–	–	+ 46.5	+ 0.23	
Maize cob carbon	–	–	+ 6.78	+ 26.91	[32]
β-cyc1odextrin	–	–	+ 14.11	+ 47.99	[38]
Bituminous shale	–	–	+ 13.8	+ 29.8	

4-CP and DCP, respectively. The efficiency of CAC in removing of the chlorophenols is very high (almost complete removal) and it decreases only slightly from 100% to with increased initial concentration. JAT1 shows the best percent removal for 4-CP at 35 °C, JAT1 and JAT2 show close values in the percent removal of DCP. JAT3 is the worst adsorbent in removing the two chlorophenols at 35 °C.

Figures 11 and 12 show the removal efficiencies of JAT1, JAT2 and JAT3 at 55 °C for 4-CP and DCP, respectively. We conclude from the two figures that at this temperature, JAT2 is the best adsorbent with a removal efficiency of 70–80% for 4-CP and 80–90% for DCP.

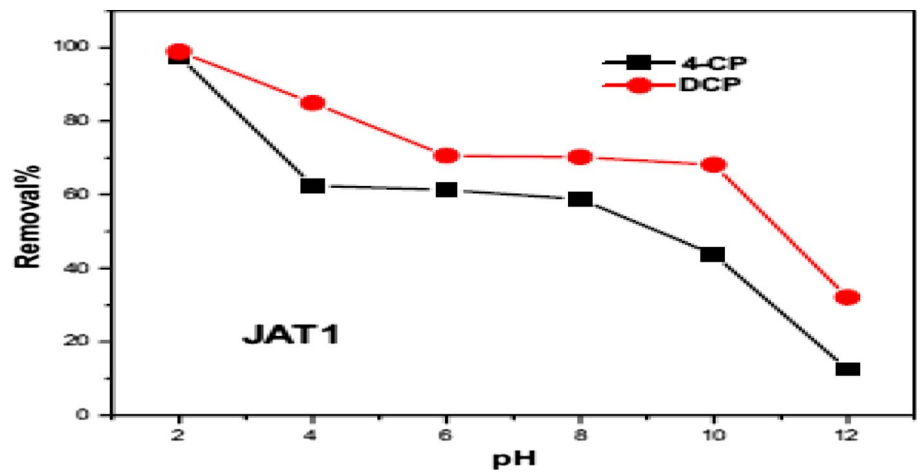**Fig. 7** Removal efficiencies of JAT1 for 4-chlorophenol and 2,4-dichlorophenol as a function of pH

Fig. 8 Removal efficiencies of JAT2 for 4-chlorophenol and 2,4-dichlorophenol as a function of pH
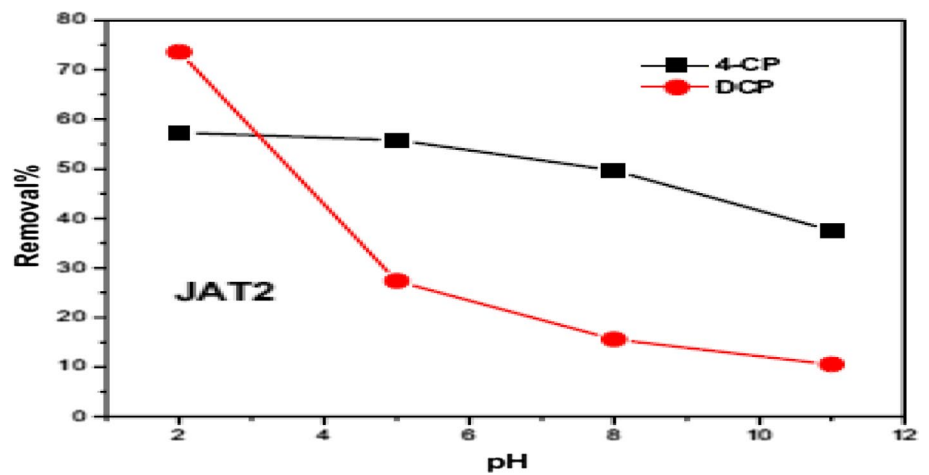

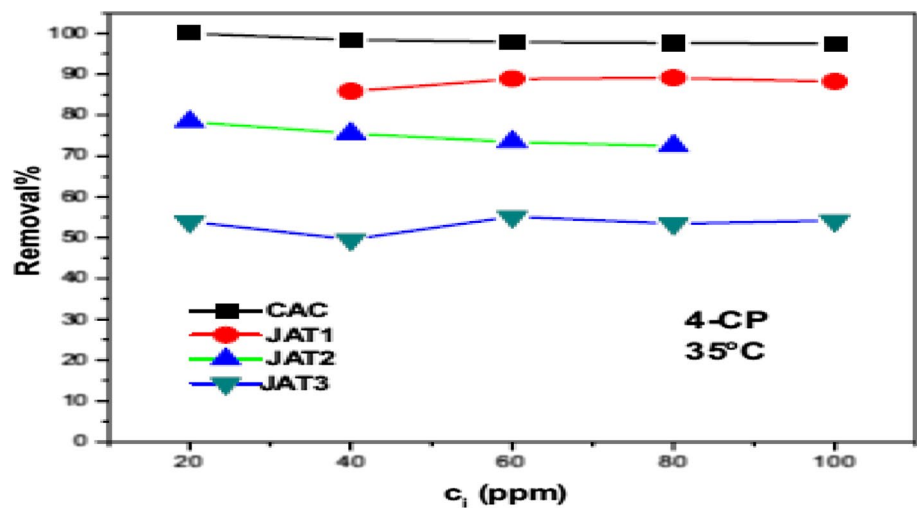**Fig. 9** Removal efficiencies of JAT1, JAT2 and CAC for 4-chlorophenol at 35 °C

Fig. 10 Removal efficiencies of JAT1, JAT2, JAT3 and CAC for 2,4-dichlorophenol at 35 °C
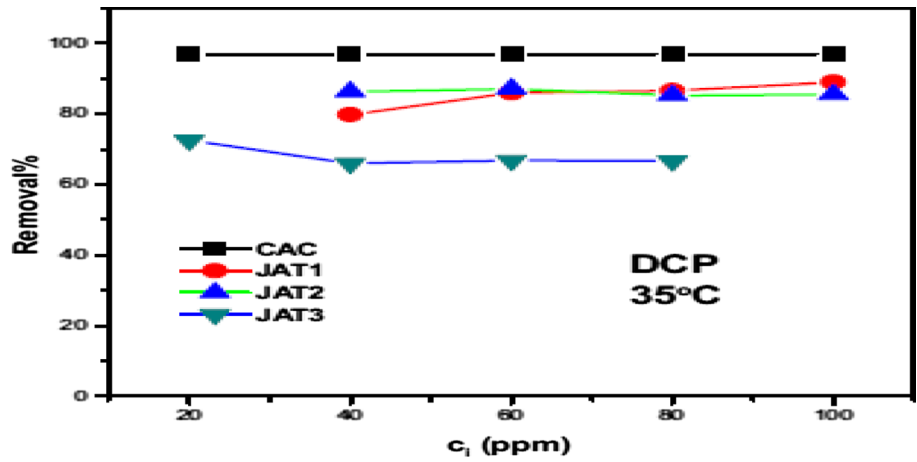

Fig. 11 Removal efficiencies of JAT1, JAT2 and JAT3 for 4-chlorophenol at 55 °C
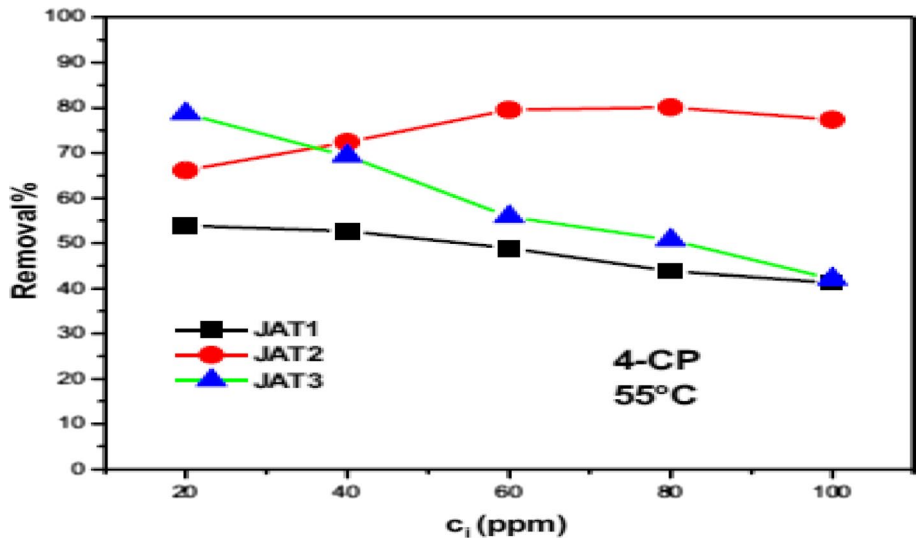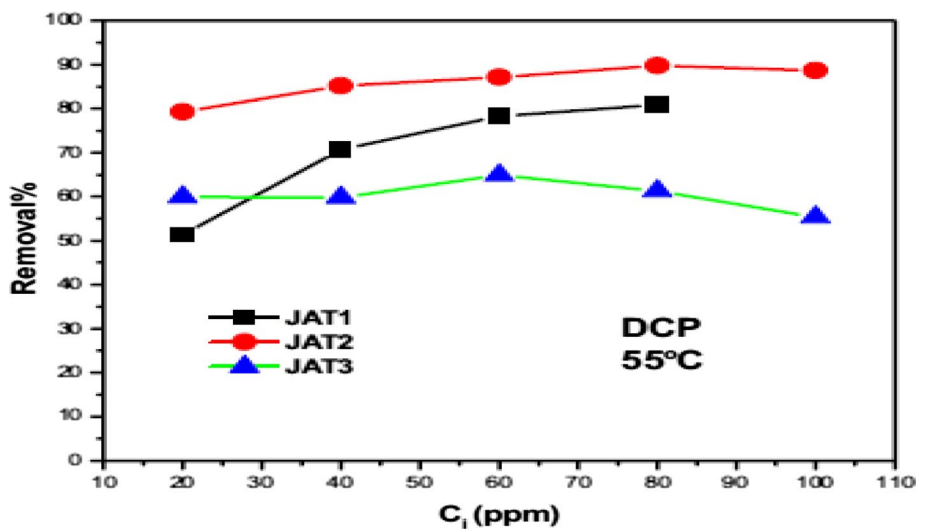

Fig. 12 Removal efficiencies of JAT1, JAT2 and JAT3 for 2,4-dichlorophenol at 55 °C

4 Conclusion

In this study, Jatropha seed shells (JSS) from Yemeni plant have been tested for studying adsorption of treated seeds shells to remove chlorophenols compounds. The washed and well-milled Jatropha seed was subjected to three different kinds of treatments. The three adsorbents were characterized with respect to the nature and amount of the acid groups at the surface by means of Boehm titration. Most of the acidic groups on the surface were found to be phenolic in nature (37.5% in the case of JAT1 and 60% in the case of JAT2). The remaining acid functionalities are carboxylic in JAT2 with no significant amounts of laconic groups are present. In JAT1, the rest is carboxylic and laconic with close percent. This result was supported by the FTIR transmission measurements of the three adsorbents.

The effect of adsorption temperature is summarized as follows: For the adsorption of DCP on JAT2 and JAT3, the heat of adsorption is slightly negative indicating that the removal efficiency decreases slightly with increasing temperatures. In the case of the adsorption of 4-CP on JAT2, the heat of adsorption is slightly positive indicating that the removal efficiency increases slightly with increasing temperatures. In the case of the adsorption of 4-CP on JAT2, the heat of adsorption is slightly positive indicating that the removal efficiency on JAT2, the heat of adsorption is slightly positive indicating that the removal efficiency increases slightly with increasing temperatures. The removal efficiency on JAT1 decreases for both compounds as the temperature is decreased.

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