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New eco-friendly composite beads from biomass activated carbon for removal of highly toxic 2,4-dichlorophenol from aqueous medium: equilibrium, modeling and thermodynamic studies

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ABSTRACT

In the present study, we prepared activated carbon beads from biomass. Fourier transform infrared spectroscopy, scanning electron microscopy and value of point of zero charges were used to characterize the physico-chemical and morphological properties of the prepared beads. The adsorbent properties of the beads were tested by adsorbing highly toxic pollutant 2,4-dichlorophenol in batch system. Effect of contact time, temperature, pH and initial 2,4-dichlorophenol concentrations on the adsorption was studied. Results showed that the amount of 2,4-dichlorophenol uptake increased with increasing initial 2,4-dichlorophenol concentrations and contact time. Increasing temperature increases the adsorption capacity. This indicates that the adsorption process is endothermic. Adsorption of 2,4-dichlorophenol followed pseudo-second-order kinetics, Langmuir and Freundlich adsorption isotherm models. Materials used for adsorbent preparation are natural, with no pollutant contamination and low cost. The adsorbents have high adsorption capacity of 297.80 and 532.60 mg/g, respectively, for AC and AC/A beads. AC/A beads were highly efficient after three cycles of adsorption–desorption.

Keywords: Calcium alginate; Activated carbon; 2,4-DCP; Adsorption; Biomass

1. Introduction

Water resources are invaluable and essential for our life. The contamination of these highly important resources by different toxic substances is an environmental problem. Phenolic compounds represent an important class of these toxic substances in water. 2,4-Dichlorophenol (2,4-DCP), a typical chlorinated phenol, has been listed as priority pollutants by the US Environment Protection Agency [1,2]. This typical phenolic compound is used as an intermediate in fabrication of herbicides, insecticides, antiseptics, preservatives, disinfectants and other organic compounds [3]. It can cause serious problems because of its high toxicity. It is highly mutagenic, carcinogenic and therefore has highly harmful effects on humans. As a consequence, decreasing concentration of this compound or completely removing it from water and wastewater is indispensable for protecting human health and environment. Particular attention has been focused on reducing pollution of water to assure a good quality for domestic and agricultural uses. Removal of chlorophenols by adsorption process is considered a promising technology [4]. Due to the high specific surface area and porous structure, activated carbon is the most-used adsorbent. It makes adsorption superior over other methods. However, due to the high cost of the precursor materials used from non-renewable source and using intensive energy for their production processes, it has

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become very urgent to discover new materials that reduce these problems and contribute to environmental protection.

Among the various types of low-cost adsorbents used in adsorption process, the adsorbents from agricultural residues are the best. These materials have several advantages such as renewable, usually available in large amounts, simple operation in the treatment processes, high sorption capacities, good modifiability and recoverability [5–7] and potentially less expensive than other precursor materials.

Activated carbon prepared from agricultural residues has high effectiveness in removing pollutants as dyes [8–10], heavy metals [11–13] and micropollutants such as chlorophenols [4,14] from water and wastewater. Many low-cost bioadsorbents have been used in adsorption process such as eucalyptus saw dust [15], pectate and polygalacturonate beads [16], activated lemon peel beads [17] and *Urtica dioica* leaves [18]. However, its use is still undesirable due to its difficulty in recovering or separating the powdered activated carbon from the mixture during the post-adsorption stage, which can substantially obstruct its utility in an industrial scale. For more effectiveness, regeneration and easy use, the obtained activated carbon can be encapsulated in biopolymer to form composite beads. Sodium alginate is one of the most-used biopolymer. Moreover, this polysaccharide is non-toxic, biodegradable, economical and can be easily used for encapsulation [19,20]. It also allows solutes to diffuse into the beads and come in contact with the entrapped material and often exhibit good adsorption capability. Lemon peels is one of the important low-cost raw material. It is available in large quantities in many parts of the world and it is considered as a cheap alternative to activated carbon for wastewater treatment. In previous paper, lemon peels activated with acids, encapsulated in calcium alginate showed very high efficiency toward dyes [21] and low efficiency toward chlorophenols. In this paper activated carbon beads from lemon peels were prepared for removing chlorophenols from aqueous medium. In the first step, lemon peels were treated by organic acids, calcined in the furnace at 600°C to enhance surface area and porosity. The obtained activated carbon was encapsulated with calcium alginate to form activated carbon beads adsorbent.

2. Experimental setup

2.1. Materials and methods

Lemon peels (LP) were collected locally. Sodium alginate was purchased from R&M Chemicals, (Malaysia). H_3PO_4, H_2SO_4, HCl, NaOH, $CaCl_2$ and 2,4-DCP (pKa = 7.85, MW = 163.1 g/mol and λ_{max} = 284 nm) were obtained from Sigma-Aldrich, (France). Stock solution of 2,4-DCP of concentration 1,000 mg/L was prepared by dissolving 1 g of 2,4-DCP in 1 L of distilled water.

2.2. Preparation of adsorbents

Lemon peels (LP) were washed several times with distilled water to remove dust and impurities and then dried in an oven at 50°C. The dried material was crushed to powder and sieved using a standard screen of 60 mesh to retain particles with size less than 0.25 mm. After drying, the sieved powder has undergone chemical activation step based on the method described in previous work [17] with acids CH_3COOH, HCl and H_3PO_4. Briefly, the sieved powder was dispersed in a 250 mL beaker of acid solution (0.6 M). The mixture was agitated using a magnetic stirrer at 150 rpm for 30 min at room temperature. Afterward, the supernatant was separated and the wet lemon peel was dried in the oven at 50°C for 24 h. The temperature of the oven was then increased to 120°C and maintained for 90 min. To remove the excess acid, the dried lemon peels were washed with distilled water and then were dried again in the oven at 50°C for 24 h. To develop a high surface area and high porosity, 5 g of each obtained material was calcined in the furnace for 1 h at 600°C under nitrogen atmosphere. Calcination can modify the structural properties and influence the morphology of crystalline building. The obtained adsorbent lemon peels were activated with HCl, H_2SO_4 and H_3PO_4 and calcined. The obtained mass of activated carbon (2 g) for each sample was, respectively, referred as AC1, AC2 and AC.

Gel beads were prepared according to the procedure reported in the literature [17,22]. Briefly, 2 g of activated carbon was dispersed in 100 mL of distilled water. The activated carbon was added to the stirred solution of alginate suspension (1%, w/w, V = 100 mL) and the mixture was stirred for 2 h at room temperature. Once the mixture becomes homogeneous, it was loaded in a syringe and allowed to fall dropwise into 200 mL of calcium chloride solution 0.1 M. After 10 h, the beads which were named AC/A were filtered, washed several times with distilled water and used for adsorption immediately after preparation or kept in distilled water until use.

2.3. Characterization

The functional groups present in the composite beads were analyzed in the wave number range of 400–4,000 cm^{-1} by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer FTIR spectrometer (Spectrum 1000, France) with KBr pellets technique. KBr was mixed with powder made from the grinding of beads.

Surface morphology and the presence of porosity of the AC/A beads prepared in this work were studied using scanning electron microscopy (SEM) analysis.

The pH_{pzc} (point of zero charge) is used to define a state of the surface of a dispersed solid phase. The pH_{pzc} of adsorbents is obtained by pH titration procedure according to the method described in literature [23]

2.4. Adsorption and desorption study of 2,4-DCP

Various experimental conditions, including contact time, pH (2–10), mass of wet adsorbent AC/A beads (10, 30, 50, 70, 120, 150 and 200 mg), initial concentration (50, 100, 150 and 200 mg/L) and temperature (10°C, 20°C, 30°C, 40°C) were tested for their effect on 2,4-DCP adsorption. Isotherms were studied from 10 to 1,000 mg/L of 2,4-DCP initial concentrations. In all sets of experiments 0.01 g of adsorbent was placed in 10 mL of 2,4-DCP solution and stirred with an agitation speed of 200 rpm at pH of the solution (pH≈6.4) and at room temperature (T = 24°C ± 1°C). The amount of 2,4-DCP adsorbed and removal efficiency (percentage removal of 2,4-DCP (R%)) were calculated by the following equations:

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{1}$$

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \tag{2}$$

$$R\% = \frac{\left(C_0 - C_e\right)V}{C_0} \times 100 \tag{3}$$

where C_0, C_t, C_e are, respectively, initial, at any time t and at equilibrium, concentrations of the 2,4-DCP expressed in mg/L. V is the volume of solution (L), m is the mass of wet adsorbent AC/A in (g), and q_t, q_e are respectively, the amount of 2,4-DCP adsorbed at time t and at equilibrium.

Regeneration of adsorbent is one of the significant economic factors for the treatment process. The reusability and efficiency of the composite beads were evaluated in this study by using ethanol as a regenerate agent. After the adsorption step, the spent composite beads saturated with 2,4-DCP was filtered and left in contact with solution ethanol–distilled water (50/50) for the same time duration as the previous adsorption. The adsorbent beads were washed using distilled water; dried at room temperature and reused for adsorption again with same conditions as described previously. The equilibrium concentration was calculated. The regenerated adsorbent was reused for six cycles of adsorption–desorption experiments. The percentage removal was calculated using Eq. (3).

3. Results and discussion

3.1. Selection of the best activated carbon adsorbent

Adsorption study was made with the same experimental parameters for the three adsorbents. Maximum adsorption capacities are of 236, 237 and 297 mg/g of 2,4-DCP, respectively, onto AC1, AC2 and AC surface. Based on the preliminary assessment of the different adsorbents in terms of the maximum adsorption capacity of 2,4-DCP onto adsorbents, AC was the best adsorbent among the samples tested. Therefore, all further experiments were performed using the AC and AC/A beads.

3.2. Adsorption experiment results

Experiments were made onto wet and dry beads. Results observed that the wet beads are more effective than the dry beads. The same results were found by other authors [24,25]. According to these results, the following adsorption experiments were conducted using the wet beads.

3.3. Characterization of adsorbents

The FTIR spectra of LP, AC and AC/A beads are depicted in Fig. 1. The broad band centered at 3,421–3,455 cm^{-1} is due to stretching vibration of the hydroxyl group (–OH) of typical water adsorption. The light stretch at 2,912–2,926 cm^{-1} showed the stretching of symmetric or asymmetric C–H vibration [17]. The peak observed at 1,764–1,784 cm^{-1} is due to the stretching vibration of carboxyl groups and the peak observed at 1,077 cm^{-1} is attributed to C–H in plane. The two bands at 1,629–1,634 cm^{-1} and 1,400–1,408 cm^{-1}, respectively, are affected by asymmetric and symmetric stretching vibrations of ionic carboxylic groups (–COO–). Many active functional groups were disappeared in the spectrum of AC/A, which indicate the efficiency of calcination process.

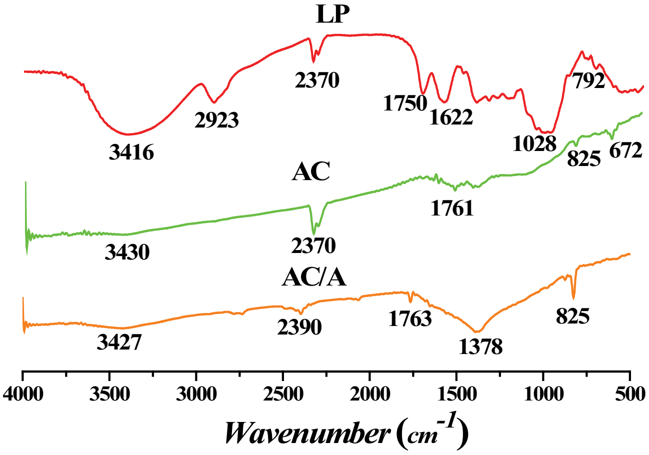

Fig. 1. FTIR spectra of LP, AC, AC/A beads.

The SEM micrograph for composite beads AC/A, taken under high magnification ((A) 134X and (B) 528X) is shown in Fig. 2. It can be seen that the surface morphology of the particles of the AC/A obtained confirm the presence of considerable number of pores.

The values of point of zero charge (pHpzc) of adsorbent AC and AC/A were found as 5.47 and 7.71. The surface of AC is acid and of AC/A is basic. For pHs of solution lower than these values, adsorbents are anion attractors and for pHs greater they are cation attractors.

3.4. Adsorption kinetics

The initial 2,4-DCP concentrations play an important role in the adsorption capacities of 2,4-DCP onto composite beads. Effect of this important parameter was studied with 2,4-DCP concentrations 50, 100, 150 and 200 mg/L. Experiments were monitored until reaching the equilibrium time. The results are presented in Fig. 3a. The increase of 2,4-DCP concentration from 50 to 200 mg/L causes an increase in adsorption capacity from 38 to 120 mg/g. The increasing initial 2,4-DCP concentrations would increase the mass transfer driving force and therefore the rate at which the 2,4-DCP molecules pass the bulk solution to the particle surface [26]. This would result in a higher 2,4-DCP adsorption. At initial contact time, affinity between adsorbent and adsorbate is strong because of the presence of a large number of vacant active sites on the adsorbent surface, so adsorption is relatively rapid during the first 5 h for all concentrations. Then, adsorption capacity varies slowly

AC/A beads

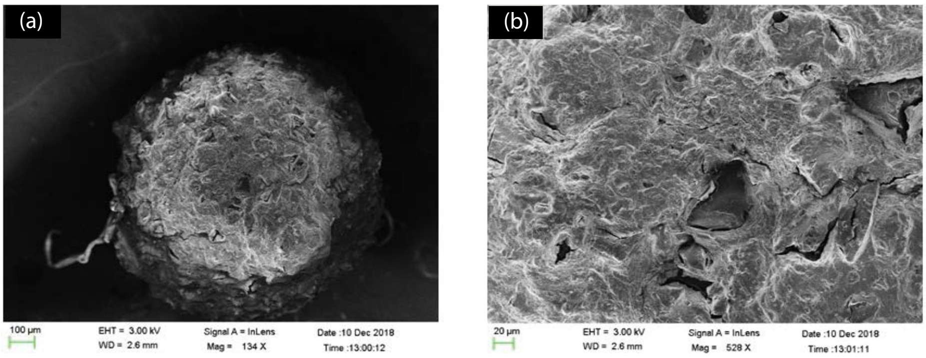

Fig. 2. SEM image of the surface of AC/A taken under (a) 134X and (b) 528X magnification.

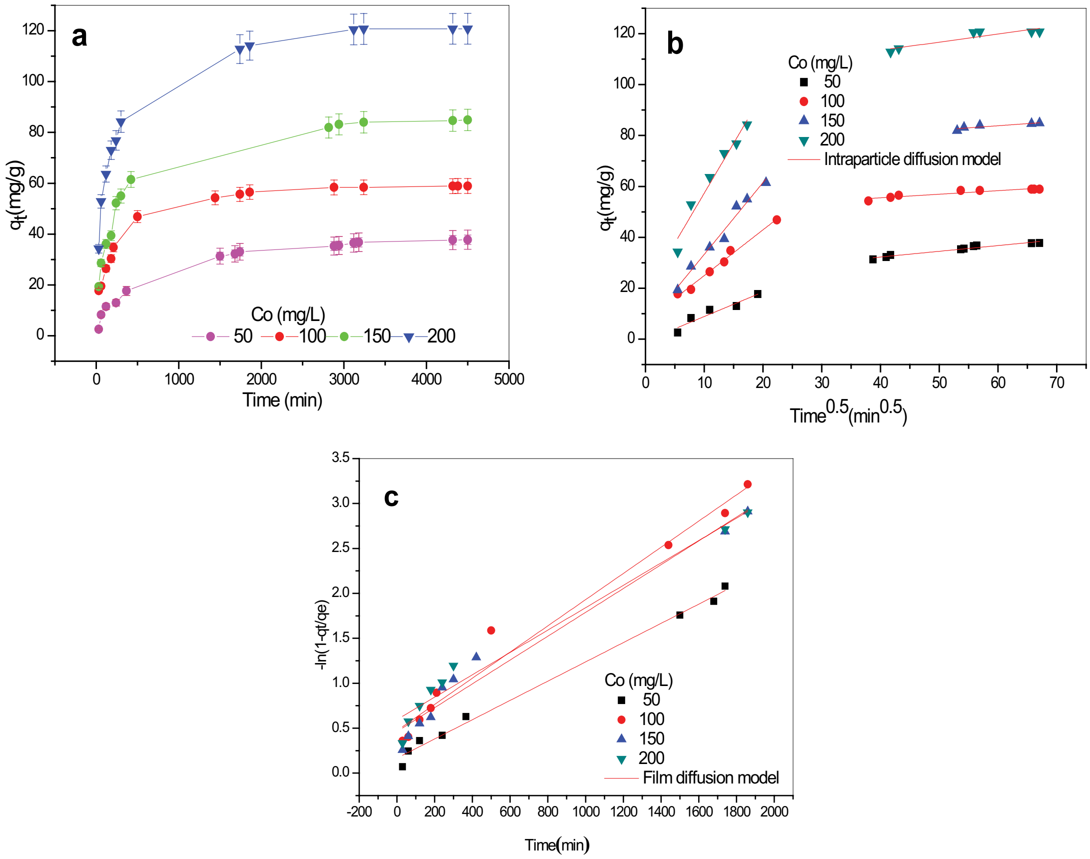

Fig. 3. (a) Adsorption kinetics of 2,4-DCP onto AC/A, (b) intraparticle diffusion and (c) film diffusion models.

until it reaches equilibrium and remains constant. Slow rate of 2,4-DCP adsorption is probably due to the electrostatic hindrance as well as the slow pore diffusion of the solute into the bulk of the adsorbent. It can be said that the 2,4-DCP is adsorbed by the exterior surface of the adsorbent and when the adsorption of exterior surface of the adsorbent reacted gets saturated, the 2,4-DCP entered into the adsorbent pores and adsorbed by the interior surface of the particles [27]. In this way, the contact time is very long and equilibrium is attained after about 2 days.

In order to investigate the kinetic mechanism, which controls the adsorption process of 2,4-DCP on AC/A surface, the pseudo-first-order, pseudo-second order, the intraparticle and the film diffusion models were used to test the experimental data.

The pseudo-first-order kinetic model is given as [28] follows:

$$q_t = q_e \cdot \left(1 - e^{-K_1 t}\right) \tag{4}$$

where K_1 (min^{-1}) is the equilibrium rate constant for pseudo-first-order sorption. q_e, q_t (mg/g) are the adsorption loading of 2,4-DCP at equilibrium and at time t (min), respectively.

The pseudo-second-order kinetic adsorption model was based on the assumption that the chemical sorption is the rate-limiting step and can be expressed in integrated and linear form using the following equation [29]:

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2} \tag{5}$$

where K_2 (g/mg min) is the rate constant of adsorption.

According to Table 1, where parameters of pseudo-first and pseudo-second-order non-linear fit are presented and from the correlation coefficients values the pseudo-second-order model was suitable for describing the kinetic data of 2,4-DCP adsorption onto the AC/A surface. The calculated adsorption capacity ($q_{e,\mathrm{cal}}$) values were very close to that of experimentally obtained ($q_{e,\mathrm{exp}}$). Similar results were found in the literature for adsorption of 2,4-DCP onto activated bentonite encapsulated with calcium alginate [30], activated carbon derived from moso bamboo [31] and activated carbon from guava seed [32].

Since pseudo-first and pseudo-second-order models cannot identify the diffusion mechanism, the intraparticle and film diffusion models were also tested. According to Weber and Morris [33], intraparticle diffusion coefficient K_{id} is given by the following equation:

$$q_t = K_{\mathrm{id}} t^{0.5} + C \tag{6}$$

where K_{id} (mg g^{-1} min$^{-0.5}$) is the rate of intraparticle diffusion controlled sorption constant and C is the intercept related to the boundary layer effect.

The process of film diffusion can be identified by the Boyd kinetic equation as follows [34]:

$$-\ln\left(1 - \frac{q_t}{q_e}\right) = K_{\mathrm{fd}} t \tag{7}$$

where K_{fd} is the liquid film diffusion constant.

Because the intraparticle diffusion was also involved in the adsorption of 2,4-DCP onto AC/A, plot of q_t vs. $t^{0.5}$ for various initial 2,4-DCP concentrations would result in a linear relationship, and intraparticle diffusion would be the controlling step if this line passes through the origin. As can be seen from Fig. 3b, the plots did not pass through the origin ($C \neq 0$), which further indicated that the intraparticle diffusion was not the sole rate-controlling step [35,36]. It may be the film diffusion and intraparticle diffusion that were concurrently operating during the adsorption process. It may be also that the film diffusion was involved in the entire investigation and played a dominant role in rate controlling [35]. In addition the plot suggests two separate linear portions. The first one is the external surface adsorption or instantaneous adsorption stage and the second portion is the gradual adsorption stage, where the intraparticle diffusion is rate limited. The two different portions of rates of adsorption observed indicate that the rate of adsorption is initially slightly faster were the adsorbate is transported to the macropores and mesopores and then slows down were the diffusion of adsorbate is into the micropores [36]. All these results confirm that the intraparticle diffusion was involved in the adsorption process but is not the sole rate limiting step.

To verify if the adsorption process is intraparticle diffusion controlled or film diffusion, the process can be identified by the Boyd kinetics using the above equation (Eq. (7)). If the plots of $-\ln(1-q_t/q_e)$ vs. t at initial concentrations are linear or non-linear but does not pass through the origin, the adsorption process follows the film diffusion mechanism. Fig. 3c shows linear plots which do not pass

Table 1
Kinetic non-linear model parameters for 2,4-DCP adsorption onto AC/A at 24°C

		Pseudo-first-order			Pseudo-second-order			
C_0 (mg/L)	$q_{e,\mathrm{exp}}$	$q_{e,\mathrm{cal}}$	K_1	R^2	$q_{e,\mathrm{cal}}$	K_2	R^2	RMSE
50	37.82	37.89	0.0013	0.964	41.02	5.67×10^{-5}	0.988	1.90
100	58.84	63.06	0.0031	0.901	60.49	11.54×10^{-5}	0.977	5.98
150	84.94	81.50	0.0040	0.895	87.35	6.89×10^{-5}	0.982	10.75
200	121.16	122.49	0.0051	0.873	121.77	7.67×10^{-5}	0.972	26.50

K_1 (1/min), K_2 (g/mg min), $q_{e(\mathrm{exp,cal})}$ (mg/g).

through the origin, explaining that film diffusion controls the 2,4-DCP adsorption rate onto AC/A. Values for the film diffusion model were higher than those of intraparticle diffusion model (Table 2) indicating also that film diffusion controls the adsorption rate of 2,4-DCP onto AC/A.

3.5. Effect of the solution pH on adsorption of 2,4-DCP onto AC/A

Adsorption capacity of 2,4-DCP onto AC/A was measured by varying pH in the range of 2–10 and the initial pH was adjusted with NaOH or HCl solutions. The effect of this important factor on the adsorption was studied at 200 mg/L initial 2,4-DCP concentration. Fig. 4 shows that adsorption capacity of 2,4-DCP onto AC/A increases with pH from 2 to 6 and a little decrease was observed for pH 7, then sharply decreases from pH 8 to 10. The effect of pH could be explained by considering the presence of ionic and molecular forms of 2,4-DCP in aqueous solution and by the surface charge of the adsorbent (point of zero charge pH_{PZC}). The point of zero charge of AC/A is of 7.71 and the dissociation constant pKa of 2,4-DCP is of 7.85. So at a pH greater than pH_{PZC} of AC/A (pH > 7.71), the adsorbent surface is negatively charged and it is a cationic attractor and because in this case, the ionised species of 2,4-DCP were higher than the unionized species (it was found to increase with pH), the 2,4-DCP adsorption capacity decreases from pH 8 to pH 10 due to the electrostatic repulsions between the negative surface charge of adsorbent (pHpzc < pH (solution)) and the chlorophenolate anions and between chlorophenolate–chlorophenolate anions in the solution [35]. While at a pH lower than pH_{PZC} and lower than 2,4-DCP pKa, the adsorption capacity was higher because the 2,4-DCP was unionized and the dispersion interaction predominated. Similar results have been reported by Hameed [26].

3.6. Effect of adsorbent mass on 2,4-DCP adsorption onto AC/A

The influence of AC/A mass on 2,4-DCP removal percentage and adsorption capacity was studied by varying the adsorbent mass from 10 to 200 mg. The adsorbent mass increased from 10 to 200 mg, the percentage of 2,4-DCP removal increases from 38% to 90% (Fig. 5). This may be due to an increase in the number of active sites of the adsorbent because with increasing amount of the adsorbent, surface area and number of active sites increases.

3.7. Effect of temperature on adsorption of 2,4-DCP

Temperature study of adsorption is carried out at four temperatures: 10°C, 20°C, 30°C and 40°C. Increasing temperature increased adsorption capacity of 2,4-DCP onto AC/A beads (Fig. 6a). This implies that the adsorption is endothermic in nature. Thermodynamic parameters including change in Gibb's free energy ($\Delta G°$), entropy ($\Delta S°$) and enthalpy ($\Delta H°$) for the adsorption of 2,4-DCP onto AC/A beads have been determined by using Eqs. (8) and (9) [37,38] as follows:

$$\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - \Delta S^{\circ}_{\text{ads}} \tag{8}$$

$$\log\left(\frac{q_e \times m}{C_e}\right) = \frac{\Delta S^{\circ}}{2.303 \times R} + \frac{-\Delta H^{\circ}}{2.303 \times R} \tag{9}$$

where m (g/L) is the adsorbent dose, R (8.314 J/K mol) is the universal gas constant, T (K) is the absolute temperature, q_e (mg/g) is the amount of 2,4-DCP adsorbed per unit mass of adsorbent, C_e (mg/L) is equilibrium concentration and q_e/C_e is called the adsorption affinity.

The values of $\Delta G°$ and $\Delta H°$ were determined from the slope and intercept of plot $\log\left(\frac{q_e \times m}{C_e}\right)$ against $1/T$ (Fig. 6b) and the values are listed in Table 3. For all temperatures used, the values of $\Delta G°$ were negative showing that the adsorption on AC/A was spontaneous. The value of $\Delta H°$ was positive, indicating adsorption endothermic and the positive values of $\Delta S°$ suggest the increased randomness at the solid/solution interface during the adsorption.

3.8. Equilibrium studies

Adsorption isotherm can be considered as an essential necessity to design adsorption system, the relationships between adsorbent and adsorbate are best explained by this essential process. The adsorption of 2,4-DCP onto AC and AC/A beads experiments was conducted by varying initial concentration of 2,4-DCP from 10 to 1,000 mg/L. Fig. 7 shows that the initial 2,4-DCP concentration was increased, the adsorption capacity of adsorbents was enhanced and then switches to saturation state at higher initial concentration. The curve tended toward a constant value of q_e, indicating the formation of a complete monolayer of DCP molecules covering the surface of the adsorbents. The maximum

Table 2
Intraparticle and film diffusion parameters for 2,4-DCP adsorption onto AC/A

		Intraparticle diffusion					Film diffusion	
		Step 1		Step 2				
C_0	K_{id}	C	R^2	K_{id}	C	R^2	K_{fd}	R^2
50	0.962	–	0.890	0.427	23.24	0.941	0.0011	0.992
100	1.797	6.992	0.985	0.735	49.89	0.856	0.0015	0.974
150	2.223	5.484	0.972	0.752	73.94	0.738	0.0013	0.965
200	3.924	18.048	0.950	1.382	100.77	0.794	0.0012	0.968

C (mg L^{-1}), K_{id} (mg g^{-1} min$^{-0.5}$).

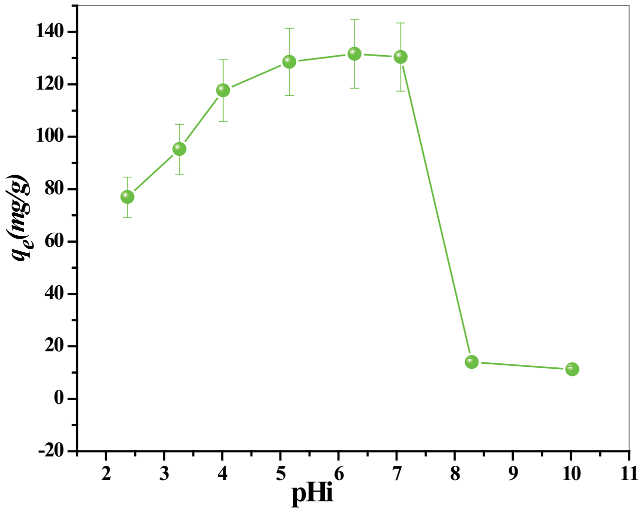

Fig. 4. Effect of pH on the removal of 2,4-DCP onto AC/A (C_0 = 200 mg L^{-1}, V = 10 mL, m = 10 mg, T = 23°C ± 2°C, contact time = 78 h).

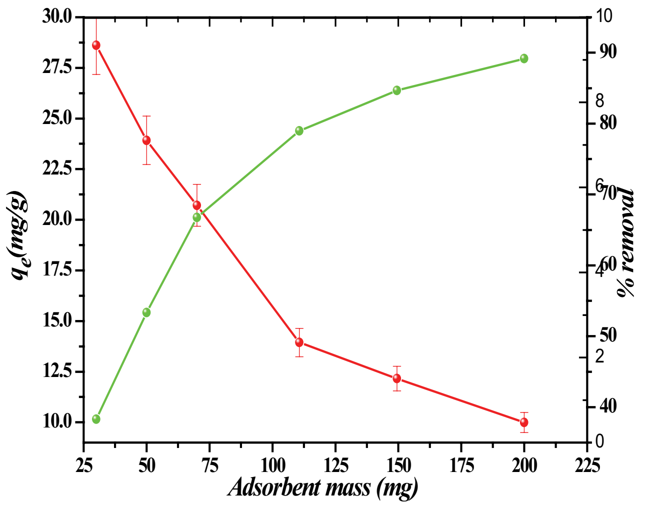

Fig. 5. Effect of adsorbent dosage on the removal of 2,4-DCP onto AC/A beads (C_0 = 200 mg L^{-1}, V = 10 mL, pH = initial pH, T = 23°C ± 2°C, contact time = 78 h).

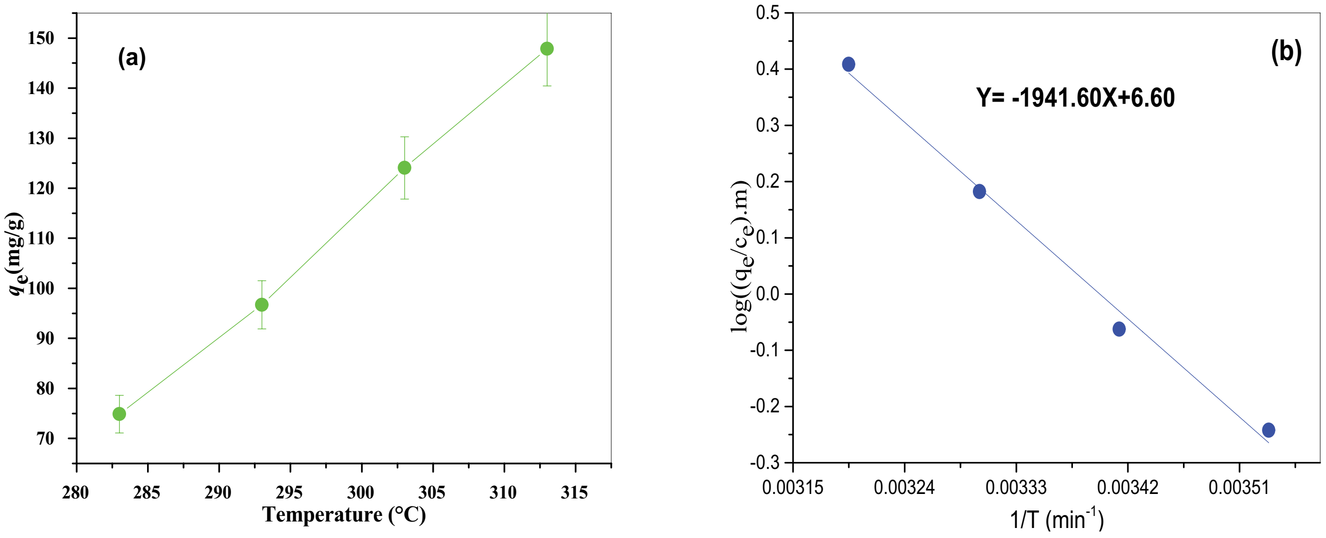

Fig. 6. (a) Effect of temperature on adsorption of 2,4-DCP onto AC/A beads, and (b) Van't Hoff equation plot.

capacity of 2,4-DCP fixed onto adsorbents founded par Langmuir model are of 297 and 532.60 mg/g, respectively for AC and AC/A beads. Adsorption capacity of AC/A beads is greater than that of AC (>1.5 times). This indicates that alginate contribute in adsorption of 2,4-DCP. The adsorption of 2,4-DCP onto pure alginate was studied and it is found that its adsorption capacity was low compared with those of adsorbent beads. It was of 85 mg/g. The prepared adsorbents are very effective, green adsorbents and low cost in the removal of chlorophenols from water medium.

In order to mention the effect of the report AC/alginate, the adsorption isotherms of 2,4-DCP onto AC/A 1/1, AC/A 2/1 and AC/A 4/1 was studied (figure not shown).

To analyze the equilibrium data of the composites beads AC/A 1/1, AC/A 2/1 and AC/A 4/1 two isotherm equations have been tested in the present study: Langmuir and Freundlich isotherms.

The Langmuir [39] isotherm is applicable to homogeneous adsorption, where the sorption of each sorbate molecule onto the surface has equal adsorption activation energy, this model isotherm is expressed using the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + q_{\max} K_L} \tag{10}$$

where q_e is the equilibrium chlorophenol concentration on adsorbent (mg/g), C_e is the equilibrium chlorophenol concentration in solution (mg/L), $q_{\max}$ is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg).

The Freundlich [40] isotherm is used for non-ideal adsorption that involves heterogeneous adsorption; this model isotherm is expressed using the following equation:

$$q_e = K_F C_e^{1/n} \tag{11}$$

where $1/n$ and K_F (mg/g) are the Freundlich constants characteristic of the system, indicators of adsorption intensity and adsorption capacity, respectively.

Parameters obtained by fitting plots of these equations to the experimental data are presented in Table 4. The Langmuir maximum capacity of 2,4 DCP onto AC, AC/A 1/1, AC/A 2/1 and AC/A 4/1 was found to be 297, 456.54, 488.1 and 532.80 mg/g, respectively. The values of correlation coefficients demonstrate good agreement with experimental data with the Langmuir and Freundlich model ($R^2 > 0.98$) indicating monolayer coverage and the homogeneous distribution of active sites onto all adsorbents. According to these results, the activated carbon prepared with phosphoric acid, calcined at 600°C and entrapped with sodium alginate AC/A 4/1 is the best and the potential adsorbent for the removal of chlorophenols.

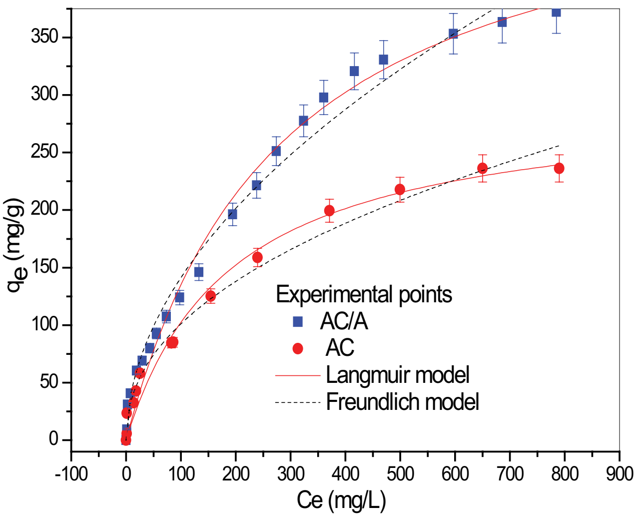

Fig. 7. Adsorption isotherms of 2,4-DCP onto AC and AC/A beads.

Table 3
Thermodynamic parameters for 2,4-DCP adsorption onto AC/A

T (K)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})	$\Delta G°$ (kJ mol^{-1})
283	16.14	0.07	–1.64
293			–1.59
303			–2.07
313			–2.28

From Table 4, the adsorption capacity of encapsulated AC increases with increasing the amount of AC in the composite beads. This finding can be attributed to more adsorption sites provided by AC/A 4/1 compared with those by AC/A 2/1 and AC/A 1/1. Activated carbon contributes more in adsorption than alginate. As at the pH of experiments (pH = 6), the great part of 2,4-DCP is unionized molecules, hence the 2,4-DCP was adsorbed by dispersive interaction.

3.9. Desorption and recycling of adsorbent

Based on the preliminary assessment of the different prepared composite beads in terms of the maximum quantities adsorbed of 2,4 DCP, the activated carbon prepared with phosphoric acid, calcined at 600°C and entrapped with sodium alginate AC/A 4/1 is among the most efficient adsorbents for 2,4 DCP with the maximum quantity adsorbed of 2,4 DCP equal to 532.80 mg/g. Therefore, the regeneration experiments of low-cost AC/A 4/1 adsorbent were investigated.

The spent AC/A must be regenerated and reused again in adsorption process. The adsorbents having this ability are considered cost-effective. On the other hand, adsorbent wastes are also more reduced. This measure reduces the cost of adsorption process and makes the wastewater treatment more economical. For this, adsorption–desorption cycles for AC/A were evaluated.

The regenerated adsorbent exhibited an excellent adsorption performance after three cycles (Fig. 8), where the AC/A showed 2,4-DCP removal of ≈68%. This removal performance decreased up to 25% at 6th cycle.

3.10. Various adsorbents for 2,4-DCP removal

The adsorption capacities of various adsorbents for removal of 2,4-DCP have been compared and presented in Table 5. As it can be seen, the maximum adsorption capacity

Table 4
Langmuir and Freundlich parameters for adsorption of 2,4-DCP onto AC and AC/A beads

	Langmuir			Freundlich		
Adsorbents	$q_{\max}$	K_L	R^2	K_F	n	R^2
AC	297.80	0.005	0.981	12.76	2.22	0.984
AC/A 4/1	532.60	0.003	0.980	12.82	1.94	0.993
AC/A 2/1	488.08	0.0025	0.987	8.35	1.81	0.991
AC/A 1/1	456.54	0.0027	0.994	7.05	1.74	0.984

$q_{\max}$(mg g^{-1}), K_L (L/mg), K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$.

Table 5
Comparison of monolayer adsorption of 2,4 DCP onto various adsorbents

Adsorbents	C_0 (mg/L)	Adsorption capacities (mg/g)	Reference
Lemon peels activated by H_3PO_4, calcined at 600°C/alginate beads	10–1,000	532.6	This study
Octadecyltrimethylammonium-bentonite/alginate beads	25–500	506.0	[30]
Activated carbon derived from moso bamboo	25–500	276.2	[31]
H_3PO_4 Activated carbon, calcined at 600°C non-encapsulated	10–1,000	297.5	This study
Hexadecyltrimethylammonium-bentonite/alginate beads	25–500	276.2	[30]
Phenyltrimethylammonium-bentonite/alginate beads	25–500	185.0	[30]
Guava seed activated carbon	5–20	32.31	[32]

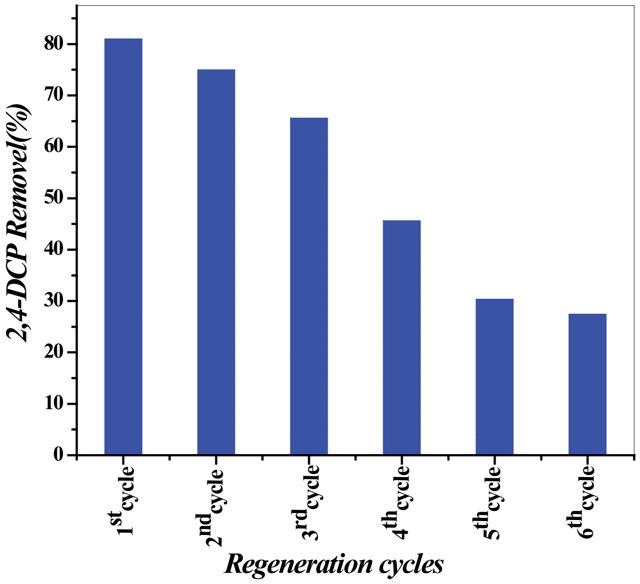

Fig. 8. Regeneration cycles of AC/A adsorbent beads.

(q_{max}) for the prepared AC/A in this study is much higher than that in the literature. AC/A is a more reliable alternative adsorbent in terms of high adsorption capacity, efficiency and fast adsorption rate.

4. Conclusion

The development of efficient adsorbents able to treat industrial wastewater containing non-biodegradable compounds as highly toxic chlorophenols has focused considerable research efforts in the latest years. The use of adsorbents prepared from agricultural residue shows some advantages: these materials are available locally, freely of charge, abundant and have been proven to be much more efficient than the conventional expensive adsorbents. This study has investigated the potential use of acid activated and calcined agricultural residue (dried lemon peel), then entrapped in calcium alginate to form beads easily used in adsorption process. Removal of 2,4-DCP from aqueous solution by the prepared adsorbents was found very high (95%) with maximum adsorption capacities of 297.80, 456.54, 488.08, 532.60 mg/g for AC, AC/A 1/1, AC/A 2/1 and AC/A 4/1, respectively. The adsorption process was spontaneous at all temperatures and endothermic. The adsorption kinetics and equilibrium isotherms of the 2,4-DCP followed pseudo-second-order and Langmuir model, respectively. The AC/A beads are recyclable and can be used in multiple adsorption cycles. Results of this study suggest that the AC/A beads (dried lemon peel activated with acid, calcined at 600°C and encapsulated with alginate) may be promising low-cost adsorbent for the removal of 2,4-DCP from wastewater. Therefore, it can be further examined and considered as a cheaper alternative to commercial adsorbents.

References

[1] X. Ruan, H. Liu, C.Y. Chang, X.Y. Fan, Preparation of organobentonite by a novel semidry method and its adsorption of 2,4 dichlorophenol from aqueous solution, Int. Biodeterior. Biodegrad., 95 (2014) 212–218.
[2] J. Yang, B. Pan, H. Li, S. Liao, D. Zhang, M. Wu, B. Xing, Degradation of p-nitrophenol on biochars: role of persistent free radicals, Environ. Sci. Technol., 50 (2016) 694–700.
[3] P. Strachowski, M. Bystrzejewski, Comparative studies of sorption of phenolic compounds onto carbon-encapsulated iron nanoparticles, carbon nanotubes and activated carbon, Colloids Surf., A, 467 (2015) 113–123.
[4] V.S. Tran, H.H. Ngo, W. Guo, J. Zhang, S. Liang, C.T. That, X. Zhang, Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water, Bioresour. Technol., 182 (2015) 353–363.
[5] H.N. Bhatti, Q. Zaman, A. Kausar, M. Iqbal, S. Noreen, Efficient remediation of Zr(IV) using citrus peel waste biomass: kinetic, equilibrium and thermodynamic studies, Ecol. Eng., 95 (2016) 216–228.
[6] H.N. Bhatti, A. Jabeen, M. Iqbal, S. Noreen, Z. Naseem, Adsorptive behavior of rice bran-based composites for malachite green dye: isotherm, kinetic and thermodynamic studies, J. Mol. Liq., 237 (2017) 322–333.
[7] S. Gao, L. Ge, T.E. Rufford, Z. Zhu, The preparation of activated carbon discs from tar pitch and coal powder for adsorption of CO_2, CH_4 and N_2, Microporous Mesoporous Mater., 238 (2017) 19–26.
[8] M.N. Mahamad, M.A.A Zaini, Z.A. Zakaria, Preparation and characterization of activated carbon from pineapple waste biomass for dye removal, Int. Biodeterior. Biodegrad., 102 (2015) 274–280.
[9] S. Shoukat, H.N. Bhatti, M. Iqbal, S. Noreen, Mango stone biocomposite preparation and application for crystal violet adsorption: a mechanistic study, Microporous Mesoporous Mater., 239 (2017) 180–189.
[10] Z. Ghani, M.S. Yusoff, N.Q. Zaman, M.F.M.A. Zamri, J. Andas, Optimization of preparation conditions for activated carbon from banana pseudo-stem using response surface methodology on removal of color and COD from landfill leachate, Waste Manage., 62 (2017) 177–187.

[11] S.Y. Lee, H.J. Choi, Persimmon leaf bio-waste for adsorptive removal of heavy metals from aqueous solution, J. Environ. Manage., 209 (2018) 382–392.

[12] A. Nayak, B. Bhushan, V. Gupta, P. Sharma, Chemically activated carbon from lignocellulosic wastes for heavy metal wastewater remediation: effect of activation conditions, J. Colloid Interface Sci., 493 (2017) 228–240.

[13] L. Zhong, Y. Zhang, Y. Ji, P. Norris, W.P. Pan, Synthesis of activated carbon from coal pitch for mercury removal in coal-fired power plants, J. Thermal Anal. Calorim., 123 (2016) 851–860.

[14] M. Achak, A. Hafidi, N. Ouazzani, S. Sayadi, L. Mandi, Low cost biosorbent "banana peel" for the removal of phenolic compounds from olive mill wastewater: kinetic and equilibrium studies, J. Hazard. Mater., 166 (2009) 117–125.

[15] L. Sun, D. Chen, S. Wan, Z. Yu. Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids, Bioresour. Technol., 198 (2015) 300–308.

[16] S. Cataldo, A. Gianguzza, A. Pettignano, I. Villaescusa, Mercury(II) removal from aqueous solution by sorption onto alginate, pectate and polygalacturonate calcium gel beads. A kinetic and speciation based equilibrium study, React. Funct. Polym., 73 (2013) 207–217.

[17] A. Aichour, H. Zaghouane-Boudiaf, C. Viseras Iborra, M.S. Polo, Bioadsorbent beads prepared from activated biomass/alginate for enhanced removal of cationic dye from water medium: kinetics, equilibrium and thermodynamic studies, J. Mol. Liq., 256 (2018) 533–540.

[18] G. Derafa, H. Zaghouane-Boudiaf, Urtica dioica leaves-calcium alginate as a natural, low cost and very effective bioadsorbent beads in elimination of dyes from aqueous medium: equilibrium isotherms and thermodynamic studies, Int. J. Biol. Macromol., 124 (2019) 915–921.

[19] K.-W. Jung, B.H. Choi, M.-J. Hwang, T.-U. Jeong, K.-H. Ahn, Fabrication of granular activated carbons derived from spent coffee grounds by entrapment in calcium alginate beads for adsorption of acid orange 7 and methylene blue, Bioresour. Technol., 219 (2016) 185–195.

[20] A. Nasrullah, A.H. Bhata, A. Naeem, M. H. Isa, M. Danish, High surface area mesoporous activated carbon-alginate beads for efficient removal of methylene blue, Int. J. Biol. Macromol., 107 (2018) 1792–1799.

[21] A. Aichour, H. Zaghouane-Boudiaf, Single and competitive adsorption studies of two cationic dyes from aqueous mediums onto cellulose-based modified citrus peels/calcium alginate composite, Int. J. Biol. Macromol. (2019), https://doi.org/10.1016/j.ijbiomac.2019.10.277.

[22] A. Benhouria, M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala, B.H. Hameed, Calcium alginate–bentonite–activated carbon composite beads as highly effective adsorbent for methylene blue, Chem. Eng. J., 270 (2015) 621–630.

[23] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater., 161 (2009) 387–395.

[24] A. Ely, M. Baudu, J.-P. Basly, M. Ould Sid'Ahmed Ould Kankou, Copper and nitrophenol pollutants removal by Na-montmorillonite/alginate microcapsules, J. Hazard. Mater., 171 (2009) 405–409.

[25] N. Boukhalfa, M. Boutahala, N. Djebri, A. Idris, Maghemite/alginate/functionalized multiwalled carbon nanotubes beads for methylene blue removal: adsorption and desorption studies, J. Mol. Liq., 2751 (2019) 431–440.

[26] B.H. Hameed, Equilibrium and kinetics studies of 2,4,6-trichlorophenol adsorption onto activated clay, Colloids Surf., A., 307 (2007) 45–52.

[27] H. Zaghouane-Boudiaf, M. Boutahala, C. Tiar, L. Arab, F. Garin, Treatment of 2,4,5-trichlorophenol by MgAl–SDBS organo-layered double hydroxides: kinetic and equilibrium studies. Chem. Eng. J., 173 (2011) 36– 41.

[28] S. Lagergren, Zur theorie der sogenannten Adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl., 24 (1898) 1–39.

[29] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[30] D. Garmia, H. Zaghouane-Boudiaf, C. Viseras. Ibbora, Preparation and characterization of new low cost adsorbent beads based on activated bentonite encapsulated with calcium alginate for removal of 2,4-dichlorophenol from aqueous medium, Int. J. Biol. Macromol., 115 (2018) 257–265.

[31] G.Q. Wu, X. Y. Sun, H. Hui, X. Zhang, J. Yan, Q.s. Zhang, Adsorption of 2,4-dichlorophenol from aqueous solution by activated carbon derived from moso bamboo processing waste, Desal. Wat. Treat., 51 (2013) 4603–4612.

[32] S.M. Anisuzzaman, Collin G. Joseph, D. Krishnaiah, A. Bono, E. Suali, S. Abang, L.M. Fai, Removal of chlorinated phenol from aqueous media by guava seed (*Psidium guajava*) tailored activated carbon, Water Resour. Ind., 16 (2016) 29–36.

[33] W.J. Weber, J.C. Morris, Water pollution symposium, Proc. Int. Conf. Pergamon, Oxford, 2 (1962) 231–266.

[34] G. Boyd, A. Adamson, L. Myers. Jr., The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, J. Am. Chem. Soc., 69 (1947) 2836–2848.

[35] H. Zaghouane-Boudiaf, M. Boutahala, Adsorption of 2,4,5-trichlorophenol by organo-montmorillonites from aqueous solutions: kinetics and equilibrium studies, J. Chem. Eng., 170 (2011) 120–126.

[36] K. Arinjay, K. Shashi, K. Surendra, Adsorption of resorcinol and catechol on granular activated carbon: equilibrium and kinetics, Carbon, 41 (2003) 3015–3025.

[37] M. Tariqul Islam, R. Saenz-Arana, C. Hernandez, T. Guinto, M.A. Ahsan, H. Kim, Y. Lin, B. Alvarado-Tenorio, J.C. Noveron, Adsorption of methylene blue and tetracycline onto biomass-based material prepared by sulfuric acid reflux, RSC Adv., 8 (2018) 32545–32557.

[38] Md. Tariqul Islam, A.H.M. Golam Hyder, R. Saenz-Arana, C. Hernandez, T. Guinto, M.A. Ahsan, B. Alvarado-Tenorioc, J.C. Noveron, Removal of methylene blue and tetracycline from water using peanut shell derived adsorbent prepared by sulfuric acid reflux, J. Environ. Chem. Eng., 7 (2019) 102816.

[39] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[40] H.M.F. Freundlich, Colloid and Capillary Chemistry, Methuen, London, 1926, UK.