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Saw-sedge *Cladium mariscus* as a functional low-cost adsorbent for effective removal of 2,4-dichlorophenoxyacetic acid from aqueous systems

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Abstract   For the first time in the published literature, a study is described concerning the use of the saw-sedge *Cladium mariscus* (*C. mariscus*) for adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous systems. Among the experiments carried out, the elemental composition of *C. mariscus* was determined (C = 48.0 %, H = 7.1 %, N = 0.95 %, S = 0.4 %), FTIR spectroscopic analysis was performed to confirm the chemical structure of the adsorbent, and porous structure parameters were measured: BET surface area ($A_{BET} = 0.6$ m^2/g), total pore volume ($V_p = 0.001$ cm^3/g) and average pore size ($S_p = 6.6$ nm). It was shown that the effectiveness of removal of 2,4-D from aqueous systems using *C. mariscus* depends on parameters of the process: contact time, system pH, mass of sorbent, and temperature. Maximum adsorption was attained for a solution at pH = 3. Further increase in the alkalinity of the tested systems led to a reduction in the effectiveness of the process. The kinetic of adsorption of 2,4-D by *C. mariscus* was also determined, and thermodynamic aspects were investigated. The experimental data obtained correspond to a pseudo-second-order kinetic model of type 1. Additionally the negative values obtained for ΔH° indicate that the process is exothermic, and the negative values of ΔG° show it to be spontaneous. As the temperature of the system increases the spontaneity of adsorption is reduced, in accordance with the exothermic nature of the process.

1 Introduction

In the last decade there has been considerable development in agriculture caused not only by the mechanization of manufacturing, but also by progress in the production of plant protection products (pesticides). However, pesticides cannot be equated only with agrotechnology. Plant protection products are commonly used in forestry, orcharding and even in backyard plots and gardens. In spite of the many advantages of using pesticides, it should be borne in mind that these substances are the main source of water pollution. This is due to the fact that these compounds easily penetrate the soil and pollute surface and ground water. Additionally, in most cases, they are toxic, carcinogenic and mutagenic (Aktar et al. 2009; Salman 2014; Shabeer et al. 2014; Sultana et al. 2014; Yang et al. 2014).

2,4-Dichlorophenoxyacetic acid (2,4-D) is the most popular pesticide or main component of plant protection products used throughout the world. It is a herbicide whose activity is based on the stimulation of cells to uncontrolled growth, which leads to the death of the plant in the final stage. It is commonly used in the cultivation of maize, soya, hazelnuts, sugar cane and spring wheat. 2,4-D is

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extremely toxic to organisms other than its targets. It is especially dangerous to aquatic organisms. It has a negative influence on the proper functioning of the human body; it is carcinogenic, mutagenic, and causes damage to the liver, kidneys and central nervous system. In addition, 2,4-D is poorly biodegradable, which means that it is stable in ambient conditions (Bradberry et al. 2004; Derylo-Marczewska et al. 2010; Garabant and Philbert 2002; Kaminski et al. 2014, Tomlin 2009).

The elimination of pesticides from water systems is a fundamental issue addressed by researchers around the world. Several techniques have been developed for the removal of organic pollution from water. The most frequently used methods, which include physical, chemical and biological processes, are photo-oxidation, chemical coagulation, sedimentation, filtration, disinfection, ion exchange, flotation, adsorption and electrochemical methods (Aksu and Kabasakal 2004; Bartczak et al. 2015; Goscianska et al. 2013, 2014; Mohammad et al. 2014; Nam et al. 2014; Ova and Ovez 2013; Pirsaheb et al. 2014; Souzaa et al. 2015; Zhang et al. 2014). In recent years, the adsorption process has become increasingly popular, as an effective method of removing pesticides from water systems. It is an attractive method because of its simplicity and low cost. In the last decade, low-cost natural-origin adsorbents have aroused increasing interest among researchers throughout the world. The use of this group of adsorbents decreases process costs, making this method an attractive alternative to conventional techniques of water and sewage purification. Saw-sedge *Cladium mariscus* (*C. mariscus*) can be included in the group of natural-origin materials (Theocharopoulos et al. 2006). It is a perennial monocot, belonging to the sedge family. It occurs on all continents except Antarctica. *C. mariscus* is an interesting material that has not previously been used and studied as an adsorbent of inorganic and organic impurities.

The phenomenon of 2,4-D adsorption is the subject of many ongoing research projects around the world. Numerous sorption materials are used for this process, including activated carbon, materials obtained from coconut shells, chitin and chitosan, and silica gel modified with cationic surfactants (Harmoudi et al. 2014; Koner et al. 2013; Njoku et al. 2014). Series of tests are performed to determine the character of the adsorbent in question, the kinetics of the process and the adsorption isotherms.

The adsorption process is a universal method for removing pesticides from aqueous systems (Ali et al. 2012). A multiplicity of studies show that this process is an alternative to conventional water treatment methods. The possibility of re-use of sorbents makes it competitive with respect to other methods of water purification.

In the present work, for the first time, an investigation was made of the use of *Cladium mariscus* as a potential adsorbent of 2,4-D. There is so far no information available in the literature concerning the use of this material, which confirms the novel nature of the present research. In the study, basic parameters of the adsorption process were determined. The adsorption kinetic was investigated using pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho 1999) models, and adsorption isotherms were determined using the Freundlich (1906) and Langmuir (1918) models. Thermodynamic aspects of the process were also investigated. An essential objective of the research was to determine the presumed mechanism of the process.

2 Materials and methods

2.1 Reagents and chemicals

The following reagents were used in the experiments: 2,4-dichlorophenoxyacetic acid (Merck KGaA, Germany) as the adsorbate, and hydrochloric acid (Chempur, Poland) and sodium hydroxide (Chempur, Poland) for pH adjustment.

2.2 Preparation of adsorbent

Cladium mariscus was collected in the vicinity of Chełm, Lublin region, Poland. The leaves of the plant were washed with distilled water and dried for 24 h at 105 °C. The next step involved reducing the adsorbent to an appropriate fineness. The plant material prepared in this way was then subjected to physicochemical analysis and used in adsorption tests.

2.3 Characterization of the biosorbent

The most important physicochemical and structural properties of the material were determined, with regard to its application as an effective adsorbent (elemental analysis, FTIR spectroscopy for identification of functional groups, and porous structure analysis). The elemental composition of *C. mariscus* was established using a Vario El Cube instrument (Elementar Analysensysteme GmbH, Germany). To identify the functional groups present in the structure of *C. mariscus*, Fourier transform infrared spectroscopy was applied. The measurements were performed using a VERTEX 70 spectrophotometer (Bruker, Germany). Substances were analyzed in a form of tablets prepared by mixing ca. 250 mg of anhydrous KBr with 1.5 mg of the sample. Spectra were produced over a wavenumber range of 4000–400 cm^{-1}, with a resolution of 0.5 cm^{-1}. To make a full physicochemical characterization of *C. mariscus* it was necessary to determine its porous

structure parameters (surface area and pore size distribution). These parameters were measured by means of low-temperature N_2 sorption using an ASAP 2020 instrument (Micromeritics Instrument Co., USA). Surface area was determined to an accuracy of ± 0.1 m^2/g, pore volume to ± 0.01 cm^3/g, and pore size to 0.01 nm.

2.4 Batch adsorption studies

The experimental studies first involved determination of the sorption capacity of *C. mariscus* with respect to 2,4-D and investigation of how selected process parameters influence the effectiveness of adsorption. The values of the variable process parameters are given in Table 1.

To determine the effect of contact time between adsorbate and adsorbent, the appropriate quantity of sorbent was weighed out (see Table 1) and was placed in conical flasks with 100 mL of model solution of 2,4-D at a specified concentration. The system was mixed using a KS 260 Basic shaker (IKA, Germany) for a specified time (1–120 min). The mixture was then filtered at reduced pressure. The effectiveness of the process was determined using a UV–Vis SPEKOL 1200 spectrophotometer (Analytik Jena AG, Germany) at wavelength 230 nm. The adsorbent was dried at 105 °C in a UE 500 drier (Memmert, Germany) and was subjected to further analysis.

To determine the influence of pH on the effectiveness of adsorption of 2,4-D, an appropriate quantity of sodium hydroxide or HCl was added to the model solution. The pH values were controlled with the use of an EL 20 pH meter (Mettler Toledo, Switzerland). After the desired pH was attained, the appropriate quantity of *Cladium mariscus* was added to the system.

The final analyzed process parameter was temperature, which was controlled using a KS 4000i incubator (IKA, Germany).

2.5 Kinetic and isothermal studies

An important element of the study was the determination of the kinetic of adsorption of 2,4-D by *C. mariscus* based on models of pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho 1999) type. To determine the kinetics of the adsorption process it was necessary to perform

calculations concerning the quantity of 2,4-D adsorbed in a given time (q_t). This was calculated from the following Eq. (1):

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

where C_0 and C_t denote the concentration of 2,4-D before and after the adsorption process (mg/L), V is the volume of model solution (L), and m is the mass of adsorbent used (g).

For the determination of adsorption isotherms using Freundlich (1906) and Langmuir models (1918), it was necessary to find the equilibrium concentration (q_e) of adsorbed 2,4-D acid on *C. mariscus*. This was calculated using the following formula (2):

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

where C_0 and C_e denote the concentration of 2,4-D before the adsorption process and in equilibrium (mg/L), V is the volume of model solution (L), and m is the mass of adsorbent used (g).

3 Results and discussion

3.1 Physicochemical characteristics of *Cladium mariscus*

Cladium mariscus, as a potential sorbent of 2,4-dichlorophenoxyacetic acid, was subjected to thorough physicochemical analysis. Elemental analysis was applied to determine the content of C, H, N and S in the plant structure (Table 2).

It also contains oxygen, which was not detected directly by this method. *C. mariscus* mainly consists of carbon and hydrogen (48.0 and 7.1 % respectively), similarly to other sorbents of plant origin (tea grounds, the seaweed *Ascophyllum nodosum*, sawdust, and the grass *Phragmites australis*—Akunwa et al. 2014; Foroughi-Dahr et al. 2015). The presence of nitrogen (0.9 %) can be explained by the occurrence of amide and amine groups in the material structure, which was also confirmed by further analysis of the FTIR spectra.

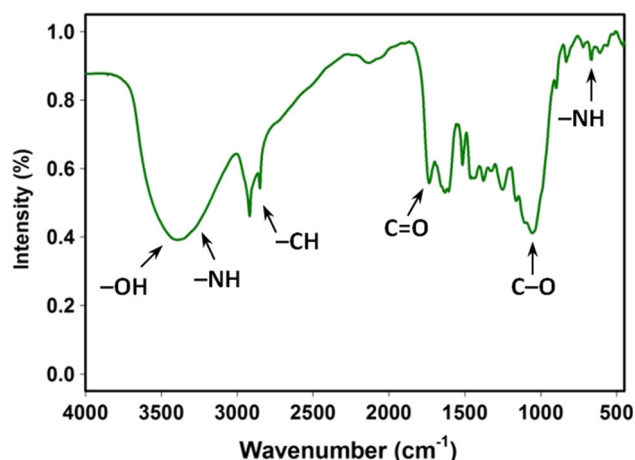**Table 1** Process conditions for the removal of 2,4-D acid by *Cladium mariscus*

Optimized parameter	Values analyzed	Adsorption process conditions
Time (min)	1, 3, 5, 10, 15, 30, 60, 120	pH 4.5; temperature 25 °C; mass of adsorbent 5 g/L; $C_0 = 20, 30, 50$ and 100 mg/L
pH	1; 2; 3; 4.5; 7; 9	Time: 60 min; temperature 25 °C; mass adsorbent 5 g/L; $C_0 = 50$ mg/L
Mass of the adsorbent (g/L)	1, 2, 5, 10, 15	Time: 60 min; temperature 25 °C; pH 4.5; $C_0 = 50$ mg/L
Temperature (°C)	25, 30, 35	Time: 60 min; mass of adsorbent 5 g/L; $C_0 = 50$ mg/L; pH = 4.5

Table 2 Elemental composition and parameters of porous structure of *Cladium mariscus*

Elemental content (%)

C	H	N	S
48.0	7.1	0.9	0.4

Parameters of porous structure

Surface area A_{BET} (m²/g)	Pore volume V_p (cm³/ g)	Pore diameter S_p (nm)
0.6	0.001	6.6

When investigating the use of adsorbents of natural origin, it is extremely important to determine their porous structure parameters. The results showed this plant to have a very low surface area of 0.6 m²/g and a pore volume of 0.001 cm³/g. However, these parameters do not exclude the application of *C. mariscus* in adsorption processes. In this case, the sorptive capacity of the material depends on the presence of specific functional groups on its surface.

To identify those groups in the structure of *C. mariscus*, FTIR spectra were obtained and analyzed (Fig. 1). The presence of hydroxyl groups was confirmed by the occurrence of bands in the range 3550–3000 cm⁻¹, derived from stretching vibrations of O–H bonds. This band substantially masks the band derived from stretching vibrations of N–H bonds (3300–3250 cm⁻¹) from amine and amide groups. The presence of aliphatic groups was indicated by the bands derived from stretching vibrations of C–H bonds in the range 3000–2800 cm⁻¹. There is also a noticeable band derived from stretching vibrations of C–O bonds in the range 1750–1700 cm⁻¹, which indicates the presence of carbonyl groups. The occurrence of ether groups was confirmed by the bands in the range 1100–1000 cm⁻¹,

derived from stretching vibrations of C–O–C and C–O groups. In the range 720–630 cm⁻¹ there are bands derived from bending vibrations of N–H bonds (amine groups). In this wavenumber range there are also vibrations proving the presence of C–C bonds, which are typical for aromatic rings.

Analysis of the FTIR spectra confirms the presence of numerous groups in the material structure and due to these groups the adsorbent can exhibit a remarkable capacity to adsorb impurities from aqueous systems.

The physicochemical analysis of the plant confirms the considerable possibilities of application of the material as an effective adsorbent of different kind of impurities.

3.2 Effect of adsorption time and kinetic study

In the first stage of the study it was investigated how the contact time between adsorbate and adsorbent influences the effectiveness of removal of 2,4-D from aqueous systems. This was done for four concentrations of 2,4-D: 20, 30, 50 and 100 mg/L (Fig. 2).

The results indicate that in the initial stage adsorption proceeded extremely rapidly. In the first 5 min the effectiveness of adsorption for each concentration was greater than 50 %. Adsorption equilibrium was reached after 30 min for an initial 2,4-D concentration of 20 or 30 mg/L, and after 60 min for 50 mg/L and for the highest analyzed concentration, 100 mg/L. The maximum adsorption yields were respectively 99.9, 99.0, 99.0 and 95.9 % for model solutions with 2,4-D concentrations of 20, 30, 50 and 100 mg/L. After the elapse of the optimum process time, no significant changes were recorded for any of the analyzed concentrations.

Fig. 1 FTIR spectrum of *Cladium mariscus*
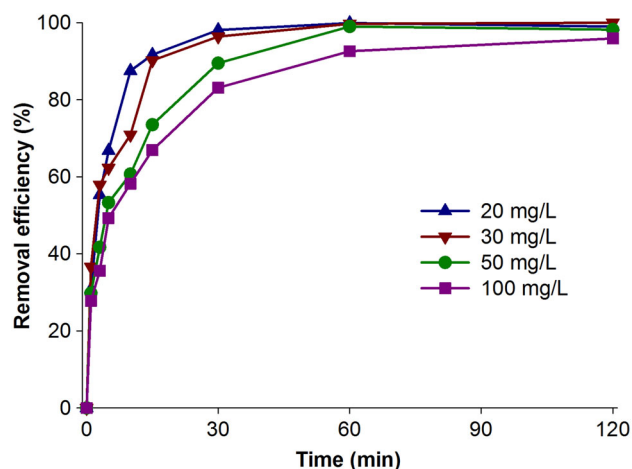
Fig. 2 Effect of contact time on 2,4-D removal by *Cladium mariscus* (2,4-D concentration 20–100 mg/L, adsorbent dose 0.5 g, pH 4.5, temperature 25 °C)

It should also be noted that the effectiveness of adsorption is also significantly influenced by the initial concentration of 2,4-D. The results indicate that as the 2,4-D concentration increases, the effectiveness of its removal decreases slightly, leading to an increase in the time required to attain an equilibrium state. This is because an increased quantity of 2,4-D anions diffuse to the sorbent surface through the boundary layer, increasing the time taken for adsorption equilibrium to be reached. The reduction in the effectiveness of adsorption with increased concentration of the solution of adsorbate results from the saturation of active sites capable of adsorbing 2,4-D.

Compared with other sorbents, the use of *C. mariscus* led to rapid attainment of adsorption equilibrium. When activated carbon was used, as described by Hammed et al. (2009), adsorption equilibrium was reached after 450 min. Aksu and Kabasakal (2005) carried out adsorption of 2,4-D on activated carbon and found equilibrium to be attained after 7 days. The properties of *C. mariscus* mean that it could be successfully used in industry, since the fast reaction time would enable a reduction in the volume of the tanks used as reactors.

A determination was also made of the kinetic of the adsorption of 2,4-dichlorophenoxyacetic acid from model solutions with the lowest and highest concentrations (20 and 100 mg/L). The kinetic of the process of adsorption of 2,4-D by *C. mariscus* was determined using a pseudo-first-order model (of Lagergren type 1898) and a pseudo-second-order model (as described by Ho 1999).

The aforementioned models present the correlations between changes in the concentration of adsorbate as a function of the time for which the adsorption process is continued until equilibrium is reached. Linear and graphical forms of the models are given in Table 3.

Here q_e and q_t (mg/g) denote the quantities of 2,4-D adsorbed at equilibrium and at time t (min), k_1 (1/min) is the rate constant for the adsorption process for the pseudo-first-order model, and k_2 (g/(mg min)) is the rate constant for the process for the pseudo-second-order model.

The kinetic parameters (Table 4) describing the pseudo-first-order as well as pseudo-second-order model type 1, 2, 3 and 4 were calculated from plots presented in Fig. 3 and 4, respectively.

Analysis of the obtained kinetic parameters (Table 4) shows that the experimental data correspond directly to the pseudo-second-order kinetic model. This is confirmed by the high correlation coefficient ($r^2 = 0.998$–0.999) obtained for the pseudo-second-order model type 1. It should also be noted that the quantities of adsorbed 2,4-D ($q_{e,cal}$) computed using that model correspond closely to the experimental values ($q_{e,exp}$). The adsorption rate coefficient (k_2) was found to decrease with increasing concentration of 2,4-D in the model solution.

Other researchers have determined the kinetics of adsorption of 2,4-D on selected adsorbents (Aksu and Kabasakal 2005; Chaparadza and Hossenlopp 2011; Gupta et al. 2006; Hameed et al. 2009; Nethaji and Sivasamy 2014; Salman and Al-Saad 2012). The kinetic parameters obtained by them are listed in Table 5. Determination of the adsorption kinetic is important for controlling the effectiveness of the removal of 2,4-D from aqueous systems. Adsorption of 2,4-D using various different types of material is described in most cases by means of a pseudo-second-order model.

The coefficients of correlation (r^2) obtained using the pseudo-second-order kinetic model of type 2, 3 and 4 (0.754–0.980) are significant lower than those obtained using the type 1 model. Additionally, the $q_{e,cal}$ computed from the pseudo-second-order kinetic models of type 2, 3 and 4 do not correspond with the $q_{e,exp}$ the same as in the case of 1st sub-type.

3.3 Effect of pH

Another important part of the study involved determining how the pH of the system influences the effectiveness of adsorption of 2,4-D from model aqueous solutions (Fig. 5).

The results show that as the pH of the solution increases (in the pH range 1–3) the effectiveness of adsorption increases, reaching a maximum at pH = 3 (yield 99.1 %). A further increase in the alkalinity of the solution causes a reduction in effectiveness, which at the highest tested pH

Table 3 Linear and graphical forms of pseudo-first and pseudo-second order kinetic models

Type of kinetic model	Linear form	Plot
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	$\log(q_e - q_t)$ vs. t
Pseudo-second order		
Type 1	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	$\frac{t}{q_t}$ vs. t
Type 2	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	$\frac{t}{q_t}$ vs. $\frac{1}{t}$
Type 3	$\frac{1}{t} = \frac{k_2 q_e^2}{q_t} - \frac{k_2 q_e^2}{q_e}$	$\frac{t}{t}$ vs. $\frac{1}{q_t}$
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - \frac{k_2 q_e^2}{q_e}$	$\frac{q_t}{t}$ vs. q_t

Table 4 Pseudo-first-order and pseudo-second-order kinetic parameters concerning adsorption of 2,4-D onto *Cladium mariscus*

Type of model kinetic		Parameter		Concentration of 2,4-D (mg/L)			
		Symbol	Unit	20	30	50	100
Pseudo-first order		$q_{e.exp}$	mg/g	4.00	5.98	9.90	19.18
		$q_{e.cal}$	mg/g	2.12	3.67	6.82	12.89
		k_1	1/min	0.12	0.10	0.07	0.05
		r^2	–	0.980	0.965	0.987	0.995
Pseudo-second order	Type 1	$q_{e.cal}$	mg/g	4.03	6.15	10.24	20.03
		k_2	g/(mg min)	0.17	0.06	0.05	0.02
		r^2	–	0.999	0.999	0.999	0.998
	Type 2	$q_{e,cal}$	mg/g	3.93	5.48	8.43	15.32
		k_2	g/(mg min)	0.17	0.13	0.06	0.03
		r^2	–	0.980	0.925	0.931	0.884
	Type 3	$q_{e,cal}$	mg/g	3.95	5.62	8.71	16.23
		k_2	g/(mg min)	0.17	0.12	0.05	0.03
		r^2	–	0.980	0.925	0.931	0.884
	Type 4	$q_{e,cal}$	mg/g	4.04	5.92	9.56	18.14
		k_2	g/(mg min)	0.15	0.09	0.04	0.02
		r^2	–	0.956	0.832	0.815	0.754
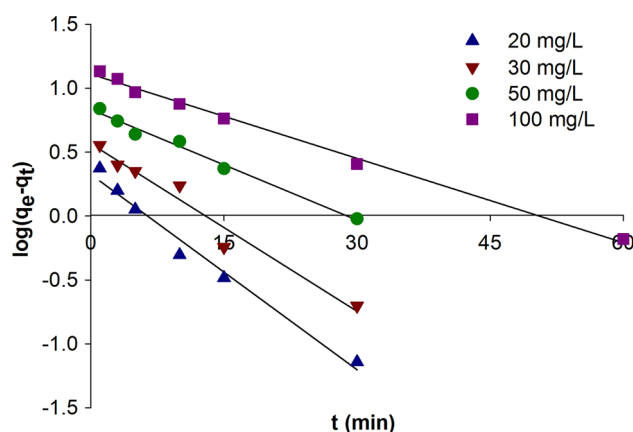
Fig. 3 Linear forms of pseudo-first-order kinetic model related with adsorption of 2,4-D by *Cladium mariscus*

value (pH = 9) was found to be 55.3 %. The pH value of the system plays a key role in defining the mechanism of adsorption of 2,4-D on the surface of *C. mariscus*.

Figure 6 shows a proposed mechanism for the adsorption of 2,4-D on the complex surface of *C. mariscus*. The presence of surface functional groups (carbonyl, amide, ether) capable of releasing a free electron pair to form a bond suggests adsorption by way of a chemical reaction. However, the protonating ability of surface functional groups (hydroxyl, amine, amide) would indicate adsorption through intermolecular interactions (including cation–dipole interactions and hydrogen bonds).

Above the pH corresponding to the pKa value (2.73), 2,4-D occurs in the form of an anion. The maximum

effectiveness of adsorption was obtained for pH = 3, which implies that the mechanism is based, to by far the greatest degree, on electrostatic interaction between the anion of 2,4-D and the surface functional groups (having a positive charge − Fig. 6). A much lesser role in the overall adsorption process is played by chemisorption and ion exchange.

3.4 Effect of adsorbent dose

Another important parameter that was analyzed is the mass of sorbent (Fig. 7). An increase in effectiveness of 2,4-D acid removal together with increasing mass of adsorbent was observed. This is because an increase in the mass of sorbent causes an increase in the adsorptive (contact) surface and an increase in the quantity of surface functional groups capable for removing 2,4-D, which leads to an increase in the effectiveness of the adsorption process. It was confirmed that adsorbent dose of 10 g/L and 60 min time is enough to completely clean the solution which contains 50 mg/L of 2,4-D.

3.5 Effect of temperature and thermodynamic studies

The last parameter analyzed was the temperature of the system (Fig. 8a). It was found that as temperature increased, the effectiveness of removal of 2,4-D slightly decreased. This suggests that the adsorption process may be of an exothermic nature.
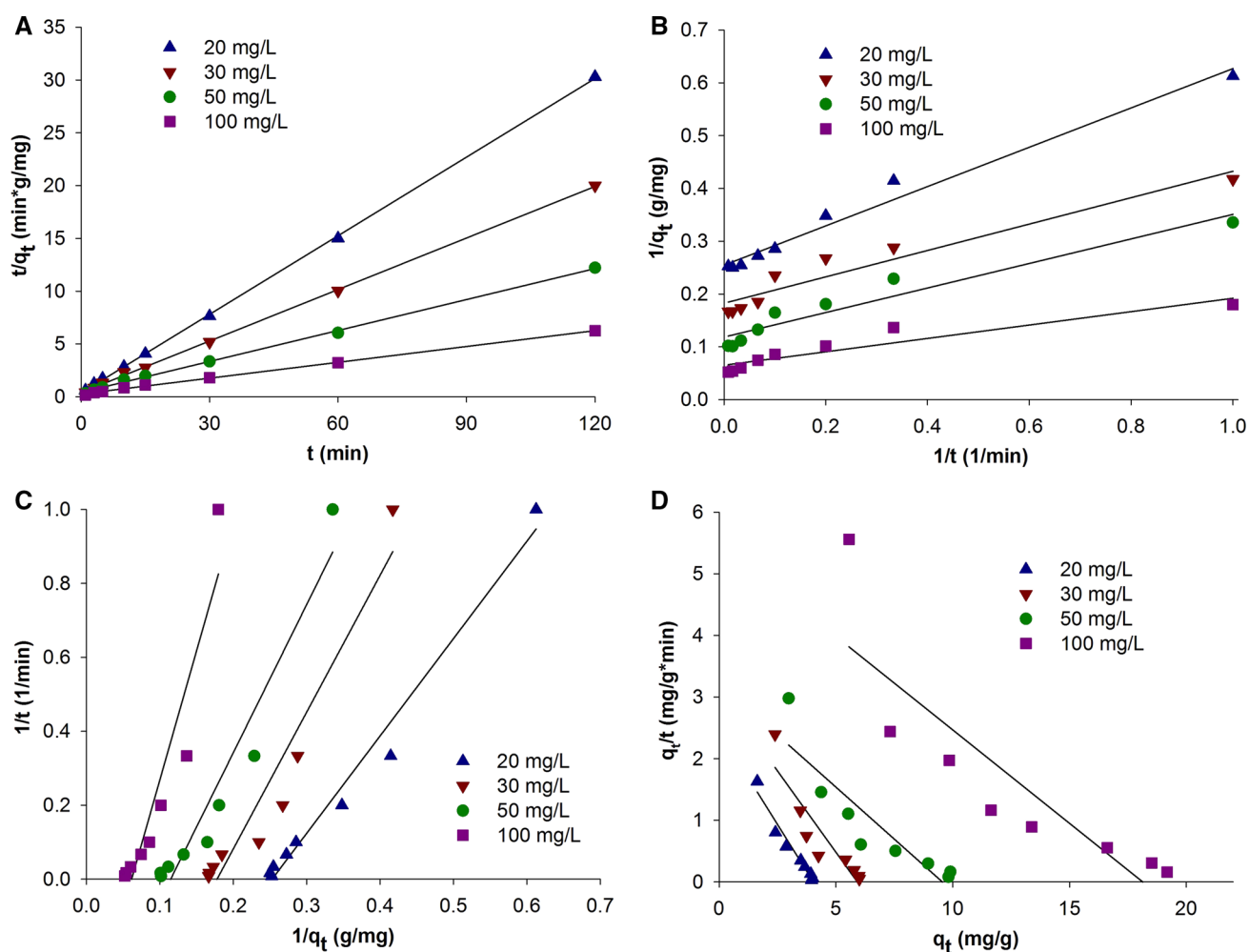
Fig. 4 Type 1 (**a**), 2 (**b**), 3 (**c**) and 4 (**d**) of pseudo-second-order kinetic model obtained using a linear method

Table 5 The kinetic parameters describe the adsorption kinetic models of 2,4-D in the selected adsorbents

Adsorbent	Type of kinetic model	r^2	k_1/k_2 (1/min) (g/(mg·min))	Reference
Activated carbon derived from date stones	Pseudo-first order	0.992	0.915	Hameed et al. (2009)
Calcined Zn-Al.-Zr layered double hydroxide	Pseudo-second order	0.990	0.004	Chaparadza and Hossenlopp (2011)
Fertilizer and steel industry wastes	Pseudo-second order	0.992	0.002	Gupta et al. (2006)
Magnetite activated carbon derived from waste biomass	Pseudo-second order	0.999	0.012	Nethaji and Sivasamy (2014)
Seeds activated carbon	Pseudo-second order	0.998	0.041	Salman and Al-Saad (2012)

This property of the process may result from the fact that interactions of anions of 2,4-D with functional groups on the plant surface are stronger than the interactions of the initially adsorbed water on the surface of the sorbent. This indicates strong electrostatic interactions between 2,4-D anions and the sorbent surface.

Other researchers studying the adsorption of 2,4-D have obtained similar results. Aksu and Kabasakal (2005), who
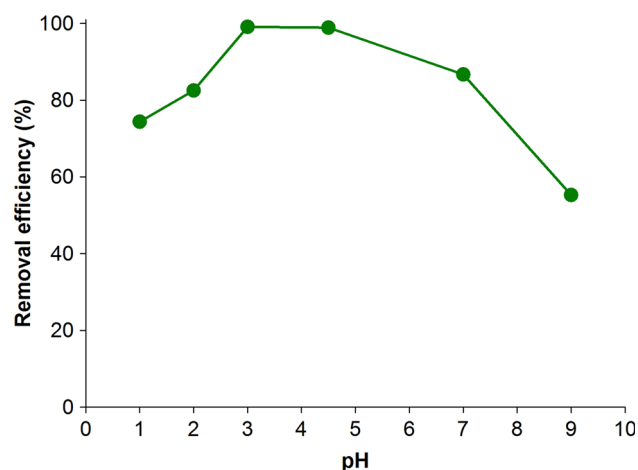
Fig. 5 Effect of pH on 2,4-D removal by *Cladium mariscus* (2,4-D concentration 50 mg/L, adsorbent dose 0.5 g, time 60 min, temperature 25 °C)

investigated the adsorption of 2,4-D on granulated activated carbon, showed the process to be exothermic. Similar results were obtained by Gupta et al. (2006), who carried out adsorption of 2,4-D using a suspension of activated carbon.

The adsorption of 2,4-D on low-cost adsorbents is not always exothermic. Koner et al. (2013) showed that

adsorption on the surface of a modified waste silica gel was endothermic.

Another important part of the work was the investigation of thermodynamic aspects of the process of adsorption of 2,4-D by *C. mariscus*. An analysis was made for four different concentrations of model solutions (20, 30, 50 and 100 mg/L) at three temperatures (25, 30 and 35 °C).

Calculations were made of the free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of the systems, using Eqs. (3–5):

$$\Delta G° = -RT \ln K_c \tag{3}$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{4}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{5}$$

where $\Delta G°$ (kJ/mol) is the change in the free energy of the system, $\Delta H°$ (kJ/mol) is the change in the free enthalpy of the system, $\Delta S°$ (kJ/mol K) is the change in the free entropy of the system, R (8.314 J/mol K) is the gas constant, K_c is the reaction equilibrium constant, and T (K) is the temperature.

The changes in enthalpy and entropy were calculated based on the plot of $\ln K_c$ against $1/T$ (Fig. 8b), using its slope $\left(-\frac{\Delta H°}{R}\right)$ and y-axis intercept $\left(\frac{\Delta S°}{RT}\right)$. The results are given in Table 6.
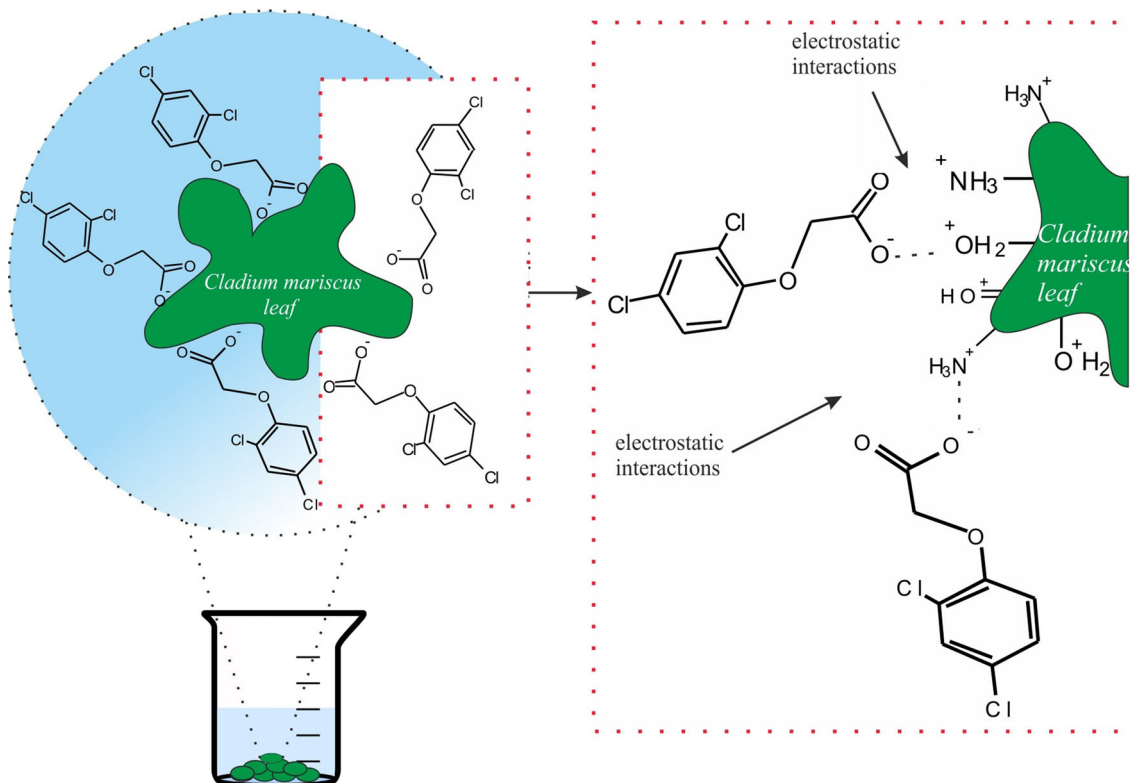

Fig. 6 Proposed mechanism of adsorption of 2,4-D on the surface of *Cladium mariscus*
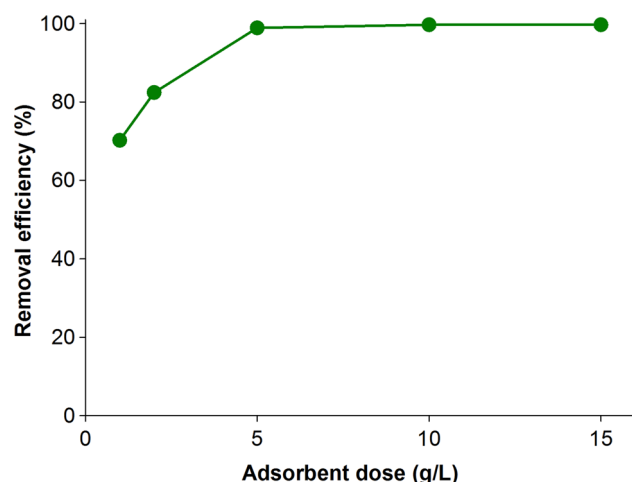
Fig. 7 Effect of adsorbent dose on 2,4-D removal by *Cladium mariscus* (2,4-D concentration 50 mg/L, pH 4.5, time 60 min, adsorbent dose 0.5 g, temperature 25 °C)

The negative values of $\Delta H°$ indicate that the process is exothermic, while the negative values of $\Delta G°$ for the process of adsorption of 2,4-D at all three temperatures show the process to be spontaneous. With increasing temperature, the degree of spontaneity of the process decreases, in accordance with the exothermic nature of the process. Furthermore, the values of change of entropy ($\Delta S°$) describe the randomness in the interactions between adsorbent and adsorbate. Nonetheless, the negative values of $\Delta S°$ point to complex interactions between adsorbent and adsorbate.

Researchers investigating different materials have obtained similar results. Salman et al. (2011a, b) and Jung et al. (2013) determined thermodynamic parameters in order to better understand the mechanism of adsorption of 2,4-D on the surface of activated carbon obtained from oil palm leaves, activated carbon from banana stalks (Salman et al. 2011a, b), and a mesoporous metal-organic framework material (Jung et al. 2013). Their results also confirm the spontaneous and exothermic nature of the adsorption of 2,4-D. It should be noted, however, that both research teams obtained positive values for the change of entropy, which may be due to the greater randomness of the interactions on the phase contact surface and the greater quantity of adsorbed water relative to 2,4-D. These results suggest that *C. mariscus* is a more effective adsorbent of this herbicide from aqueous systems.
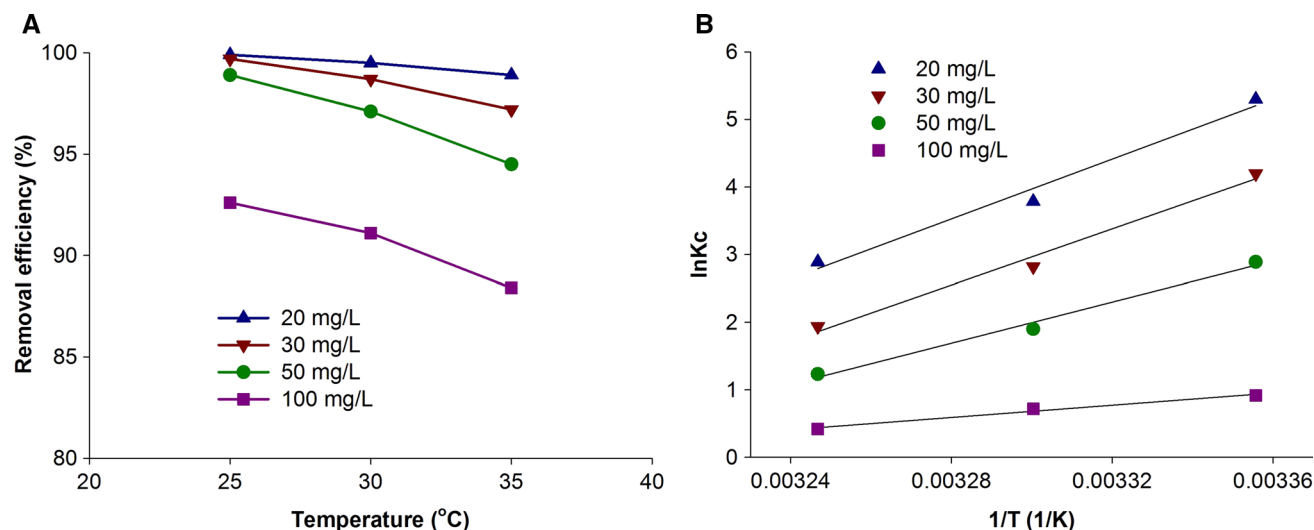

Fig. 8 Effect of temperature on 2,4-D removal by *Cladium mariscus* (2,4-D concentration 50 mg/L, pH 4.5, time 60 min) (**a**) and log K_c versus 1/T (**b**)

Concentration of 2,4-D (mg/L)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$\Delta G°$ (kJ/mol)		
			25 °C	30 °C	35 °C
20	−184.08	−574.73	−12.81	−9.93	−7.06
30	−172.66	−545.39	−10.13	−7.40	−4.68
50	−126.41	−400.57	−7.04	−5.04	−3.03
100	−37.80	−119.09	−2.31	−1.72	−1.12

Table 6 Thermodynamic parameters of the adsorption of 2,4-D onto *Cladium mariscus*

3.6 Isothermal studies

Isotherms for the adsorption of 2,4-D by *C. mariscus* were determined using the models of Freundlich and Langmuir. The diagrams in Fig. 9 show fits of the experimental data to those models based on graphs of C_e/q_e against C_e and $log(q_e)$ against $log(C_e)$. These enabled calculation of the parameters of the isotherms, which are given in Table 7.

The Freundlich isotherm (1906) is described by the following linear Eq. (6):

$$\log q_e = \log K_F + \log C_e^{\frac{1}{n}} \qquad (6)$$

where K_F (mg/g) is a measure of adsorption capacity, and $\frac{1}{n}$ denotes the intensity of adsorption.

The Langmuir isotherm equation has the following linear form (1918) (7):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (7)$$

where: C_e (mg/L) is the equilibrium concentration of ions in solution; q_e (mol/g) is the quantity of adsorbate adsorbed at equilibrium; q_m (mg/g) is the maximum sorptive capacity; b (–) is Langmuir's constant.

The linear correlation coefficients (R^2) for the two models have similar values (0.982–0.988), which indicates the complexity of the process mechanism and the heterogeneity of the adsorbent surface. The experimental data are slightly better described by Langmuir's model. Assuming the formation of a monolayer, it is possible to determine the adsorption capacity (q_m), which in the case of *C. mariscus* was found to be 65.58 mg/g. For the model assuming heterogeneity of the surface, however, the value K_F was calculated as 8.93 mg/g. Another parameter of the Freundlich model is the constant *n*. For all experiments it

was found that $n > 1$, which indicates the predominantly physical nature of the adsorption, confirming the previous assumptions concerning the adsorption mechanism.

At the next stage the adsorption capacity of the studied material was compared with that of other adsorbents (see Table 7). *C. mariscus* demonstrates a significant sorptive capacity, which means that it may be successfully used as an effective low-cost adsorbent of 2,4-dichlorophenoxyacetic acid.

3.7 FTIR spectroscopy

FTIR spectra of *C. mariscus*, 2,4-dichlorophenoxyacetic acid (2,4-D), and the product after adsorption (2,4-D concentration 50 mg/L, adsorbent dose 0.5 g, time 60 min, temperature 25 °C, pH = 4.5) are presented in Fig. 10. The most important bands are summarized in Table 8.

The FTIR spectrum of *C. mariscus* shows the presence of bands characteristic for the groups forming the structure of the adsorbent. FTIR analysis of 2,4-dichlorophenoxy-acetic acid reveals peaks at 3072, 1482 and 641 cm^{-1} associated with vibrations of aromatic structures, and signals at 3389, 1733, 1230 and 1095 cm^{-1} which can be assigned to vibrations of carboxylic groups (Nejati et al. 2013).

Most important is the spectrum of the product after adsorption of 2,4-D by *C. mariscus*. This shows the presence of bands at 3408, 3278, 2920, 2853, 1738, 1634, 1478, 1315, 1236, 1092, 1057 and 1055 cm^{-1}, which are characteristic for the structural vibrations of both the sorbent and 2,4-D (Pavlovic et al. 2005). The peaks at 3069 and 642 cm^{-1} correspond to other vibrations of groups present in the 2,4-dichlorophenoxyacetic acid structure. The presence of all of these signals confirms the successful
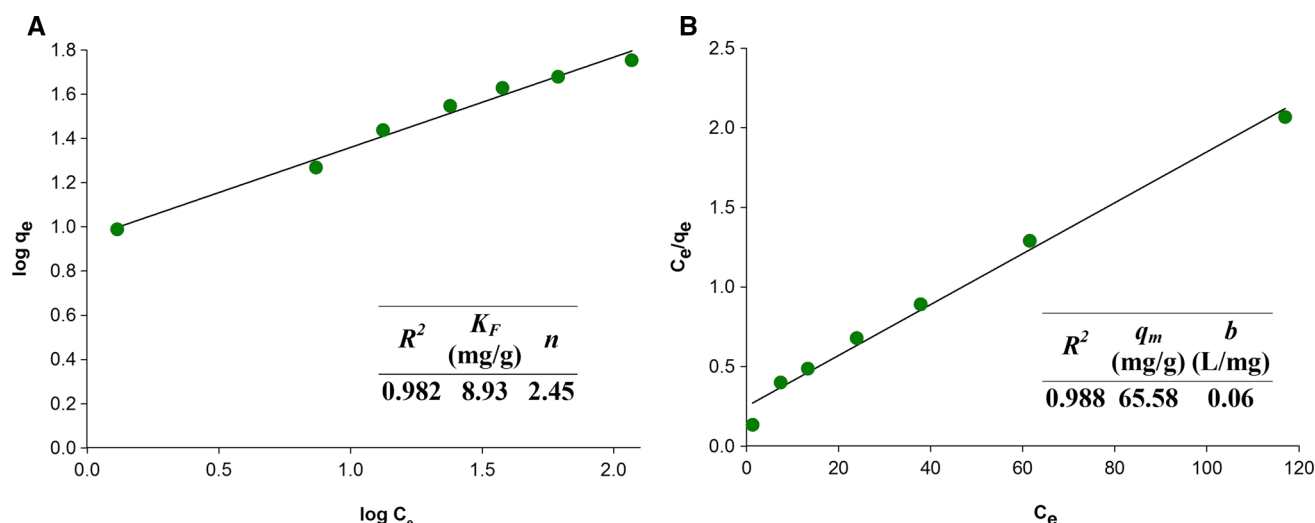

Fig. 9 Linear adsorption isotherms models of Freundlich (**a**) and Langmuir (**b**), and isotherm constants for 2,4-D with *Cladium mariscus*

Table 7 Comparison of adsorption capacity towards removal of 2,4-D acid by other adsorbents

Adsorbent type	q_m (mg/g)	Reference
Powdered activated carbon	97.4	Aksu and Kabasakal (2005)
Cladium mariscus	65.58	This study
Blast furnace sludge	30.0	Gupta et al. (2006)
Blast furnace dust	21.0	Gupta et al. (2006)
Modified silica gel	17.7	Koner et al. (2013)
Surface modified activated carbon (AC F400AN)	11.76–16.25	Son Tran et al. (2015)
Chitosan	11.0	Harmoudi (2014)
Commercial activated carbon (AC F400)	8.13–10.48	Son Tran et al. (2015)
Chitin	6.0	Harmoudi (2014)
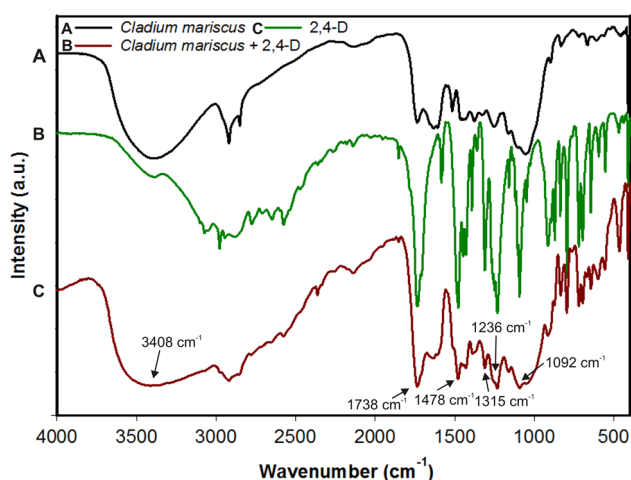
Fig. 10 FTIR spectra of C*ladium mariscus*, 2,4-dichlorophenoxyacetic acid, and the product after the adsorption process

adsorption of the organic compound onto the sorbent surface (Cavani et al. 1991). It is also interesting that the intensity of the signal corresponding to stretching vibrations of –OH groups was greater on the spectrum after the adsorption process, which confirms previous observations.

The slight shifts in the maximal wavenumbers of the peaks in the spectrum of the product after adsorption compared with the spectra of *C. mariscus* and 2,4-dichlorophenoxyacetic acid might suggest that the interactions between adsorbent and adsorbate are based on hydrogen bonds Hajdú et al. 2012.

4 Conclusions

In this study, for the first time in the scientific literature, research has been carried out on the process of adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous systems using saw-sedge *C. mariscus*, collected in the east part of Lublin region. *C. mariscus* consists chiefly of carbon (48 %) and hydrogen (7 %). The presence of these elements can be explained by the occurrence of surface functional groups on the surface of the material, as was confirmed by FTIR analysis. The plant material has a relatively small BET surface area ($A_{BET} = 0.6$ m^2/g) and a total pore volume of $V_p = 0.001$ cm^3/g. Hence the sorptive capacity of this material, considering the low surface area, is conditioned by the presence of functional groups on its surface. The effectiveness of removal of 2,4-D from

Table 8 Maximal vibrational wavenumbers (cm^{-1}) of *Cladium mariscus*, 2,4-dichlorophenoxyacetic acid, and products after adsorption

Vibrational assignment	*Cladium mariscus*	2,4-D acid	*Cladium mariscus* + 2,4-D acid
O–H stretching	3414	3389	3408
N–H stretching	3267	–	3278
C$_{Ar}$–H stretching	–	3072	3069
C–H stretching	2916, 2846	2980	2920, 2853
C=O stretching	1734	1733	1738
N–H stretching	1625	–	1634
C$_{Ar}$=C$_{Ar}$	1465	1482	1478
C–O–C asymetric	1322	1307	1315
C–OH deformational	1247	1230	1236
C–O stretching	1054	1095	1092, 1055
C–O–C symetric	1054	1058	1057
C$_{Ar}$–Cl stretching	–	641	642

aqueous systems using *C. mariscus* is dependent on four basic process parameters, namely the contact time between adsorbate and adsorbent, the pH of the system, the mass of sorbent used, and the temperature. The results show that in the initial stage the process of adsorption proceeds extremely rapidly. Depending on the solution concentration, equilibrium was attained after different contact times of adsorbate with adsorbent (30 min for concentrations of 20 and 30 mg/L, 60 min for 50 and 100 mg/L). It was also found that the pH has a significant influence on the effectiveness of removal of 2,4-D. Maximum adsorption was attained for a solution at pH = 3. Further increase in the alkalinity of the tested systems led to a decrease in the effectiveness of adsorption. It was also shown that the effectiveness of removal of 2,4-D increases as the mass of material used increases. This is due to the greater contact surface between adsorbate and adsorbent. It was also shown that with an increase in the temperature at which the adsorption process took place, the effectiveness of removal of 2,4-D decreased slightly. The inverse proportionality of the effectiveness of adsorption of 2,4-D with respect to temperature implies that the process is exothermic.

An investigation was made of the kinetic of adsorption of 2,4-D by *C. mariscus*. The experimental data corresponded to a pseudo-second-order kinetic model of type 1. The adsorption rate constant (k^2) decreased with increasing concentration of 2,4-D in model solution.

Detailed thermodynamic analysis showed values of $\Delta H°$ to be negative, which confirms the exothermic nature of the process. Meanwhile, negative values of $\Delta G°$ for the process of adsorption of 2,4-D at all analyzed temperatures indicate that the process is spontaneous.

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