



RESEARCH PAPER

# Nitrate Removal by Sorbent Derived from Waste Lignocellulosic Biomass of *Lagenaria vulgaris*: Kinetics, Equilibrium and Thermodynamics

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## Abstract

The equilibrium, sorption kinetics and thermodynamic parameters of nitrate ions sorption using a cationic modified *Lagenaria vulgaris* shell as a sorbent were studied. The sorption of nitrate ions was carried out from synthetic aqueous solutions in a batch mode. For this purpose, a sorbent based on waste lignocellulosic biomass was utilized. The cationic quaternary ammonium sorbent was obtained by chemical modification of raw *Lagenaria vulgaris* shell using (3-chloro-2-hydroxypropyl) trimethylammonium chloride reagent. The obtained results of nitrate sorption from synthetic solutions of different concentrations (2–100 mg/L) were examined by non-linear regression analysis of different reaction kinetic and multi-linear diffusion models. To describe the sorption equilibrium in the liquid–solid system, the experimentally obtained data were fitted with typical non-linear models of sorption isotherms (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Sips isotherms). To determine the thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ), nitrate sorption experiments on CMLVS sorbent were performed at different temperatures (20, 40, 60 °C), under previously determined optimal conditions. Nitrates desorption and CMLVS sorbent regeneration was also studied.

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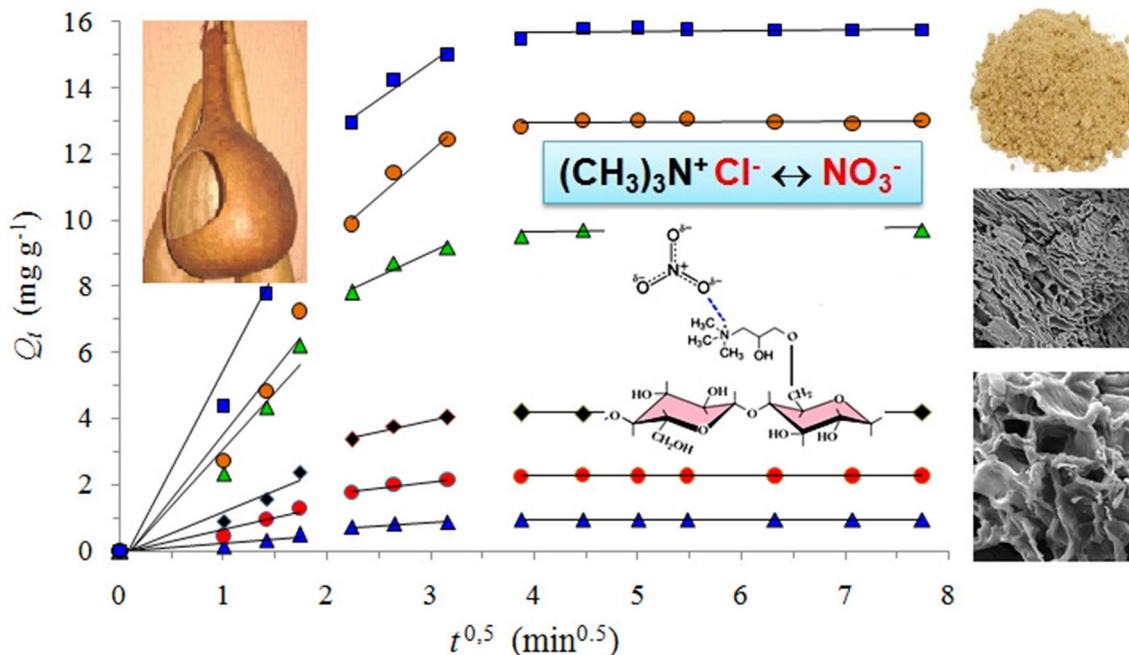
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## Graphic Abstract



## Highlights

- The exploitation of waste lignocellulosic biomass of *Lagenaria vulgaris* shell as a valuable sorbent for anionic pollutants, primarily for nitrates, is proposed.
- Equilibrium, sorption kinetics and thermodynamic parameters of nitrate sorption using the cationic modified sorbent are characterized.
- The sorption capacity of the sorbent (15.869 mg/g) is comparable to the results of other cationically modified lignocellulosic agricultural wastes.
- The nitrate-loaded sorbent can be effectively regenerated in HCl and used repeatedly in the sorption–desorption cycles.

**Keywords** Sorption · Nitrate · *Lagenaria vulgaris* · Kinetics · Equilibrium · Thermodynamics

## Introduction

Regardless of numerous regulations in the field of environmental protection, the reality is an increasing amount of wastewater, both industrial and municipal, which contains various organic and inorganic substances. Discharge of wastewater into watercourses leads to deterioration of the quality of natural waters, which are less and less for the

survival of the living world. Thus, various pollutants are increasingly identified in natural waters, as well as the presence of nitrates, which are the subject of this paper.

The presence of nitrates in lower concentrations is not a problem, with regard to the use of nitrates as fertilizers by plants, which significantly reduces the concentration of nitrates in surface waters. However, the main environmental problem stems from groundwater, from where nitrates spread to the environment, primarily in drinking water (Majumdar and Gupta 2000). On the other hand, it is known that in aerated soils, nitrogen compounds oxidize to soluble nitrate, which can penetrate into the saturated zone. For these reasons, it is very important to map locations susceptible to nitrate pollution, as well as to monitor the nitrate content in waters. Thus, water monitoring literature data were indicated elevated nitrate concentrations of 266 mg/L at several locations in Texas, given that the maximum contaminant level for nitrate in drinking water was 44.27 mg/L according to U.S. EPA (Hudak 2010).

Nitrates are responsible for the eutrophication of fresh water and the sea, and have a detrimental effect on aquatic ecosystems because they hinder the survival and reproduction of a large number of life forms (Wiesmann et al. 2006). Also, water contaminated with nitrates is not for consumption. Nitrates in natural waters, primarily in drinking water, pose a great danger to human and animal health, since they

can cause methemoglobinemia (Fewtrell 2004), and non-Hodgkin's lymphoma (Ward et al. 1994). In addition, when they reach the body, nitrates are reduced to nitrites, which in reaction with amines lead to the formation of potentially carcinogenic nitrosamines (Oram 2015). In this regard, according to recommendation of the World Health Organization (WHO 2016), EU guidelines and the Drinking Water Ordinance, the limit of nitrate in water is 50 mg/L, and the maximum allowable concentration (MAC) for nitrate is 10 mg/L expressed over nitrogen.

In order for nitrate-contaminated water to become usable, purification is needed, which is a very expensive process. Numerous methods and techniques have been developed to remove nitrates from water. They are most often mentioned in the literature: biological treatment (Wiesmann et al. 2006), denitrification (Soares 2000), reverse osmosis (Schoeman and Steyn 2003), electrodialysis (Abou-Shady et al. 2012), ion exchange (Zhan et al. 2011; Ebrahimi and Roberts 2013), adsorption (Ozturk and Bektas 2004; Bhatnagar and Sillanpa 2011; Cengeloglu et al. 2006; Mishra and Patel 2009), and reduction by zerovalent iron (Su and Puls 2004). The disadvantages of these methods are technological and economic limitations, which relate to the requirements of water pretreatment, high operating costs, lower efficiency, and the creation of by-products and concentrated waste streams, which is a new problem due to their disposal (Soares 2000).

One of the important alternatives in wastewater treatment was adsorption by activated carbon, due to the simplicity and efficiency of removing various pollutants (Kostić et al. 2019). However, in addition to the high cost of production and the complex regeneration process, the occurrence of secondary contaminants is an important limiting factor in the application of this technique today. Therefore, recent research has focused on the utilization of various agro-industrial waste biomasses (Gupta et al. 2009). Due to their unique properties, such as adsorptivity, biocompatibility, biodegradability and hydrophilicity, biomasses are functional ecological materials (Keranen et al. 2015). In addition to widely researched native biomasses, sorbents based on chemically modified agro-industrial waste are of special interest for these purposes (Loganathan et al. 2013). In this regard, chemical modification was performed by cationizing the lignocellulosic material to allow binding of anions, such as nitrates. Cationization involves the introduction of a quaternary ammonium groups into the structure of the lignocellulosic material. Several methods have been described in the literature, such as cationization via epichlorohydrin and dimethylamine (Orlando et al. 2002) or *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHTAC) reagents (Marković Nikolić et al. 2018a).

Valuable waste from agriculture that can be utilized for these purposes is lignocellulosic biomass of bottle gourd

(*Lagenaria vulgaris*) shell (LVS). The sorption potential of this biomass has already been proven by the examples of removing cationic pollutants from aqueous solutions (Mitić-Stojanović et al. 2011; Bojić et al. 2013, 2017). Biodegradability, macroporous and structural properties, as well as high content of OH functional groups, are the characteristics of the lignocellulosic LVS and represent a good basis for improving the existing sorption characteristics. In that sense, cationically modified LVS biomass using epichlorohydrin and trimethylamine has been shown to be an effective sorbent for the pre-concentration and immobilization of phosphates from synthetic aqueous solutions to environmental cleanup (Marković Nikolić et al. 2020).

In our previous publication, the synthesis success, structural performance and preliminary sorption properties (for phosphates and nitrates) of a new cationic sorbent based on LVS biomass modified by grafting CHTAC reagent were reported (Marković Nikolić et al. 2018a). In preliminary isotherm studies, using only the Freundlich and Langmuir models, it was found that nitrate sorption better followed the Langmuir model with a maximum sorption capacity of 16.53 mg/g. However, a significant relative deviation of the sorption capacity compared to the experimentally obtained value indicated the necessary application of other models for describing the nitrate sorption, such as Sips, Temkin, and Dubinin-Radushkevich isotherms. In this regard, an explanation of the mechanism and kinetics of nitrate sorption required more detailed analysis, which is a novelty of this research. Therefore, the aim of this paper is to investigate the sorption potential of CMLVS sorbent for the removal of nitrates from synthetic solutions, with special emphasis to kinetic, equilibrium and thermodynamic studies of the sorption process.

## Materials and Methods

### Materials

As a starting material for the production of cationic sorbent, naturally dried lignocellulosic biomass of bottle gourd shell (LVS), after removal of the inner pulp, was used. The constituents, physical and chemical properties of the LVS biomass, determined according to the standard procedures of the Association of Official Analytical Chemists (AOAC) and the American Association of Cereal Chemistry (AACC), are described in our previous publications (Marković Nikolić et al. 2018a, 2020).

An initial nitrate stock solution (100 mg N/L) was prepared by dissolving  $\text{KNO}_3$  of analytical purity (Merck, Germany) in demineralized water (18 M $\Omega$ ). Standard solutions for making a calibration diagram (0.5, 1.0, 1.5, 3.0, 4.0, 5.5 and 7.0 mg N/L), as well as synthetic solutions for

nitrate sorption (2, 5, 10, 30, 50 and 100 mg N/L), were prepared by further diluting the initial solution to the desired concentration.

### Sorbent Preparation

Modification of LVS biomass to cationic sorbent was performed according to a known chemical procedure (Marković Nikolić et al. 2018a). Washed, dried, milled and sieved (to a particle size of 0.5–1.0 mm) LVS biomass (9 g) was suspended in 5 M NaOH solution (45 mL). The suspension was stirred for 30 min at room temperature using a magnetic stirrer (150 rpm). Cationization of the biomass was performed in a reaction vessel (250 mL, three-neck round bottom flask) by gradually adding 60 wt% CHTAC reagent (45 mL). The chemical reaction was maintained for a further 14 h with a condenser at 80 °C and constant stirring (150 rpm). The resulting reaction mixture was transferred to a vessel with demineralized water (2 L). The modified cationic sorbent was converted to the chloride form by adjusting the pH of the solution to 2 (5 M HCl). The suspension was filtered and the resulting product was washed with demineralized water and dried at 60 °C to constant weight. Thus, prepared cationic modified sorbent (CMLVS) was used in all further nitrate sorption experiments.

### Sorbent Characterization

Elemental analysis (CHN/O), structural (FTIR) and morphological (SEM–EDX) characterization of the LVS biomass and CMLVS sorbent are described in our previous publications dealing with the study of phosphate sorption (Marković Nikolić et al. 2018a, 2019). The LVS biomass is a typical representative of the lignocellulosic material which in terms of textural surface characteristics is characterized by low porosity and low specific surface area (about 1 m<sup>2</sup>/g), determined by the BET method in previous studies (Mitić-Stojanović 2011). The analysis showed that nitrogen saturation is achieved at relatively low gas pressure values. The sorbed gas volume in equilibrium (0.28 cm<sup>3</sup>/g) indicated a low specific surface area of the material, without pronounced porosity. The surface of the shell is characterized mainly by micropores (1.048 m<sup>2</sup>/g) of small volume (4.96 × 10<sup>-4</sup> cm<sup>3</sup>/g), while the remaining specific surface is represented by macropores and surface elements of much larger dimensions than standard pores (cavities and channels). These results are very similar to the porosity and specific surface area (1.075 m<sup>2</sup>/g) of the prepared CMLVS sorbent, which shows that the biomass treatment did not affect the textural properties of the sorbent surface (Marković Nikolić et al. 2018a). Additionally, the CMLVS sorbent is characterized by a p*H*<sub>PZC</sub> of 7.04 and a high content of added quaternary ammonium groups (1.39 mmol N/g), which represent active centers (NR<sub>4</sub><sup>+</sup>Cl<sup>-</sup>) on the sorbent surface and

are responsible for the sorption of nitrate anions through ion exchange (Marković Nikolić et al. 2018a).

### Batch Sorption

Sorption experiments were conducted in batch mode by adding 100 mg of sorbent in 50 mL of nitrate solution of different concentrations, under selected conditions. A series of experiments was performed by varying: sorbent dose (0.5–6.0 g/L), nitrate solution concentration (2–100 mg/L), temperature (20–60 °C), solution pH (2–10), mixing speed (50–500 rpm) and contact time (0–60 min). After the given time intervals, 2 mL aliquot was taken and filtered through a 0.45 μm microfiltration membrane. Then, 1 mL of HCl (1 M) was added to each aliquot before measuring the absorbance on a UV–VIS spectrophotometer (Cary-100 Conc., Varian). Nitrate concentration (expressed as N–NO<sub>3</sub>) was determined from a calibration diagram ( $A = 0.014 + 0.237 C$ ,  $R^2 = 0.999$ ) at 220 nm, according to standard 4500-NO<sub>3</sub> methods (American Public Health Association—APHA 2000). Since some soluble organic substances can affect the absorbance value (Narayana and Sunil 2009), measurements were performed at two wavelengths (220 and 275 nm) to correct the nitrate content. The amount of sorbed nitrates (mg N/g) was calculated from the following equation:

$$Q = (C_0 - C_t) \times V/m, \quad (1)$$

where  $C_0$  is the initial nitrate concentration (mg/L),  $C_t$  is the nitrate concentration in time  $t$  (mg/L),  $V$  is the sorbate volume (L), and  $m$  is the sorbent mass (g).

### Desorption Experiment

The desorption experiment was adapted according to a known procedure applied to the quaternized agricultural sorbents (Xu et al. 2010). Desorption test of the sorbed nitrate was studied in a batch system (20 ± 0.2 °C, 150 rpm, 60 min). The nitrate-loaded CMLVS sorbent (from the initial nitrate solution of 50 mg/L at 20 ± 0.2 °C) was shaken in 0.1 M HCl solution (50 mL) during 90 min. Thereafter, the sorbent was filtered and washed with demineralized water. The regenerated CMLVS sorbent was reused in the subsequent sorption experiments. The sorption and regeneration cycles were repeated five times. To calculate the percentage recovery values (%RV = 100  $Q_{\text{DESORBED}}/Q_{\text{SORBED}}$ ), a comparison of the obtained values with those observed in the initial sorption step was used.

### Mathematical Analysis of Results and Statistics

All nitrate sorption experiments were performed in triplicate to define mean and statistical parameters. Statistical analysis of the experimental results is expressed through

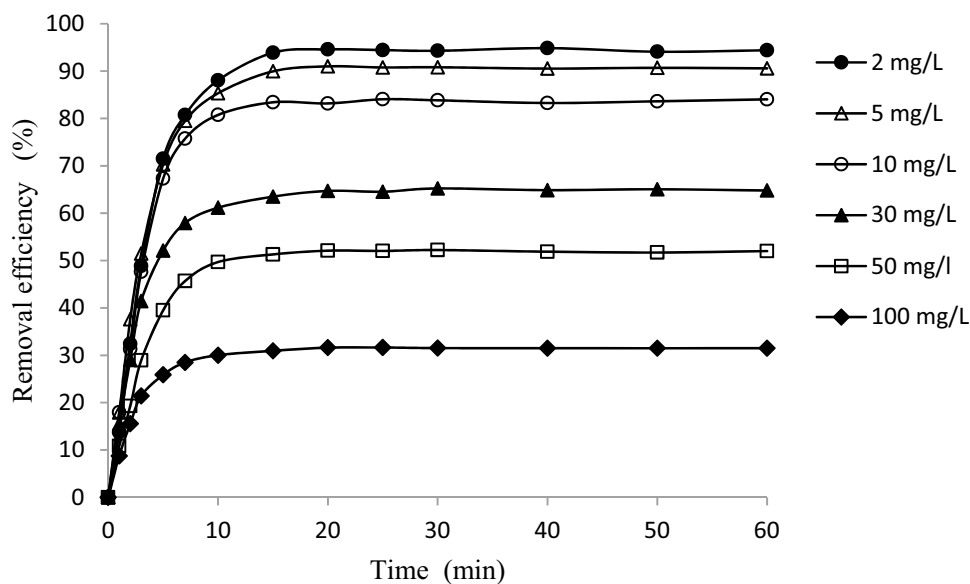
the parameters: sum of the squares of the errors (SSE), relative standard deviation (RSD, %), and average relative error (ARE, %). Characteristic parameters of the applied kinetic models and sorption isotherms were estimated by non-linear (Levenberg–Marquardt method) regression analysis using OriginPro 9.0 software (OriginLab Corporation, USA), as described in the literature (Marković Nikolić et al. 2018b, 2019). The significance level was 0.05. The best match of the applications was verified using the lowest Chi-square distribution ( $\chi^2$ ) and highest coefficient of determination ( $R^2$ ).

## Results and Discussion

### Effect of Initial Nitrate Concentration

The effect of initial nitrate concentration on the sorption capacity of CMLVS sorbent was monitored in the range of concentrations 2–100 mg/L, at pH  $6.5 \pm 0.1$ , sorbent dose 2 g/L, speed 150 rpm, at temperature  $20 \pm 0.2$  °C for 60 min. The nitrate removal efficiency is presented in Fig. 1. It can be seen from the plot that all dependency curves have the same shape. As the initial concentration of the solution increases, the sorbed amount of nitrate per unit mass of sorbent increases, which can be explained by the higher driving force of mass transfer. The removal of nitrate from the solution takes place very quickly during the first 10 min, and then more slowly up to 30 min, when the system enters equilibrium. The slower phase of nitrate removal is conditioned by the decrease in the driving force of mass transfer over time (Bhatnagar and Sillanpa 2011).

**Fig. 1** Effect of initial nitrate concentration on nitrate removal efficiency using CMLVS sorbent

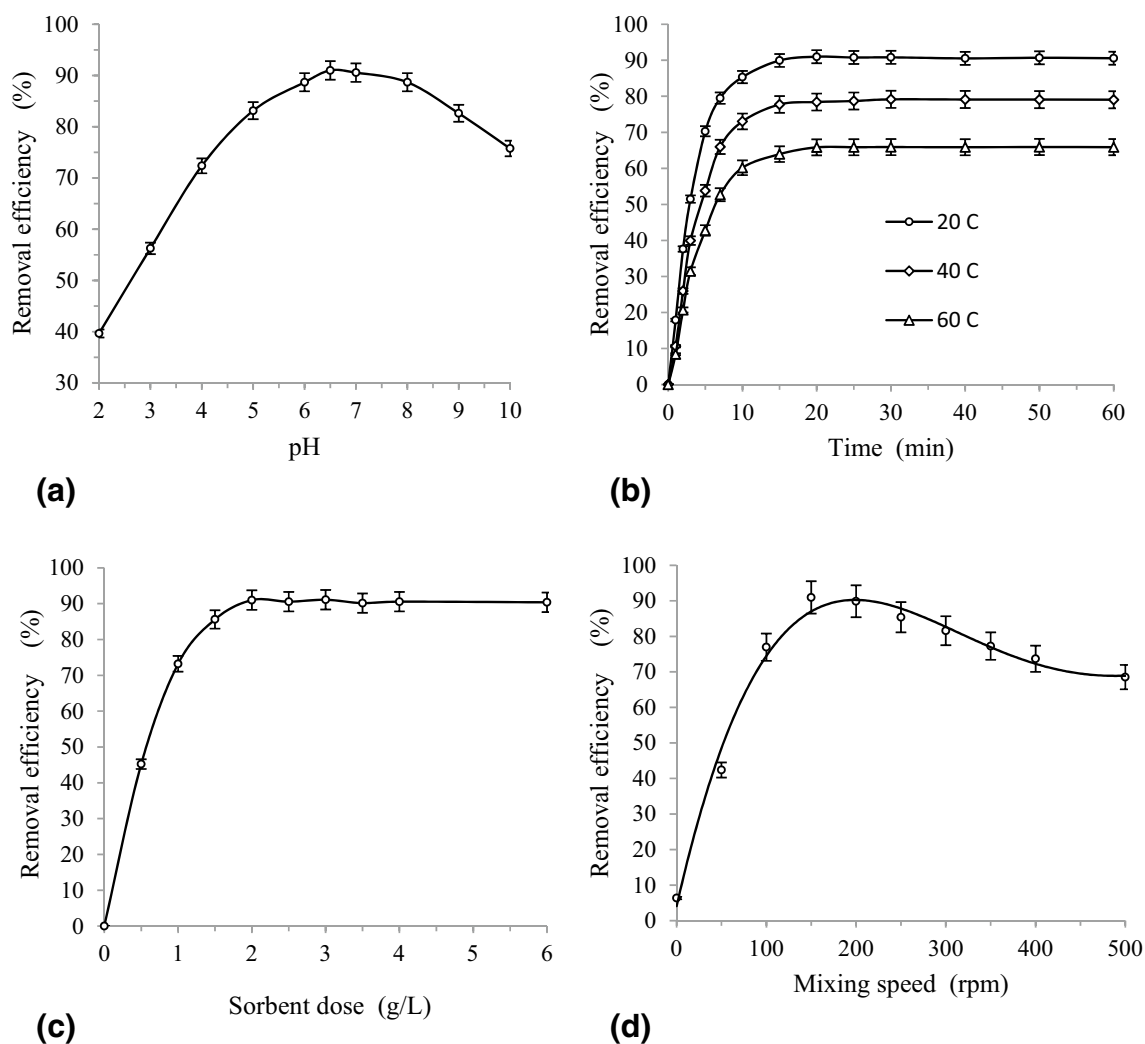


### Effect of pH Value

An important parameter that controls nitrate sorption is the pH value of the solution (Loganathan et al. 2013). The effect of pH value on nitrate sorption by CMLVS sorbent was monitored in the range from 2.0 to 10.0. The nitrate removal efficiency at different pH values is shown in Fig. 2a. As can be seen from the plot, with an increase in pH from 2 to 4, almost twice the efficiency of nitrate removal is achieved (from 39.6% to 72.4%). With a further increase in pH, the removal efficiency increases and reaches its maximum of 91% at pH 6.5. Contrary to expectations, since the surface of the sorbent at pH < 5 is positively charged, the lower nitrate removal efficiency can be explained by the presence of competing  $\text{Cl}^-$  ions (added via HCl to reduce the pH value) (Loganathan et al. 2013). On the other hand, at pH > 8, the number of negatively charged centres on the sorbent surface increases. This leads to electrostatic repulsion, as a result of which the nitrate removal efficiency is lower. Also, with increasing pH, the number of competing  $\text{OH}^-$  ions that interfere with nitrate sorption significantly increases (Marković Nikolić et al. 2018a). Given that the nitrate removal efficiency does not change significantly when the pH of the solution is between 6 and 7, this pH range can be accepted as optimal for nitrate sorption on the CMLVS sorbent.

### Effect of Temperature

Nitrate sorption by CMLVS sorbent was monitored at three temperatures (20, 40 and 60 °C), at pH  $6.5 \pm 0.1$ , for a sorbent dose of 2 g/L and an initial nitrate concentration of 5 mg/L. The effect of temperature on the nitrate removal efficiency is shown in Fig. 2b. The plot shows that during the first 10–15 min, nitrate is rapidly removed from the solution



**Fig. 2** Effect of pH (a), temperature and contact time (b), sorbent dose (c) and mixing speed (d) on the nitrate removal efficiency by CMLVS sorbent

at all temperatures. After this period, the sorption process slows down until a state of equilibrium is reached. With an increase in temperature from 20 to 40 °C, the efficiency of nitrate removal from the solution decreases from 90.8% (2.27 mg/g) to 79.2% (1.98 mg/g). With a further increase in temperature to 60 °C, the removal efficiency decreases to 65.9% (1.65 mg/g). The negative effect of temperature increase on nitrate removal efficiency can be explained by forced desorption of anions from the sorbent surface (Loganathan et al. 2013).

### Sorbent Dose Effect

The sorbent dose is an important parameter because it determines the capacity of the sorbent as an anion exchanger for a given initial nitrate concentration, under the applied conditions. The effect of sorbent dose on nitrate sorption

was investigated in the range of 0.5 to 6.0 g/L, for an initial anion concentration of 5 mg/L, at pH  $6.5 \pm 0.1$ , temperature  $20 \pm 0.2$  °C and a stirring speed of 150 rpm. The obtained results are presented in Fig. 2c. For the minimum sorbent dose (0.5 g/L), the nitrate removal efficiency was 45.2% (1.13 mg/g). With increasing the dose of sorbent to 2 g/L, the removal efficiency reaches a maximum of 91% (2.28 mg/g). It is obvious that a higher dose of sorbent enables a larger total available surface area, as well as a positive charge, so the electrostatic interaction of the sorbent with nitrates is also higher. However, with a further increase in the sorbent dose above 2 g/L, there is no tendency to increase the removal efficiency. This phenomenon can be explained by the effect of the initial concentration gradient between the solid phase and the solution. For a given volume of solution and amount of sorbent, the initial concentration gradient increases with increasing solution concentration.

Decreasing the amount of added sorbent affects the concentration gradient, analogous to increasing the concentration of the solution (Kumara et al. 2007). Also, with an increase in the amount of sorbent in the same volume of solution, agglomeration of particles can occur, and thus a decrease in the surface area of the sorbent, i.e. reducing the number of active nitrate-binding centers. Thus, increasing the sorbent dose leads to a scattering of the concentration gradient between the sorbent and the solution. This directly affects the reduction of the amount of sorbed anions per unit mass of sorbent. Based on the obtained results, the dose sorbent of 2 g/L was selected as optimal for further experiments of the sorption process.

### Effect of Mixing Speed

The effect of mixing speed on the efficiency of nitrate removal from aqueous solution using CMLVS sorbent was investigated in the range of magnetic stirrer speed from 50 to 500 rpm, at initial nitrate concentration of 5 mg/L, sorbent dose 2 g/L, pH value  $6.5 \pm 0.1$ , contact time 30 min and temperature  $20 \pm 0.2$  °C. The obtained results of testing the influence of mixing speed are shown in Fig. 2d. In the system without mixing, the efficiency of nitrate removal is very low (6.3%) because there is precipitation and grouping of sorbent particles, which reduces its available surface. Also, there is a partial separation of particles on the surface of the solution, which causes uneven contact of the sorbent with the sorbate. Therefore, the efficiency of nitrate removal is lower. However, with an increase in the mixing speed (up to 150 rpm), an even suspension of all present particles is ensured, without a vortex effect, which leads to a sharp increase in nitrate sorption and a maximum sorption efficiency of 90.95% is achieved. Increasing the mixing speed above 200 rpm leads to the appearance of vortices and a certain number of sorbent particles lose contact with the solution. This directly affects the gradual reduction of the efficiency of nitrate removal from the aqueous solution. Since the mixing speed of 150 rpm proved to be optimal, it was used in all subsequent experiments.

### Reaction Kinetic Models

Kinetic models of pseudo-first, pseudo-second and  $n$ th order were used to describe the nitrate sorption process on CMLVS sorbent. Graphical presentations of the experimental data agreement with the mentioned models are shown in Fig. 3. Typical kinetic and statistical parameters determined by non-linear regression analysis are shown in Table 1.

Analysis of the obtained experimental data for the kinetic model of the pseudo-first order (Table 1) showed that the determination coefficients ( $R^2$ ) have high values (0.993–0.998) in the entire range of the examined initial

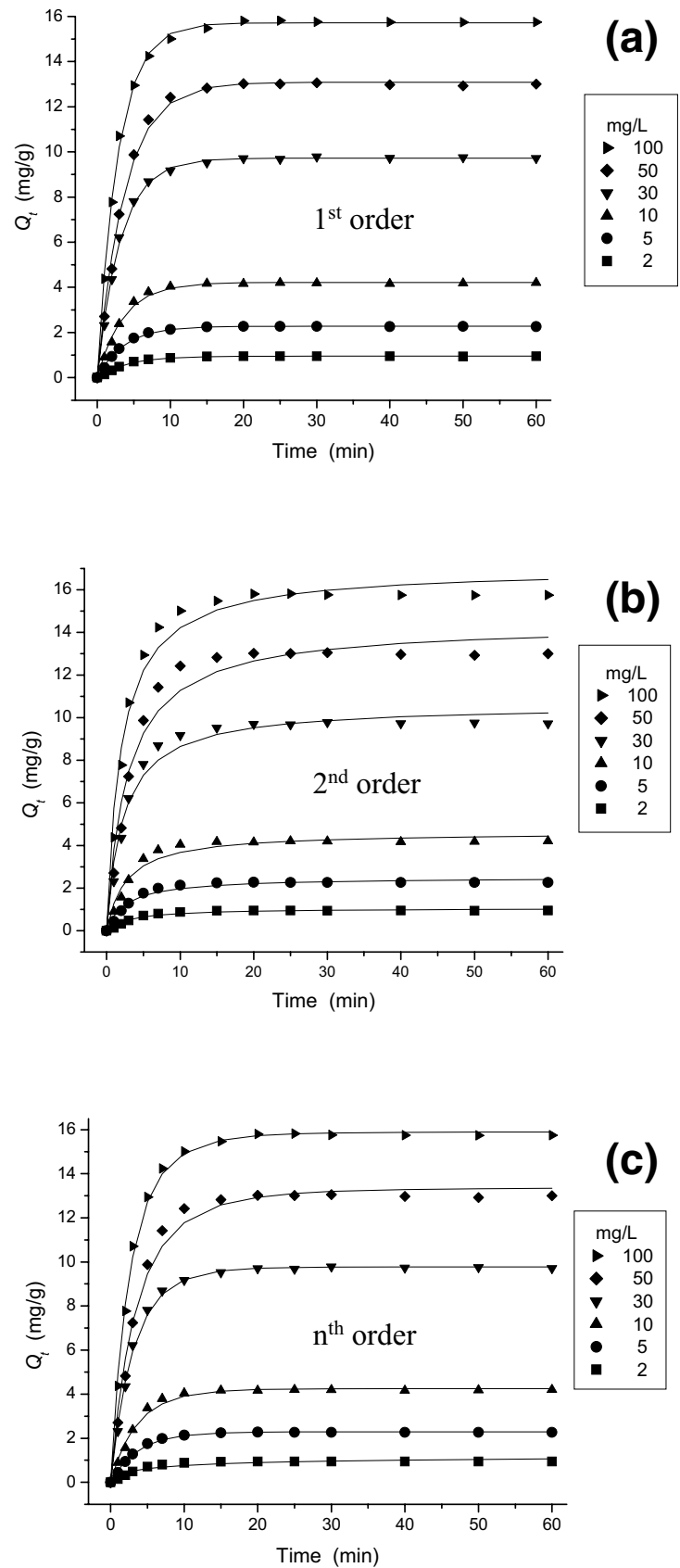
nitrate concentration. The calculated values of the sorption capacity ( $Q_{e \text{ calc.}}$ ) are relatively close to the obtained experimental values, with an acceptable relative deviation in the range of 0.19–1.06%. However,  $R^2$  for the non-linear kinetic model of the pseudo-second order was significantly less favorable (0.964–0.981) compared to the model of the pseudo-first order. Accordingly, the calculated values of sorption capacity were slightly higher than the experimentally obtained values in the whole range of the initial nitrate concentration, with a significant relative deviation from 8.02% to 12.30%. Based on these facts, it can be concluded that the kinetics of nitrate sorption on CMLVS sorbent is better described by a non-linear pseudo-first order model, which is in accordance with the literature data (Wang et al. 2007). This is supported by the fact that the Lagergren model in real systems corresponds mainly to physisorption from a solution of sorbates lower concentrations, while Ho's model is based on the assumption that the process follows the mechanism of hemisorption (Wang et al. 2007).

In addition to the mentioned kinetic models, a pseudo  $n$ th-order model was used to describe the nitrate sorption process on the CMLVS sorbent. Typical kinetic ( $n$ ,  $k_n$  and  $Q_e$ ) and statistical ( $R^2$ ,  $\chi^2$  and SSE) parameters for the non-linear kinetic model of the pseudo  $n$ th order are given in Table 1. The values of correlation (0.996–0.999) and determination coefficients (0.993–0.998), in the whole range of tested initial nitrate concentrations (2–100 mg/L), indicate that the applied kinetic model of the  $n$ th order agrees very well with the experimental data. This is confirmed by other statistical parameters. The Chi-square distribution values ( $\chi^2$ ) range from 0.0008 to 0.06 in the whole examined range of the initial nitrate concentration. Very small SSE values (0.009–0.6) are correlated with the relative deviation of the calculated values of equilibrium sorption capacity (0.10–0.78%). The values of the kinetic parameter  $n$  are very close to unity (0.966–1.065), which indicates that nitrate sorption most likely behaves according to the pseudo-first order model. The rate constants  $k_n$  (0.247–0.309) are very close to the constants  $k_1$  (0.243–0.349), in contrast to the constants  $k_2$  (0.317–0.508) which show a significant deviation. By comparing the data obtained by non-linear regression for all three examined models with experimental results (Fig. 3), a very good agreement of data for pseudo-first and pseudo  $n$ th order is observed.

### Diffusion Kinetic Models

To investigate the mechanism and kinetics of nitrate sorption on CMLVS sorbent from a solution of initial concentrations of 2–100 mg/L, at optimal process parameters ( $m_s = 2$  g/L; pH  $6.5 \pm 0.1$ ;  $T = 20 \pm 0.2$  °C;  $t = 60$  min; 150 rpm), the Weber–Morris model was used. Stacking of the experimental data with the intraparticle diffusion model for a given

**Fig. 3** Pseudo-first order kinetics (a), pseudo-second order kinetics (b) and kinetics of  $n$ th order (c) for nitrate sorption on CMLVS sorbent





**Table 1** Kinetic and statistical parameters of non-linear regression of pseudo-first, pseudo-second and *n*th-order models for nitrate sorption using CMLVS sorbent

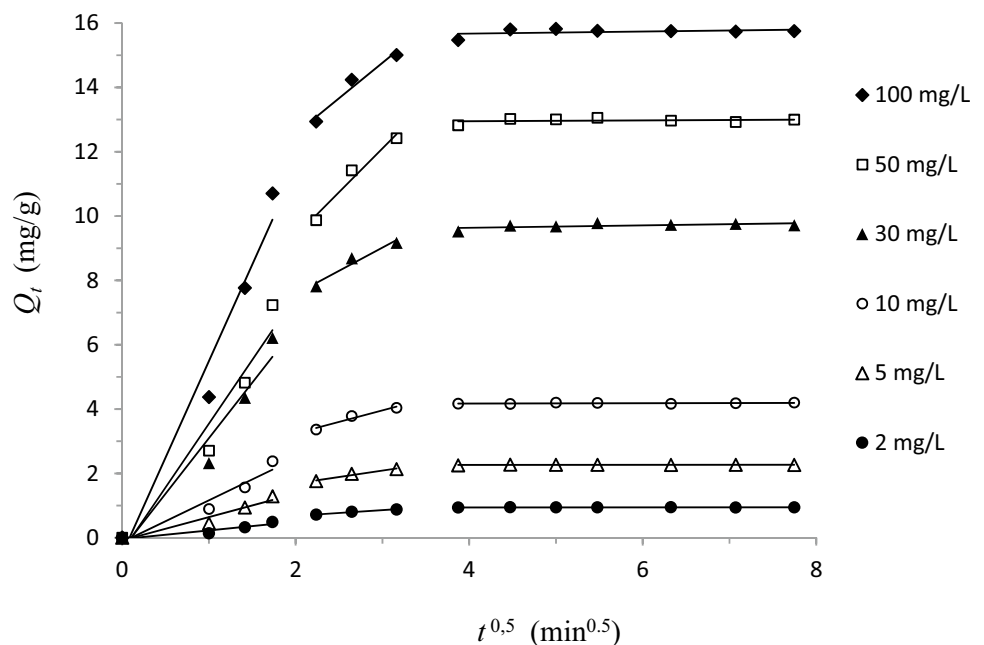
Models	Parameters	Initial nitrate concentration (mg/L)					
		2	5	10	30	50	100
	$Q_{e \text{ exp.}}$ (mg/g)	0.94	2.27	4.19	9.78	13.06	15.76
Pseudo-first order	$Q_{e \text{ calc.}}$ (mg/g)	0.95	2.28	4.22	9.72	13.08	15.71
	RSD (%)	1.06	0.31	0.67	0.67	0.19	0.29
	$k_1$ (min <sup>-1</sup> )	0.244	0.277	0.281	0.314	0.266	0.349
	$\chi^2$	0.001	0.001	0.012	0.021	0.064	0.038
	$R^2$	0.993	0.998	0.994	0.998	0.997	0.998
Pseudo-second order	$Q_{e \text{ calc.}}$ (mg/g)	1.06	2.50	4.64	10.60	14.42	17.02
	RSD (%)	12.31	10.26	10.59	8.38	10.42	8.02
	$k_2$ (g/mg/min)	0.317	0.377	0.383	0.442	0.360	0.508
	$\chi^2$	0.004	0.016	0.080	0.242	0.635	0.519
	$R^2$	0.964	0.974	0.964	0.978	0.970	0.981
	SSE	0.051	0.201	0.961	2.910	7.629	6.229
<i>n</i> th order	$Q_{e \text{ calc.}}$ (mg/g)	0.95	2.27	4.23	9.74	13.07	15.73
	RSD (%)	0.32	0.26	0.79	0.46	0.11	0.16
	<i>n</i>	0.97	0.97	0.98	1.06	0.96	1.04
	$k_n$ (g <sup>n-1</sup> mg <sup>1-n</sup> /min)	0.247	0.272	0.276	0.266	0.285	0.309
	$\chi^2$	0.001	0.002	0.014	0.038	0.056	0.046
	$R^2$	0.993	0.998	0.994	0.997	0.998	0.998
	SSE	0.009	0.018	0.151	0.418	0.624	0.515

range of the tested nitrate concentrations is presented in Fig. 4. The values of characteristic kinetic ( $k_{id}$  and  $C_{id}$ ) and statistical parameters of the intraparticle diffusion model, determined by multi-linear regression analysis for the range of tested nitrate concentrations, are presented in Table 2.

The Weber–Morris diffusion model shows characteristic multi-linearity (Fig. 4), since nitrate sorption takes place

in three stages. Each stage is characterized by the different slopes, which indicates different rates of the sorption process over time. The sorption rate of each stage increases proportionally with the increase of the initial nitrate concentration, due to the higher driving force of the process. In the whole range of tested initial concentrations, the first sorption period is very fast and ends after 5 min. This phase is characterized

**Fig. 4** Intraparticle diffusion model for nitrate sorption on CMLVS sorbent



**Table 2** Kinetic and statistical parameters of the intraparticle diffusion model for nitrate sorption using CMLVS sorbent

Parameters		Values					
$C_0$ (mg/L)		2	5	10	30	50	100
$Q_e$ exp. (mg/g)		0.94	2.27	4.19	9.78	13.06	15.76
$Q_e$ calc. (mg/g)		0.94	2.25	4.15	9.49	12.89	15.54
ARE (%)		0.21	0.57	0.95	3.05	1.26	1.39
Stady I (to 5 min)	$k_{id}$	0.268	0.724	1.300	3.455	3.968	6.003
	$C_{id}$	-0.040	-0.082	-0.137	-0.360	-0.421	-0.511
	$R^2$	0.896	0.939	0.941	0.948	0.942	0.964
Stady II (to 15 min)	$k_{id}$	0.177	0.400	0.715	1.443	2.718	2.201
	$C_{id}$	0.326	0.885	1.810	4.690	3.950	8.158
	$R^2$	0.982	0.962	0.955	0.947	0.963	0.955
Stady III (after 15 min)	$k_{id}$	0.000	0.001	0.005	0.037	0.012	0.032
	$C_{id}$	0.941	2.258	4.152	9.485	12.890	15.540
	$R^2$	0.039	0.040	0.157	0.390	0.056	0.151

by the transport of anions through a negligible boundary diffusion layer (with respect to mixing 150 rpm) to the external surface of the sorbent, on which the primary sorption process takes place. The second stage of the process (5–15 min) is diffusion in the particles, with the corresponding linear dependences having a smaller slope (lower  $k_{id}$  values), suggesting a decrease in the overall process rate (Table 2). As the initial nitrate concentration increases, the  $k_{id}$  values increase and range from 0.177 to 2.718 mg/g/min<sup>0.5</sup>. The determination coefficients of the second stage are more favorable compared to the first stage. The sorption process is characterized by the third-slowest stage, after a period of 15 min, which represents the depletion of the anion from the solution and the state of equilibrium (saturation of the active centers on the sorbent). This stage is characterized by very small rate constants, with a very wide range of unfavorable coefficients of determination (0.039–0.390), with a dominant boundary layer thickness effect (0.941–15.540 mg/g) in limiting the process rate. Considering the fact that fitting data according to the Weber–Morris model cannot be represented by a linear line passing through the coordinate origin, it can be concluded that intraparticle diffusion is not the only mechanism that controls the process rate (Marković Nikolić et al. 2018b). The process of nitrate sorption on CMLVS sorbent is probably of a complex nature and is based on both surface sorption and diffusion in the sorbent particles (Nethaji and Rahman 2011).

A corresponding graphical presentation of the experimental data agreement according to the Chrastil's diffusion model, for the examined range of initial nitrate concentrations (2–100 mg/L), at optimal process parameters ( $m_S = 2$  g/L; pH  $6.5 \pm 0.1$ ;  $T = 20 \pm 0.2$  °C;  $t = 60$  min; 150 rpm), is shown in Fig. 5.

The characteristic kinetic parameters of the Chrastil's model, determined by non-linear regression analysis, are shown in Table 3. High values of the determination

coefficients (0.998–0.999) and small values of relative deviation (0.12–1.03%) indicate a very good agreement of the experimental with the calculated sorption capacity according to Chrastil's diffusion model. The values of the heterogeneous structural diffusion resistance constant (parameter  $n$ ) are relatively high and range from 1.048 to 1.532. It should be borne in mind that the parameter  $n$  also shows the characteristic of the reaction order. Thus, when the diffusion resistance is small, the value of  $n$  is approaching 1 and the reaction is then of the first order. Conversely, when the diffusion resistance is higher, then the parameter  $n$  will be in the range of 0.5 to 0.6. In the case when  $n > 1$ , a consecutive reaction can be expected (Carrillo et al. 2005). Taking into account that in these studies all obtained values of  $n > 1$  for the entire range of concentrations, a consecutive reaction of nitrate sorption on the CMLVS sorbent can be assumed.

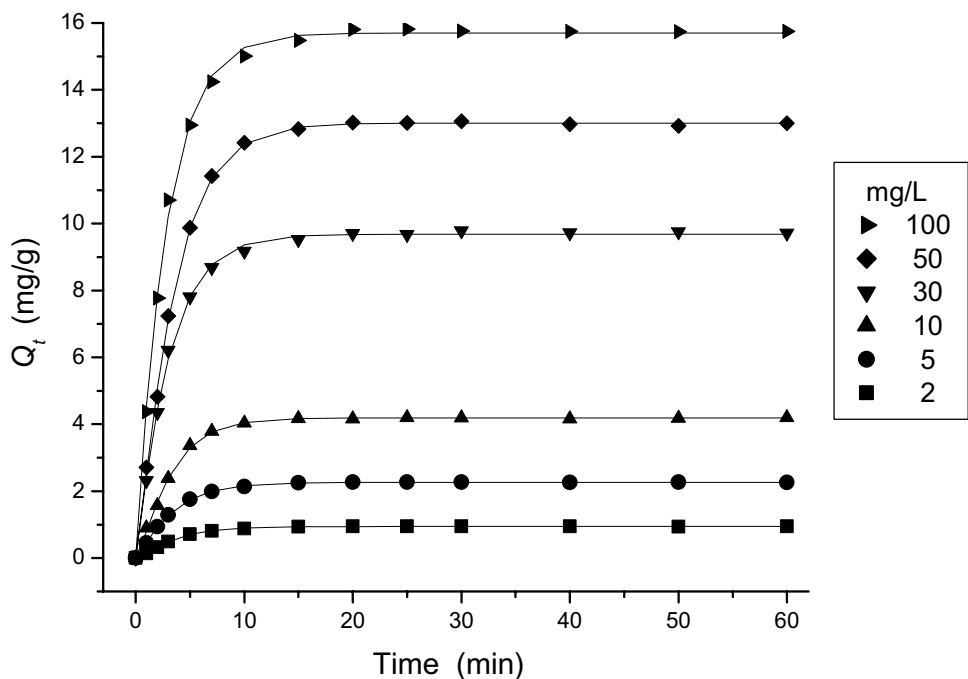
### Equilibrium Studies of the Nitrate Sorption

To describe the sorption equilibrium in the liquid–solid system, the experimentally obtained equilibrium data were fitted with typical models of sorption isotherms (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and Sips isotherms). Graphical presentations of the agreement of equilibrium experimental data with sorption isotherms are shown in Fig. 6. All isothermal parameters of these models were obtained by applying non-linear regression, using Origin Pro 9.0 software (Table 4).

### Langmuir Isotherm

Based on the non-linear regression of equilibrium data (Fig. 6), the values of maximum sorption capacity and Langmuir constant, as well as the corresponding statistical data (Table 4), it can be concluded that Langmuir model is suitable for describing nitrate sorption on CMLVS sorbent

**Fig. 5** Chrastil’s diffusion model for nitrate sorption on CMLVS sorbent



**Table 3** Kinetic and statistical parameters of the Chrastil’s diffusion model for nitrate sorption using CMLVS sorbent

Parameters	Initial nitrate concentration (mg/L)					
	2	5	10	30	50	100
$Q_{e \text{ exp.}}$ (mg/g)	0.94	2.27	4.19	9.78	13.06	15.76
$Q_{e \text{ calc.}}$ (mg/g)	0.94	2.27	4.19	9.68	13.00	15.70
$K_c$ (L/g/min)	0.174	0.167	0.189	0.179	0.165	0.182
$n$	1.532	1.249	1.442	1.161	1.295	1.048
ARE (%)	0	0.26	0.12	1.03	0.42	0.40
$\chi^2$	0.0001	0.0002	0.003	0.014	0.012	0.039
$R^2$	0.999	0.999	0.998	0.998	0.999	0.998
SSE	0.0007	0.002	0.029	0.158	0.132	0.432

compared to other applied models. The relatively large values of the determination coefficient, as well as the small values of  $\chi^2$  and SSE, confirm that Langmuir model agrees well with the equilibrium data. The maximum sorption capacity of the sorbent calculated using the Langmuir model (16.53 mg/g) shows a relative deviation of 4.9% compared to the experimentally obtained value (15.76 mg/g). Characteristically, the average relative errors are higher for lower initial nitrate concentrations (< 10 mg/L). The value of Langmuir sorption equilibrium constant ( $K_L = 0.169$  L/mg) indicates a high affinity of nitrate ions for CMLVS sorbent. Also, the shape of the isotherm  $R_L = f(C_0)$  confirms the spontaneity of the nitrate sorption process (Marković Nikolić et al. 2018a). The calculated values of the Langmuir dimensionless separation factor (0.056–0.747) in the range  $0 < R_L < 1$  confirm the spontaneity of the sorption process, where the spontaneity increases with the increase of initial nitrate concentration in the examined range (2–100 mg/L). Based on Langmuir

model, it can be concluded that nitrate sorption takes place in the monomolecular layer, on the energy uniform surface of CMLVS sorbent with a finite number of active binding centers, without mutual interaction and trans-migration of ions on the sorbent surface (Marković Nikolić et al. 2018a).

**Sips Isotherm**

Based on the sorption isotherms (Fig. 6) and characteristic parameters obtained by non-linear regression of equilibrium data (Table 4), it can be seen that the Sips model is the most suitable for describing nitrate sorption on the CMLVS sorbent. Good agreement with the equilibrium data is confirmed by the determination coefficient ( $R^2 = 0.999$ ) and small values of statistical parameters  $\chi^2$  (0.053) and SSE (0.159). Based on the equilibrium sorption constant ( $K_S = 3.958$  L/g), the constant proportional to the sorption energy ( $(\alpha_s = 0.191$  L/mg) and the exponential

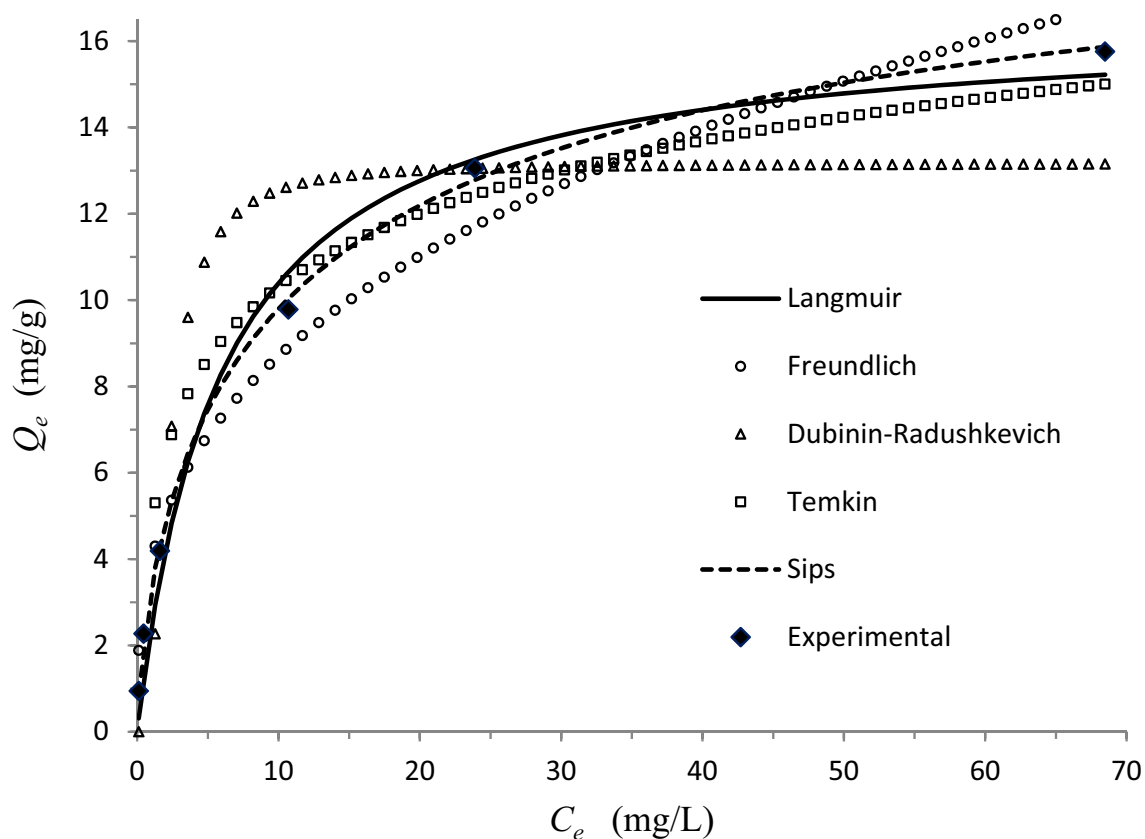


Fig. 6 Sorption isotherms by non-linear regression for the nitrate sorption on CMLVS sorbent

Table 4 Non-linear regression coefficients of sorption isotherms and corresponding statistical data

Isotherms	Constants	Statistical parameters			
		$R^2$	$\chi^2$	SSE	
Langmuir	$Q_{max}$ (mg/g)	16.532	0.983	0.764	3.056
	$K_L$ (L/mg)	0.169			
Freundlich	$K_F$ (mg/g) (mg/L) <sup>1/n</sup>	3.957	0.971	1.332	5.330
	1/n	0.341			
Dubinin-Radushkevich	$n_F$	2.932	0.887	5.201	20.807
	$Q_{DR}$ (mg/g)	13.165			
	$K_{DR}$ (mol <sup>2</sup> /kJ <sup>2</sup> )	$8.5 \times 10^{-7}$			
Temkin	$E$ (J/mol)	769.23	0.963	1.702	6.811
	$K_T$	6.950			
	$b_T$ (J/mol/K)	1018.84			
Sips	1/ $b_T$	$9.8 \times 10^{-4}$	0.999	0.053	0.159
	$K_S$ (L/g)	3.958			
	$\beta_S$	0.672			
	$\alpha_S$ (L/mg)	0.191			

factor ( $\beta_S = 0.672$ ), the equilibrium sorption capacity of the sorbent for nitrates of 15.869 mg/g was calculated, with a satisfactory average relative error of 0.7%.

### Freundlich Isotherm

The statistical parameters of the Freundlich model obtained by non-linear regression of equilibrium data (Table 4) indicate that the agreement of the applied isotherm with the experimental results is not satisfactory. Since the value of the Freundlich parameter  $n_F$  is greater than 1, it can only be assumed that it is a favored sorption of nitrate on the CMLVS sorbent.

### Dubinin-Radushkevich Isotherm

Based on the values of mean free sorption energy according to this model ( $E = 0.769$  kJ/mol), it can be assumed that physisorption has a large share in the nitrate-binding mechanism. However, the theoretical monolayer saturation capacity ( $Q_{DR} = 13.165$  mg/g) is significantly below the equilibrium sorption capacity of the sorbent (15.759 mg/g), with a relative deviation of 16.5% (Table 4). This fact, the relatively low value of the  $R^2$  coefficient, as well as the high values of statistical parameters, indicate that the Dubinin-Radushkevich model is not suitable for describing the equilibrium sorption of nitrate on the sorbent.

### Temkin Isotherm

The value of the Temkin constant  $b_T$  (1.018 kJ/mol/K) indicates a pronounced ionic interaction between nitrates and quaternary  $-R_3N^+$  sorbent groups, i.e. the dominance of ion exchange as a binding mechanism. However, the relatively lower value of the determination coefficient ( $R^2 = 0.963$ ), unfavorable statistical values ( $\chi^2 = 1.7$  and  $SSE = 6.8\%$ ), as well as a large relative deviation (especially at low initial nitrate concentrations), indicate a discrepancy between the calculated and experimentally obtained sorption capacity (ARE of 6.4%), which is why this model cannot be fully accepted (Table 4).

### Thermodynamics of Nitrate Sorption

To determine the thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ), nitrate sorption experiments on CMLVS sorbent were performed at different temperatures (20, 40, 60 °C), under previously determined optimal conditions: initial nitrate concentration 5 mg/L, sorbent dose 2.0 g/L, pH  $6.5 \pm 0.1$ ,

contact time 60 min and mixing speed 150 rpm. The values of the characteristic thermodynamic parameters were determined from the dependence  $\ln(K_e) = f(1/T)$  (Table 5). Equilibrium  $K_e$  constants at certain temperatures were calculated on the basis of equilibrium values of nitrate concentrations on the sorbent surface and in solution ( $C_s/C_e$ ). The characteristic thermodynamic parameters ( $K_e$ ,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) as well as the corresponding determination coefficients ( $R^2$ ), are presented in Table 5. Based on negative  $\Delta G$  values in the range from  $-20$  to  $0$  kJ/mol at the tested temperatures, it can be concluded that nitrate sorption under these conditions is a spontaneous process. However, the increase in temperature affects the increase of the  $\Delta G$  value, which indicates that the spontaneity of the process decreases. The negative value of the enthalpy change, which refers to the establishment of different interactions between the sorbent and the sorbate, indicates the exothermic process of nitrate sorption. Considering that the value of  $\Delta H$  indicates the nature of the bond between sorbent and sorbate, based on the enthalpy change of  $-33.173$  kJ/mol, it can be concluded that nitrate sorption on CMLVS sorbent takes place by the mechanism of ion exchange, which is characterized by the value of  $\Delta H$  in the range of  $20$ – $80$  kJ/mol (Marković Nikolić et al. 2018b). It is characteristic that with increasing temperature from  $20$  to  $60$  °C, the value of the equilibrium constant  $K_e$  decreases (in the range  $9.893$ – $1.934$ ), which suggests that nitrate-binding is simultaneously accompanied by the appearance of desorption from the sorbent surface at higher temperatures. The negative value of the change in entropy ( $-94.364$  J/mol/K) indicates that there is a decrease in the disorder on the contact surface of the phases, due to the loss of translational degrees of freedom on the sorbent surface, which is in accordance with the ion exchange mechanism (Marković Nikolić et al. 2018b).

### Cost Analysis of Sorbent Preparation

The cost of sorbent production is an important factor that must be considered in order for a water treatment process to be cost-effective for its practical application (Singh and Srivastava, 2020). The total cost of sorbent production is affected by several steps, such as its availability (waste collection), processing requirements, treatment conditions, and reuse (Gupta et al. 2009). The basic technological operations that contribute to the total cost in this study are: grinding,

**Table 5** Thermodynamic parameters for the nitrate sorption on CMLVS sorbent at different temperatures

Temperatures (K)	$K_e$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)	$R^2$
$\ln(K_e) = f(1/T)$		$y = 3990.x - 11.35$			0.996
293	9.893	$-5.583$	$-33.173$	$-94.364$	0.996
313	3.798	$-3.251$			
333	1.934	$-1.607$			

sieving, rinsing, drying, activation, cationization, stirring, heating and neutralization. The cost for each step and the total cost for the preparation of 1 kg sorbent were calculated stepwise to gain insight into the approximate costs included in this study. The individual costs for processing raw material are estimated as follows: 1.0 EUR for washing and rinsing with demineralized water; 0.5 EUR for grinding and sieving LVS up to particle size 0.5–1.0 mm; 0.2 EUR to activate LVS with NaOH solution; 4.0 EUR for cationization of LVS (modification by 60 wt% of CHTAC); 0.1 EUR for pH adjustment (using HCl and NaOH). The electricity cost per kWh in Serbia [power (kWh) × time (h) × per unit cost] is estimated as follows: 1.5 EUR for stirring (1 kWh × 15 h × 0.1 EUR/kWh); 4.2 EUR for heating (3 kWh × 14 h × 0.1 EUR/kWh). In addition, the bottle gourd shell (LVS) was collected from agriculture as waste lignocellulosic biomass with free of cost. The biomass was naturally dried, which is not included in the processing price. Thus, the approximate total cost for the preparation of 1 kg sorbent is estimated to be 11.5 EUR. The preparation cost of CMLVS sorbent was found to be reasonable and comparable to other quaternized adsorbents (\$7–\$25/kg) based on the CHTAC reagent (Wartelle and Marshall 2006), and possess potential for largescale application.

### Desorption Study

Given that the sorption of nitrate from the aqueous solution is not selective, the nitrate-loaded sorbent can be regenerated easily by desorption of sorbed nitrate using a solution of simple salts or reagents, such as HCl or NaOH (Loganathan et al. 2013). In this study, the nitrate desorption method with 0.1 M HCl reagent was used. The nitrate-loaded CMLVS sorbent, obtained from an initial nitrate solution of 50 mg/L, and with an experimental sorption capacity of 13.06 mg/g was tested. The sorption/desorption cycles were repeated five times. Desorption efficiency (%RV) during five successive cycles changes as follows: 99.08%, 97.99%, 95.66%, 92.71% and 87.20%. The obtained results show that this sorbent has a high regeneration capacity in acidic solution (still higher than 90% in the fourth cycle). Applied desorption tests confirmed that the HCl reagent has good nitrate desorption ability. This suggests that nitrate desorption from CMLVS is most probably an ion-exchange reaction (i.e., a reverse reaction). Thereby, Cl<sup>-</sup> ions (from HCl solution) displace nitrate ions from the sorbent (Xu et al. 2010). In addition, it was observed that the sorption capacity of CMLVS sorbent (13.06 mg/g) decreased only slightly in the fourth cycle (11.25 mg/g), suggesting that the sorbent can be repeatedly used to remove nitrate from water. However, in these desorption tests, a small weight loss of the sorbent was observed after four cycles (≈ 6%). The HCl solution

appears to cause the destruction of cellulose/hemicellulose structure in the sorbent, resulting in the decrease in the weight loss of the sorbent (Xu et al. 2011). Therefore, the sorption capacity of the CMLVS sorbent for nitrate decreases to 9.92 mg/g after the fifth cycle, indicating that the sorbent efficiency decreases by about 24% after five consecutive cycles of sorption/desorption. This phenomenon was also observed in other quaternized sorbents during desorption of various anions after treatment with HCl solution, for which weight loss of about 5% (cotton stalk), 12–18% (wheat straw) or 25% (chitosan beads) is reported (Xu et al. 2011). In general, when agricultural waste is used to obtain a sorbent, the exhausted sorbent can be disposed of on agricultural lands, where it can provide nitrate fertility and improve the physical, chemical and biological condition of the soil (Loganathan et al. 2013).

### Comparison of Sorption Capacity

The results of nitrate removal using CMLVS sorbent were compared with a control sample (LVS biomass) to present the effect of grafted CHTAC groups on nitrate removal, as well as with other cationic modified sorbents to determine the efficiency of CMLVS sorbent. In this study, it was found that LVS biomass does not show sorption properties for nitrates ( $Q_{\max} = 0.02$  mmol/g), which confirms the success of biomass modification using CHTAC and explains the significant increase in nitrate removal efficiency by the obtained CMLVS sorbent ( $Q_{\max} = 1.13$  mmol/g). The sorption capacity of CMLVS is comparable to the results of other cationic sorbents tested for nitrate removal under similar conditions (Loganathan et al. 2013). The CMLVS sorbent showed approximate sorption capacity with cationized pine sawdust ( $Q_{\max} = 1.09$  mmol/g) (Keränen et al. 2015), modified rice straw ( $Q_{\max} = 1.18$  mmol/g) and rice hull ( $Q_{\max} = 1.21$  mmol/g) (Orlando et al. 2002), or even almond shell activated carbon impregnated by zinc ( $Q_{\max} = 1.20$  mmol/g) (Rezaee et al. 2008). However, CMLVS has a lower sorption capacity than some lignocellulosic agricultural wastes grafted with various amine groups for the production of anion exchangers (Loganathan et al. 2013). Thus, the modified moringa oleifera husk, rice husk, sugarcane bagasse, and pine bark are reported to have higher adsorption capacities (4.5–5.3 mmol/g), which were approximately equal to the capacity of the commercial anion exchanger Amberlite IRA-900 (Orlando et al. 2002). It should be borne in mind that the differences values of the sorption capacity between these modified biomasses are dependent primarily on the amount of cellulose and lignin present, then from the modification reagent, as well as the applied sorption conditions (such as temperature, pH, mixing rate, sorbent dose and initial nitrate concentration).

## Conclusion

This study indicated the possibility of exploiting waste lignocellulosic biomass to cationically modified LVS as a valuable sorbent for removing nitrate from aqueous solution. The reaction kinetic of nitrate sorption on CMLVS sorbent is best described by a non-linear pseudo-first-order model, which is consistent with the pseudo  $n$ th-order model ( $n$  in the range of 0.96–1.06). This is supported by the fact that the Lagergren model in real systems corresponds mainly to physisorption from a solution of sorbates lower concentrations. Anion exchange mechanism is dominant sorption process. The diffusion models have shown that there are limiting factors, such as surface reaction and diffusion in the boundary layer, and pores of the sorbent. A comparative analysis of the sorption isotherms used to describe nitrate sorption on the CMLVS sorbent indicated the following order of agreement of the model with the experimental results: Sips  $\approx$  Langmuir  $>$  Freundlich  $>$  Temkin  $>$  Dubinin-Radushkevich. The equilibrium nitrate sorption capacity was 15.869 mg/g for the sorbent, with a satisfactory average relative error of 0.7%. Based on Langmuir model, it can be concluded that nitrate sorption takes place in the monomolecular layer, on the energy uniform surface of CMLVS sorbent with a finite number of active binding centers, without mutual interaction and trans-migration of ions on the sorbent surface. Based on thermodynamic parameters, it was estimated that the nitrate sorption process is spontaneous and exothermic in the temperature range from 20 to 60 °C. The results of desorption tests show that the CMLVS sorbent has a high regeneration capacity in HCl solution ( $>$  90%), without significant weight loss after four cycles. The studied CMLVS sorbent shows relatively good sorption efficiency of nitrates, and possibly other anionic pollutants, and can be considered a cost-effective alternative material to prevent eutrophication.

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## Compliance with Ethical Standards

**Conflict of Interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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