

# Evaluation of Adsorption Capacity of Chitosan-Cinnamaldehyde Schiff Base

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## Abstract

The aim of this study was to evaluate the adsorption capacity of the Schiff base chitosan-cinnamaldehyde for its application in dairy wastewater pre-treatment. Chemical oxygen demand (COD) reduction was used to evaluate the adsorption efficiency. The maximum COD percentage reduction of 33.5% was obtained at 40.0 C, pH 9.0, adsorbent dose 20 g L<sup>-1</sup>, contact time 240 min and agitation speed 100 rpm. Temkin isotherm fitted well the equilibrium data of COD uptake ( $R^2 = 0.987$ ), whereas the kinetic data were described by the pseudo-second order model ( $R^2=0.993$ ). Enhancement of the adsorption efficiency up to 6.4% in dependence of the initial COD concentration of the dairy wastewater was observed by adsorption with the Schiff base chitosan-cinnamaldehyde adsorbent compared to the non-modified chitosan at the same experimental conditions. The results indicated that the Schiff base chitosan-cinnamaldehyde can be used as an adsorption agent that could be applied before the biological unit in the wastewater treatment plant for the load reduction.

**Key words:** Chitosan-cinnamaldehyde, Schiff base, adsorption, wastewater, COD removal efficiency.

## INTRODUCTION

Deacetylation of chitin affords chitosan, with enormous application in food processing waste recovery [1-3], chemical [4] and pharmaceutical industries [5] and biotechnology [1]. Chitosan can be easily characterized as a promising material not only due to its physical properties and applications to many fields, but also for its adsorption potential [6].

Muzzarelli and Tubertini [7] described the synthesis and adsorption potential of chitosan for the removal of metal ions from organic and sea waters. Numerous papers have been reported regarding the use of chitosan as adsorbent for decontamination of wastewaters [6]. Researchers have attempted to prepare chitosan-based adsorbent materials modifying the molecules of chitosan due to the existence of proper positions in its chemical structure. It leads to the design of chitosan derivatives with superior properties - enhancement of adsorption capacity and resistance in extreme media conditions. Zhou et al. [8] synthesized chitosan-modified biochars for heavy metal environmental remediation and it was found that it had great advantage over many traditional adsorbents. Several workers have reported the use of cross-linking treatments (via Schiff base formation) using several chemical reagents such as glutaraldehyde and epichlorohydrin [9-11] for removal of metal ions. Other researchers synthesized chitosan-zinc oxide nanocomposite materials for application in milk processing industry wastewater [12]. As a result of the treatment with these materials, the turbidity and COD were reduced.

Dairy industry is one of the largest food industry worldwide contributes to pollution in a great extent. Dairy wastewater is distinguished by the high biological oxygen demand (BOD) and chemical oxygen demand (COD) contents, high levels of dissolved or suspended organic components like whey proteins, lactose, fats and minerals,

nutrients such as ammonia and phosphates [13]. The decomposition of these substances often cause discomfort to the surrounding population and therefore requires proper attention before disposal [14]. Dairy wastewaters coming from different sources are mixed, pH adjusted and then directed to biological unit for treatment. Higher loading of the biological unit leads to many operation difficulties. Therefore, the wastewater physicochemical pre-treatment such as coagulation, flocculation and adsorption, which might be applied before the biological treatment unit in the wastewater treatment plant reduce the load [14, 15, 16]. Some authors reported effective removal of COD and suspended solids by optimizing coagulant dosage and pH in the treatment of wastewater [17, 18]. Several workers investigated that low molecular weight crab shell chitosan [17] and rice husk [19] could be applied as effective adsorbents for removal of pollutants from dairy wastewater. There are no reports in the literature about the application of the Schiff base chitosan-cinnamaldehyde for pollution removal. Therefore, the aim of this study is to evaluate the adsorption capacity of the Schiff base chitosan-cinnamaldehyde and to investigate the possibility of its applications in dairy industries for wastewater pre-treatment.

## MATERIALS AND METHODS

### Materials

Chitosan with a molecular weight of 100 – 300 kDa and degree of deacetylation 80 % was purchased from Across Organics (Belgium). Cinnamaldehyde was obtained from Jean Niel (France). Other chemicals were of analytical grade and they were used without further purification. Synthetic wastewater was prepared from whey obtained from yellow cheese processing plant by dilution with distilled water to the usual raw dairy wastewater pollution measured by COD.

### Schiff base chitosan-cinnamaldehyde preparation

The Schiff base chitosan-cinnamaldehyde was synthesized by described method with slight modifications [20]. Chitosan was dispersed in 50 mL methanol. Then aldehyde dissolved in anhydrous ethanol (20 mL) was added dropwise to the suspension under high-intensity ultrasound at 30–40 °C for 5 h. The product was filtered and the unreacted aldehyde was removed by extraction with ethanol in Soxhlet apparatus for 12 h. The resulting Schiff base chitosan-cinnamaldehyde was dried at 40 °C for 24 h and stored in desiccator.

### FTIR spectroscopy

The FTIR spectra of chitosan and Schiff base chitosan-cinnamaldehyde were recorded in KBr pellets by Nicolet Avatar 330 FTIR, Thermo Science, (USA) spectrophotometer. The scanning range was 400 – 4000  $\text{cm}^{-1}$ .

### Batch adsorption experiments

All experiments were carried out at temperature of 40.0  $\pm$  0.5 °C in batch mode. The batch experiments were conducted in 100 mL flasks using a water bath shaker at constant agitation speed (100 rpm). Adsorption experiments were conducted in different batches for all the experimental conditions like pH of the solution, adsorbent contact time, adsorbent dose and initial COD concentration. The pH values were measured by using of pH-meter „Microsyst Labline” MS 2006. The pH was corrected using diluted NaOH (0.1 mol  $\text{L}^{-1}$ ) or HCl (0.1 mol  $\text{L}^{-1}$ ) solutions. Each flask was filled with a known volume of sample having desired pH and stirring process was initiated. The samples were withdrawn at predetermined time intervals, filtered and analyzed for COD concentration.

The effect of pH was studied with a constant initial concentration (3875  $\pm$  10 mg  $\text{L}^{-1}$ ), adsorbent dose (0.1 g 10 mL $^{-1}$ ) and constant time, but at the pH values from 6.0 to 9.0. The samples were agitated for 60 min, filtered and then analyzed for residual COD concentration.

To determine the contribution of the adsorbent dose on COD reduction, 10 mL of sample were treated with different doses of adsorbent ranging from 0.05 to 0.25 g 10 mL $^{-1}$ . The other conditions were as follows: contact time 60 min, pH 9.0  $\pm$  0.2, and initial COD concentration 3875  $\pm$  10 mg  $\text{L}^{-1}$ .

### Kinetics experiments

Batch kinetic experiments were carried out at pH 9.0  $\pm$  0.2 and 40.0  $\pm$  0.5 °C. For this purpose, 0.20 g of adsorbent were contacted with 10 mL of wastewater with initial COD concentration 3875  $\pm$  10 mg  $\text{L}^{-1}$  in 100 mL Erlenmeyer glass flasks placed in a shaking water bath at 100 rpm. The treated samples were withdrawn at different time intervals from 60 to 360 min, filtered and were analyzed for residual COD concentration.

### Equilibrium experiments

The equilibrium adsorption experiments were carried out by keeping all other conditions constant (40.0  $\pm$  0.5 °C, 10 mL solution, 0.20 g adsorbent, pH 9.0  $\pm$  0.2 and

treatment time 360 min), except changing the initial COD concentration as follow: 3875  $\pm$  10; 2538  $\pm$  8; 1977  $\pm$  6 and 1575  $\pm$  9 mg  $\text{L}^{-1}$ .

### Analytical methods

The COD of the wastewater samples was measured spectrophotometrically [21] before and after treatment with adsorbent. The water sample is oxidized with a hot sulfuric solution of potassium dichromate, with silver sulfate as the catalyst. Chloride is masked with mercury sulfate. The concentration of green  $\text{Cr}^{3+}$  ions is determined photometrically. The COD uptake was calculated from the difference between the initial and the final COD concentrations (1):

$$q = \frac{(C_0 - C_f)}{m} \cdot V \quad (1)$$

where, q - the uptake (mg adsorbate/g adsorbent),  $C_0$  and  $C_f$  - the initial and final COD concentrations (mg  $\text{L}^{-1}$ ), m - the adsorbent amount (g) and V- the solution volume (L).

The COD reduction efficiency (RE, %) was estimated by the following equation (2):

$$RE = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (2)$$

### Kinetic modeling

The Lagergren pseudo-first order model was used due to its simplicity and good fit. This model is most commonly used to describe the adsorption of a solute from a liquid solution. It is based on the assumption that the rate is proportional to the number of free site [22]. The linearized form of this model is given by equation (3):

$$\lg(q_e - q) = \lg q_e - \frac{K_{1,ads} t}{2.303} \quad (3)$$

where  $K_{1,ads}$  is the kinetic constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ),  $q_e$  and q (mg  $\text{g}^{-1}$ ) are the amounts adsorbed at equilibrium and at time t (min), respectively.

The linear plot of  $\lg(q_e - q)$  versus t was plotted to evaluate this kinetic model (3) and to determine the rate constant and  $q_e$  from the slope and intercept, respectively.

In the pseudo-second order model, the rate limiting step is the surface adsorption that involves chemisorption, where the adsorbate removal from a solution is due to physicochemical interactions between the two phases. The rate of sorption is proportional to the square of the number of unoccupied sites [22]. The model is usually represented by its linearized form (4):

$$\frac{t}{q} = \frac{1}{K_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (4)$$

here  $K_{2,ads}$  (g  $\text{mg}^{-1} \text{min}^{-1}$ ) is the pseudo-second order rate constant of adsorption. The  $q_e$  and  $K_{2,ads}$  parameters are calculated from the slope and intercept of the plot  $t/q$  versus t.

### Sorption isotherm modeling

Equilibrium isotherm equations are used to describe experimental sorption data.

The Freundlich isotherm which has been widely used in correlating equilibrium data can be expressed by the following linearized logarithmic form [23]:

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (5)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of COD removed per unit mass of the adsorbent,  $C_e$  ( $\text{mg L}^{-1}$ ) is the residual COD concentration of the aqueous solution,  $K_F$  and  $n$  are Freundlich constants and measures of adsorption capacity and adsorption intensity, respectively

The Langmuir isotherm is based on three assumptions: namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy [23]. This isotherm can be described by the following linearized form:

$$q_e = q_{max} - \frac{1}{K_L} \cdot \frac{q_e}{C_e} \quad (6)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium amount of COD adsorbed,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of COD in the solution,  $q_{max}$  ( $\text{mg g}^{-1}$ ) and  $K_L$  ( $\text{L mg}^{-1}$ ) are Langmuir constants representing the maximum monolayer adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

For the Langmuir isotherm analysis, the separation factor ( $R_L$ ) value is of special importance:  $R_L = 0$  (irreversible isotherm),  $R_L = 1$  (linear isotherm),  $R_L > 1$  (unfavorable isotherm) and  $R_L < 1$  (favorable isotherm) [24].

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial COD concentration in the solution.

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm [25] contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. The Temkin isotherm can be described by the following linearized form:

$$q_e = \frac{RT}{b_T} \ln A_T + \left( \frac{RT}{b_T} \right) \ln C_e \quad (8)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is amount of adsorbate in the adsorbent at equilibrium,  $R$  and  $T$  are universal gas constant ( $8314 \text{ J mol}^{-1}\text{K}^{-1}$ ) and temperature (K), respectively,  $A_T$  ( $\text{L g}^{-1}$ ) - Temkin isotherm equilibrium binding constant,  $b_T$  - Temkin isotherm constant,  $C_e$  ( $\text{mg L}^{-1}$ ) is equilibrium concentration.

The Chi-square error analysis function (9) was used to find out the best fit model to the obtained experimental data [16]:

$$CHI^2 = \sum_{i=1}^n \frac{(q_{e,i,exp} - q_{e,i,cal})^2}{q_{e,i,exp}} \quad (9)$$

All experiments were performed in triplicate. The data were analyzed and presented as mean values.

## RESULTS AND DISCUSSION

### Schiff base chitosan-cinnamaldehyde characterization

FTIR spectroscopy was used to confirm the synthesis of the Schiff base chitosan-cinnamaldehyde. The FTIR spectra of

chitosan (A) and Schiff base (B) samples were shown and compared (Fig. 1). Both spectra exhibited the absorption bands at 1153, 1070, 1024, and 897  $\text{cm}^{-1}$ , which was assigned to the carbohydrate moiety. Among the bands characteristic to chitosan, in the FTIR spectra of the Schiff base chitosan-cinnamaldehyde, a new peak was found at 1635  $\text{cm}^{-1}$ , attributed to C=N vibrations of imines. A broad band at 3439  $\text{cm}^{-1}$  corresponding to the stretching vibration of OH bonds was observed. New distinctive peaks at 688  $\text{cm}^{-1}$ , 750  $\text{cm}^{-1}$ , 1450  $\text{cm}^{-1}$  and 1491  $\text{cm}^{-1}$  typical for the phenyl residue of cinnamaldehyde were observed in the Schiff base (B) spectrum. Additionally, the characteristic absorption peak at 1597  $\text{cm}^{-1}$  almost disappeared, representing a decrease in  $-\text{NH}_2$  group content. This indicated that the amino groups on chitosan reacted with cinnamaldehyde to form a Schiff base chitosan-cinnamaldehyde.

### Effect of pH

The effect of pH was studied in the range of 6.0–9.0, based on the stability of the Schiff base in alkaline medium. The pH value of the solution was an important controlling parameter in the process of adsorption. The effect of pH on COD reduction efficiency in wastewater was shown (Fig. 2). Increasing the pH from 6.0 to 9.0 led to increasing of the COD reduction. The maximum reduction efficiency of 20.0% was observed at pH 9.0, hence this value was used for the rest of the experimental work.

### Effect of adsorbent dosage

The adsorbent dosage played an important role in the adsorption process. The results of the adsorbent dosage effect on COD reduction in wastewater were presented (Fig. 3). When the adsorbent dose was increased from 5 to 25  $\text{g L}^{-1}$  the COD reduction efficiency increased from 13.5 to 27.4%. An increase in the dose beyond 20  $\text{g L}^{-1}$  had no significant effect ( $p < 0.05$ ) on COD reduction hence this value was used for the rest of the experiments. It was observed that the percentage removal was found to be increasing with increase in dosage and the results were similar with the previous investigations [14, 17]. This could be attributed to a large number of vacant binding sites (as a result of grafting the extra functional groups), which were available for adsorption during the initial stages.

### Effect of contact time and kinetic modeling

Equilibrium time is another important operational parameter for the adsorption process effectiveness. The effect of contact time on COD uptake was presented in Fig. 4 (by data points). The COD reduction kinetics data indicated that after 240 min the equilibrium was reached and the equilibrium COD uptake was found to be 64.9  $\text{mg g}^{-1}$ . The established highest COD reduction efficiency was 33.5%.

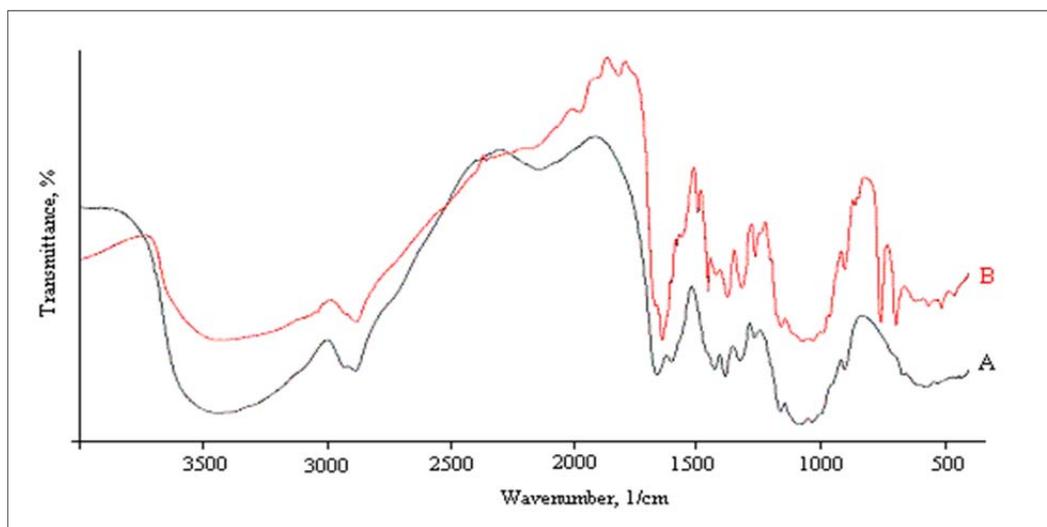
Different kinetics models have been used to investigate the sorption mechanism and potential rate controlling steps, which are helpful for selecting optimum operating conditions for the full-scale batch process [23]. The pseudo-first order and pseudo-second order models were applied in this study to modeling the experimental data. Results from linear regression analysis were presented (Fig. 5 and 6) and the kinetic parameters calculated for the used models are shown in Table 1.

**Table 1. Kinetic parameters for the adsorption of COD on the Schiff base chitosan-cinnamaldehyde**

Pseudo-first order model				Pseudo-second order model			
$q_e$ , mg g <sup>-1</sup>	$K_{1,ads}$ , min <sup>-1</sup>	$R^2$	CHI <sup>2</sup>	$q_e$ , mg g <sup>-1</sup>	$K_{2,ads}$ , g (mg min) <sup>-1</sup>	$R^2$	CHI <sup>2</sup>
72.93	0.019	0.82	3.2	70.92	0.014	0.99	1.0

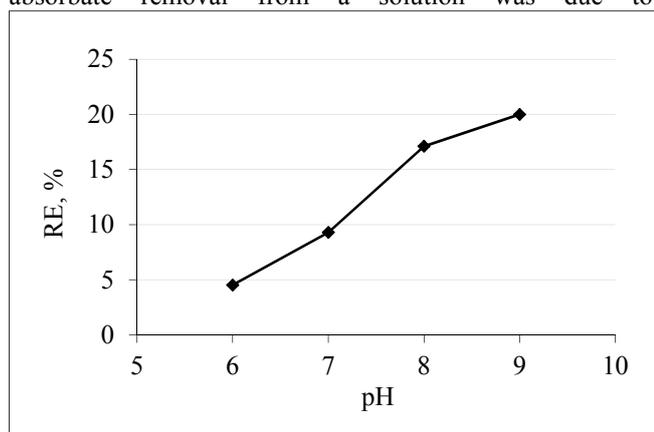
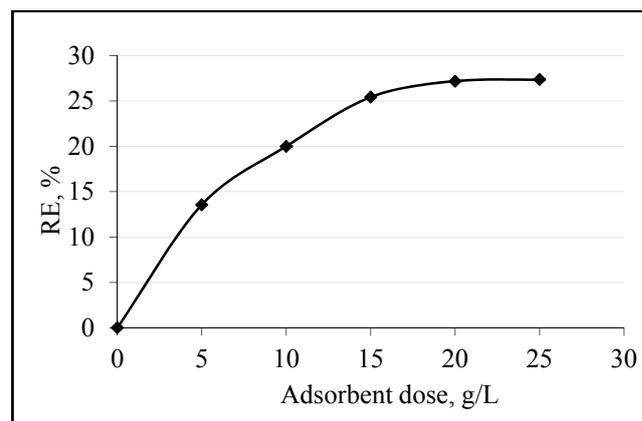
**Table 2. Isotherm model parameters for the adsorption of COD on the Schiff base chitosan-cinnamaldehyde**

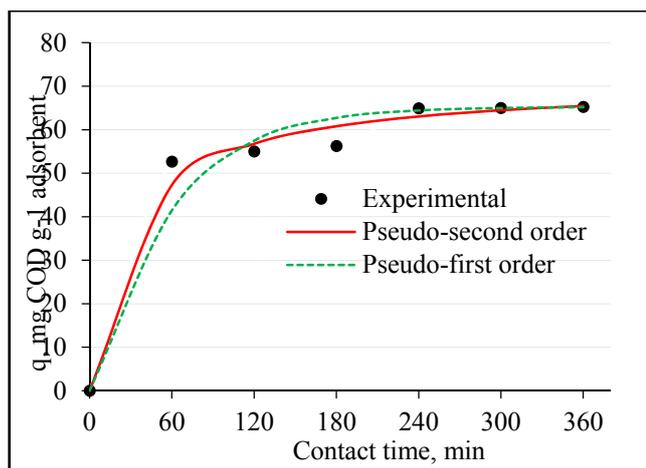
Freundlich model			Langmuir model			Temkin model		
$K_F$	n	$R^2$	$q_{max}$ , mg g <sup>-1</sup>	$K_L$ , L mg <sup>-1</sup>	$R^2$	$b_T$	$A_{T,1}$ , L g <sup>-1</sup>	$R^2$
$3 \times 10^{-7}$	0.41	0.87	17.38	$3.4 \times 10^{-4}$	0.89	$3.2 \times 10^4$	$8.9 \times 10^{-4}$	0.99

**Fig. 1.** FTIR – spectra of chitosan (A) and Schiff base chitosan-cinnamaldehyde (B).

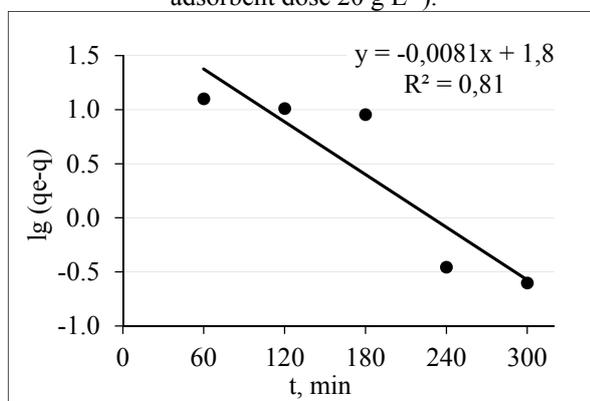
Data from Table 1 for coefficients of determination ( $R^2$ ) and the CHI-square error proved that the pseudo-second order model provided the best fit for the kinetic data. Therefore, probably the rate limiting step was the surface adsorption that involved chemisorption, where the adsorbate removal from a solution was due to

physicochemical interactions between the two phases [22]. Pathak et al. [19] also reported that the second-order kinetic model was the best choice to describe the adsorption of pollutants from dairy wastewater by using of rice husk as adsorbent.

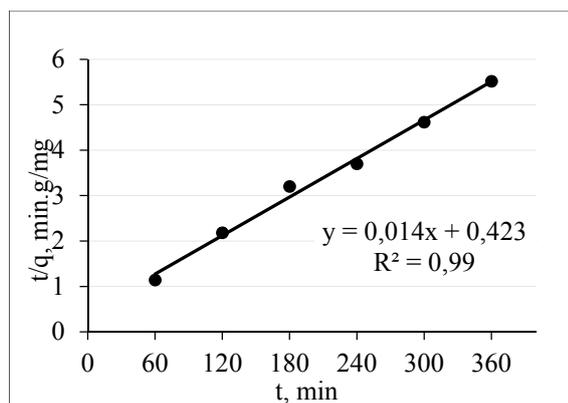
**Fig. 2.** Effect of pH on COD reduction efficiency ( $C_0 = 3875 \pm 10$  mg L<sup>-1</sup>, temperature 40 °C, adsorbent dose 10 g L<sup>-1</sup>, contact time 60 min).**Fig. 3.** Effect of adsorbent dose on COD reduction efficiency ( $C_0 = 3875 \pm 10$  mg L<sup>-1</sup>, temperature 40 °C, pH 9.0, contact time 60 min).



**Fig. 4.** Kinetics of COD uptake and fits of used kinetic models ( $C_0 = 3875 \text{ mg L}^{-1}$ , temperature  $40 \text{ }^\circ\text{C}$ , pH 9.0, adsorbent dose  $20 \text{ g L}^{-1}$ ).



**Fig. 5.** Plot of  $\lg(q_e - q)$  vs.  $t$  according to the pseudo-first order model ( $C_0 = 3875 \text{ mg L}^{-1}$ , temperature  $40 \text{ }^\circ\text{C}$ , pH 9.0, adsorbent dose  $20 \text{ g L}^{-1}$ ).

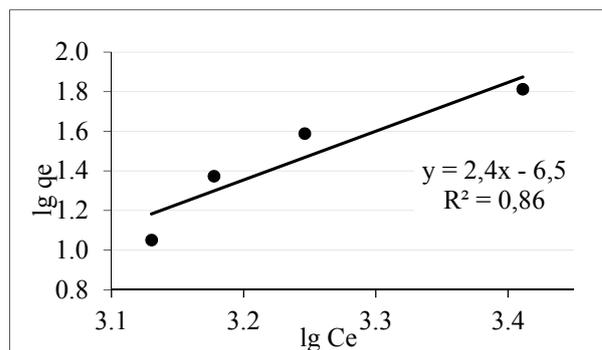


**Fig. 6.** Plot of  $t/q$  vs.  $t$  according to the pseudo-second order model ( $C_0 = 3875 \text{ mg L}^{-1}$ , temperature  $40 \text{ }^\circ\text{C}$ , pH 9.0, adsorbent dose  $20 \text{ g L}^{-1}$ ).

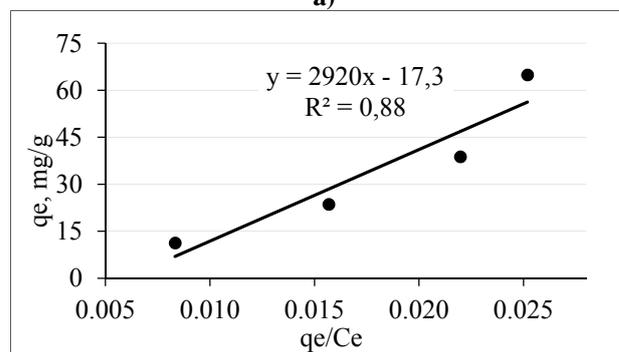
#### Sorption isotherm modeling

The experimental data for equilibrium adsorption were fitted to the Freundlich, Langmuir and Temkin isotherm models (Fig. 7). Isotherm model parameters calculated for the used models were shown (Table 2). The results from the adsorption isotherm study indicated that the experimental data were described by the Temkin model with higher coefficient of determination in comparison to the Freundlich and Langmuir models. The calculated values

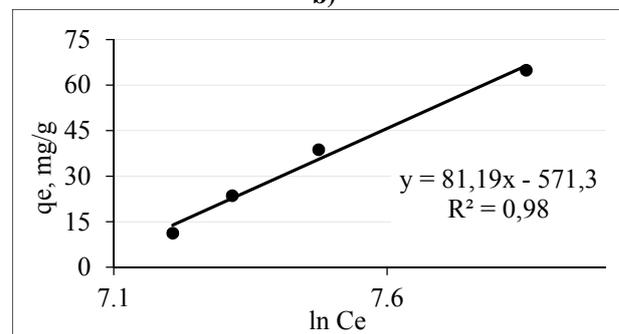
of the Langmuir separation factor were  $R_L < 1.0$ , which corresponded to the favorable isotherm type. Similar results were obtained by Pathak et al. [19].



a)



b)



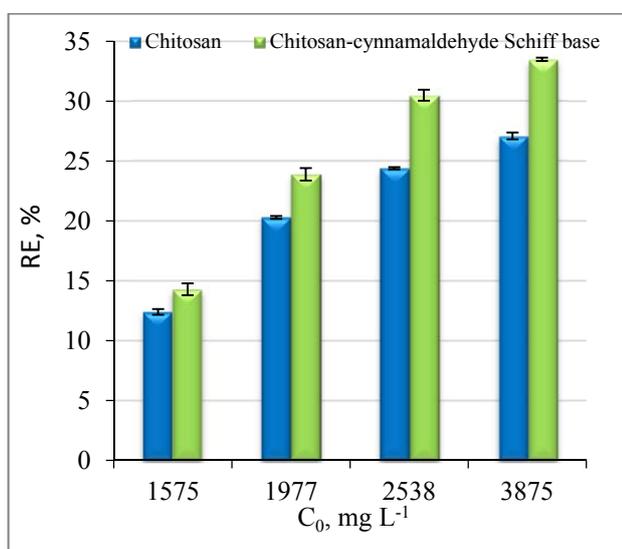
c)

**Fig. 7.** Sorption isotherm modeling a) Freundlich plot b) Langmuir plot and c) Temkin plot for COD reduction using Schiff base chitosan-cinnamaldehyde adsorbent ( $40.0 \text{ }^\circ\text{C}$ , pH 9.0, adsorbent dose  $20 \text{ g L}^{-1}$ , contact time 360 min).

#### Comparison of COD reduction efficiency between chitosan and Schiff base chitosan-cinnamaldehyde adsorbents

The results for COD reduction efficiency in application of chitosan and Schiff base chitosan-cinnamaldehyde as adsorbents at different initial COD concentrations ( $C_0$ ,  $\text{mg L}^{-1}$ ) were presented (Fig. 8). The enhancement of adsorption efficiency between 1.9 and 6.4% in dependence on initial COD concentration of dairy wastewater was observed by the adsorption with Schiff base chitosan-cinnamaldehyde adsorbent compared to chitosan. This is probably due to increases of adsorption sites resulting from chitosan modification [6].

At lower pH, the amino groups in chitosan are protonated and make it positively charged and since particles in the effluent are negatively charged, the electrostatic interaction will be stronger [17]. Chitosan is a very attractive adsorbent by allowing the molecules to bind negatively charged surface via ionic or hydrogen bonding or electrostatic interaction. When pH is increased, surface charge of chitosan is decreased so the charge neutralization becomes less important. The probable mechanism for wastewater treatment using Schiff base chitosan-cinnamaldehyde could be explained with modifying process by grafting reactions. The addition of extra functional groups to chitosan increases the number of adsorption sites and consequently the adsorption capacity. The mechanism of bridging probably becomes the major mechanism of interaction between adsorbent and pollutants.



**Fig. 8.** COD reduction efficiency in application of chitosan and Schiff base chitosan-cinnamaldehyde as adsorbents (40.0 °C, pH 9.0, adsorbent dose 20 g L<sup>-1</sup>, contact time 360 min).

### CONCLUSIONS

For the first time, a wastewater treatment study was carried out using Schiff base chitosan-cinnamaldehyde. Enhancement of the adsorption efficiency up to 6.4% in dependence on initial COD concentration of dairy wastewater was observed by adsorption with Schiff base chitosan-cinnamaldehyde adsorbent, compared to chitosan at the same experimental conditions. The major advantage of the Schiff base chitosan-cinnamaldehyde as adsorbent

material was the possibility of its application at alkaline medium. Chemical oxygen demand of the investigated wastewater was found to be on pH, adsorbent dosage and contact time dependent. The maximum percentage reduction of COD concentration of 33.5% was observed at 40.0 °C, pH 9.0, adsorbent dose 20 g L<sup>-1</sup>, contact time 240 min, and agitation speed 100 rpm. The results from this study indicated that Schiff base chitosan-cinnamaldehyde could be applied for physicochemical pre-treatment by adsorption of dairy wastewater before biological unit of the wastewater treatment plant to reduce the load.

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