Evaluation of Adsorption Capacity of Chitosan-Citral Schiff Base for Wastewater Pre-Treatment in Dairy Industries

Desislava K. Tsaneva[1], Milena I. Nikolova[2], Tsvetko V. Prokopov[2], Albena S. Stoyanova[3], Panteley P. Denev[1]*

1 - University of Food Technologies, Department of Organic and Inorganic Chemistry, 26 Maritsa blvd. 4002 Plovdiv, BULGARIA
2 - University of Food Technologies, Department of Engineering Ecology, 26 Maritsa blvd. 4002 Plovdiv, BULGARIA
3 - University of Food Technologies, Department of Tobacco, Sugar, Vegetable and Essential Oils, Perfumery and Cosmetics, 26 Maritsa blvd. 4002 Plovdiv, BULGARIA
* Corresponding author: desi_gb12@mail.bg

Abstract. In this study, we aimed to evaluate the adsorption capacity of the Schiff base chitosan-citral for its application in dairy wastewater pre-treatment. Chemical oxygen demand (COD) reduction was the factor used to evaluate the adsorption efficiency. The maximum COD percentage reduction of 35.3% was obtained at 40.0 °C, pH 9.0, adsorbent dose 15 g L^{-1}, contact time 180 min and agitation speed 100 rpm. It was found that the Langmuir isotherm fitted well the equilibrium data of COD uptake (R^2 = 0.968), whereas the kinetic data were best fitted by the pseudo-second order model (R^2=0.999). Enhancement of the adsorption efficiency up to 29.8% in dependence of the initial COD concentration of the dairy wastewater was observed by adsorption with the Schiff base chitosan-citral adsorbent compared to the non-modified chitosan at the same experimental conditions. The results indicated that the Schiff base chitosan-citral can be used for dairy wastewater physicochemical pre-treatment by adsorption, which might be applied before the biological unit in the wastewater treatment plant to reduce the load.

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

Introduction

Natural biopolymers attract much attention due to their biocompatibility and biodegradability (HENRIKSEN *et al.*, 1993; OHKAWA *et al.*, 2000; PETER, 1995). Chitin is the most abundant nitrogen containing biopolymer in nature and it is found widely in the shells of crabs, lobster, krill and shrimp. Chitin is used commercially to produce chitosan, a positively charged biopolymer with applications in food processing waste recovery (PETER, 1995; SAVANT & TORRES, 2000; TORRES *et al.*, 1999; AHMED & PYLE, 1999; SHAHIDI *et al.*, 1999), chemical industries (CHEN, 1998), biomedical and pharmaceutical industries (LEE *et al.*, 2001), and biotechnology (PETER, 1995). 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 (KYZAS & BIKIARIS, 2015).

Since the primary research work of MUZZARELLI & TUBERTINI (1969), who described the synthesis and adsorption

evaluation of chitosan for the removal of metal ions from organic and sea waters, numerous papers have been published regarding the use of chitosan as adsorbent for decontamination of wastewaters (or effluents, sea waters, drinking water samples, etc.) from various pollutants, either organic or inorganic species (KYZAS & BIKIARIS, 2015). The investigation of DEVI *et al.,* (2012) showed that low molecular weight crab shell chitosan (MW 20 kDa) could be effectively used as adsorbent in the treatment of dairy wastewater.

In more recent years, researchers have attempted to prepare chitosan-based adsorbent materials modifying the molecules of chitosan. ZHOU *et al.,* (2013) synthesized chitosan-modified biochars in efforts to produce a low-cost adsorbent for heavy metal environmental remediation. Characterization results showed that the coating of chitosan on biochar surfaces could improve its performance as a soil amendment or an adsorbent and had great advantage over many traditional adsorbents. Other researchers synthesized chitosan–zinc oxide nanocomposite materials for the application in milk processing industry wastewater (THIRUGNANASAMBANDHAM & SIVAKUMAR, 2016). As a result, the turbidity and COD were reduced after treatment with these materials.

The major advantage of chitosan is the existence of modifiable positions in its chemical structure. Several workers have reported the use of cross-linking treatments (via Schiff base formation) using several chemical reagents such as glutaraldehyde (SUGUNA *et al.,* 2010; WAN NGAH *et al.,* 2005), epichlorohydrin (WAN NGAH *et al.* 2005; VIEIRA & BEPPU, 2006), *etc.* for removal of metal ions, preventing the dissolution of chitosan in acidic solutions and to improve its metal ion adsorption properties.

The modifications of chitosan with grafting (inserting functional groups) or cross-linking reactions (joining the macromolecular chains each other) lead to the formation of chitosan derivatives with superior properties (enhancement of adsorption capacity and resistance in extreme media conditions, respectively). In the case of grafting reactions, the addition of extra functional groups to chitosan increases the number of adsorption sites and consequently the adsorption capacity. On the other hand, the cross-linking reactions slightly decrease the adsorption capacity, because some functional groups of chitosan (i.e., amino or hydroxyl groups) are bound with the cross-linker and cannot interact with the pollutant (KYZAS & BIKIARIS, 2015).

Dairy industry is one of the largest types of food industry, contributes to a great extent to pollution. In dairy industries, water has been a key processing medium. Water is used throughout all steps of the dairy industry including cleaning, sanitization, heating, cooling and floor washing — and naturally, the requirement of water is huge. Dairy wastewater is distinguished by the high biological oxygen demand (BOD) and chemical oxygen demand (COD) contents, high levels of dissolved or suspended solids including fats, oils and grease, nutrients such as ammonia or minerals and phosphates and therefore requires proper attention before disposal (SARKAR *et al.,* 2006). Dairy wastewater generally does not contain conventional toxic chemicals like those listed under EPA's Toxic Release Inventory. However, it has high concentration of dissolved organic components like whey proteins, lactose, fat and minerals (MUKHOPADHYAY *et al.,* 2003) and it is also malodorous, because of the decomposition of some of the contaminants causing discomfort to the surrounding population.

In general, dairy wastewaters coming from different sources are mixed, pH

adjusted and then directed to biological unit for treatment. The higher loading of the biological unit leads to operational 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 to reduce the load, became the main focus of the researchers (CHI & CHENG, 2006; SARKAR *et al.*, 2006; KUSHWAHA *et al.*, 2010).

Coagulation and flocculation pro-cesses are commonly used to remove suspended solids and organics. Many studies were performed to investigate the effective removal of COD and suspended solids by optimizing coagulant dosage and pH in the treatment of wastewater (DEVI *et al.*, 2012; AMUDAA & AMOOB, 2007). Some authors reported that low molecular weight crab shell chitosan (DEVI *et al.*, 2012) and rice husk (PATHAK *et al.*, 2016) 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-citral for pollution removal, therefore the aim of this work is to evaluate the adsorption capacity of the Schiff base chitosan-citral and to investigate the possibility of its applications in dairy industries for wastewater pre-treatment. Chemical oxygen demand (COD) reduction was the factor used to evaluate the adsorption efficiency.

Materials and Methods

Chitosan with a molecular weight of 100000 – 300000 Da and degree of deacetylation 78,98% (calculated in previous study by conductometric titration) was purchased from Across Organics (Belgium); Citral was obtained from Givaudan (France); other chemicals (methanol, ethanol) were of reagent grade and 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-citral preparation

The Schiff base chitosan-citral was synthesized as per method described earlier with slight modifications (JIN *et al.*, 2009). Chitosan was dispersed in 50 mL of methanol. Then aldehyde dissolved in anhydrous ethanol (20 mL) was added dropwise to the solution under high-intensity ultrasound at 30 – 40 °C for 5 h. When the reaction ended, the product was filtered, and the unreacted aldehyde was extracted in a Soxhlet apparatus with anhydrous ethanol for 12 h. The resulting Schiff base chitosan-citral was dried at 40 °C for 24 h and stored in desicator with sillica gel.

FTIR-spectroscopy

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

Batch adsorption experiments

All experiments were carried out at a temperature of 40.0 ± 0.5 °C (based on preliminary experiments) in batch mode. The batch experiments were conducted in different flasks of 100 mL capacity using a water bath shaker at constant agitation speed (100 rpm) in order to ensuring constant mixing. Adsorption experi-ments 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 desired pH was maintained using diluted NaOH (0.1 mol L^{-1}) or HCl (0.1 mol L^{-1}) solutions. Each flask was filled with a

known volume of sample having desired pH and stirring was initiated. The samples were withdrawn from the shaker at predetermined time intervals, filtered through filter paper and analyzed for COD concentration.

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

The effect of pH was studied with constant initial concentration (3750 mg L^{-1}), adsorbent dose (0.1 g 10 mL^{-1}) and constant time, but varying the pH values from 6.0 to 9.0 using diluted NaOH or HCl solutions. 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 0.2 g 10 mL^{-1}. The other conditions were: contact time 60 min, pH 9.0 ± 0.2, and initial COD concentration 3750 mg L^{-1}.

Kinetics experiments

Batch kinetic experiments were carried out at pH 9.0 ± 0.2 and 40.0 ± 0.5 °C. For this purpose, 0.15 g of adsorbent were contacted with 10 mL of wastewater with initial COD concentration 3750 mg L^{-1} in 100 mL Erlenmeyer glass flasks on a water bath shaker at 100 rpm. At different time intervals ranging from 60 to 240 min the treated samples were withdrawn, filtered and was analyzed for residual COD concentration.

Equilibrium experiments

The equilibrium adsorption experiments were carried out by keeping all other conditions constant (40.0 ± 0.5 °C, 10 mL solution, 0.15 g adsorbent, pH 9.0 ± 0.2 and treatment time 240 min), except changing the initial COD concentration as follow: 3750, 2500, 1875, and 1500 mg L^{-1}.

Analytical methods

In this research, we studied the reduction in COD only. The COD of the wastewater samples was measured spectrophotometrically in accordance to the standard method ISO 15705 (2002) 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 Cr^{3+} ions is than determined photometrically.

The pH values of samples were measured by using of pH-meter „Microsyst Labline" MS 2006.

The COD uptake was calculated from the difference between the initial and the final COD concentrations as follows:

$$q = \frac{(c_0 - c_f)}{m} \cdot V$$

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

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

$$RE = \frac{(c_0 - c_f)}{c_0} \cdot 100$$

Kinetic modeling

The following kinetics models were used in this study to model experimental data:

The Lagergren pseudo-first order model was employed 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 (EL-NAAS *et al.*, 2010).

The linearized form of this model is given by:

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

(3)

where K_1,ads is the kinetic constant of pseudo-first order adsorption (min^{-1}), q_e and q (mg 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 used, 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 squire of the number of unoccupied sites (EL-NAAS *et al.*, 2010).

The model is usually represented by its linearized form as follow:

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

where $K_{2,ads}$ (g mg^{-1} 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.

In recent years, Elovich's model has been successfully used to describe the adsorption of pollutants from aqueous solutions (EL-NAAS *et al.*, 2010).

The linearized form of this model is given by the following equation:

$$q = \frac{1}{b}ln\ (ab) + \frac{1}{b}ln\ t$$

where a (g mg^{-1} min^{-1}) is the initial adsorption rate and 1/b (mg g^{-1}) is a parameter related to the number of sites available for adsorption.

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:

$$lg\ q_e = lg\ K_F + \frac{1}{n}lg\ C_e$$

where q_e (mg g^{-1}) is the amount of COD removed per unit mass of the adsorbent, C_e (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. A higher n value (lower value of 1/n) implies stronger sorbent-pollutant interaction whereas 1/n equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites (FEBRIANTO *et al.*, 2009).

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 (FEBRIANTO *et al.*, 2009).

(4)

This isotherm can be described by the following linearized form:

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

where q_e (mg g^{-1}) is the equilibrium amount of COD adsorbed, C_e (mg L^{-1}) is the equilibrium concentration of COD in the solution, q_{max} (mg g^{-1}) and K_L (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.

(5)

For the Langmuir isotherm analysis, the separation factor (R_L) value is of special importance:

$$R_L = \frac{1}{1 + K_L C_0}$$

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

FOO & HAMEED, (2010) described four possibilities for the separation factor values, which determine the isotherm type: $R_L = 0$ (irreversible isotherm), $R_L = 1$ (linear isotherm), $R_L > 1$ (unfavorable isotherm) and $R_L < 1$ (favorable isotherm).

The Chi-squire error analysis function was used to find out the best fit model to the obtained experimental data (KUSHWAHA *et al.*, 2010). It is given as:

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

Results and Discussion

Schiff base chitosan-citral characterization

FTIR spectroscopy was used to confirm the structure of the Schiff base chitosan-citral. The FTIR spectra of chitosan (A) and Schiff base (B) samples are shown in Figure 1. Both spectra exhibit the absorption peaks at 1151, 1066, 1026, and 895 cm^{-1}, which can be assigned to the saccharide moiety. Among the bands characteristic to chitosan, in the FTIR spectra of the Schiff base chitosan-citral, a new peak was generated at 1647 cm^{-1}, attributed to C=N vibrations of imines. The figures exhibit a broad band at 3439 cm^{-1}, which corresponds to the stretching vibration of –NH$_2$ and OH bonds. Additionally, the characteristic absorption peak at 1597 cm^{-1} almost disappears, representing a decrease in –NH$_2$ group content, which indicates that the amino groups on

chitosan reacted with citral to form a Schiff base chitosan-citral.
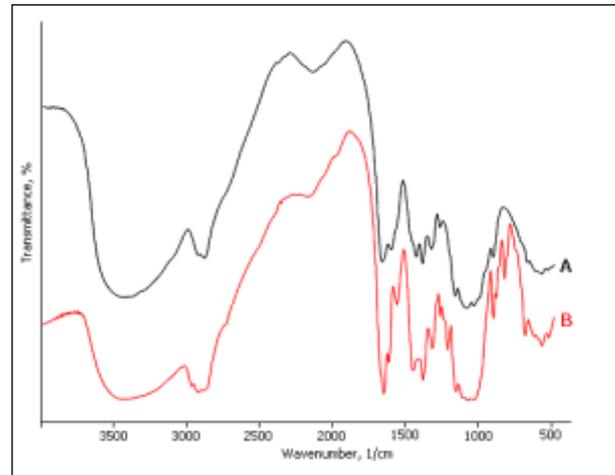
Fig. 1. FTIR – spectra of chitosan (A) and Schiff base chitosan-citral (B).

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 is an important controlling parameter in the process of adsorption. The effect of pH on COD reduction efficiency in wastewater is shown in Figure 2.
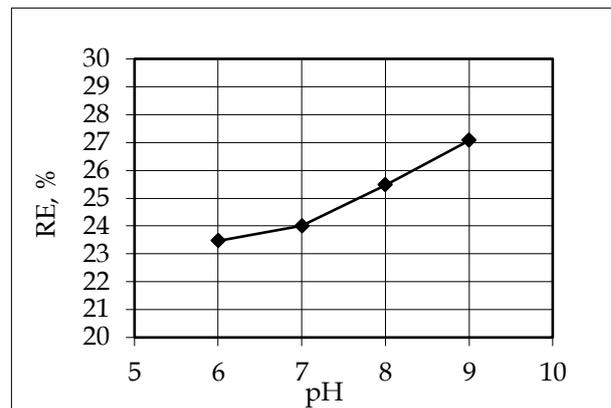
Fig. 2. Effect of pH on COD reduction efficiency (C_0 = 3750 mg L^{-1}, adsorbent dose 10 g L^{-1}, contact time 60 min).

Increasing the pH from 6.0 to 9.0 led to increasing of the COD reduction. The maximum reduction efficiency of 27.5% 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 on the adsorbent dosage effect on COD reduction in wastewater are presented in Figure 3. When the adsorbent dose was increased from 5 to 15 g L^{-1} the COD reduction efficiency increased from 18.3 to 28.4%. An increase in the dose beyond 15 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 investigations made by SARKAR *et al.,* (2006) and DEVI *et al.,* (2012). This could be attributed to a large number of vacant binding sites (as a result of grafting the extra functional groups), which are available for adsorption during the initial stages.
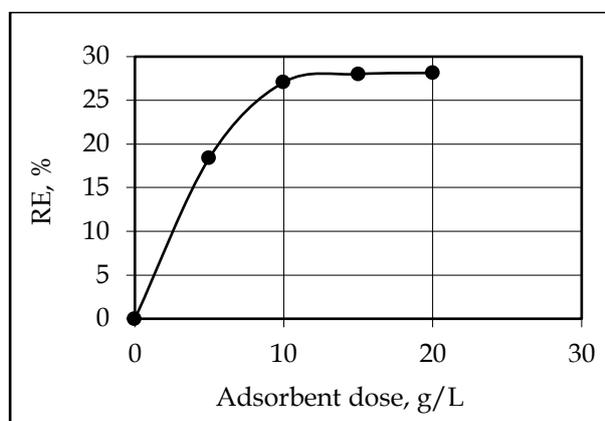
Fig. 3. Effect of adsorbent dose on COD reduction efficiency (C$_0$ = 3750 mg L^{-1}, pH 9.0, contact time 60 min).

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 is

presented in Figure 4 (by data pints). The COD reduction kinetics data indicated that after 180 min the equilibrium was reached and the equilibrium COD uptake was found to be 88.7 mg g^{-1}. The established highest COD reduction efficiency was 35.3%.
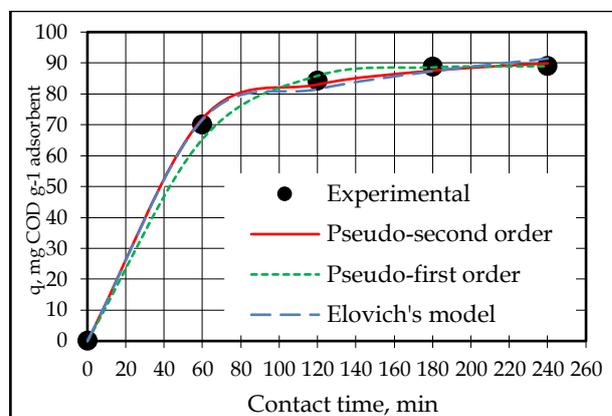
Fig. 4. Kinetics of COD uptake and fits of used kinetic models (C$_0$ = 3750 mg L^{-1}, pH 9.0, adsorbent dose 15 g L^{-1}).

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 (FEBRIANTO *et al.,* 2009). The pseudo-first order, pseudo-second order and Elovich's models were employed in this study to modeling the experimental data. Results from linear regression analysis are presented in Figures 5, 6 and 7, and the kinetic parameters calculated for the used models are shown in Table 1.

Data from Table 1 for coefficients of determination (R^2) and the CHI-squire error proved that the pseudo-second order model provided the best fit for the kinetic data. Therefore, probably the rate limiting step is the surface adsorption that involves chemisorption, where the absorbate removal from a solution is due to physicochemical interactions between the two phases (EL-NAAS *et al.,* 2010). PATHAK *et al.* (2016) 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.
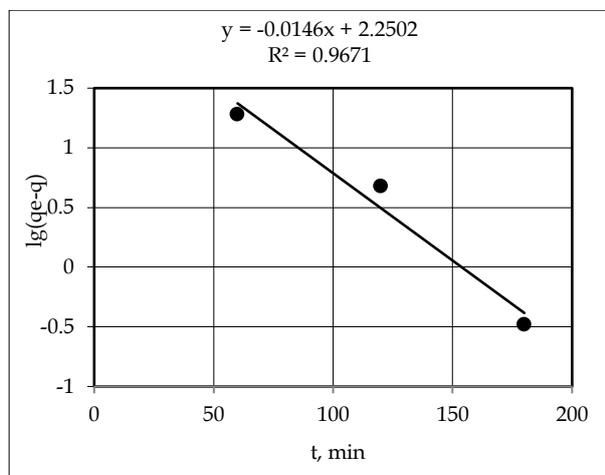
Fig. 5. Plot of $lg(q_e – q)$ vs. t according to the pseudo-first order model ($C_0 = 3750$ mg L^{-1}, pH 9.0, adsorbent dose 15 g L^{-1}).
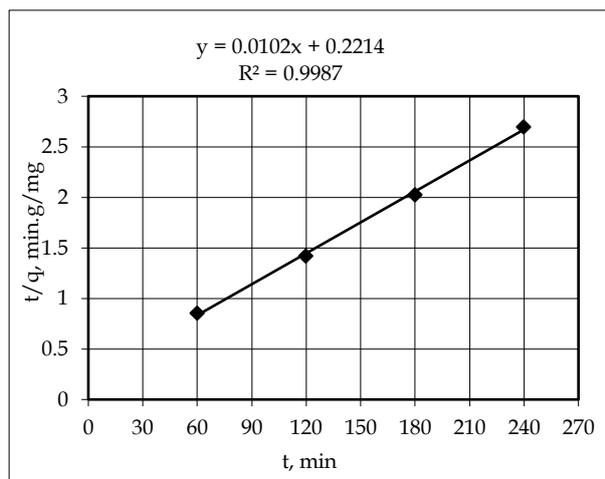
Fig. 6. Plot of t/q vs. t according to the pseudo-second order model ($C_0 = 3750$ mg L^{-1}, pH 9.0, adsorbent dose 15 g L^{-1}).
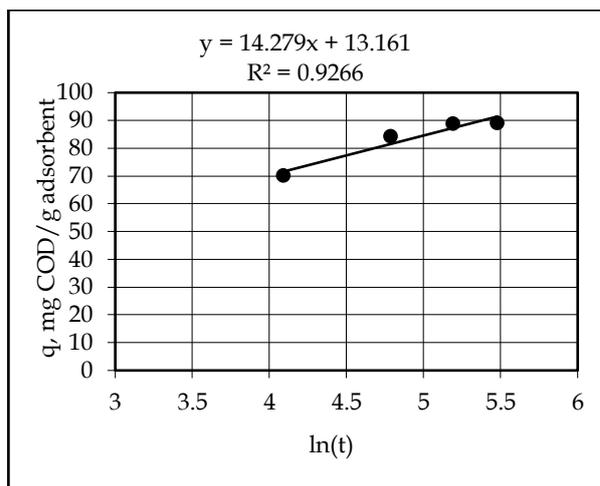
Fig. 7. Plot of q vs. Ln(t) according to the Elovich's model ($C_0 = 3750$ mg L^{-1}, pH 9.0, adsorbent dose 15 g L^{-1}).

Sorption isotherm modeling

The experimental data for equilibrium adsorption were fitted to the Freundlich and Langmuir isotherm models as presented in Figures 8 and 9. Isotherm model parameters calculated for the used models are shown in Table 2. The results from the adsorption isotherm study indicated that the experimental data were the best fit by the Langmuir model with higher coefficient of determination and lower Chi-squire error in comparison to the Freundlich model. A higher n value (lower value of 1/n) obtained for Freundlich model implies stronger sorbent-pollutant interaction, whereas 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.* (2016).

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

Pseudo-first order model				Pseudo-second order model				Elovich's model			
q_e, mg g^{-1}	$K_{1,ads}$, min^{-1}	R^2	CHI^2	q_e, mg g^{-1}	$K_{2, ads}$, g (mg min)$^{-1}$	R^2	CHI^2	a, mg (g min)$^{-1}$	1/b, mg g^{-1}	R^2	CHI^2
177.9	0.034	0.967	0.34	98.0	4.7×10^{-4}	0.999	0.09	0.176	14.3	0.927	0.21

y = 0.3978x + 0.622
R² = 0.8253
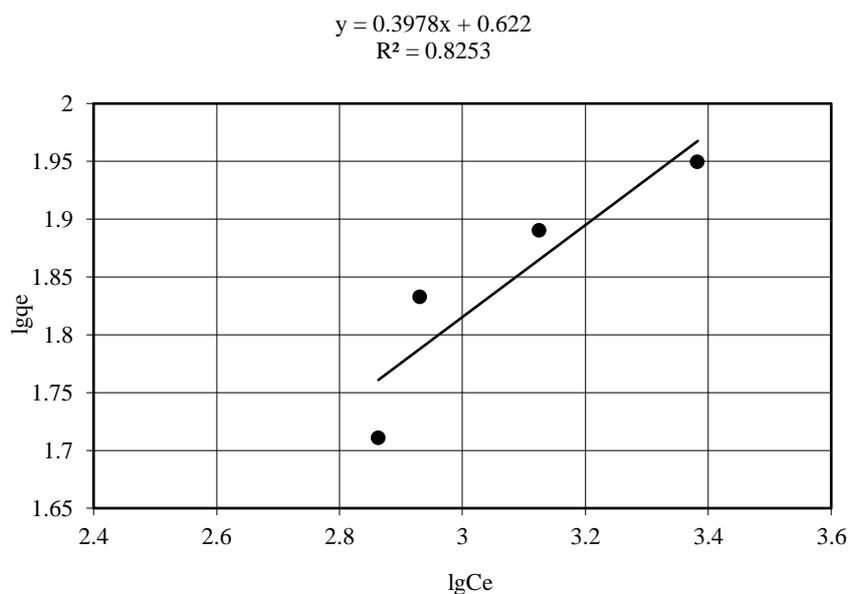
Fig. 8. Freundlich plot for COD reduction using Schiff base chitosan-citral adsorbent (40.0 °C, pH 9.0, adsorbent dose 15 g L^{-1}, contact time 240 min).

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

Langmuir model				Freundlich model			
q_{max}, mg g^{-1}	K_L, L mg^{-1}	R²	CHI²	K_F	n	R²	CHI²
119.0	1.27x10^{-3}	0.968	1.32	4.19	2.5	0.825	1.82

y = 0.0084x + 6.6206
R² = 0.9678
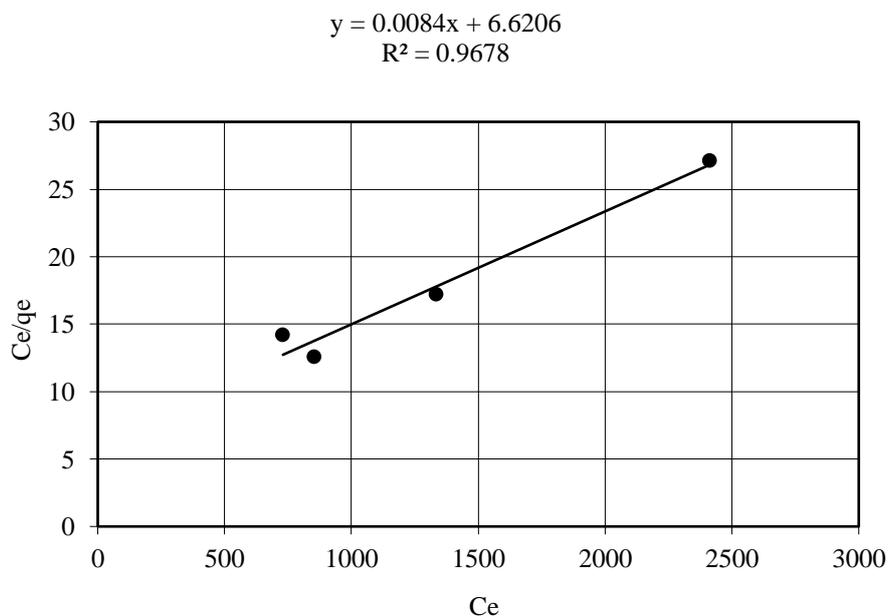
Fig. 9. Langmuir plot for COD reduction using Schiff base chitosan-citral adsorbent (40.0 °C, pH 9.0, adsorbent dose 15 g L^{-1}, contact time 240 min).

The results for COD reduction efficiency in application of chitosan and Schiff base chitosan-citral as adsorbents at different initial COD concentrations (C_o, mg L^{-1}) are presented in Figure 10. The enhancement of adsorption efficiency between 23.2 and 29.8% in dependence of initial COD concentration of dairy wastewater was observed by adsorption with Schiff base chitosan-citral adsorbent compared to chitosan. This is probably due to increases of adsorption sites resulting from chitosan modification (KYZAS & BIKIARIS, 2015).

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 strong DEVI *et al.,* (2012). 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-citral 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.
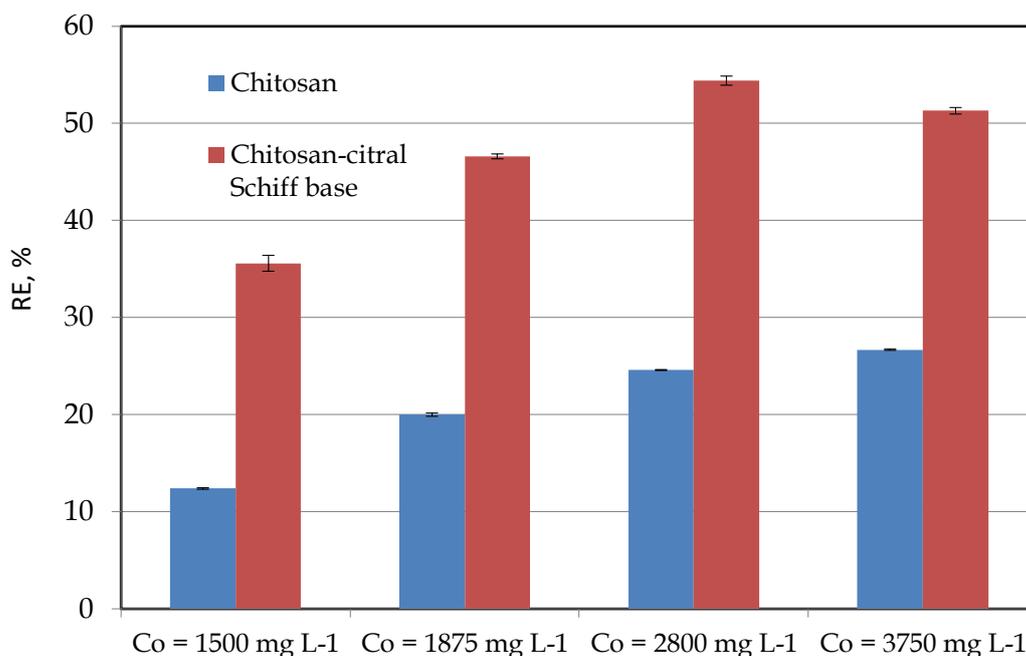
Fig. 10. COD reduction efficiency in application of chitosan and Schiff base chitosan-citral as adsorbents (40.0 °C, pH 9.0, adsorbent dose 15 g L^{-1}, contact time 240 min).

Conclusions

For the first time, a wastewater treatment study was carried out using Schiff base chitosan-citral. Enhancement of the adsorption efficiency up to 29.8% in dependence of initial COD concentration of dairy wastewater was observed by adsorption with Schiff base chitosan-citral adsorbent, compared to chitosan at the same experimental conditions. The major advantage of the Schiff base chitosan-citral as adsorbent material is the possibility of its application at alkaline medium. The results from this study indicated that Schiff base chitosan-citral could be

applied for physicochemical pre-treatment by adsorption of dairy wastewater before biological unit of the wastewater treatment plant to reduce the load. Chemical oxygen demand (COD) of the investigated wastewater was found to be on pH, adsorbent dosage and contact time dependent. The maximum percentage reduction of COD concentration of 35.3% was observed at 40.0 °C, pH 9.0, adsorbent dose 15 g L^{-1}, contact time 180 min, and agitation speed 100 rpm. It was found that the Langmuir isotherm fitted well the equilibrium data of COD uptake (R^2 = 0.968), whereas the kinetic data were best fitted by the pseudo-second order model (R^2 = 0.999).

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