

## SORPTION OF METHYLENE BLUE ONTO ORANGE AND LEMON PEEL

DAJANA KUČIĆ, SNEŽANA MILJANIĆ<sup>1</sup>, MIRELA ROŽIĆ

Faculty of Graphic Arts, University of Zagreb, Croatia

<sup>1</sup>Faculty of Science, University of Zagreb, Croatia

e-mail: [dajana.kucic@grf.hr](mailto:dajana.kucic@grf.hr)

This study examines the sorption of methylene blue on the cheap unconventional bio sorbents, citrus fruits: oranges and lemons. Bio sorbents which was used was: orange and lemon peel, seeds and pulp. The results are compared with results of sorption to mineral sorbents, zeolite clinoptilolite, Pyrolox and Birm. Sorption kinetics and the influence of pH on the sorption of methylene blue on orange and lemon peel was examined. Sorption isotherm of methylene blue onto the orange end lemon peel was determined at 25°C with the initial concentrations of methylene blue 50 – 1000 mg/dm<sup>3</sup>. The sorption kinetic data were analyzed using pseudo–first–order and pseudo–second–order models. It was found that the pseudo-second-order kinetic model was the best applicable model to describe the sorption kinetics. When the pH of the solution dyes was 2-3, the sorption of methylene blue was slightly weaker than at pH 3-6. In the studied concentration range 50-1000 mg/dm<sup>3</sup> sorption of methylene blue on orange and lemon peel was linear, with sorption efficiency of approximately 100%. The capacity of zeolite for methylene blue was 20 mg/g. Sorption capacity of citrus waste was significantly higher than in the mineral sorbents (zeolite, Pyrolox, Birm).

**Key words:** bio sorbents, orange and lemon peel, methylene blue, sorption isotherms, kinetics.

**Sorpcija metilenskog modrila na koru naranče i limuna.** U ovom radu proučavana je sorpcija metilenskog modrila na nekonvencionalne jeftine biosorbense, agrume: naranču i limun. Upotrijebljeni su otpaci: kora, koštice i pulpa. Rezultati su uspoređeni s rezultatima sorpcije na mineralnim sorbensima zeolitu klinoptilolitu, Pyroloxu i Birmu. Ispitana je kinetika sorpcije i utjecaj pH vrijednosti na sorpciju metilenskog modrila na korama naranče i limuna. Određene su i izoterme sorpcije na korama naranče i limuna te na zeolitu. Eksperimentalni podaci ispitivanja kinetike sorpcije analizirani su uporabom dva kinetička modela: model pseudo – prvog i model pseudo – drugog reda. Model pseudo – drugog reda bolje opisuje kinetiku sorpcije metilenskog modrila na korama naranče i limuna. Pri pH vrijednostima otopine bojila 2-3, sorpcija metilenskog modrila je nešto slabija nego pri pH vrijednostima 3-6. U ispitivanom koncentracijskom području od 50 do 1000 mg/dm<sup>3</sup> sorpcija metilenskog modrila na korama naranče i limuna je linearna uz efikasnost sorpcije približno 100%. Kapacitet zeolita za metilensko modrilo je 20 mg/g. Kapacitet sorpcije otpadaka agruma kao biosorbensa za uklanjanje metilenskog modrila iz vodenih otopina, je znatno veći u odnosu na mineralne sorbense (zeolit, Pyrolox, Birm).

**Ključne riječi:** biosorbensi, kora naranče i limuna, metilensko modrilo, izoterme sorpcije, kinetika.

### INTRODUCTION

Removal of synthetic dyestuffs from aqueous solution is necessary because of the frequent appearance of these dyestuffs in waste waters generated from graphic and

textile industries. The presence of dyes in water is undesirable since even a very small amount of these coloring agents is highly visible and may be toxic to the aquatic environment. Therefore, removal of dyes is an important aspect of waste water treatment

before discharge[1]. There are a variety of waste water treatment, biological treatment, chemical treatment, physical treatment and chemical – physical treatment of which is the most common sorption.

The most commonly used sorbent is activated carbon, but there are certain problems with its use. The high capital and regeneration cost of the activated carbon limits its large-scale applications for the removal of dyes and other aquatic pollutants. Therefore, there is a growing interest in using low-cost, easily available materials for the sorption of dye colors[2].

One of the important agricultural wastes is peel of different fruits. In this work

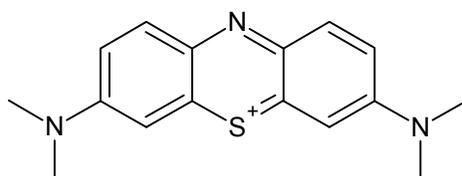
were used orange and lemon peel. The components of lemon and orange peel are: pectin, hemicellulose, lignin, chlorophyll pigments and low-molecular hydrocarbons. These components contain different functional groups such as carboxyl (COOH) and hydroxyl (OH)[3].

The aim of these work was investigated the sorption capacity of citrus waste as a bio sorbents for removal of methylene blue from aqueous solutions and the results compared with results of sorption to mineral sorbents, zeolite clinoptilolite, Pyrolox and Birm. Sorption isotherms and kinetics of the sorption process were also studied.

## MATERIALS AND METHODS

### Model water

Wastewater which was used in the experiments was prepared by dissolving methylene blue in distilled water concentration,  $\gamma(\text{MB}) = 1 \text{ g/dm}^3$ . Structure of methylene blue is shown in Figure 1.



**Figure 1.** Structure of methylene blue.  
**Slika 1.** Struktura metilenskog modrila.

### Sorbents

Orange and lemon waste were used for the sorption of methylene blue. The orange and lemon waste was first cut into small pieces, extensively washed with tap water to remove adhering dirt and soluble components such as tannins, resins, reducing

sugar and colouring agents, and then oven-dried at 80°C until constant weight (24 hours). The washed and dried material was crushed and sieved to obtain a particle size lower than 3 mm. They also used mineral sorbents: zeolite clinoptilolite,  $w(\text{clinoptilolite}) = 70\%$ , Pyrolox and Birm.

### Batch kinetic studies of methylene blue to orange and lemon peel

Kinetic experiments were carried out by adding a fixed amount of sorbent (0,25 g) into 50 cm<sup>3</sup> plastic bottles containing 25 cm<sup>3</sup> different initial concentrations (50-1000 mg/dm<sup>3</sup>) of dye solution. The temperature was controlled at 25°C. Agitation was provided at 250 rpm for 30 min, 1h, 3h, 7h, 15h and 24h. The dye concentrations were determined colorimetrically. The amount of

sorption at time  $t$ ,  $q_t$  (mg/g), was calculated by (1)

$$q_t = \frac{(c_0 - c_t) \cdot V}{m} \quad (1)$$

where  $c_0$  and  $c_t$  (mg/ dm<sup>3</sup>) are the liquid-phase concentrations of dye at initial and any time  $t$ .  $V$  (dm<sup>3</sup>) is the volume of the solution and  $m$  (g) is the mass of dry sorbent used.

### Equilibrium studies

Sorption experiments were identical to those of equilibrium tests. The aqueous samples were taken at time of 24 hours. The amount of sorption at equilibrium,  $q_e$  (mg/g), was calculated by (2)

$$q_e = \frac{(c_0 - c_e) \cdot V}{m} \quad (2)$$

where  $c_e$  is the liquid-phase concentrations of dye at equilibrium.

### Effect of solution pH

The effect of initial solution pH was determined by agitating 0,25 g of lemon and orange peel and 25 cm<sup>3</sup> of dye solution of initial basic dye concentration of 25 mg/dm<sup>3</sup>

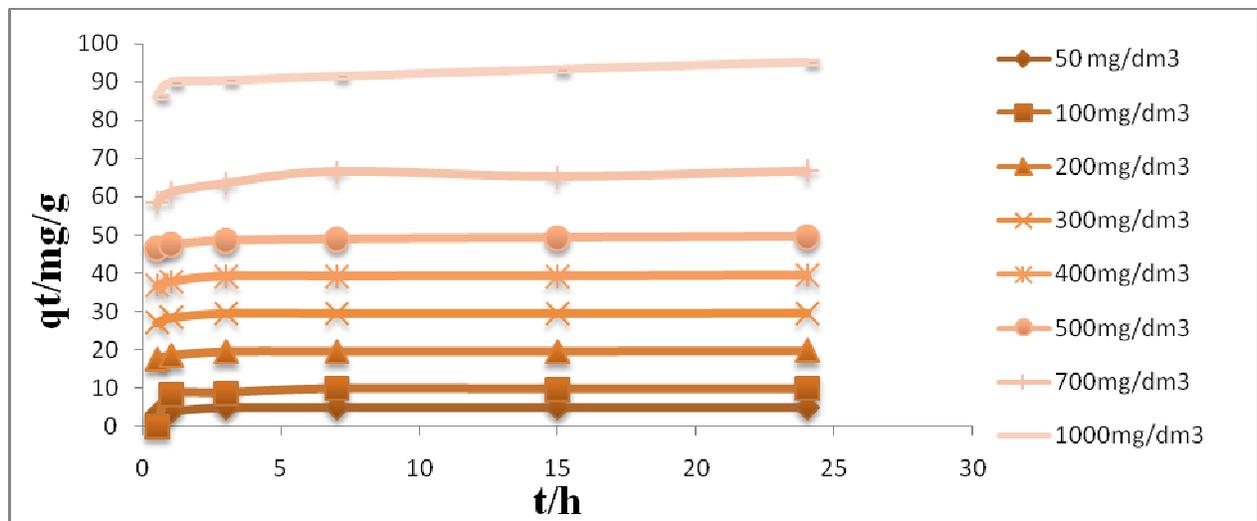
at different solution pH ranging from 2 to 10. Agitation was provided for 3 hours contact time which is sufficient to reach equilibrium with a constant agitation speed of 250 rpm. The pH was adjusted by adding a few drops of diluted NaOH or HCl.

## RESULTS AND DISCUSSION

### Sorption kinetics

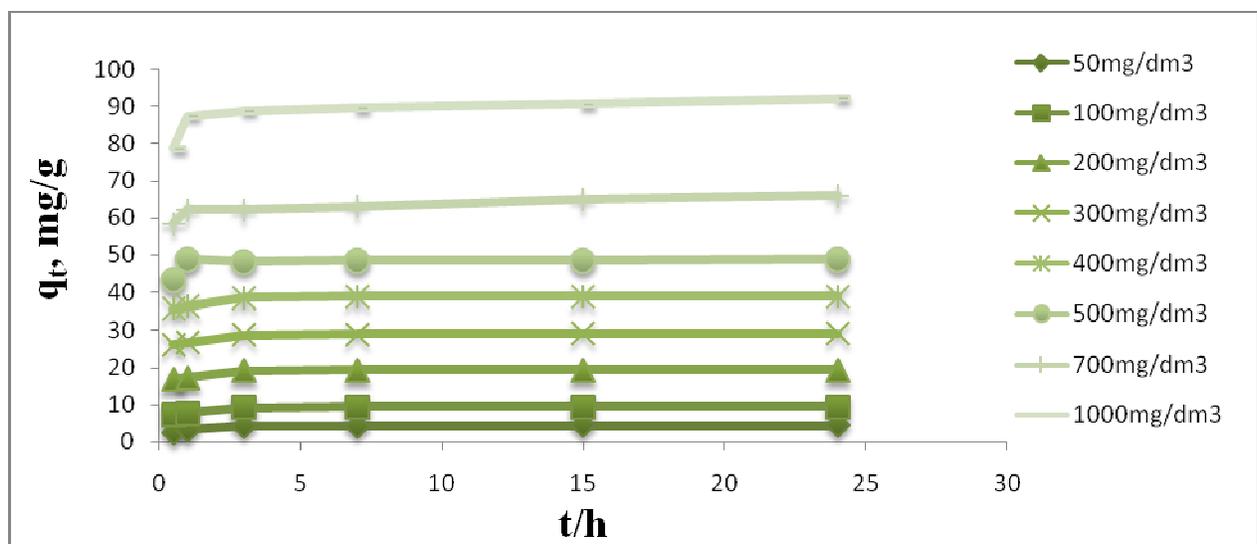
When designing a sorption processing system, it is desirable to know the rate at which the sorbate uptake will occur[4].

Therefore, the first step was testing the kinetics of sorption of methylene blue. Figure 2. and 3. illustrates the sorption of methylene blue for different initial concentrations of methylene blue between 50 and 1000 mg/dm<sup>3</sup> as a function of contact time.



**Figure 2.** Sorption of methylene blue on orange peel, pH = 6,5.

**Slika 2.** Sorpcija metilenskog modrila na koru naranče pH = 6,5.



**Figure 3.** Sorption of methylene blue on lemon peel, pH = 6,5.

**Slika 3.** Sorpcija metilenskog modrila na koru limuna pH = 6,5.

Figure 2. and figure 3. shows similar data for the orange and lemon peel. The effect of contact time on the removal of methylene blue by the orange and lemon peel at initial concentrations 50-500 mg/dm<sup>3</sup> showed rapid adsorption of dye in the first three hours. Such short times coupled with high removals indicate a high degree of affinity for the dye groups pointing towards chemisorption. The

adsorption rate decreased gradually and the adsorption reached equilibrium in about 7 hours for the initial concentration of 500 – 700 mg/dm<sup>3</sup>. At high initial concentrations (> 1000 mg/dm<sup>3</sup>), the time necessary to reach equilibrium was more than 24 hours (sorption of dyestuffs is still slightly growing). This observation could be explained by the theory that in process of

dye sorption, initially the dye molecules have to first encounter the boundary layer effect and then diffuse from boundary layer film onto sorbent surface and then finally, they have to diffuse into the porous structure of the sorbent. Therefore, methylene blue solutions of higher initial concentrations will take relatively longer contact time to attain equilibrium due to higher amount of dye molecules[5].

The experimental data for the sorption of methylene blue on orange and lemon peel were fitted using the pseudo-first-order (eq. 3) and pseudo-second-order kinetic models (eq. 4).

The Lagergren's equation is one of the most widely used rate equations to describe the sorption of an sorbate from the liquid phase. The linear form of pseudo-first-order equation is given as: (eq. 3):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Integrating this for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives (eq. 4):

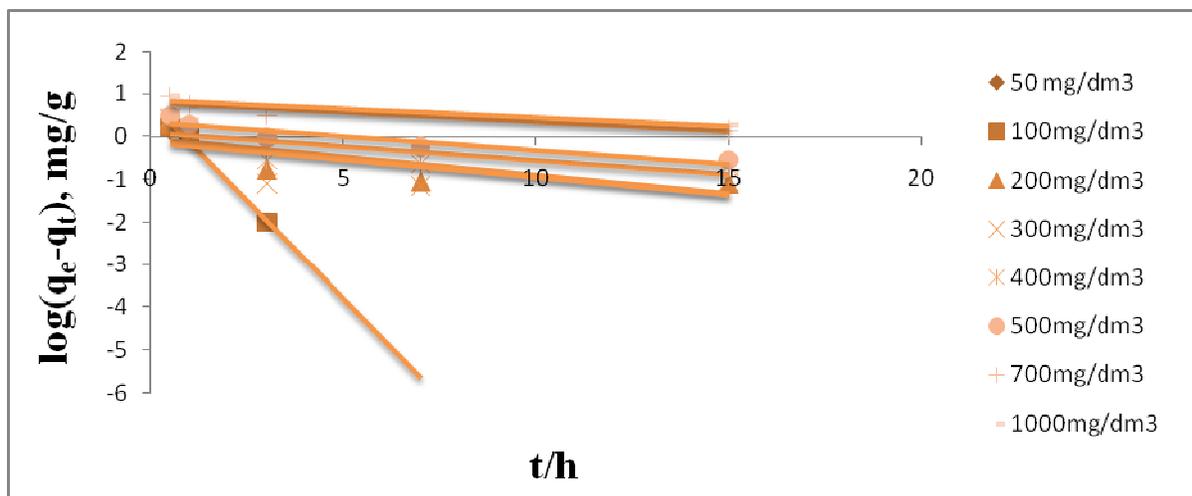
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where  $k_1$  is the rate constant (1/h),  $q_e$  the amount of solute sorbed on the surface at equilibrium (mg/g),  $q_t$  the amount of solute sorbed at any time (mg/g)[1]. The value of the sorption rate constant ( $k_1$ ) for methylene blue sorption by orange and lemon peel was determined from the plot of  $\log(q_e - q_t)$  against  $t$  (Figs.4.,6.).

The pseudo-second-order equation based on equilibrium sorption is expressed as:

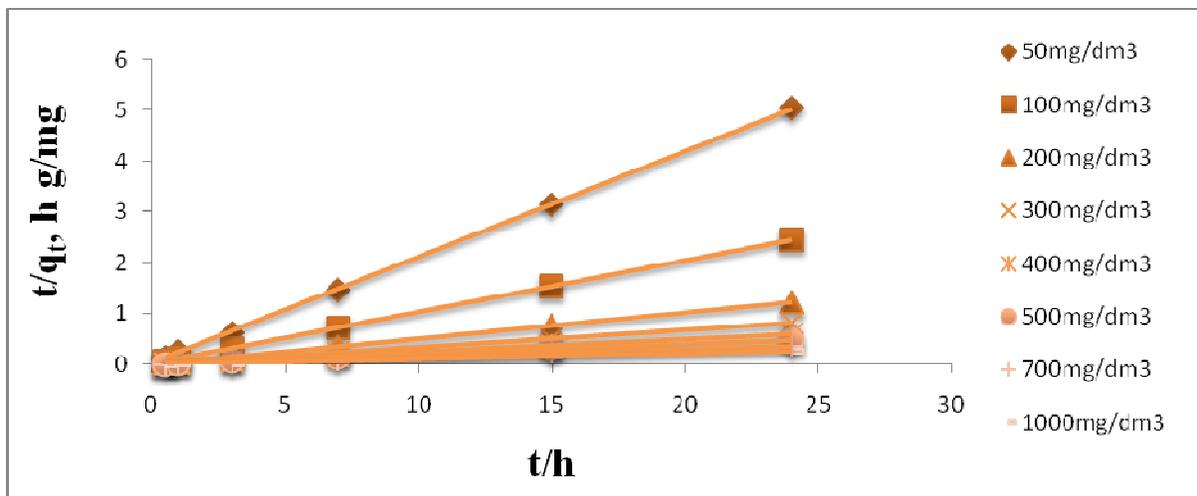
$$\frac{t}{q_t} = \frac{1}{k_2 q_r^2} + \frac{1}{q_r} t \quad (5)$$

where  $k_2$  (g/mg h) is the pseudo-second-order rate constant determined from the plot of  $t/q_t$  versus  $t$ , as shown in Fig. 5. and Fig. 7.



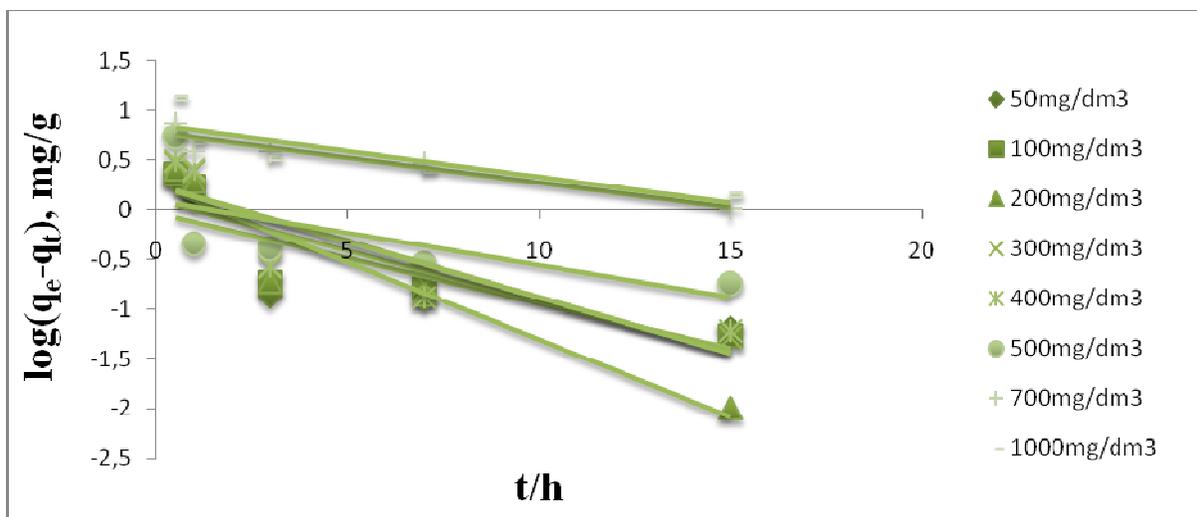
**Figure 4.** Pseudo-first-order sorption kinetics of methylene blue on orange peel.

**Slika 4.** Linearni oblik kinetičkog modela sorpcije pseudo – prvog reda na koru naranče.



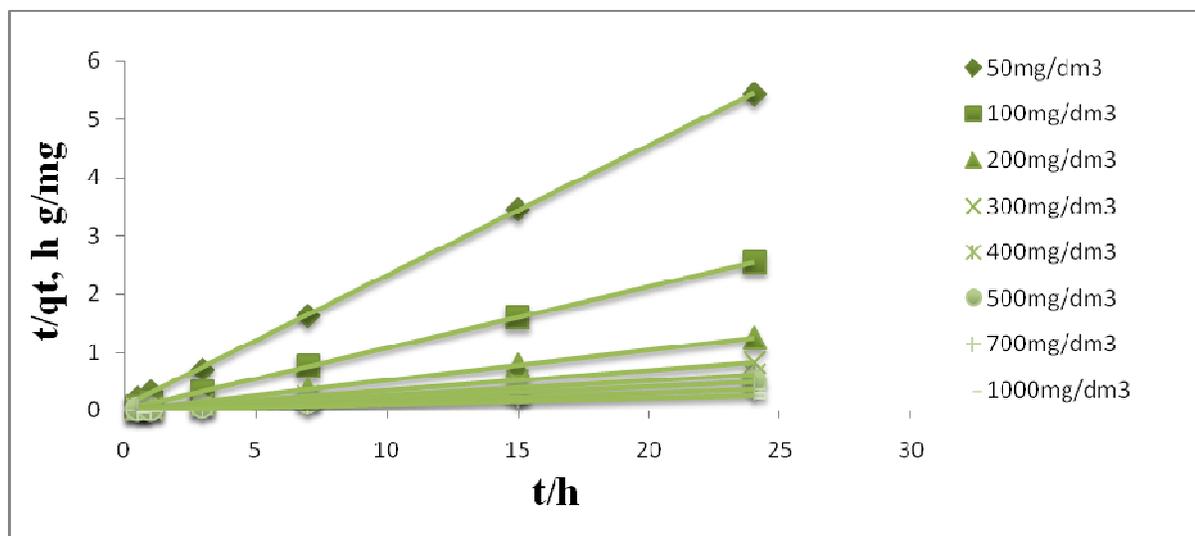
**Figure 5.** Pseudo-second-order sorption kinetics of methylene blue on orange peel.

**Slika 5.** Linearni oblik kinetičkog modela sorpcije pseudo – drugog reda na koru naranče.



**Figure 6.** Pseudo-first-order sorption kinetics of methylene blue on lemon peel.

**Slika 6.** Linearni oblik kinetičkog modela sorpcije pseudo – prvog reda na koru limuna.



**Figure 7.** Pseudo-second-order sorption kinetics of methylene blue on lemon peel.

**Slika 7.** Linearni oblik kinetičkog modela sorpcije pseudo – drugog reda na koru limuna.

The parameters of pseudo-first and pseudo-second-order model for orange and lemon peel are summarized in Table 1. and Table 2. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the sorption processes. Although the correlation coefficients,  $R^2$ , for the application of the pseudo-first-order model are reasonably high in some cases, the calculated  $q_e$  is not equal to experimental  $q_e$ , suggesting the sorption of orange and lemon peel is not likely to be pseudo-first order for the initial concentrations examined[1].

For most of the papers found in the bibliography whose data have been modelled using this equation, a good fit between experimental and theoretical model data were obtained in the early stages of sorption. In fact, the pseudo-first-order approach assumes that the uptake rate is limited by

only one process or mechanism acting on a single class of sorbing sites. So, this model does not seem to be appropriate for a heterogeneous surface, since multiple sorption sites and mass transfer effect may exist[4].

The calculated  $q_e$  values agree very well with the experimental values for the case of pseudo-second-order kinetics, and a regression coefficient of above 0,99 shows that the model can be applied for the entire sorption process and confirms the chemisorption of methylene blue onto orange and lemon peel[1]. The pseudo-second-order model is based on the assumption that the rate-limiting step may be a chemical sorption involving valence forces through the sharing or exchange of electrons between sorbent and sorbate[4]. Contrary to the pseudo-first order equation, this model adequately predicts the sorption behaviour over the whole sorption period.

**Table 1.** Comparison of the pseudo-first-order, pseudo-second-order sorption rate constants and calculated and experimental  $q_e$  values obtained at different initial methylene blue concentrations for orange peel.

**Tablica 1.** Konstante brzina sorpcije metilenskog modrila na koru naranče prema modelima pseudo – prvog i pseudo-drugog reda te eksperimentalne i izračunate  $q_r$  vrijednosti pri različitim koncentracijama bojila; MB=metilensko bojilo.

Orange peel	$q_{r,exp}$ (mg/g)	Pseudo – first-order			Pseudo – second-order		
$\gamma(\text{MB}), \text{mg/dm}^3$		$k_1$ (1/h)	$q_{r,calc}$ (mg/g)	$R^2$	$k_2$ (g/mg h)	$q_{r,calc}$ (mg/g)	$R^2$
50	4,76	2,08	0,53	0,9851	1,37	4,81	0,9999
100	9,75	2,13	0,64	0,9884	1,27	9,79	1
200	19,70	0,20	0,74	0,6305	1,14	19,72	1
300	29,56	0,19	0,90	0,4424	0,92	29,59	1
400	39,49	0,15	1,28	0,5678	0,58	39,53	1
500	49,46	0,15	2,18	0,8731	0,34	49,51	1
700	66,60	0,10	6,22	0,8489	0,14	66,67	0,9998
1000	95,03	0,09	6,96	0,9001	0,07	95,24	0,9998

**Table 2.** Comparison of the pseudo-first-order, pseudo-second-order sorption rate constants and calculated and experimental  $q_e$  values obtained at different initial methylene blue concentrations for lemon peel.

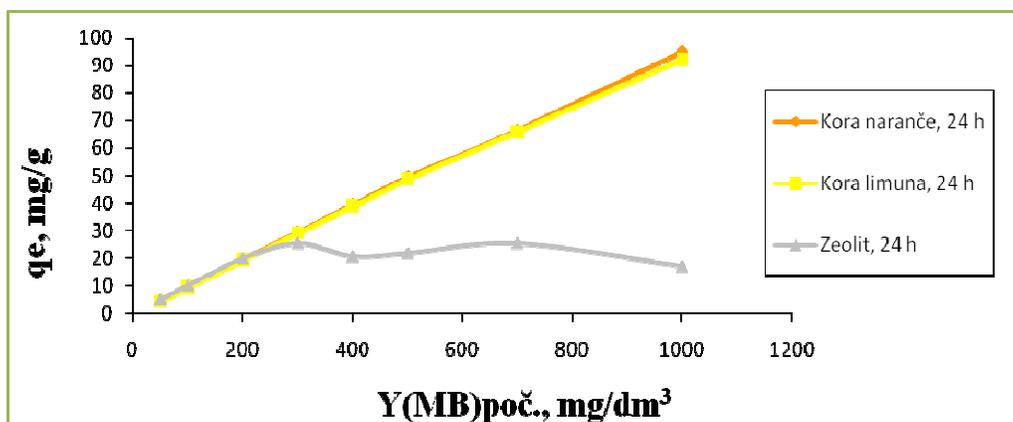
**Tablica 2.** Konstante brzina sorpcije metilenskog modrila na koru limuna prema modelima pseudo – prvog i pseudo-drugog reda te eksperimentalne i izračunate  $q_r$  vrijednosti pri različitim koncentracijama bojila; MB=metilensko bojilo.

Lemon peel	$q_{r,exp}$ (mg/g)	Pseudo – first-order			Pseudo – second-order		
$\gamma(\text{MB}), \text{mg/dm}^3$		$k_1$ (1/h)	$q_{r,calc}$ (mg/g)	$R^2$	$k_2$ (g/mg h)	$q_{r,calc}$ (mg/g)	$R^2$
50	4,41	0,21	0,93	0,6592	0,66	4,47	0,9999
100	9,39	0,24	1,25	0,7579	0,65	9,46	1
200	19,27	0,36	1,77	0,9081	0,66	19,34	1
300	29,10	0,26	1,78	0,8048	0,53	29,15	1
400	38,84	0,26	1,75	0,7633	0,55	38,91	1
500	48,60	0,15	1,22	0,4477	0,53	48,54	1
700	65,93	0,11	5,86	0,8994	0,09	66,23	0,9998
1000	92,1	0,12	7,05	0,7197	0,09	92,59	0,9999

### Isotherm studies

Sorption isotherms are basic requirements for designing any sorption system. Figure 8. shows the sorption isotherms of methylene blue onto orange and lemon peel and zeolite clinoptilolite. From Figure 8. it can be seen that the capacity of

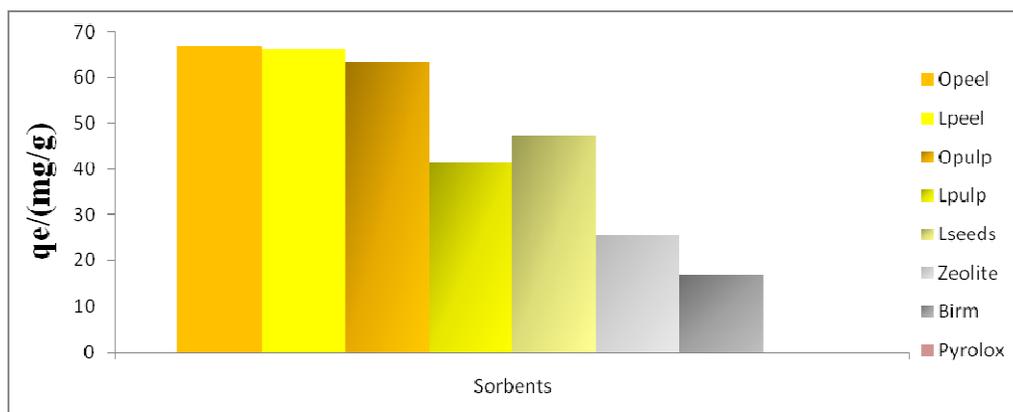
zeolite is about 20 mg/g. The capacity of orange and lemon peel was not determined because the highest used concentration of methylene blue ( $1000 \text{ mg/dm}^3$ ) was not sufficient to determined capacity. It can be concluded that the capacity of orange and lemon peel for methylene blue is much higher than the capacity of zeolite.



**Figure 8.** Sorption isotherms of methylene blue onto orange and lemon peel and zeolite.  
**Slika 8.** Izoterme sorpcije metilenskog modrila na korama naranče, limuna te na zeolitu.

In Figure 9. is given the sorption of methylene blue onto different sorbents (orange and lemon peel, orange and lemon pulp, zeolite, Pyrolox and Birm) at concentration of methylene blue  $700 \text{ mg/dm}^3$  after 24 hours. From Figure 9 it can be seen

that the best sorbents are orange and lemon peel and orange pulp. Lemon pulp and lemon seeds was sorbing less methylene blue. Of all examined sorbents the worst was Pyrolox, where there was no sorption.

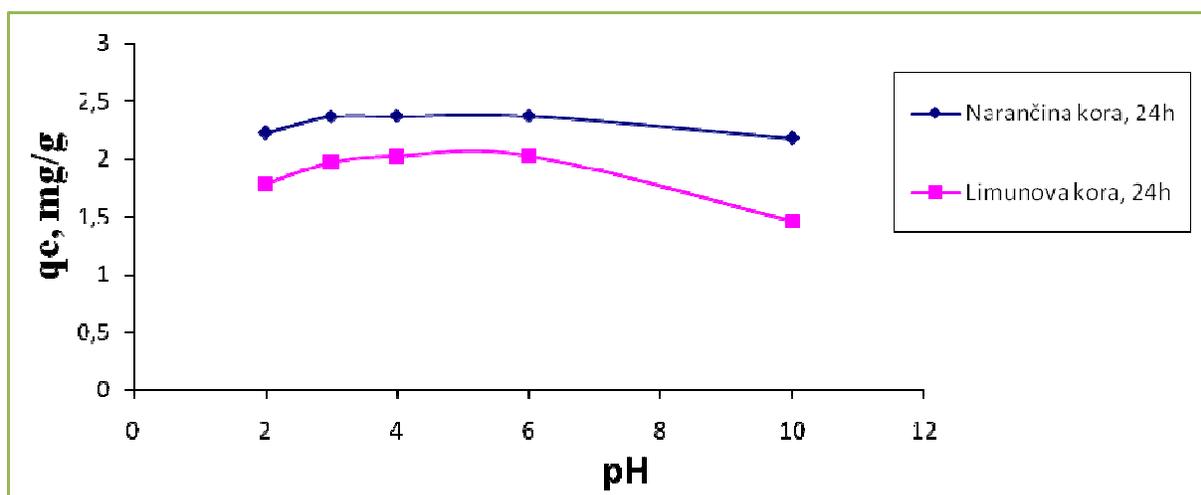


**Figure 9.** Sorption of methylene blue onto different sorbents,  $\gamma$  (MB) =  $700 \text{ mg/dm}^3$ ,  $t = 24 \text{ h}$ .  
**Slika 9.** Usporedba različitih sorbensa pri koncentraciji metilenskog modrila,  $\gamma$ (MB) =  $700 \text{ mg/dm}^3$ ;  $t = 24 \text{ h}$ .

### Effect of solution pH on dye sorption

The effect of initial pH on equilibrium uptake capacity of orange and lemon peel was studied at  $25 \text{ mg/dm}^3$  initial methylene blue concentration and at  $25^\circ\text{C}$ . Figure 10. shows that the sorption of methylene blue was minimum at the initial pH = 2 and increased with pH up to 4 and then remained nearly constant over the initial pH ranges of 4 – 7. Cellulose fibers are negatively charged due to functional groups related to the base

polymer whose dissociation depends on the pH of the solution. The main carriers of negative charge are carboxyl groups[6]. Carboxylic acids are weaker than inorganic acids, but much stronger than the alcohol and phenol. Most unsubstituted carboxylic acids at room temperature has an approximate value of  $\text{pK} = 3\text{-}5$ . Therefore, the lower sorption of methylene blue at  $\text{pH} < 4$  can be overwritten to a lower dissociation of carboxyl groups.



**Figure 10.** Effect of solution pH on the sorption of methylene blue on orange and lemon peel ( $\gamma_0 = 25 \text{ mg/dm}^3$ ,  $T = 25^\circ\text{C}$ ).

**Slika 10.** Utjecaj pH vrijednosti otopine na sorpciju metilenskog modrila na korama naranče i limuna,  $\gamma(\text{MB}) = 25 \text{ mg/dm}^3$ ;  $T = 24^\circ\text{C}$ .

### CONCLUSIONS

The present work shows that orange and lemon peel are an efficient sorbents for the removal of methylene blue from aqueous solution and it may be an alternative to more costly sorbents such as activated carbon. Kinetic studies suggest that methylene blue sorption on orange and lemon peel sorbents could be described more favorably by the pseudo-second-order kinetic model. Sorption rate constants,  $k_2$ , for orange and lemon peel decrease with increasing concentration of

methylene blue in the solution. When the pH of the solution was 2-3, the sorption of methylene blue was slightly weaker than at pH 3-6 due to poor dissociation of carboxyl groups. In the studied concentration range  $50\text{-}1000 \text{ mg/dm}^3$  sorption of methylene blue on orange and lemon peel is a linear, with sorption efficiency of approximately 100%. The capacity of zeolite for methylene blue is  $20 \text{ mg/g}$ . Sorption capacity of citrus waste is significantly higher than in the mineral sorbent (zeolite clinoptilolite, Pyrolox, Birm).

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