ISSN 1848-0071
582.746.21+535.375.5=111
Recieved: 2014-01-15
Accepted: 2014-03-05
Original scientific paper

# METHYLENE BLUE SORPTION CHARACTERISATION ONTO ORANGE AND LEMON PEELS

**MIRELA ROŽIČ, IRA SENJI, SNEŽANA MILJANIĆ[1]**

University of Zagreb, Faculty of Graphic Arts, Zagreb, Croatia
[1]University of Zagreb, Faculty of Science, Department of Chemistry, Zagreb, Croatia
e-mail: mirela.rozic@grf.hr

Chemical properties of cationic biosorbents, the orange peel and the lemon peel, have been studied. ATR and Raman spectra indicated that the functional groups in the peels structure responsible for dye sorption are carboxyl groups (COOH and COOM, M=$Na^+$,$K^+$,$Ca^{2+}$,$Mg^{2+}$) and hydroxyl groups (OH). Increasing the mass of the peels in water suspensions a decrease in dissociation of both, the –COOH and –COOM groups was obtained. Sorption isotherms of methylene blue onto the biosorbents had two sorption plateaus. Hence the carboxyl groups interacted with methylene blue up to the first plateau, while sorption by also the hydroxyl groups occurred from the first to the second plateau. A very good agreement between the amounts of the carboxyl groups estimated in the peels and the amounts of the dye molecules sorbed onto the peels was obtained.

**Key words:** biosorbent, peel, characterization, methylene blue.

**Karakterizacija sorpcije metilenskog modrila na kore naranče I limuna.** Ispitivana su kemijska svojstva kationskih biosorbensa, kore naranče i kore limuna. ATR i Raman spektri pokazuju da su funkcijske skupine u strukturi kora na kojima dolazi do sorpcije bojila karboksilne (COOH i COOM, M=$Na^+$,$K^+$,$Ca^{2+}$,$Mg^{2+}$) i hidroksilne (OH) skupine. Povćanjem mase kora u vodenim suspenzijama smanjuje se stupnj disocijacije COOH i –COOM skupina. Izoterme sorpcije metilenskog modrila na biosorbensima sastoje se od dva sorpcijska platoa. Karboksilne skupine djeluju s metilenskim modrilom do prvog platoa, dok se od prvog do drugog platoa metilensko modrilo sorbira na hidroksilne skupine. Dobiveno je vrlo dobro slaganje između količina karboksilnih skupina u korama i količina sorbiranih molekula bojila.

**Ključne riječi:** biosorbens, kora, karakterizacija, metilensko modrilo.

## INTRODUCTION

Water resources are of critical importance to both natural ecosystem and human developments. Increasing environmental pollution from industrial wastewater particularly in developing countries is of major concern. Many industries like dye industries, textile, paper and plastics use dyes in order to color their products hereby consuming substantial volumes of water. As a result they generate a considerable amount of colored wastewater. The presence of small amount of dyes (less than 1 mg $dm^{-3}$) is highly visible and undesirable. Many of these dyes are also toxic and even carcinogenic and pose a serious threat to living organisms [1].

Among the various types of dyes, many cationic dyes, such as methylene blue, are used in paint production and dyeing. Applications of methylene blue include paper and hair coloring, cottons and wools dyeing, paper stock coating, etc. Methylene blue is also employed in microbiology, surgery, diagnostics, trace analysis of anionic surfactants present in aqueous streams and as a sensitizer in photo oxidation of organic pollutants. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue may cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [2].

Dyes are extremely stable due to their complex aromatic molecular structure, and are thus difficult to biodegrade. Hence, there is a need to treat the wastewaters containing toxic dyes before they are discharged into the waterbodies [3].

Some physico-chemical methods like coagulation, flocculation, membrane separation, oxidation, etc. are available for the treatment of dyes. Major drawbacks of these methods are high sludge production, handling and disposal problems, high cost, technical constraints, etc. [1].

The increasing awareness and concern about the environment inspired research of new efficient technologies that would be capable of treating inexpensively wastewaters polluted by dyes [1]. Adsorption has been reported to be efficient and economical for the treatment of wastewaters containing dyes, pigments and other colorants [4]. Granular activated carbon has been used successfully, but is cost-prohibitive. This led to search for cheaper biosorbents derived from agricultural and wood wastes [3]. Biosorption has many advantages including low cost, the selective removal of pollutants, biosorbent regeneration and metal recovery potentiality as well as no sludge generation [5].

Several sorbents are currently used which are by-products from agriculture products such as wool, rice, straw, peat moss, coconut fibre, etc. Adsorption/ biosorption using low cost adsorbents could be technically feasible and economically viable sustainable technology for the treatment of wastewater streams. Low cost adsorbents are nothing but materials that require little processing, are abundant in nature or are a byproduct or waste material from another industry [1].

Fruit waste materials are typically generated in large quantities by the fruit juice industry. These materials have received little scientific attention, in spite of their high quantity of pectin, which contains carboxylate groups. The plant cell wall polysaccharide pectin consists mostly of polygalacturonic acid, partially esterified with methyl groups. Pectin polymers with a low degree of esterification (low methoxyl pectin) can cross-link through calcium bridging between two deprotonated carboxylate groups [6].

Orange peel (OP) and lemon peel (LP) are one of the valuable agriculture biomass wastes, principally consisting of cellulose, hemicellulose, lignin and pectin substances [7]. In the world, oranges take up 75% of the total citrus fruits [8]. Thus, a lot of the orange and lemon peels are available throughout the world.

The present work has been done in order to evaluate the application potential of OP and LP as an inexpensive and environment friendly material for the removal of methylene blue (MB) from aqueous solutions. The present study reports sorption potential of the peels through measurement of sorption isotherms, in batch conditions. Characterization of biosorbents has been performed by means of vibrational spectroscopy (infrared and Raman) and by determination of carboxylic groups (acidic and alkaline) present in the peels.

## MATERIALS AND METHODS

### Materials

Methylene blue (MB), a cationic dye of molecular formula $C_{16}H_{18}N_3SCl$, was purchased from Kemika, Zagreb, Croatia, and its chemical structure is shown in Fig. 1. Model wastewaters used in the experiments were prepared by dissolving the dye in deionised water resulting in concentrations from 0.17 to 5.90 mmol $dm^{-3}$. The concentrations of the dye were measured with a DR/890 Hach colorimeter.

Orange and lemon peels were cut in small pieces of size 1–3 mm. They were used as sorbent materials after the following treatment: 10 g of peels were vigorously stirred in 2 $dm^3$ of distilled water in a beaker (at a speed of 400 rpm) by a magnetic stirrer at a room temperature of 25±1°C during 4 hours, then filtered, washed with distilled water for several times and after filtration oven-dried at 80 °C for 24 hours.

### FT-infrared spectroscopy

FT-infrared spectra were taken on a Bruker Equinox 55 spectrometer using the technique of attenuated total reflectance (ATR). For the measurement of solid samples the PIKE MIRacle ATR sampling accessory with a diamond/ZnSe crystal plate and a pressure clamp was used.

Solid samples were grounded in an agate mortar prior to placement on the ATR crystal. The ATR spectra were recorded in the single reflection configuration, in the spectral range between 4000 and 600 $cm^{-1}$ at the resolution of 4 $cm^{-1}$. 32 scans were averaged for a spectrum.

### FT-Raman spectroscopy

FT-Raman spectra were taken on a Bruker Equinox 55 interferometer equipped with the FRA 106/S Raman module using Nd-YAG laser excitation at 1064 nm and the laser power of 500 mW. Raman spectra were recorded from the solid samples on an aluminium holder. Spectra were taken in the 3500–100 $cm^{-1}$ range. To obtain a good spectral definition, 128 scans at the spectral resolution of 4 $cm^{-1}$ were averaged for a spectrum.

### Determination of the carboxyl groups in peels

Amounts of the protonated carboxyl groups in biosorbents were determined by potentiometric titration. Suspensions of 0.120 g, 0.500 g and 1.000 g of a peel in 100 $cm^3$ of distilled water were titrated with NaOH ($c$ = 0.1 mol $dm^{-3}$) up to pH 11. The change in pH of suspension was measured throughout the titration. The amount of the protonated carboxyl groups (–COOH) per gram of a sorbent (mmol $g^{-1}$) was evaluated using the equivalence point volume of NaOH according to the expression:

$$n(-\mathrm{COOH}) = \frac{V(\mathrm{NaOH}) \cdot c(\mathrm{NaOH})}{m(\mathrm{sorbent})} \quad (1)$$

Amounts of the deprotonated carboxyl groups (–$COO^-$) were determined by measuring exchangeable $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ ions in the peels. Samples were prepared by suspending 0.120 g, 0.500 g and 1.000 g of a biosorbent in 100 $cm^3$ of HCl, $c = 0.1$ mol $dm^{-3}$. The suspensions were kept at the room temperature for 5 days and periodically agitated. After that period, the supernatant containing metal ions was separated from the precipitate by centrifugation, and the concentrations of $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ ions were determined by atomic absorption spectrometry (AA-6800, Shimadzu).

### Sorption of methylene blue onto peels

Dye equilibrium isotherms were determined by mixing 0.120 g, 0.500 g and 1.000 g of a biosorbent material with dye solutions of different concentrations, 0.17–5.90 mmol $dm^{-3}$. The volume of the dye solutions was 100 $cm^3$. The prepared mixtures were agitated in 250 $cm^3$ conical flasks for a period of 24 hours at the room temperature. The contact time was previously determined by kinetics tests under the same conditions [9]. The equilibrium dye uptake, $q_e$, (mmol dye / g sorbent) was determined as follows:

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

where $c_0$ (mmol $dm^{-3}$) and $c_e$ (mmol $dm^{-3}$) are initial and equilibrium dye concentration, respectively, $V$ is the volume of solution ($dm^3$), and $m$ is the sorbent mass (g) in dry form.

## RESULTS AND DISCUSSION

### FT-infrared spectroscopy and FT-Raman spectroscopy

Orange peel and lemon peel consist of soluble and insoluble monomers and polymers. Water soluble fraction contains glucose, fructose and sucrose, while pectin, cellulose, hemicellulose and lignin make up between 50% and 70% of insoluble fraction. Sorption to biomaterials is attributed to active functional groups in the insoluble polymer fraction. ATR and Raman spectra of the lemon and orange peel were measured in order to identify these functional groups.

The bands in the ATR spectra are assigned to vibrations of different functional groups in the structure of the peels (Fig. 2). Very broad bands peaking at 3330 $cm^{-1}$ (LP) and 3336 $cm^{-1}$ (OP) correspond to the O–H stretching and indicate presence of the "free" and associated OH groups, alone and those in the protonated carboxyl groups [10]. Bands appearing at 2922 $cm^{-1}$ (LP), 2921 $cm^{-1}$ (OP), 2852 $cm^{-1}$ (LP) and 2853 $cm^{-1}$ (OP) are assigned to the antisymmetrical and symmetrical C–H stretching vibrations of the methylene, methoxy and methyl groups in carbohydrates [10–12]. Deformations of the corresponding groups give rise to bands around 1435 $cm^{-1}$ and 1365 $cm^{-1}$. In the spectra of both, the orange peel and the lemon peel, a band at 1733 $cm^{-1}$ is attributed to the stretching of the C=O bond in the ester groups [10–12]. The band of the stretching of the C=O group that participates in hydrogen bonding (the associated carbonyl group) is observed at 1645 $cm^{-1}$ in the orange peel spectrum, while in the lemon peel spectrum this band is overlapped by an intense band at 1616 cm$^{-1}$, assigned to the antisymmetrical stretching of the dissociated carboxyl groups ($COO^-$) [12]. Whereas the band of the antisymmetrical stretching mode of the $COO^-$ groups in the orange peel appears at 1607 cm$^{-1}$, it is very likely that the stretching of the C=O bond in the protonated carboxyl groups (COOH) contributes to the band at 1645 cm$^{-1}$ in the OP spectrum [10]. In the spectra of both, the lemon and orange peel, bands associated with the symmetrical stretching of the dissociated carboxyl groups ($COO^-$) are obtained at 1419 cm$^{-1}$ [11]. The C–O stretching in the deprotonated carboxyl group ($COO^-$) is observed at 1316 cm$^{-1}$ (LP) and 1319 cm$^{-1}$ (OP). Bands of medium intensity at 1235 cm$^{-1}$ (LP) and 1234 cm$^{-1}$ (OP) as well as broad intense bands in the spectral range between 1100 cm$^{-1}$ and 1000 cm$^{-1}$ are attributed to stretching vibrations of the C–O bonds in carbohydrate molecules [11]. The ATR spectra clearly show that the dominant functional groups in the studied peels structure are protonated carboxyl groups (COOH), deprotonated carboxyl groups ($COO^-$) and hydroxyl groups (OH). In addition, higher intensity of the bands assigned to vibrations of the deprotonated carboxyl groups (1616 cm$^{-1}$ and 1316 cm$^{-1}$) in the LP spectrum, in comparison with the OP spectrum, implies that there is more $COO^-$ groups in the lemon peel than in the orange peel.

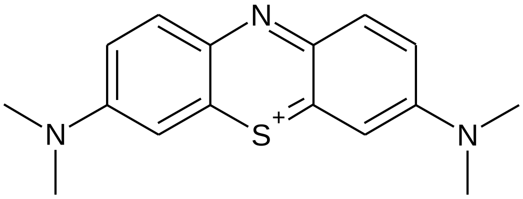


**Figure 1.** Chemical structure of methylene blue
**Slika 1.** Kemijska struktura metilenskog modrila

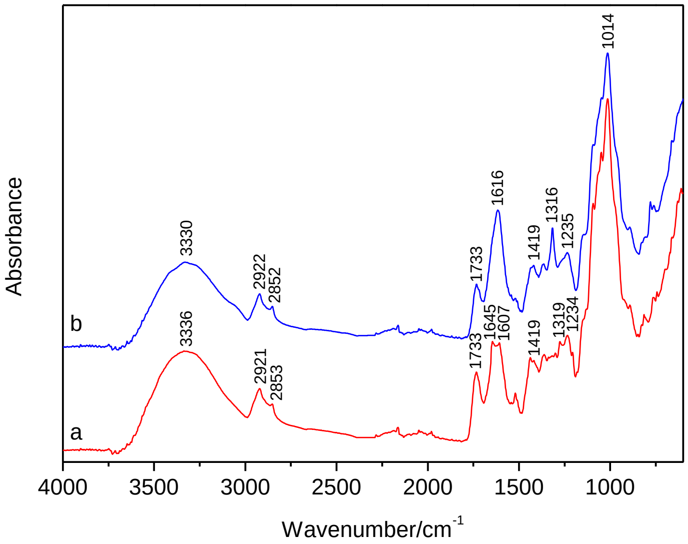


**Figure 2.** ATR spectra of a) the orange peel and b) the lemon peel
**Slika 2.** ATR spektar a) kore naranče i b) kore limuna

Raman spectra of the orange and lemon peel are shown in Fig. 3. A broad intense band at 2938 cm$^{-1}$ with the shoulder around 2910 cm$^{-1}$ is attributed to the antysimmetrical and symmetrical C–H stretching in the methylene and methyl groups. Bending vibrations of the corresponding groups are observed around 1460 cm$^{-1}$ and 1330 cm$^{-1}$. A weak band at 1742 cm$^{-1}$ (LP) and 1743 cm$^{-1}$ (OP) is assigned to the stretching of the carbonyl group in esters. A broad pattern of the overlapping bands in the spectral range between 1670 cm$^{-1}$ and 1570 cm$^{-1}$ is assigned to the CC stretchings in the phenol groups of lignin and to the stretching mode of the carbonyl groups (1627 cm$^{-1}$ (LP), 1624 cm$^{-1}$ (OP)) in pectin. Bands originated from the symmetrical stretching of the dissociated carboxyl groups in pectin are obtained at 1609 cm$^{-1}$ (LP) and 1605 cm$^{-1}$ (OP), while the symmetrical stretching of the respective groups produce bands at 1373 cm$^{-1}$ (LP) and 1378 cm$^{-1}$ (OP). A band at 1304 cm$^{-1}$ in the orange peel spectrum is associated with the COH bending in the protonated carboxyl group, whereas a corresponding shoulder is observed at 1308 cm$^{-1}$ in the lemon peel spectrum. Bands below 1200 cm$^{-1}$ correspond mainly to the C–O bond stretching as well as deformations of the COC and CCO groups of glucopyranose in the structures of pectin, cellulose and hemicellulose. Even though the LP and OP spectra resemble each other, a medium intensity band at 895 cm$^{-1}$, ascribed to the out of plane bending of the O=C–O group in carboxylic acid is more intense in the LP spectrum than in the OP spectrum. On the other hand, a low intensity band at 768 cm$^{-1}$, assigned to the in plane bending of the O=C–O group in ester, is stronger in the OP spectrum.

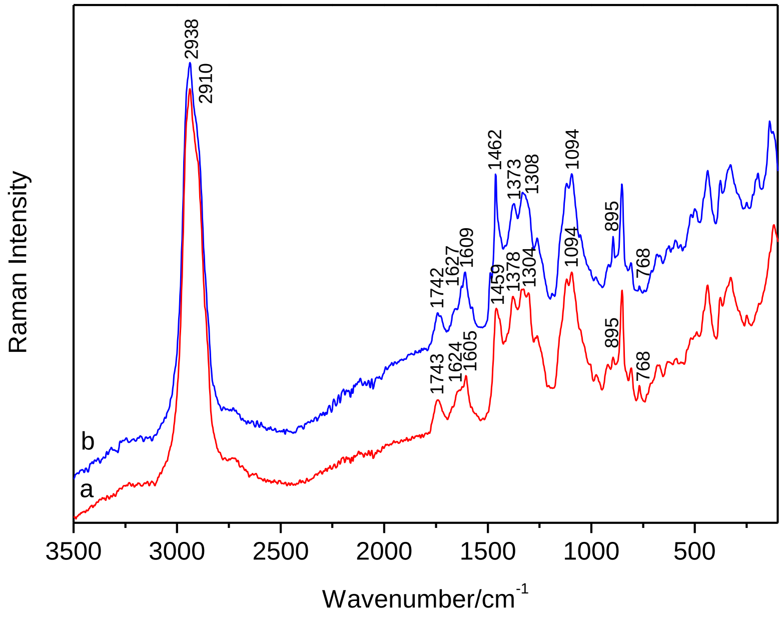


**Figure 3.** Raman spectra of a) the orange peel and b) the lemon peel
**Slika 3.** Raman spektar a) kore naranče i b) kore limuna

Providing structural data about interacting species, vibrational spectroscopy has been already used as a very useful tool in study of the interaction mechanism involved in the treatment of wastewater [13]. Here, FT-IR spectroscopy has been applied to reveal interactions between methylene blue and the studied peels. Fig. 4 shows the ATR spectrum of methylene blue, while the ATR spectra of OP and LP before and after sorption of the dye from the methylene blue solutions (0.62 mmol dm$^{-3}$ and 4.13 mmol dm$^{-3}$) on 0.120 g of the peels are given in Figs. 5 and 6. Bands that correspond to vibrations of the aromatic moiety of methylene blue appear in the spectra of the peels with the sorbed dye (Figs. 5.b,c and 6.b,c) [14,15]. In comparison with the spectrum of methylene blue (Fig.4), significant shifts to higher wavenumbers in the spectra of the peels treated with the dye solution of the lower concentration (0.62 mmol dm$^{-3}$) are observed for the CN stretching band (from 1593 cm$^{-1}$ to 1601 cm$^{-1}$ (LP) and 1600 cm$^{-1}$ (OP)) as well as for the CS stretching band (from 1222 cm$^{-1}$ to 1231 cm$^{-1}$ (LP) and 1232 cm$^{-1}$ (OP)). Bands of the CC stretching in the aromatic rings, on the other hand, are either very slightly downshifted (1–2 cm$^{-1}$) or appear at the same wavenumbers as in the spectrum of the dye. Due to an extensive overlap in the 1650–1250 cm$^{-1}$ range, bands originating from the peel could not be analyzed. Nevertheless, observed spectral changes indicate that methylene blue is sorbed onto the peels most likely due to interactions of the positively charged central ring of the dye molecule with the carboxyl groups in the peels structure. When treated with the dye solution of the higher concentration (4.13 mmol dm$^{-3}$), bands that originate from the aromatic dye system are also present in the spectra, but the prominent change concerns the band of the O–H stretchings from the constituents of the peels. If compared to the spectra of the untreated bisorbents (Figs. 5.a and 6.a), this band shifts to the lower values for approximately 15 cm$^{-1}$ and 50 cm$^{-1}$ for the peels exposed to the lower and higher dye concentration, respectively. The obtained downshifts are attributed to the weakening of the O–H bonds due to participation of the hydroxyl groups in interactions with methylene blue, which become more pronounced while increasing concentration of the dye. Apart from the carboxyl groups, interactions with the hydroxyl groups from the peel structure also contribute to the sorption of methylene blue.

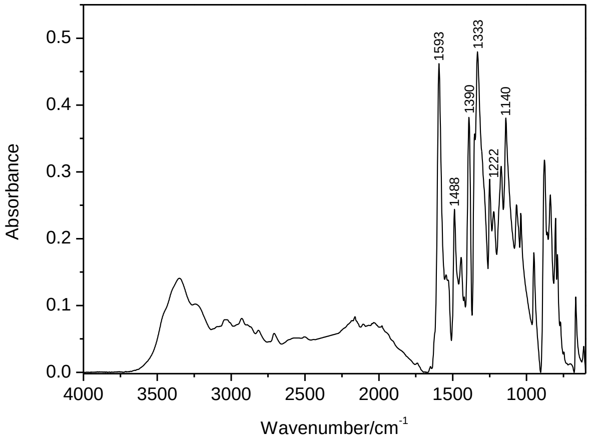


**Figure 4.** ATR spectrum of methylene blue
**Slika 4.** ATR spektar metilenskog modrila

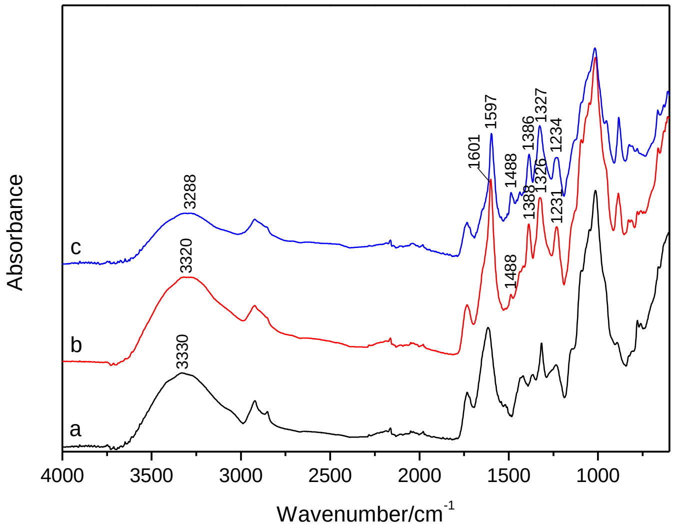


**Figure 5.** ATR spectra of a) the lemon peel, b) the lemon peel after sorption of 0.62 mmol dm$^{-3}$ methylene blue, c) the lemon peel after sorption of 4.13 mmol dm$^{-3}$ methylene blue; *m*(peel)= 0.120 g, *V*(dye solution) = 100 cm$^3$

**Slika 5.** ATR spektar a) kore limuna, b) kore limuna nakon sorpcije metilenskog modrila iz otopine 0.62 mmol dm$^{-3}$, c) kore limuna nakon sorpcije metilenskog modrila iz otopine 4.13 mmol dm$^{-3}$; *m*(kora)= 0.120 g, *V*(otopine bojila) = 100 cm$^3$

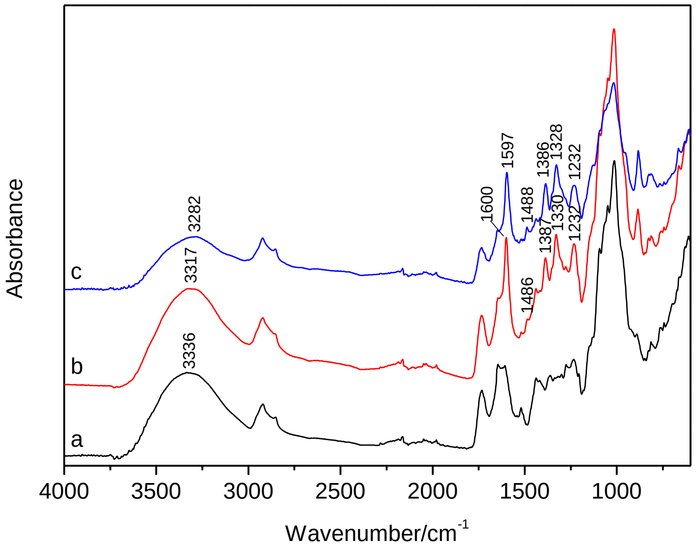


**Figure 6.** ATR spectra of a) the orange peel, b) the orange peel after sorption of 0.62 mmol dm$^{-3}$ methylene blue, c) the orange peel after sorption of 4.13 mmol dm$^{-3}$ methylene blue; *m*(peel)= 0.120 g, *V*(dye solution) = 100 cm$^3$

**Slika 6.** ATR spektar a) kore naranče, b) kore naranče nakon sorpcije metilenskog modrila iz otopine 0.62 mmol dm$^{-3}$, c) kore limuna nakon sorpcije metilenskog modrila iz otopine 4.13 mmol dm$^{-3}$; *m*(kora)= 0.120 g, *V*(otopine bojila) = 100 cm$^3$

## Determination of the carboxyl groups in peels

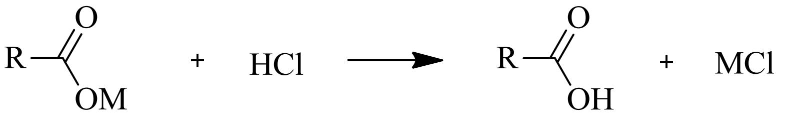
The carboxyl groups are the main carriers of a charge in OP and LP. The phenol hydroxyl groups are much weaker acids and alkaline conditions (pH > 9) are needed for their ionization. In general, different types of hydroxyl groups in alcohols are weak acids which are ionized only in strongly alkaline solutions [16].

Amounts of the protonated carboxyl groups (–COOH) in biosorbent samples were determined by potentiometric titration. Suspensions of 0.120 g, 0.500 g and 1.000 g of peels in 100 $cm^3$ water were titrated with 0.1 M NaOH. Results of the potentiometric titrations are shown in Fig. 5. The shape of the titration curves indicate only one type of the acidic groups in the sorbents, which dissociates in the pH range from 4 to 11 (–COOH). Increasing the sorbent mass in suspensions, slopes of the curves relative to the volume axis decrease. The equivalence point is estimated from the inflection point of the potentiometric curve. To obtain a more accurate value, the first derivative curve, $\Delta pH/\Delta V$, as a function of the added NaOH volume is used, when the maximum of the calculated curve corresponds to the equivalence point. However, the maxima of the first derivative curves are obtained only for the suspensions containing the lowest mass of biosorbent (0.120 g/100 $cm^3$). During titrations of suspensions with the higher content of peels, changes in pH with the addition of the alkaline solution decrease. Using the values of the NaOH volume at the equivalence point, amount of the protonated –COOH groups in biosorbent samples are calculated (Table 1). The highest amounts of the protonated carboxyl groups per 1 g of a biosorbent, 0.340 mmol $g^{-1}$ (OP) and 0.290 mmol $g^{-1}$ (LP), result from the titrations of the suspensions with the lowest mass of peels. The obtained data can be explained by the fact that carboxylic acids are weak acids, and its dissociation depends on the concentration of the acid in solution [17]. As the concentration of the carboxylic acids increases (i.e. mass of biosorbents in solution), the percent dissociation decreases, lowering concentration of the $H^+$ ions per 1 g of a sorbent which can be neutralized with the $OH^-$ ions.

**Table 1.** Amounts of the protonated carboxyl groups in the biosorbent samples
**Tablica 1.** Količine protoniranih karboksilnih skupina u uzorcima biosorbensa

| *m*(peel)/g | *n*(–COOH)/mmol $g^{-1}$ |
|---|---|
| LP | |
| 0.120 | 0.290 |
| 0.500 | 0.210 |
| 1.000 | 0.180 |
| OP | |
| 0.120 | 0.340 |
| 0.500 | 0.220 |
| 1.000 | 0.195 |

Except for the protons from the –COOH groups, cationic dyes in solution can be exchanged with the metal cations, which are primarily electrostatically bound with the –COO$^-$ groups in sorbents. In order to estimate amounts of the deprotonated carboxylic groups (–COO$^-$) in peels, concentrations of the $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ ions are determined in suspensions of 0.120 g, 0.500 g and 1.000 g biosorbent prepared in 100 cm$^3$ HCl. The metal cations exchange with the protons from the acid by reaction:



(3)

where M are $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$.

According to the chemical reaction (3) the amounts of $K^+$, $Na^+$, ½ $Ca^{2+}$, ½ $Mg^{2+}$ are equivalent with the amount of the –COO$^-$ groups in the biosorbents. Results of measurements of the respective ions in the supernatants of the acidic suspensions by atomic absorption spectrometry are given in Table 2. The highest concentrations of the exchanged cations per one gram of the sorbent, related to the highest amounts of the –COO$^-$ groups, characterize the suspensions with the lowest mass of the peels. Increasing the biosorbent mass, the bases weaken resulting in the lower amounts of the –COO$^-$ groups evaluated per one gram of the peel. In addition, the results suggested that the lemon peel contains a larger amount of the –COO$^-$ groups than the orange peel, which is in agreement with the data obtained from the ATR and Raman spectra (Fig. 2).

The total amounts of the exchangeable cations, $H^+$, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$, i.e. the total ion exchange capacity of the peels determined in the suspensions of 0.120 g sorbent / 100 cm$^3$ are 0.640 mmol g$^{-1}$ for the lemon peel and 0.615 mmol g$^{-1}$ for the orange peel. The total amounts of the –COOH and –COO$^-$ groups for 0.500 g and 1.000 g of the peel in the 100 cm$^3$ suspensions are 0.456 mmol g$^{-1}$ (LP) and 0.393 mmol g$^{-1}$ (OP), and 0.407 mmol g$^{-1}$ (LP) and 0.356 mmol g$^{-1}$ (OP), respectively.

**Table 2.** Amounts of the deprotonated carboxyl groups in the biosorbent samples
**Tablica 2.** Količine deprotoniranih karboksilnih skupina u uzorcima biosorbensa

| $m$(peel)/g | $n$(1/z $M^{z+}$)/mmol g$^{-1}$ | | | | $n$(–COO$^-$)/mmol g$^{-1}$ |
|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ | |
| LP | | | | | |
| 0.120 | 0.224 | 0.040 | 0.082 | 0.004 | 0.350 |
| 0.500 | 0.190 | 0.037 | 0.018 | 0.001 | 0.246 |
| 1.000 | 0.174 | 0.036 | 0.015 | 0.002 | 0.227 |
| OP | | | | | |
| 0.120 | 0.131 | 0.035 | 0.085 | 0.024 | 0.275 |
| 0.500 | 0.106 | 0.028 | 0.013 | 0.026 | 0.173 |
| 1.000 | 0.099 | 0.028 | 0.009 | 0.025 | 0.161 |

## Sorption of methylene blue onto peels

Sorption isotherms of the lemon peel and the orange peel for methylene blue are shown in Figs. 6 and 7. The sorption isotherm is a fundamental expression that correlates the sorbent and the concentration of sorbate in bulk solution at constant temperature under equilibrium conditions. Isotherms concerning 0.120 g and 0.500 g of the peels are characterized by two sorption plateaus. Very similar two-stage-shape behavior has been already obtained in the study by Schiewer and Patil [6]. The observed shape of the sorption curves is attributed to different interactions involved in sorption of methylene blue onto the peels dependent on the dye concentration. It is very likely that at dye concentrations lower than 2.50 mmol dm$^{-3}$ methylene blue interact with the protonated and deprotonated carboxyl groups in the peels structure, while at dye concentrations higher than 2.50 mmol dm$^{-3}$ interactions between the dye and the hydroxyl groups get more pronounced (Fig. 6). Involvement of the –OH groups in interactions with methylene blue is also suggested by the ATR spectra (Fig. 2). According to the first sorption plateau 0.650 mmol g$^{-1}$ and 0.615 mmol g$^{-1}$ of methylene blue is sorbed onto 0.120 g of the lemon peel and the orange peel, respectively, from the dye solution of 2.56 mmol dm$^{-3}$. The amounts of the sorbed dye are very similar to the amounts of the –COOH and–COO$^{-}$ groups determined in the peels, 0.640 mmol g$^{-1}$ (LP) and 0.615 mmol g$^{-1}$ (OP).

Increasing the mass of the biosorbent in solution, the first sorption plateau shifts towards higher concentrations of the dye (Fig. 7). Hence the first plateau is reached during sorption of 3.13 mmol dm$^{-3}$ and 4.70 mmol dm$^{-3}$ methylene blue onto 0.500 g and 1.000 g of the sorbent, respectively. The values of the dye sorbed from the 3.44 mmol dm$^{-3}$ methylene blue solution onto 0.500 g of the biosorbent, 0.450 mmol g$^{-1}$ for the lemon peel and 0.405 mmol g$^{-1}$ for the orange peel, resemble the amounts of the carboxyl groups determined in the peels (0.456 mmol g$^{-1}$ (LP) and 0.393 mmol g$^{-1}$ (OP)). A very good agreement is also obtained with the amounts of the carboxyl groups present in 1.000 g of the peels (0.407 mmol g$^{-1}$ (LP) and 0.356 mmol g$^{-1}$ (OP)) for which amounts of methylene blue sorbed on the lemon peel, 0.386 mmol g$^{-1}$, and on the orange peel, 0.350 mmol g$^{-1}$, from the 4.70 mmol dm$^{-3}$ dye solution are evaluated. Unlike the sorption isotherms observed for the suspensions containing 0.120 g and 0.500 g of the peels, the sorption curve of the 1.000 g biosorbent lacks the second plateau, implying involvement of the hydroxyl groups in interactions with the dye in a lesser degree in the studied concentration range. Nevertheless, close values of the concentrations of the dye sorbed onto the peels and the amounts of the carboxyl groups in the structure of the peels indicate potential application of the methylene blue sorption as a method for determination of the total amount of the carboxyl groups in the peels, i.e. the total ion exchange capacity of the peels.

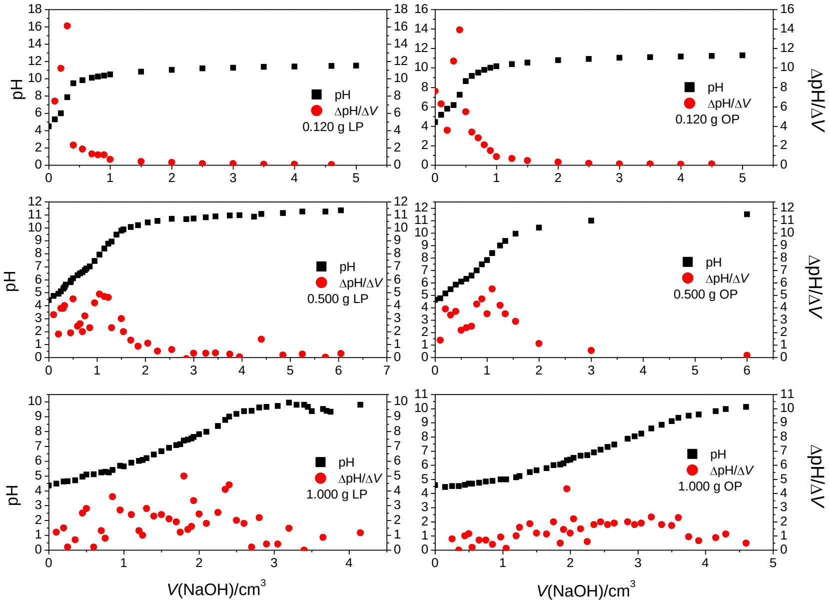


**Figure 7.** Potentiometric titration curves and first derivative curves ΔpH/ΔV for titrations of aqueous suspensions of the lemon and orange peels with 0.1 M NaOH; *m*(peel) = 0.120 g, 0.500 g and 1.000 g; *V*(suspension) = 100 cm$^3$

**Slika 7.** Krivulje potenciometrijske titracije i diferencijalne krivulje ΔpH/ΔV za titracije vodenih suspenzija kora limuna i naranče s 0.1 M NaOH; *m*(kore) = 0.120 g, 0.500 g i 1.000 g; *V*(suspenzije) = 100 cm$^3$

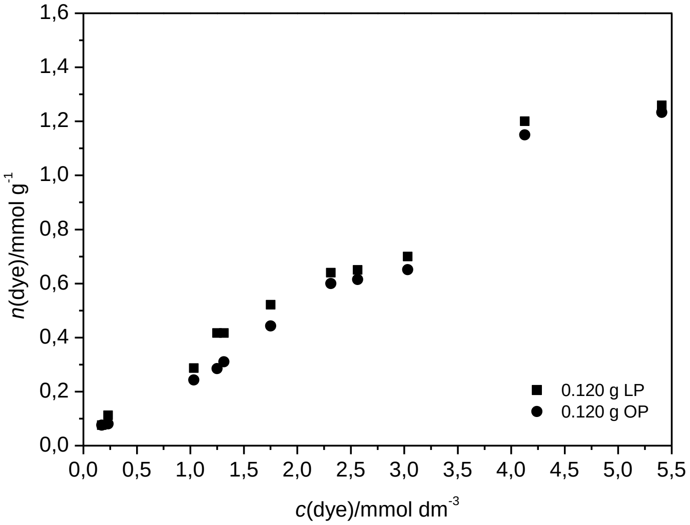


**Figure 8.** Isotherm of methylene blue sorption onto the lemon and orange peels; *m*(biosorbent) = 0.120 g, *V*(dye solution) = 100 cm$^3$, *t* = 24 h

**Slika 8.** Izoterma sorpcije metilenskog modrila na kore limuna i naranče; *m*(biosorbens) = 0.120 g, *V*(otopine bojila) = 100 cm$^3$, *t* = 24 h

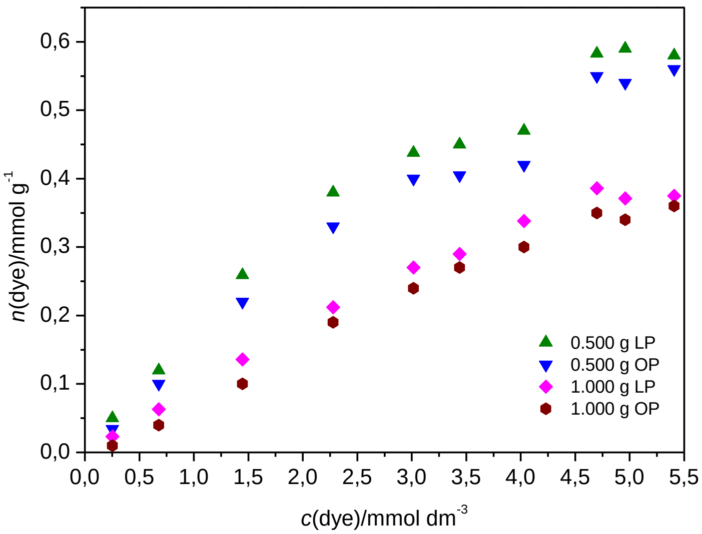


**Figure 9.** Isotherms of methylene blue sorption onto the lemon and orange peels; *m*(biosorbent) = 0.500 g and 1.000 g, *V*(dye solution) = 100 cm$^3$; *t* = 24 h

**Slika 9.** Izoterme sorpcije metilenskog modrila na kore limuna i naranče; *m*(biosorbens) = 0.500 g, i 1.000 g, *V*(otopine bojila) = 100 cm$^3$, *t* = 24 h

## CONCLUSION

From the above study it may be concluded that the orange and lemon peels have great potential to be used as low cost sorbents for effective removal of cationic dyes from water. Vibrational spectra point to the carboxyl and hydroxyl groups as the dominant functional groups in the structure of the studied biosorbent samples.

An increase in a sorbent dose at a constant dye concentration leads to an increase in methylene blue sorption but also to saturation of the sorption sites during the sorption process. At the higher peel to solute concentration ratios, there is a lower percent dissociation of the –COOH and –COOM groups so the portion of $H^+$, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ ions, which can be exchanged with the cationic dye from the solution, diminishes. The two-stage-shape behavior of the measured sorption isotherms is due to two different binding sites with distinctive affinities for the dye. The binding sites with the stronger affinity for the dye are –COOH and –COOM groups, which become saturated at the dye concentrations indicated by the first plateau of the sorption curves, while the binding sites with the lesser affinity for the dye are –OH groups. Similar values of the amounts of the carboxylic groups determined in the peels and the amounts of the cationic dye sorbed onto the peels imply that the sorption of methylene blue can be used as a method for determination of the total ion exchange capacity of the peels.

## REFERENCES

[1] M. Jayarajan, R. Arunachalam, G. Annadurai, Agricultural wastes of jackfruit peel nano-porous adsorbent for removal of rhodamine dye, Asian J. Appl. Sci. 4 (3) (2011), pp. 263-270.

[2] H. Benaissa, Equilibrium study of methylene blue sorption from aqueous solutions by a low-cost waste material: almond peel, Eleventh International Water Technology Conference, IWTC11 2007 Sharm El-Sheikh, Egypt 895.

[3] A. Saeed, M. Sharif, M. Iqbal, Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption, J. Hazard. Mater. 179 (2010), pp. 564-572.

[4] R. Gong, Y. Liu, Y. Jiang, C. Li, Isothermal, kinetic and thermodynamic studies on basic dye sorption onto tartaric acid esterified wheat straw, African Journal of Biotechnology 8 (24) (2009), pp. 7138-7147.

[5] G.K. Nagda, V.S. Ghole, Biosorption of congo red by hydrogen peroxide treated tendu waste, Iran. J. Environ. Health. Sci. Eng., 6 (3) (2009), pp. 195-200.

[6] S. Schiewer, S. B. Patil, Modeling the effect of pH on biosorption of heavy metals by citrus peels, J. Hazard. Mater. 157 (2008), pp. 8-17.

[7] B. Chen, Z. Chen, Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures, Chemosphere 76 (2009), pp. 127-133.

[8] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloids Surf. A 317 (2008), pp. 512-521.

[9] D. Kučić, S. Miljanić, M. Rožić, Sorption of methylene blue onto orange and lemon peel, The Holistic Approach to Environment 1 (2011), pp. 39-49.

[10] A.B. Perez Marin, M.I.Agilar, V.F. Meseguer, J.F. Ortuno, J. Saez, M. Llorens, (2009), Biosorption of chromium (III) by orange waste: Batch and continuous studies, Chem. Eng. J. 155 (2009), pp. 199-206.

[11] N. Feng, X. Guo, S. Liang, Adsorption study of copper (II) by chemically modified orange peel, J. Hazard. Mater. 164 (2009), pp. 1286–1292.

[12] S. Schiewer, A. Balaria, Biosorption of $Pb^{2+}$ by original and protonated citrus peel: Equilibrium, kinetics, and mechannism, Chem. Eng. J. 146 (2009), pp. 211–219.

[13] H. Zhang, Y. Tang, X. Liu, Z. Ke, X. Su, D. Cai, X. Wang, Y. Liu, Q. Huang, Z. Yu, Improved adsorptive capacity of pine wood decayed by fungi Poria cocos for removal of malachite green from aqueous solutions, Desalination 274 (2011), pp. 97-104.

[14] Z. Yu, S.S.C. Chuang, Probing methylene blue photocatalytic degradation by adsorbed ethanol with in situ IR, J.Phys. Chem. C 111 (2007), pp. 13813–13820.

[15] E.I. Unuabonah, G.U. Adie, L.O. Onah, O.G. Adeyemi, Multistage optimization of the adsorption of methylene blue dye onto defatted Carica papaya seeds, Chem. Eng. J. 155 (2009), pp. 567–569.

[16] E. Sjostrom, R. Alen, Analytical methods in wood chemistry, pulping, and papermaking, Springer, 1998.

[17] Levine, I. N., Physical Chemistry, sixth ed., McGraw Hill Companies, New York, 2009.