Plant waste materials from restaurants as the adsorbents for dyes

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Abstract

This paper has demonstrated the valorization of inexpensive and readily available restaurant waste containing most consumed food and beverage residues as adsorbents for methylene blue dye. Coffee, tea, lettuce and citrus waste have been utilized without any pre-treatment, thus the adsorption capacities and dye removal efficiency were determined. Coffee waste showed the highest adsorbent capacity, followed by tea, lettuce and citrus waste. The dye removal was more effective as dye concentration increases from 5 up to 60 mg/L. The favorable results obtained for lettuce waste have been especially encouraged, as this material has not been commonly employed for sorption purposes. Equilibrium data fitted very well in a Freundlich isotherm model, whereas pseudo-second-order kinetic model describes the process behavior. Restaurant waste performed rapid dye removal at no cost, so it can be adopted and widely used in industries for contaminated water treatment.

Keywords: adsorption, dye, restaurant waste, isotherms, kinetics.

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The discharge of dyes in the environment is a matter of concern for both toxicological and aesthetic reasons. Many industries use dyes in order to color their products. As a result, they generate a considerable amount of colored wastewater. Most of the dyes are toxic, mutagenic and carcinogenic [1]. Furthermore, wastewater containing dyes is very difficult to be treated, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents [2]. Many techniques have been investigated for such purposes [3–14], but adsorption is considered to be relatively superior to others, because of low cost, simplicity of design and ability to treat dyes in more concentrated form [15]. Besides activated carbons, these are well known commercial adsorbents, some waste materials may also offer an inexpensive and renewable additional alternative for such processes. Waste materials have little or no economic value and often present a disposal problem [16].

According to the authors' knowledge, no attempt has been made to use restaurant food waste for removal of dyes from contaminated waters. Restaurants daily generate large quantities of food residues. Thus, coffee and tea waste, followed by lettuce and mix of citrus fruit waste have been utilized for sorption purposes. This waste is inexpensive and does not require an additional pre-treatment step before its application. In addition, an efficient management of such waste is very desirable. Methylene blue (MB) dye was selected as a model compound in adsorption experiments. It is a basic dye with the structure of heterocyclic aromatic chemical compound [17] that has been widely applied, including coloring paper, temporary hair colorations, dyeing cottons, wools, and coating for paper stock [18]. In water streams, it can cause some harmful effects on human health [18].

The aim of this study was to evaluate the adsorption capacity of restaurant waste, without any pre-treatment, for methylene blue dye removal from its aqueous solutions. The work has been designed to represent a comparative review of coffee, tea, lettuce and citrus residues capabilities for MB uptake efficiency. The second objective was to investigate the sorption equilibrium behaviors using several most commonly used isotherm models. Finally, kinetic studies have been conducted in order to determine the rate of MB adsorption and analyze the mechanism of the process for each of the tested adsorbents.

MATERIAL AND METHODS

Materials

Coffee residues, as well as tea, lettuce and citrus residues were obtained from „Hotel-Restaurant Hyatt", Belgrade, Serbia. All materials, one by one, separately, were rinsed well with distilled water to remove any dirt, and then were dried in an oven at 110 °C for 24 h. Dry materials were crushed and powdered. The pow-

dered materials (except for coffee residues) were sieved to obtain a particle size < 0.5 mm. Obtained samples were stored in sealed vials and used for further experimental work.

Preparation of dye stock solution

Methylene blue (MB) dye was obtained from Acros Organics, New Jersey, USA. A stock solution of 100 mg/L of the dye was prepared by dissolving 0.1 g in 1 L of distilled water. The working concentrations of the dye in aqueous solutions were varied from 5 to 60 mg/L by diluting the MB stock solution with distilled water. Fresh dilutions of desired dye concentrations were prepared at the beginning of each experiment, without any adjustment of pH values.

Dye adsorption experiments

100 mL of MB solutions with different initial concentrations of 5–60 mg/L were placed in a series of 250 mL Erlenmeyer flask. 0.70 g of the adsorbent was added into each flask and placed in translatory shaker (IKA – KS 4000i control, Staufen, Germany) at room temperature (27 °C), at 120 rpm, for the time period of 180 min. After a certain time, samples were collected, filtered and analyzed by UV/Vis spectrophotometer (Ultrospec 3300 pro, Amersham Biosciences, USA) at 668 nm for residual dye concentration. This experimental procedure has been repeated for each adsorbent individual. The MB removal in the aqueous solution was computed by monitoring the dye removal percentage (Eq. (1)) and adsorption capacity (Eq. (2)):

$$\text{MB removal (\%)} = 100\left(\frac{c_i - c_e}{c_e}\right) \qquad (1)$$

$$q = \frac{(c_i - c_e)V}{m_{ads}} \qquad (2)$$

where c_i and c_e are the initial and equilibrium MB concentrations (mg/L), respectively, q is the adsorption capacity (mg/g), m_{ads} is adsorbent dose (g) and V is solution volume (L) [19]. All the experiments were performed in triplicate and their mean values have been reported here.

Adsorption isotherms

Equilibrium experiments were conducted by contacting of 100 mL of different initial dye concentrations (5, 10, 20, 40, 50 and 60 mg/L) with 0.70 g of the adsorbent in six different capped 250 mL Erlenmeyer flasks. The contact was made using a translatory shaker at a constant agitation speed of 120 rpm, at room temperature of 27 °C. The agitation has been made for 180 min. Samples were collected, filtered and analyzed spectrophotometrically at 668 nm.

The most widely used isotherm models, named Langmuir, Freundlich, Temkin–Pyzhev and Dubinin––Radushkevich, have been employed for adsorption isotherm modeling of the experimental data.

The Langmuir model assumes that the adsorbent surface contains energetically homogenous cites, where the monolayer surface coverage is formed with no interactions between the molecules adsorbed [20]. The model can be presented in the linear form of modified Langmuir-2 Equation:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{c_e} + \frac{1}{q_m} \qquad (3)$$

where q_e (mg/g) is the amount of dye adsorbed per unit weight of adsorbent, q_m (mg/g) indicates the monolayer sorption capacity of adsorbent and the Langmuir constant K_L (L/mg) is a direct measure of the intensity of adsorption [20].

The Freundlich isotherm model considers multilayer and heterogeneous surface adsorption [21]. The linear form of the model is given by the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log c_e \qquad (4)$$

where K_F (mg/g)(L/g)^n and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively [21].

The Temkin–Pyzhev isotherm also describes the behavior of an adsorption system on a heterogeneous surface [22,23]. It includes the assumption that the heat of adsorption of all the molecules in the layer decreases linearly with increasing surface coverage. The model equation is represented as follows:

$$q_e = \frac{RT}{b_T}\ln c_e + \frac{RT}{b_T}\ln A \qquad (5)$$

where R is the gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and A and b_T are the isotherm constant (mL/mg) and Temkin–Pyzhev constant (J/mol), respectively [22].

The Dubinin–Radushkevich isotherm is partly analogous to the Langmuir isotherm and it is relatively more commonly applied to distinguish between the physical and chemical adsorption [22]. It considers that the adsorption takes place on a single type of uniform pores, but it does not suppose a homogeneous surface or constant adsorption potential [22]. The model equation is described as follows:

$$\ln q_e = -\beta\varepsilon^2 + \ln q_m \qquad (6)$$

where β is a constant related to the mean free energy of adsorption per mol of an adsorbate (mol^2/J^2) while ε is the Polanyi potential, equal to $RT\ln(1 + 1/c_e)$ [22].

Kinetic studies

Adsorption kinetic experiments were conducted under the same conditions as previously described adsorption isotherms procedure. Samples were taken at predetermined time intervals, filtered and analyzed spectrophotometrically.

The controlling mechanism of the adsorption process was investigated by fitting pseudo-first- and second-order kinetic models to the experimental data.

The pseudo-first-order model considers a reversible equilibrium of adsorbates between a liquid and a solid phase [24]. The linearized first-order kinetic model is given as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

where q_e and q_t are the amount of dye adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of pseudo-first-order kinetics [21].

The pseudo-second order kinetics assumed that the rate-limiting step might be the chemical adsorption, in which concentrations of both adsorbate and adsorbent were involved [22]. The linearized second-order kinetic model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where q_e and q_t have the same meaning as mentioned previously and k_2 (g/(mg min)) is the rate constant for the pseudo-second-order kinetics [21].

Adsorption mechanism

An intraparticle diffusion model was defined by using the following equation [21]:

$$q_t = k_{pi}t^{1/2} + c_i \tag{9}$$

where k_{pi} (mg/(g min$^{1/2}$)) is the rate parameter of stage i, and is obtained from the slope of the straight line of q_t *versus* $t^{1/2}$. C_i is the plot intercept and represents the boundary layer effect [21].

Statistical analysis

Results are shown as the mean ± standard deviation (*SD*). One-way analysis of variance (ANOVA) was applied for each parameter. Tukey test was used as a test a posteriori with a level of significance of 95%. All statistical analyses were performed using the Origin Pro 8 software package.

RESULTS AND DISCUSSION

Effect of contact time on dye removal

Increasing the duration of contact time causes an increased amount of dye uptake (Figure 1). The adsorp-tion of MB onto coffee and tea waste was rapid during the initial stage of the contact period. It occurred within the first 30 min and then gradually slowed down while it reached equilibrium. In terms of effectiveness and efficiency of adsorption process, completion of the process within a short time is extremely important for industrial applications [25]. Similar results have been obtained by Nasuha *et al.* (2010) [17] for the initial adsorption stage of MB onto rejected tea within the first 40 min. The fast adsorption at the initial stage may be due to the fact that a large number of surface sites are available for adsorption. After a lapse of time, the remaining surface sites are difficult to be occupied, probably because of the repulsion between the solute molecules of the solid and bulk phases make it took long time to reach equilibrium [21]. In addition, the later process regime may also be followed by slower adsorption inside the pores of adsorbents [1].The same observations have been previously reported by Dutta *et al.* (2011) these have investigated the MB removal using citrus fruit peel [26].

MB uptake onto citrus waste, as well as lettuce waste, was in a constant increase during the examined contact time, except in a case of two lowest concentrations of 5 and 10 mg/L, where the dye uptake was almost insignificant. These materials require extended contact time for the establishment of process equilibrium. Nevertheless, results obtained in this study have been improved, in terms of faster reaching the equilibrium, compared to literature reports. For example, Ahmad and Rahman (2011) [21] have noted that contact time of 5 h was required for reaching the equilibrium in the process of RBO3R dye adsorption onto coffee husks (with the initial dye concentrations of 25––50 mg/L), while the other study by Oliveira *et al*. (2008) [27] indicated that 12 h of the contact time assured attainment of equilibrium onto coffee husks for all initial MB concentrations evaluated up to 400 mg/L. In addition, adsorption equilibrium has been reached within 5 h for methylene blue adsorption onto tea waste, wherein the dye concentrations were in a range of 20–50 mg/L [28].

Effect of concentration on dye removal

The amount of MB adsorbed per unit of mass of adsorbent increased with the increase in initial concentration, bearing in minds all of tested adsorbents. Raising the dye concentration from 5 to 60 mg/L allows the adsorbents to increase their sorption capacities. The phenomenon has also been reported previously in the literature [17,28–32]. The initial dye concentration provides an important driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases [21]. At higher initial dye concentrations, the number of molecules competing for the available sites on the surface of activated carbon was
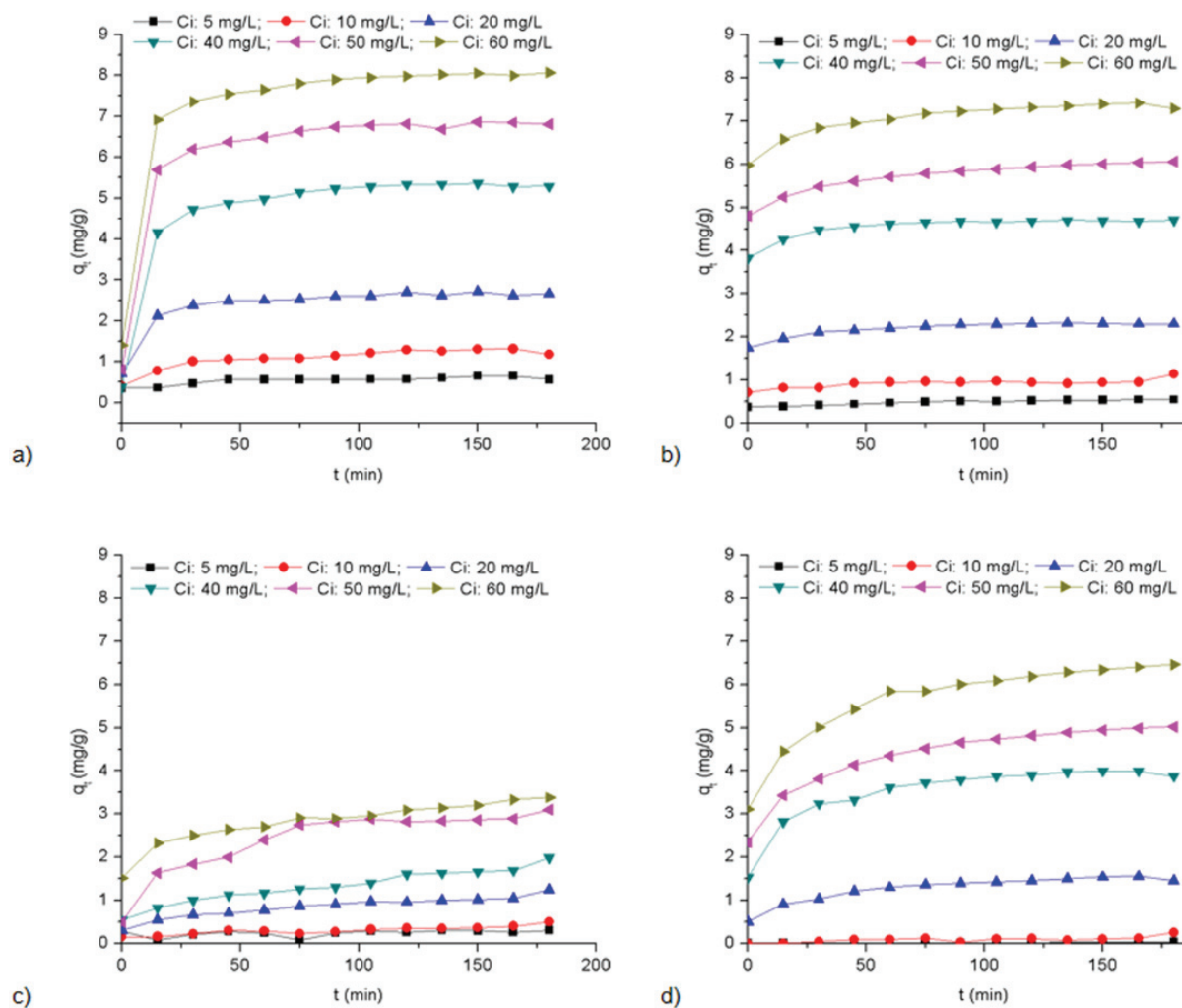
Figure 1. Effect of contact time on methylene blue dye adsorption onto: coffee waste (a), tea waste (b), citrus waste (c) and lettuce waste (d), at various initial dye concentrations (adsorbent mass: 7g/L, 120 rpm, 27 °C).

high, hence resulting in higher adsorption capacity. In fact, the ratio of the initial number of dye molecules to the available surface area is lower at a lower initial concentration compared to higher initial concentration [21]. Some researchers have observed the fast adsorption of dye at lower concentrations, as an indication that dyes adsorption occurs mainly on the surface of the adsorbent [27]. As the dye concentration increases, the adsorption process will probably occur in two stages: the first one at the adsorbent surface (faster) and the second one (slower) in the adsorbent pores [27]. It appears that in our investigation the dye concentration had not affected the adsorption speed.

Coffee waste expressed maximum adsorption capacity (8.07 mg/g), followed by tea waste (7.42 mg/g), lettuce waste (6.46 mg/g) and citrus waste (3.38 mg/g), respectively. It was observed that the adsorption capacities depend upon the sources of the raw materials used. Bearing in mind that many raw materials have been modified by various physical and chemical treatments (these include the use of more or less expensive

and adverse chemicals) in order to affect and improve the adsorption capacity, this study aims with the exemption of usage of any chemical agents and immediate utilization of raw restaurant waste. In addition, their cost approaches zero. The adsorption capacity of these unconventional adsorbents was due to their nature composition, and the variations in the content of polymers such as polysaccharides, lignin, hemicelluloses and cellulose, proteins, fats and a variety of other elements [33].

It is not uncommon that coffee and tea residues have been already applied as adsorbents for many types of adsorbates, and the obtained results were more or less improved, compared with the literature reports. Their main role in this investigation basically consisted as a reference point for assessing the effectiveness of other types of tested adsorbents. The research reports about the dye adsorption onto lettuce waste have been weak. It was an interesting that such rare type of adsorbent showed very good sorption capabilities, even better than those obtained for citrus

waste. In this respect, it may be suggested that dye sorption studies should take into further consideration lettuce waste as potential effective and available low cost adsorbent.

Coffee and tea waste performed better adsorption affinity in MB dye, compared to some heavy metals, evidenced by the following literature reports. Oliveira *et al.* (2008) [34] noted that adsorption capacities of untreated coffee husks were in a range from 5.57 up to 7.50 mg/g for copper, zinc, cadmium and chrome removal from its aqueous solutions. Also, Ahluwalia and Goyal (2005) [35] reported adsorption capacity of waste tea leaves for nickel removal of 5 mg/g. In addition, results presented in this paper were higher than those found for other nonspecific types of bio materials for MB adsorption capacity. For example, Ncibi *et al*. (2007) [36] reported adsorption capacities of 0.44 up to 4.64 mg/g of *Posidonia oceanica* (L.) fibers for MB uptake, as dye concentration raises from 10 to 50 mg/L, respectively. Another study by Hana *et al*. (2006) [32] noted chaff capacity for MB uptake of 3.60 mg/g after 60 min of contact.

It should be noted that higher adsorption capacities have been previously reported for MB uptake by tea waste [17], as well as orange peel [37]. Those materials were also utilized without any pretreatment, but some additional effects have been included in the investigation, like varying the pH of the dye solution and temperature, as well. Temperature effects have been exempted in this study, in terms of overall cost reduction, while preliminary experimental results showed that pH variations of initial dye solutions did not significantly affect the process efficiency (data not shown). Thus, pH remained unmodified during the entire period of the process duration. Some literature reports also testify about irrelevant pH effects in dye adsorption experiments [32].

The dye removal percentages of all tested adsorbents have been presented in Table 1.

Maximum obtained dye removal percentage was attained with coffee waste, followed by tea waste, lettuce waste and citrus waste, respectively. A comparative review of the effect of time on the percentages of MB removal of all tested adsorbents is graphically presented on Figure 2.
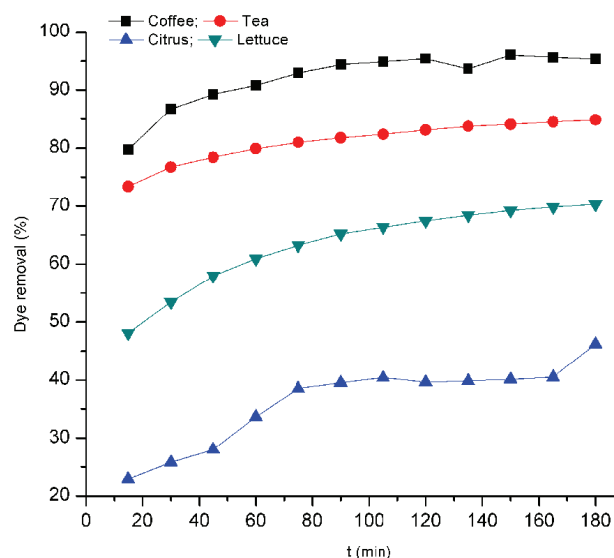

Figure 2. Effect of time on methylene blue dye removal on coffee, tea, lettuce and citrus waste (c_i: 50 mg/L, adsorbent mass: 7g/L, 120 rpm, 27 °C).

It was calculated that coffee waste removed almost 90% of initial dye concentration within 30 min from the start of the experiment, at the initial MB concentration of 60 mg/L. For the specified period of time, tea waste removed 80%, lettuce waste 60 % and citrus waste 30 % of the initial dye concentration. The results presented in this paper have been improved compared to previously reported. Oliveira *et al.* (2008) [27] noted that the amount of MB adsorbed onto coffee husks ranged from 70 to 85% after 2 h and from 90 to 96% after 12 h of contact, while Hana *et al*. (2006) [32] reported MB removal efficiency by chaff of 95% up to 60 min. Some researchers have observed the decline of MB removal percentage as the initial dye concentration increased [1,15,29]. Nevertheless, reported concentrations were much higher than those presented in this paper. The researchers explained that the increased number of dye molecules leads to saturation of adsorbent surface, and thus most of the dye adsorption took place slowly inside the pores [1]. The mentioned phenomena have not been observed within the range of concentrations tested in this paper. Thus, it might be said that dye molecules have been predominantly adsorbed on the outer surface.

Table 1. Maximum dye removal percentages for different methylene blue dye initial concentrations on coffee, tea, lettuce and citrus waste (adsorbent mass: 7 g/L, 120 rpm, 27 °C)

Adsorbent	c_i / mg L^{-1}					
	5	10	20	40	50	60
Coffee waste	91.41±0.37	92.20±0.34	94.44±0.38	93.86±0.09	96.03±0.13	94.16±0.13
Tea waste	76.61±0.54	79.41± 0.36	81.14±0.55	82.43±0.61	84.83±0.54	86.57±0.51
Lettuce waste	32.98±0.90	38.52±0.69	54.52±0.55	70.11±1.02	70.52±0.68	75.68± 1.16
Citrus waste	43.29±0.68	35.29±0.58	43.56±0.88	45.70±0.98	46.52±0.65	49.35±0.77

Equilibrium adsorption Isotherms

The adsorption equilibrium provides fundamental physiochemical data for evaluating the applicability of the sorption process as a unit operation [18]. The suitability of isotherm models has been mostly compared by judging the correlation coefficients, R^2. Isotherm model parameters are presented in Table 2. Only the Langmuir isotherm parameters were omitted due to wrong experimental data fitting. The Langmuir model calculations resulted in obtaining of negative parameter values, indicating to it's completely incompatibility to fit the actual sorption system. This fact might be the first note referring that adsorbents surfaces were not homogenous nor we can exclude assumptions that the interactions exist between adsorbed molecules.

The Freundlich isotherm model exhibited better experimental fit than both the Temkin–Pyzhev and Dubinin–Radushkevich, respectively, for all of tested adsorbents. This assumption primary indicates that the sorption process was based on sorption on a heterogeneous surface or surface supporting sites of varied affinities [21]. By comparing K_F values, it was confirmed that the highest sorption capacity possesses coffee waste, followed by tea, lettuce and citrus waste. Regarding to *n* values it was generally established that values of *n* > 1 illustrate that adsorbate is favorably adsorbed on the adsorbent whereas *n* < 1 demonstrate the adsorption process is chemical in nature [20,21]. *n* values obtained for all types of adsorbents were less than 1, demonstrated the adsorption process might be chemical in nature.

These results were somewhat expected. As raw materials were used, without any pre-treatment, it was unlikely that their surface contains homogenous cites, as the Langmuir model suggests. Literature reports about pre-treated coffee residues, these are used as dye adsorbents showed good agreement with Langmuir

isotherm [21]. The same was observed for tea waste [30], as well as orange peel [31].

Kinetic study

Adsorption kinetics describes the rate of adsorbate uptake governing the contact time of adsorption reaction [18,38]. The results showed that the sorption process followed a pseudo-second-order mechanism for all tested adsorbents, based on the high correlation coefficient values (Table 3). Further, compared with experimental results ($q_{e,exp}$), the values of $q_{e,cal}$ for the pseudo-second-order model were much more reasonable than those for the pseudo-first-order model. Most of the $q_{e,cal}$ values of the pseudo-first-order model deviated significantly from the experimental values. The best fit showed tea and coffee waste, followed by lettuce and citrus waste. Also, pseudo-second order model was developed on the principle that the rate limiting step may be chemisorption promoted by either valency forces, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the parties involved [27].

The pseudo-second-order kinetic plot for the adsorption of MB dye onto coffee, tea, lettuce and citrus waste is presented in Figure 3. The specified model follows the process with an overall tested range of concentrations.

Previous researchers have also reported the pseudo--second-order mechanism of MB adsorption onto coffee husks [27], spent tea [17,29], orange peel [31], and other adsorbents, such as rice husks [18]. In addition, this kinetic model was common for some other adsorbed dyes and heavy metals onto coffee and tea waste [1,21,30,39].

Table 2. Isotherm constants for methylene blue dye adsorptions on coffee, tea, lettuce and citrus waste (adsorbent mass: 7 g/L, 120 rpm, 27 °C)

Isotherm model	Coffee waste	Tea waste	Lettuce waste	Citrus waste
Freundlich				
R_F^2	0.9942	0.9923	0.9778	0.9671
n	0.6031	0.7815	0.6956	0.8775
K_f / (mg/g) (L/mg)$^{1/n}$	0.9698	0.4236	0.0903	0.0707
Temkin–Pyzhev				
R_T^2	0.9292	0.8659	0.8116	0.8359
b_T / J mol^{-1}	522.38	768.86	940.36	2432.3
A	1.2210	0.7562	0.3173	0.3173
Dubinin–Radushkevich				
R_D^2	0.9397	0.8581	0.6732	0.6233
β / mol^2 J^{-2}	6.5920	1.1711×10^{-6}	3.7696×10^{-6}	3.6628×10^{-6}
q_m / mg g^{-1}	8.0422	5.3682	3.4446	1.8651

Table 3. Kinetic constants for methylene blue adsorption on coffee, tea, lettuce and citrus waste, at 50 mg/L of dye concentration (adsorbent mass: 7 g/L, 120 rpm, 27 °C)

Adsorbent	Pseudo-first order kinetic model			Pseudo-second order kinetic model			$(q_e)_{exp}$[b] mg/g
	$(q_e)_{cal}$[a] mg/g	k_1 1/min	R^2	$(q_e)_{cal}$ mg/g	k_2 g/(mg min)	R^2	
Coffee waste	2.0850	1.6863	0.4668	6.7654	5.7952	0.9978	6.6876
Tea waste	1.2530	1.2578	0.9712	6.0861	3.4971	0.9994	6.0601
Lettuce waste	2.6975	1.4142	0.9706	5.1440	1.4762	0.9963	5.0201
Citrus waste	1.3717	0.9253	0.6995	3.1260	1.4474	0.9848	3.2994

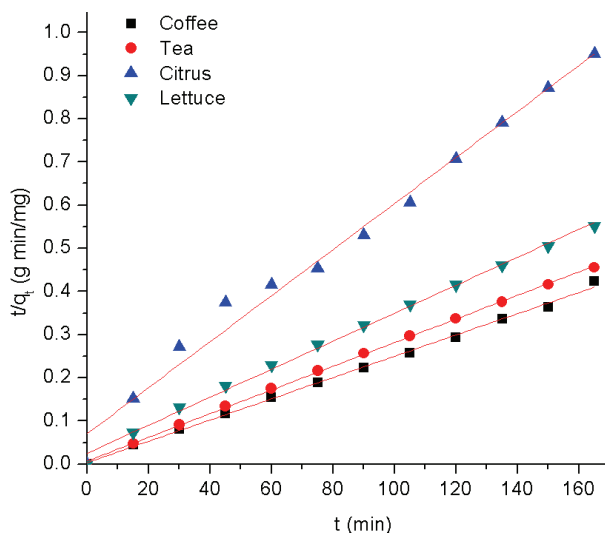[a]Calculated adsorption capacity; [b]experimental adsorption capacity

Figure 3. Pseudo-second-order kinetic plot for the adsorption of methylene blue dye on coffee, tea, lettuce and citrus waste (c_i:50 mg/L, adsorbent mass: 7 g/L,120 rpm,27 °C).

Adsorption mechanism

An intraparticle diffusion model was employed in order to further clarify the adsorption mechanism and determine rate controlling steps [25,40]. In accordance with the applied model, the plot of q_t *versus* $t^{1/2}$ should be linear if the intraparticle diffusion occurs. Further, if the plot passes through the origin, the rate limiting process is only due to the intraparticle diffusion [21].

The results of experimental data fitting within intraparticle diffusion model are presented in Figure 4 and corresponding parameters are obtained in Table 4. It was found that the sorption process exhibit multilinearity and tends to be followed by two stages (Fig. 4). The same multilinearity pattern has also been reported previously by various researchers, thus indicating that the process involves more than one kinetic stage [18,21,25,40]. The first initial linear stage may be referred to an instantaneous adsorption and is probably due to an electrostatic attraction between the dye molecules and the external surface of the adsorbent [21,40]. The second stage is a gradual adsorption stage, ascribed to the intraparticle diffusion [21,40]. It may be also regarded as the solute diffusion from larger pores

to the micropores causing a slow adsorption rate [14,40].

Vadivelan and Kumar (2005) [18] had noted that the adsorption of methylene blue dye onto the low cost rice husk based adsorbent followed similar two-portion intraparticle diffusion pattern, as well as adsorption of acid violet onto orange peel [41]. Another type of adsorbates, such as phenols, demonstrated that adsorption onto tea waste also occurred in the same manner as previously described [20].

From the Figure 4, it was clear that intraparticle diffusion was not the fully operative mechanism, since slopes of the plots do not pass through the origin and this observation might be applied to all of tested adsorbents. However, the process does not occur identically at all examined concentrations. The linear plots for lower concentrations (5 and 10 mg/L) tend to pass very close to the origin. With further increase of initial dye concentrations, the intercept values increase, too, indicating to the greater contribution of surface sorption in the process [21]. This deviation from the origin may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption [42]. Almost all the intercepts reported here were positive, indicating that relatively rapid adsorption occurs within a short period of time. Also, the k_{pi} values increase as the dye initial concentrations increase. It might be concluded that intraparticle diffusion tends to be rate controlling step for lower dye concentrations, while for higher concentrations the other mechanism, such as film diffusion, is considered to be involved.

CONCLUSIONS

Inexpensive and readily available restaurant waste, including coffee, tea, lettuce and citrus residues, have been tested for methylene blue efficiency removal andtheir adsorption capacities were determined. Coffee waste showed highest adsorption capacity, and therefore the highest dye removal efficiency. Thereupon, there are tea as well as lettuce and citrus waste, respectively, with considerate adsorption capabilities. The dye removal was more effective as dye concen-
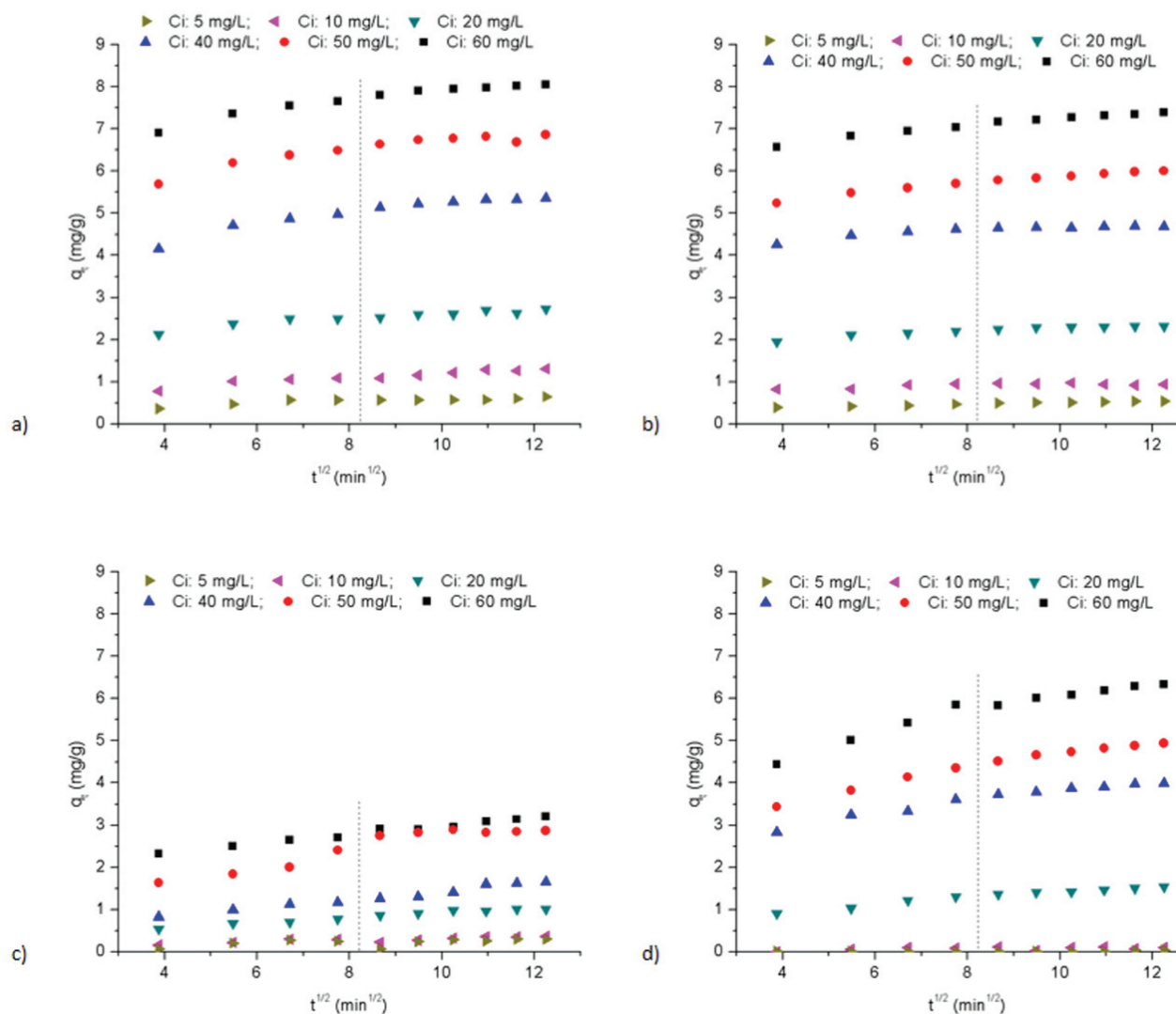
Figure 4. Intraparticle diffusion model plots for the adsorption of methylene blue dye onto coffee waste (a), tea waste (b), lettuce waste (c) and citrus waste (d) (adsorbent mass: 7 g/L, 120 rpm, 27 °C).

Table 4. Intraparticle diffusion model constants and correlation coefficients for adsorption of methylene blue dye on coffee, tea, lettuce and citrus waste (adsorbent mass: 7 g/L, 120 rpm, 27 °C)

Adsorbent	Parameter	Concentration, mg/L					
		5	10	20	40	50	60
Coffee waste	k_{pi} / mg g^{-1} min$^{-1/2}$	0.1954	0.4327	0.4652	1.0146	0.9467	0.9892
	c_i / mg g^{-1}	0.3297	0.6389	2.0039	3.9003	5.4639	6.6097
	R^2	0.7529	0.9225	0.8667	0.8861	0.8476	0.9205
Tea waste	k_{pi} / mg g^{-1} min$^{-1/2}$	0.1434	0.1120	0.3150	0.3445	0.6777	0.7285
	c_i / mg g^{-1}	0.3211	0.7943	1.8642	4.2085	4.9843	6.2946
	R^2	0.9706	0.4812	0.8989	0.7738	0.9672	0.9659
Lettuce waste	k_{pi} / mg g^{-1} min$^{-1/2}$	0.0207	0.0641	0.5724	1.0500	1.3821	1.6701
	c_i / mg g^{-1}	0.0079	0.0054	0.6718	2.4457	2.8769	3.8716
	R^2	0.3680	0.2880	0.9556	0.9407	0.9657	0.9226
Citrus waste	k_{pi} / mg g^{-1} min$^{-1/2}$	0.1522	0.1697	0.4516	0.7804	1.2882	0.8032
	c_i / mg g^{-1}	0.0556	0.0958	0.3345	0.4222	1.0410	1.9362
	R^2	0.3232	0.7516	0.9747	0.9700	0.8705	0.9839

tration increases from 5 up to 60 mg/L. Sorption isotherm results asserted that the sorption process was based on interactions on a heterogeneous surface as all of adsorbents followed Freundlich model. Kinetic analysis revealed that pseudo-second-order model was the primary process mechanism, but also there was the tendency that intraparticle diffusion model follows the process at very low dye concentrations.

Restaurant waste performs well in removing the MB at no cost, so it can be adopted and widely used in industries for contaminated water treatment as a concept of waste-to-wealth. Further process investigation may include the form of integrated and comprehensive restaurant waste for treatment of industrial effluents, containing not only dyes, but also other pollutants, like heavy metals, etc.

Acknowledgements

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IZVOD

ISKORIŠĆENJE SIROVOG OTPADA IZ RESTORANA ZA ADSORPCIJU BOJA

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Metilen plavo je bazna boja sa strukturom heterocikličnog aromatičnog jedinjenja, koja se u dobu savremenog društva često koristi za bojenje raznih tipova materijala. Efluenti iz industrije boja predstavljaju jednu od najproblematičnijih vrsta otpadnih voda za tretiranje, usled njihove velike biološke i hemijske potrebe za kiseonikom. Pored toga, toksičnost i teško razgradiva priroda boja mogu značajno uticati na fotosintetičku aktivnost vodenog sveta. Adsorpcijom na čvrstim nosačima mogu se ukloniti, odnosno, svesti na minimum razni tipovi zagađivača, zbog čega ova tehnika ima široku primenu u kontroli zagađenja voda. S tim u vezi, ispitivana je mogućnost iskorišćenja sirovog otpada iz restorana za adsorpciju i uklanjanje boje metilen plavo iz vodenih rastvora. U radu su određivani adsorpcioni kapaciteti otpadnih sirovina najčešće konzumiranih namirnica, uključujući kafu, čaj, zelenu salatu i mešavinu citrusnog voća (citrusa). Proces adsorpcije izveden je u šaržnom režimu, uz mešanje na tresilici, u uslovima ambijentalne temperature. Efikasnost procesa praćena je u zavisnosti od promene koncentracije boje u radnim rastvorima. Pokazano je da otpadna kafa ispoljava najviši adsorpcioni kapacitet, a za njom otpadni čaj, zelena salata i citrusi, redom. Nakon 30 min odigravanja reakcije, na kafi se vezalo gotovo 90%, dok na čaju 80%, zelenoj salati 60% i citrusima 30% od početne koncentracije rastvora boje. Vezivanje boje na adsorbentima bilo je efikasnije u slučajevima kada je koncentracija rastvora boje rasla od 5 do 60 mg/L. Na osnovu ispitivanja najčešće primenjivanih modela izotermi za definisanje adsorpcione ravnoteže, pronađeno je da su ravnotežni podaci, u slučajevima svih vrsta adsorbenata, bili u skladu sa Frojndlihovom adsorpcionom izotermom. S tim u vezi, smatra se da je proces odigravanja reakcije baziran na interakcijama između molekula boje i funkcionalnih grupa na heterogenoj površini adsorbenata. Kinetika i mehanizam reakcija opisani su po principu modela pseudo-drugog reda, koji se zasniva na pretpostavci da hemisorpcija, odnosno stvaranje hemijskih veza između adsorbenta i adsorbata, kontroliše celokupan tok reakcija. Iskorišćenjem sirovog otpada iz restorana može se doći do ekonomski isplativog rešenja za brzo i efikasno uklanjanje toksičnih i teško razgradivih boja iz vodenih rastvora. Smatra se da ova vrsta otpadnog materijala može naći svoju primenu u brojnim adsorpcionim procesima, u prvom redu onim koji se zasnivaju na tretmanima prečišćavanja otpadnih i pijaćih voda.