Removal of cationic dyes using chemically activated tangerine (*Citrus reticulata*) by-products and zeolites

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Abstract

The by-products of fruit processing are the most abundant lignocellulosic biomasses in the world. Fruit residues, mostly thrown away, cause not only environmental pollution e.g. peels, seeds and unused flesh generated in the different steps of processing chains but also are a source of biocomponents. Moreover, they can be used as raw materials to produce high efficiency filters for the purification of drinking waters and wastewaters. Adsorbents, which derived from the chemical modification of tangerine peels (TP) tangerine stones (TS) and clinoptilolite (CL) were mixed (100% TS (A), 50%TS.+50%CL. (B), 20%TS.+80%CL. (C), 100%TP. (D), 50%TP.+50%CL. (E), 20%TP.+80%CL. (F) w./w.) in powder form and were activated with HCL acid (4M). Their adsorptive properties were studied with methylene blue dye solution (MB). The increase in the adsorption capacity of each sample (% dye adsorption), follows the order: 20%TP+80%CL > 20%TS+80%CL ≈ 50%TS+50%CL ≈ 50%TP+50%CL > 100% TS ≈ 100%TP w./w., respectively. The implementation of different kinetic models, i.e. pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion shows that the pseudo-second order kinetic model describes better the experimental adsorption data of MB on tangerine stone and tangerine peels while the sorption data of MB on mixtures follows initially intraparticle diffusion model and then pseudo second order kinetic model. In conclusion, chemically activated tangerine peels or stone alone or in combination with minerals such as zeolites can be used as filters for the purification of water from organic compounds such as dyes reducing the by-product amounts released to the environment.

Keywords: tangerine peels, tangerine stone, zeolite, adsorption, methylene blue dye, kinetic analysis

Introduction

Industrial wastewaters contain synthetic dyes from textile, paper, pharmaceutical and leather industries leading to negative consequences to aquatic life [1]. Methylene blue (MB), a typical cationic dye, is presented in large quantities in the environment causing serious problems to human health such as high blood pressure, gastrointestinal pain, and nausea [2,3]. Several methods are being used to eliminate these pollutants from aquatic environments including chemical coagulation, ion exchange, electrolysis, biological treatments and adsorption [4]. Among these methods, adsorption through activated adsorbents is highly effective, cheap and eco-friendly for the removal of dyes and pigments as well as other organic and inorganic polluters [5,6].

Citrus fruits belong to the family *Rutaceae* and are broadly dispersed to tropical and subtropical regions. They considered the most cultivated fruits in the world with oranges being the most consumable fruits between all citrus fruits. According to 2019 estimation, citrus processing led to 17.41 million tons of wastes [7]. One-third of the total citrus fruits are processed, and thousands of tons of by-products produced during citrus juice processing [8]. Among these agro-industrial by-products are tangerine peels and stones. Such by-products may be used as briquettes for their high heating value [7] or to convert to essential oils, pectin, fertilizer and succinic acid through fermentation techniques [9]. New approaches show their use as filters for the removal of organic compounds or heavy metals for water or soil [10].

In the present work, the development of new adsorptive materials is studied combing the properties of agro-food by-products and minerals. These adsorbents are derived from the lignocellulosic wastes of the juice industry and more specifically from tangerine peels (TP) and stones (TS) in combination with clinoptilolite (CL), an abundant zeolite with low cost, either separately or in mixtures, in different proportions chemically activated with HCL acid. The MB adsorption capacity of the materials is examined. Different kinetic models (pseudo-first order, pseudo-second order, elovich and intraparticle diffusion) are applied to MB adsorption data.

Materials and Methods

New adsorptive materials were prepared from the chemical modification of tangerine by-products and zeolites appropriate for dye removal. Different proportions of tangerine peels (TP), tangerine stones (TS) and clinoptilolite (CL) were mixed (100% TS (A), 50%TS.+50%CL. (B), 20%TS.+80%CL. (C), 100%TP. (D), 50%TP.+50%CL. (E), 20%TP.+80%CL. (F), w./w.) in powder form and were activated with HCL acid (4M). Then, the samples were placed in an orbital shaker for 24 h at 24ºC. They were filtered and washed several times with distilled water until the filtrate pH remained neutral (~7). After that, the samples were dried in an oven at 110ºC for 24 h.

0.14 g of each adsorbent were mixed with 14mL of dye and placed in test tubes in a proportion of 10g of adsorbent/L of dye. Then, the samples were stirred and centrifuged for 5 min at 5000 rpm. The absorbance of each sample was measured in the VIS spectrophotometer (λ = 664 nm). The adsorbed amount (q_t) of the adsorbate onto the adsorbent was determined from the difference between the initial amount of adsorbate (q_o) in the solution and the measured amount of the adsorbate, expressed as %, i.e. $(q_t/q_o)\cdot 100$. The above procedure was repeated three times for each sample. The initial dye concentration was equal to 0.033g/L.

Different kinetic models were used to investigate the mechanism of adsorption [11]. The pseudo-first order kinetic model is given by the following equation:

$$\log(q_e - q_t) = logq_e - \frac{K_L}{2.303}t$$

where q_e and q_t are the amounts, g, of dye adsorbed per unit mass of adsorbent at equilibrium and at time, t, respectively and K_L is the equilibrium rate constant of pseudo-first order adsorption ($gg^{-1}min^{-1}$). The slope of the plot of $\log(q_e\text{-}q_t)$ versus t was used to determine K_L and the intercept q_e.

The pseudo-second order kinetic model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_{se}q_e^2} + \frac{t}{q_e}$$

where K_{se} is the equilibrium rate constant of pseudo-second order adsorption ($gg^{-1}min^{-1}$). The slope of the plot of t/q_t versus t was used to determine q_e and the intercept K_{se}.

Elovich equation can be expressed by the following equation:

$$q_t = \frac{1}{p}\ln(mp) + \frac{1}{p}lnt$$

where m ($gg^{-1}min^{-1}$) is the initial sorption rate and the parameter p (gg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption. The slope of the plot of q_t versus lnt was used to determine p and the intercept m.

When the diffusion is the prevailing mechanism then the intraparticle diffusion model can be defined as follows:

$$q_t = K_D t^{0,5} + C$$

where K_D ($gg^{-1}min^{-0.5}$) is the intraparticle diffusion rate and C is a constant

Results and Discussions

The adsorption of MB on chemically modified tangerine by-products and clinoptilolite is shown in Fig.1. The adsorption ability of methylene blue follows the order: 20%TP+80%CL > 20%TS+80%CL ≈ 50%TS+50%CL ≈ 50%TP+50%CL > 100% TS ≈ 100%TP w./w., respectively (Fig. 1). It is observed that the mixtures of tangerine peel or tangerine stone with zeolite, i.e. clinoptilolite, present higher adsorption than the chemically activated raw materials alone. Generally, the increase in the amount of zeolite in the mixture leads to higher adsorption ability of the materials. The adsorption curves for all the materials reach equilibrium after a certain time, which differ among them.

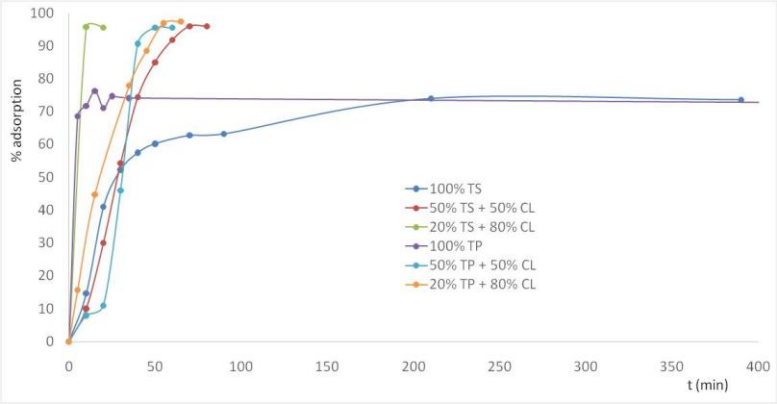


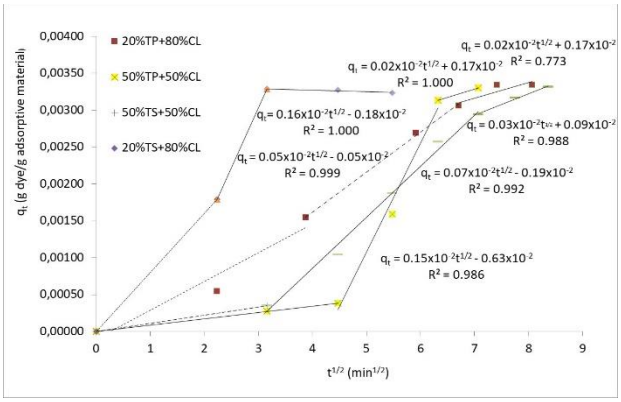
Fig. 1 Percentage of methylene blue adsorption from its aqueous solutions on different mixtures of tangerine by-products and zeolites activated with HCL acid (4M) versus time, t, at a ratio of 10 g adsorbent L^{-1} adsorbate

Moreover, the maximum adsorption of MB on the materials and the adsorption time are presented in table 1. The highest maximum MB adsorption is observed in 20% w./w. TP and 80% w./w. CL (F) after 65 min while the lowest maximum MB adsorption is observed in 100% w./w. TP (D) after 15 min.

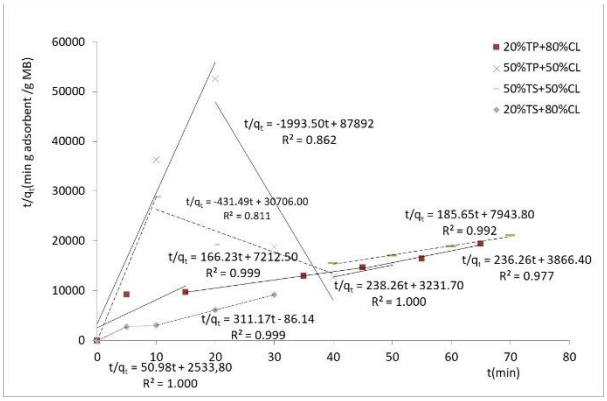
Table 1: Maximum percentage of MB adsorption and the related time

Samples	% maximum MB adsorption	t(min)
A	73.99	210
B	95.95	70
C	95.55	30
D	73.83	15
E	95.55	55
F	97.36	65

Different kinetic models (pseudo-first order, pseudo-second order, elovich and intraparticle diffusion) were applied to MB adsorption data indicating that the adsorption process follows different mechanisms in the mixtures of tangerine stone, peels and clinoptilolite. By ignoring the movement of the adsorbate molecules from the bulk liquid to the liquid film surrounding the adsorbent, the adsorption process in porous media can be separated into three stages [12]: a) diffusion through the solution to the external surface of the adsorbent (film mass transfer), b) diffusion within the pores or capillaries of the adsorbent internal structure to the sorption sites, c) rapid uptake of adsorbate on the adsorbent leading to equilibrium. The first and the second step are the rate limiting step while the last one is assumed to be rapid.



(a)



(b)

Fig.2(a) Application of Intraparticle diffusion model and (b) pseudo-second order kinetic model to the experimental adsorption data of methylene blue dye (MB) on chemically modified mixtures of tangerine peels (TP), tangerine stones (TS) and clinoptilolite (CL)

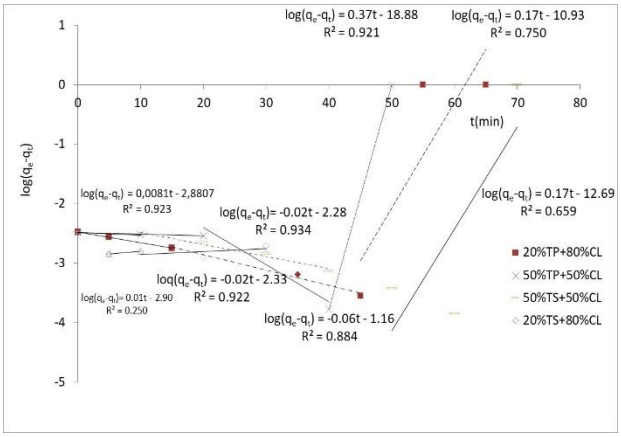
The experimental curves which give the amount of adsorbate (MB) adsorbed per unit mass of adsorbent (gg^{-1}) are plotted versus $t^{1/2}$ (Fig.2a). Three different regions can be distinguished (see Table 2).

Table 2: The regions according to Fig.2a for the adsorption of MB on chemically activated mixtures of TP or TS with CL.

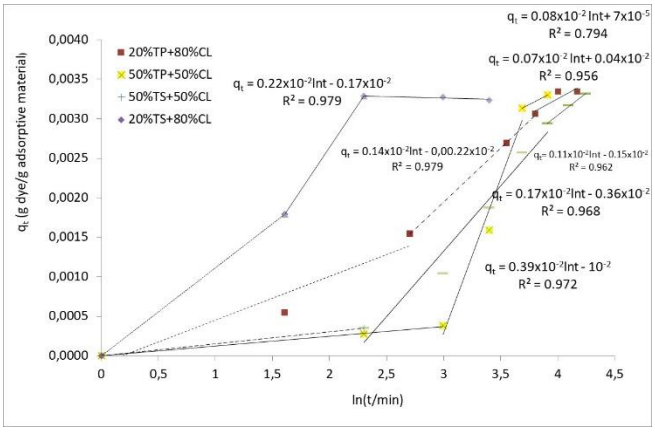
Materials	Regions (t in min)		
	A	B	C
20%TP+80%CL	0-15	15-45	45-65
50%TP+50%CL	0-20	20-40	40-50
20%TS+80%CL	0-10	10-40	40-70
50%TS+50%CL	0-5	5-10	10-30

According to literature [12] the initial portion (from the origin up to the first experimental point), A region is due to external mass transfer and then two linear region follow representing the intraparticle diffusion. Comparing the correlation coefficient factors after the application of intraparticle diffusion model to the experimental data, it seems that Intraparticle diffusion model describes well the B region for all materials (R^2>0.98). As far as the C region may concern, mixtures of 50% w./w. TP or TS with 50%w./w. of CL present high correlation coefficient factors for the application of Intraparticle diffusion model to the experimental adsorption data. The rate parameter for the diffusion in the B and C region is attributed to macropore diffusion and mesopore or transitional pore diffusion [12].

Figs. 2(b), 3(a) and 3(b) show the application of pseudo-second order, pseudo-first order and Elovich equation models to the MB adsorption data. It seems that pseudo-second order model fits well to the experimental data of the C region for all materials and of the B region only for the materials 20% w./w. TP or TS with 80%w./w. of CL. Pseudo-first order kinetic model and Elovich model present low correlation coefficient values for all regions.



(a)



(b)

Fig.3(a) Application of pseudo-first order kinetic model and (b) Elovich model to the experimental adsorption data of methylene blue dye (MB) on chemically modified mixtures of tangerine peels (TP), tangerine stones (TS) and clinoptilolite (CL)

Table 3 summarizes the results of the kinetic parameters of the two models, i.e. pseudo-second order, intraparticle diffusion, that fit well to MB adsorption data for the B and C region. The correlation coefficient values, R^2, are near unity.

According to Fig.4. the adsorption data of MB dye on tangerine peel (100%w./w.) and tangerine stone (100%w./w.) fit well to the pseudo-second order kinetic model indicating that the the overall rate of dye

adsorption is controlled by the chemisorption process. All the other kinetic models, i.e. intraparticle diffusion model, pseudo-first order and Elovich model, show correlation coefficient factors less than unity indicating that they cannot describe well MB adsorption data on TP and TS.

Table 3: Kinetic parameters of the two models (pseudo-second order, intraparticle diffusion model) based on the adsorption of MB from chemically activated mixtures of TS or TP with CL

Materials	Pseudo-second order						Intraparticle Diffusion			
	B region			C region			B region		C region	
	K_{SE}	q_E	R^2	K_{SE}	q_E	R^2	K_D	R^2	K_D	R^2
20-80% w./w. TP-CL	3.83	$0.60x10^{-2}$	0.999	14.44	$0.42x10^{-2}$	0.977	$0.05x10^{-2}$	0.999	-	-
50-50% w./w. TP-CL	-	-	-	17.57	$0.42x10^{-2}$	1.000	$0.15x10^{-2}$	0.986	$0.02x10^{-2}$	1.000
50-50% w./w. TS-CL	-	-	-	4.34	$0.54x10^{-2}$	0.992	$0.07x10^{-2}$	0.992	$0.03x10^{-2}$	0.988
20-80% w./w. TS-CL	1.03	$0.19x10^{-1}$	1.000	1124.06	$0.32x10^{-2}$	0.999	$0.16x10^{-2}$	1.000	-	-

where K_D, K_{SE} and q_E is expressed in $gg^{-1}min^{-1/2}$, $gming^{-1}$, gg^{-1}, respectively

According to the results, the sorption data of MB on tangerine stone (100% TS) and tangerine peels (100% TP) activated with HCL 4M follows pseudo second order kinetic model showing that the chemical sorption of methylene blue onto TP or TS is prevalent. The kinetic parameters of pseudo second order kinetic model follow: K_{SE} = 16.85 $mingg^{-1}$, q_E = $2.47x10^{-3}$ gg^{-1} for 100%w./w. TS and K_{SE} = 1150.07 $mingg^{-1}$, q_E = $2.47x10^{-3}$ gg^{-1} for 100%w./w. TP. The sorption data of MB on mixtures of clinoptilolite and tangerine stone or tangerine peels activated with 4M HCL follow intraparticle diffusion model and pseudo second order kinetic model indicating that initially the prevailing mechanism is physical adsorption and then chemical adsorption of MB onto mixtures. In literature [13], plum and apricot kernels have been used as adsorbents for the removal of heavy metals (lead and chromium) from wastewaters and their kinetic analysis has shown that the pseudo-second order kinetic model fitted well the experimental data.

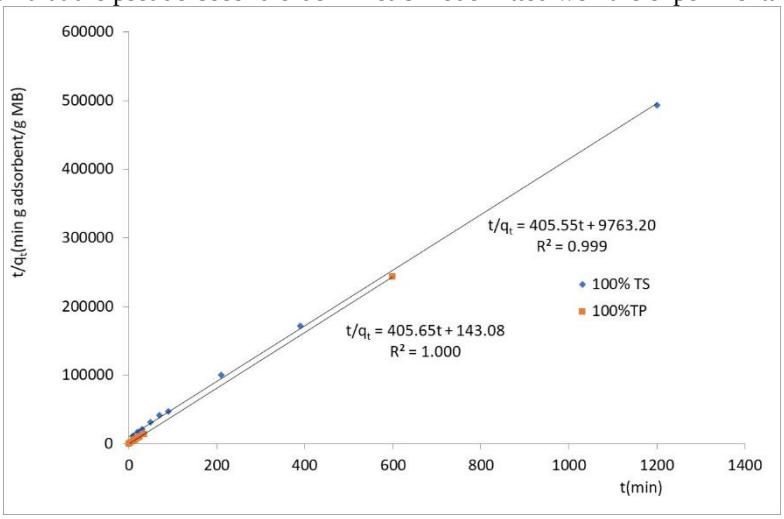


Fig.4 Application of pseudo-second order kinetic model to the experimental adsorption data of methylene blue dye (MB) on chemically modified tangerine peels (TP) and tangerine stones (TS).

Conclusions

- The adsorption ability of methylene blue follows the order: 20%TP+80%CL > 20%TS+80%CL ≈ 50%TS+50%CL ≈ 50%TP+50%CL > 100% TS ≈ 100%TP w./w., respectively
- The adsorption data of MB on tangerine stone or tangerine peels activated with HCL 4M follows pseudo second order kinetic model while the adsorption data of MB on mixtures of clinoptilolite and tangerine stone or tangerine peels activated with HCL 4M follows initially intraparticle diffusion model and then pseudo second order kinetic model
- Adsorbents consisting of both activated food by-products and zeolites combine unique low-cost abilities and are promising materials in water purifiers as filters.

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