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

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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 [2]. Several methods are being used to eliminate these pollutants from aquatic environments including chemical coagulation, ion exchange, electrolysis, biological treatments and adsorption [3]. 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 [2,3].

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 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. 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). Different kinetic models (pseudo-first order, pseudo-second order, elovich and intraparticle diffusion) were applied to MB adsorption data.

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. 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

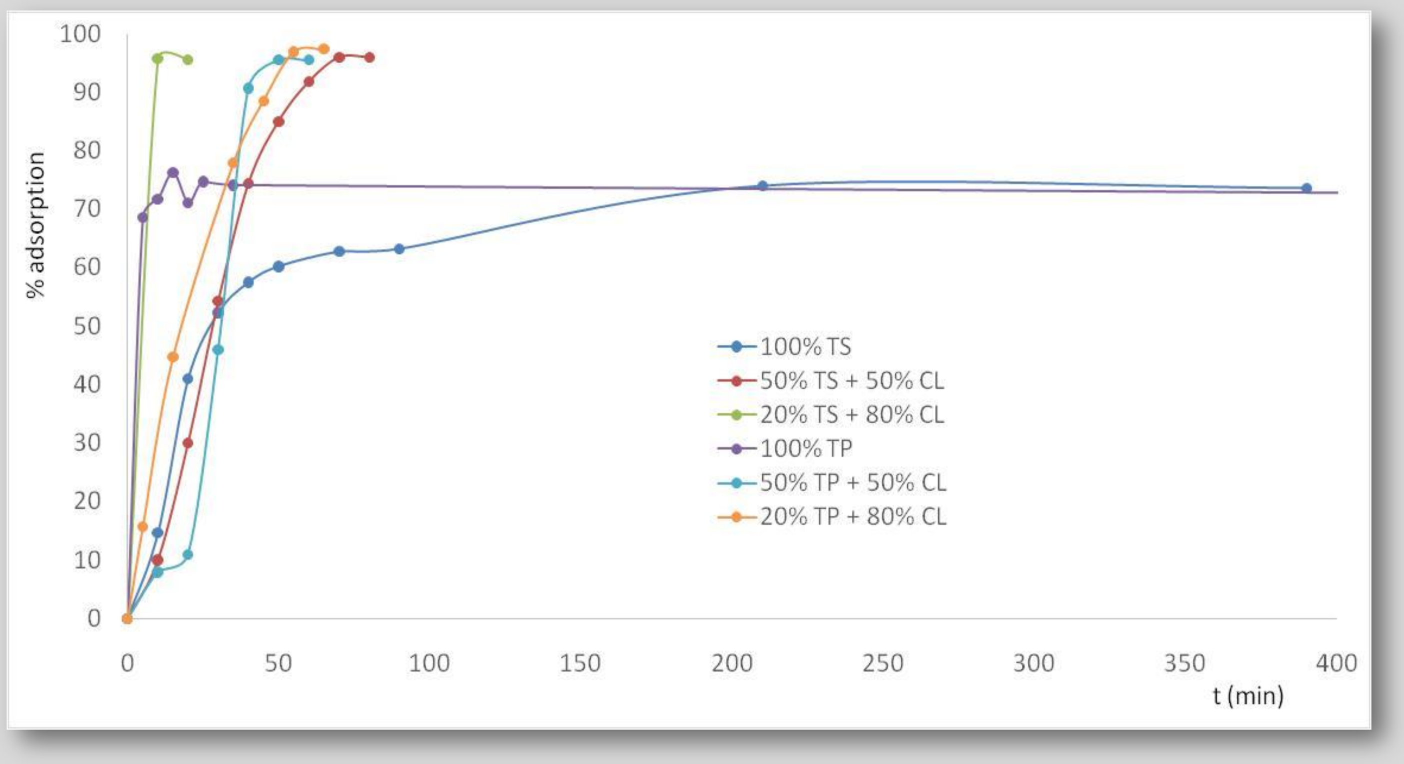

Fig. 1 Percentage of methylene blue adsorption from its aqueous solutions on different mixtures of tangerine by-products and zeolites activated with HCL acid (4M) versus time, t, at a ratio of 10 g adsorbent L^{-1} adsorbate

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 [4]: 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 steps are the rate limiting steps while the last one is assumed to be rapid. 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 1).

Table 1: 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 [4] 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.

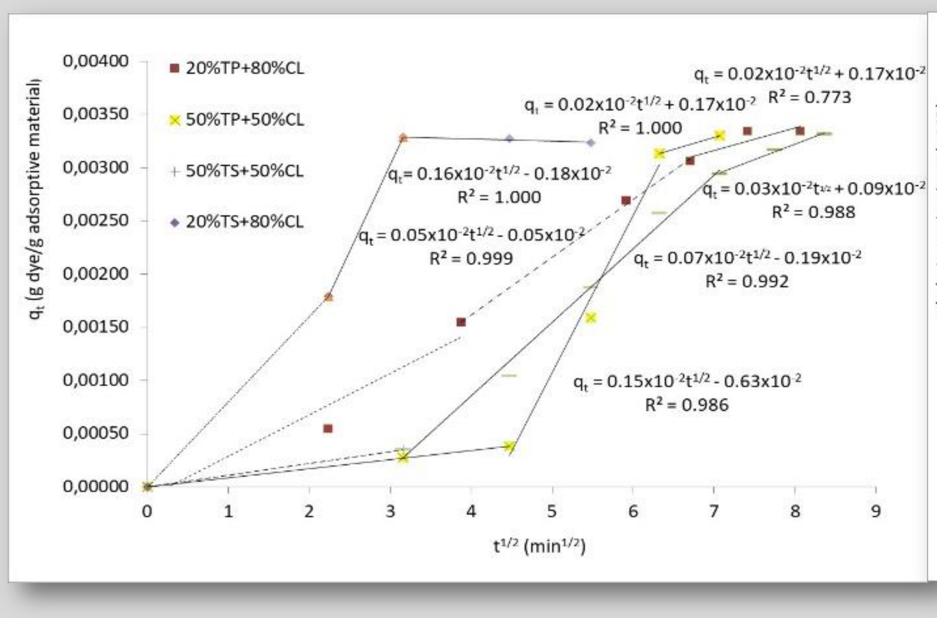

Fig.2(a)

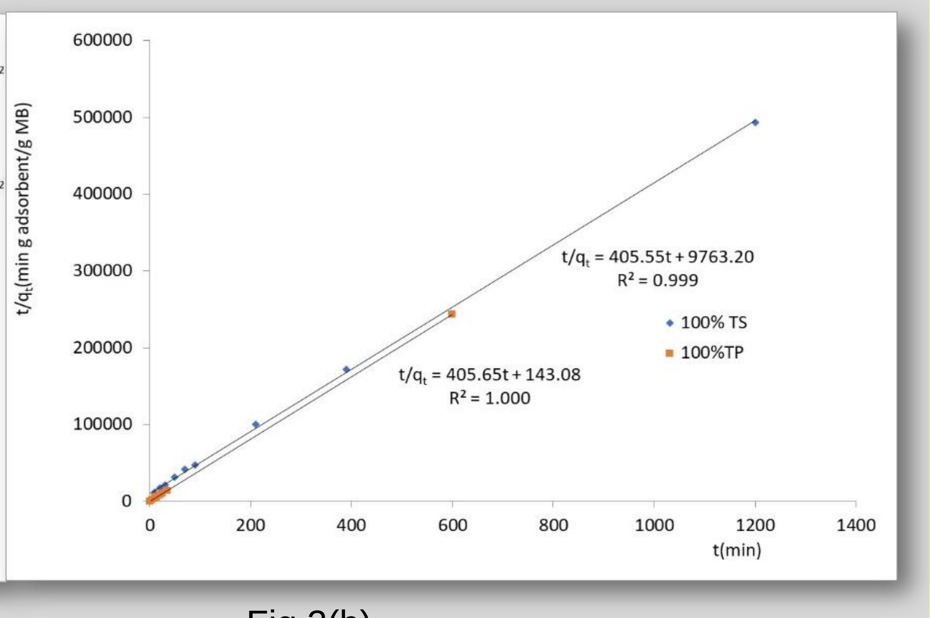

Fig.2(b)

Fig.2(a) Application of Intraparticle diffusion 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). **Fig 2(b)** 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).

Comparing the correlation coefficient factors after the application of intraparticle diffusion and pseudo-second order model (table 2) to the experimental data, it seems that Intraparticle diffusion model describes well the B region for all materials and pseudo-second order describes well the C region, (R^2>0.98). As far as the kinetic analysis of TP or TS may concern (Fig. 2b), pseudo-second order fits well to the experimental adsorption data indicating that the chemical sorption of MB onto TP or TS is the prevailing mechanism.

Table 2: 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
F	3.83	$0.60x10^{-2}$	0.999	14.44	$0.42x10^{-2}$	0.977	$0.05x10^{-2}$	0.999	-	-
E	-	-	-	17.57	$0.42x10^{-2}$	1.000	$0.15x10^{-2}$	0.986	$0.02x10^{-2}$	1.000
B	-	-	-	4.34	$0.54x10^{-2}$	0.992	$0.07x10^{-2}$	0.992	$0.03x10^{-2}$	0.988
C	1.03	$0.19x10^{-1}$	1.000	1124.06	$0.32x10^{-2}$	0.999	$0.16x10^{-2}$	1.000	-	-

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 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.
- Adsorbents consisting of both activated food by-products and zeolites combine unique low-cost abilities and are promising materials in water purifiers as filters.

Reference

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