Production and characterization of carbonaceous materials derived from shrimp by-products



I. Fotodimas¹, A. Zapantioti¹, Z. Ioannou¹, D. Sarris¹, G. Kanlis²

¹Department of Food Science and Nutrition, University of the Aegean, 81400, Myrina, Lemnos, Greece

²Department of Fisheries and Aquaculture, University of Patras, 30200, Mesolongi, Greece

Keywords: shrimp biomass, methylene blue adsorption, carbonization, FTIR analysis, kinetic models Presenting author emails: zioan@teemail.gr



UNIVERSITY OF THE

Introduction

The intensive production of shrimp by-products from processing industries has increased significantly in recent years. The deposition of shrimp by-product in the environment causes problems such as the increase of the biochemical oxygen demand (BOD) on the wastewaters and the creation of strong odors to the environment due to the degradation of biomass (Bataille & Bataille, 2008). Although the by-products of shrimp processing have valuable bioactive substances, i.e., chitin, with high financial interest, they are not utilized but usually discarded in the environment (Djellouli et al., 2019; Karthi et al., 2022). Moreover, the shrimp shells can be converted into products with high additional value such as carbonaceous materials through a pyrolysis processes (Liu et al., 2021). In this study, shrimp wastes are used to produce new adsorbents via the pyrolysis process. The data of these experiments are evaluated and fitted to various adsorption kinetic models. The produced materials are characterized by FTIR analysis, and their adsorptive abilities are determined by the discoloring abilities of methylene blue dye (MB).

Experimental

Two different marketable type of shrimps, i.e., Argentine red shrimp *Pleoticus mullieri* (SPM) and Pacific white farmed shrimp *Litopenaeus vannamei* (SLV), were used. All samples were rinsed with running water and then the shrimp wastes were separated into shells (SPMS, SLVS) and tails (SPMT, SLVT). Each shrimp waste sample was dried and then was fully crushed by a blender, grounded by a mortar, sieved up to $200\mu m$, and then stored in a shady place at $20^{\circ}C$. Finally, the specimens were then carbonized in an oven under an inert atmosphere and the temperature rise rate was 5°C/min (Fig. 1). The carbonaceous materials were weighted before and after the carbonization process. The discoloring abilities of the carbonaceous materials were also determined with the use of MB dye in a concentration of 0.032 g/L. The absorbance of each sample was measured with the use of ONDA V-10 Plus spectrophotometer ($\lambda = 664$ nm). The adsorption of MB onto carbonized materials was investigated with the use of FTIR analysis. The kinetic study of MB adsorption on carbonaceous adsorbents was also examined with the application of five different models, i.e., pseudo-second order, Lagergren, Elovich, Power and Intraparticle diffusion model. The equations of the five models are described in Table 1.



Fig. 1: Flow chart to produce adsorbent materials via the pyrolysis process from shrimp by-products

Table 1: Kinetic equations of five different models, i.e., pseudo-first order, pseudo-second order, Elovich and Intraparticle diffusion

Intraparticle diffusion model	$\mathbf{q}_t = \mathbf{K}_{\mathbf{D}} \ t^{1/2} + \mathbf{Z}$	Eq. (1)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_{SE}q_e^2} + \frac{t}{q_e}$	Eq. (2)
Lagergren	$log(q_e - q_t) = log q_e - \frac{K_L t}{2.303}$	Eq. (3)
Elovich	$q_t = \frac{1}{p}\ln(mp) + \frac{1}{p}\ln t$	Eq. (4)
Power	$\log q_t = \log a + n \log t$	Eq. (5)

where: q_t the amount of adsorbate adsorbed per unit mass of adsorbent (mg g⁻¹), at time, t (min), K_D the intraparticle diffusion rate constant (mg g⁻¹) $min^{-1/2}$), Z the constant related to the thickness of the boundary layer (mgg⁻¹), K_{SE} the rate constant of pseudo second order adsorption $(gmg^{-1} min^{-1})$, q_e the amount of adsorbate adsorbed per unit mass of adsorbent (carbonaceous materials) (mg g⁻¹) at equilibrium, K_L the rate constant of pseudo first order adsorption (min⁻¹), m the initial adsorption rate (mg g⁻¹ min⁻¹), p is related to the extent of surface coverage and activation energy for chemisorption (gmg⁻¹), n is the order of the physical phenomenon (e.g. adsorption) and α is the initial rate of the power function (mg g^{-1} min⁻ⁿ).

Results & Discussion





According to the weight loss percentage of all adsorbents (Fig. 2), it seems that SPMT presents the highest weight loss while SPMS the lowest. The weight loss increased significantly on the materials: SPMT (67.6%) > SLVT(62.8%) > SLVS (61.6%) >SPMS (58.0%), respectively. The results show that shrimp waste tails reduce significantly their weight compared to shells.



Figure 4: FTIR spectra of the carbonized biomass before and after MB adsorption for (a) *Pleoticus mullieri* species (SPM) and (b) *Litopengeus*

Comparing the FTIR spectra of the adsorbents before and after MB adsorption (Fig. 4), it seems that the peaks at 1638-1634 cm⁻¹ may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The peaks at 2372-2314 cm⁻¹ is due mainly to stretching vibrations of C-N or O-C-O (Raspolli et al., 2015; Feng



According to Fig.3, the decrease in MB adsorption percentage on carbonaceous materials follows the order: SPMS>SLVT>SLVS>SPMT. The results have shown that the carbonaceous material derived from shrimp shell of *Pleoticus* mullieri species (SPMS) has a maximum percentage of MB adsorption equal to 99.9% compared to shrimp tail of *Pleoticus mullieri* species (SPMT, 86.5%), when the adsorbent to adsorbate rate is equal to 1.0 g/L. All the other carbonaceous materials derived from shrimp species Litopenaeus vannamei (SLV) presented

Figure 3:MB adsorption percentage from aqueous intermediate values of MB adsorption percentage solution on carbonaceous materials in a proportion from aqueous solutions. Similar results were also of adsorbent to adsorbate solution equal to 1.0 g/L presented to other studies (Ho and McKay, 1999).

Table 2: Kinetic parameters of pseudo-second order model in a proportion of adsorbent to adsorbate solution equal to 1.0 gL⁻¹

Material	q _{e, exper.}	Pseudo-second order			
code		K _{SE}	q _{e, theor.}	R ²	
SPMS	31.99	9.73x10 ⁻⁴	32.05	1.00	
SPMT	27.70	0.13x10 ⁻⁴	27.62	1.00	
SLVS	29.68	0.11x10 ⁻⁴	29.76	1.00	

Comparing the experimental $(q_{e,exp})$ and theoretical $(q_{e,theor.})$ values of adsorbate adsorbed per unit mass of adsorbent at equilibrium and the correlation coefficient factor, r^2 of the models (Table 2), it seems that pseudo-second order fits well for all adsorbents indicating that chemisorption is the prevailing step. All the other models, i.e., Lagergren, Elovich, Power and Intraparticle diffusion, present low correlation coefficient factors

vannamei (SLV).	et al., 2020; Larkin et al., 2011).	SLVT	31.20 0	0.10x10 ⁻⁴ 31.	.25 1.00	correlation coefficient factors.		
Conclusions								
The adsorption capacity of MB decreases according to the o SPMS. The lowest weight loss of the carbonaceous material SI	order: SPMS>SLVT>SLVS>SP SPMS leads to the highest MB ac	MT while the v dsorption.	veight loss d	ecreases acco	ording to the	order SPMT > SLVT > SLVS >		
According to FTIR analysis, the peaks at 1636cm ⁻¹ may be carbonaceous materials.	attributed to C=C stretching "	'in plane" vibra	tions of the	aromatic rin	g of MB ind	icating the adsorption of MB on		
For all the adsorbents studied, chemical reaction seems significant in the rate-controlling step and the pseudo-second order chemical reaction kinetics provide the best correlation of the experimental data.								
	Acknowledge	ements						
Authors are grateful to G. Hotos, D. Avramidou, K. Vidalis and X. Douvi for providing laboratory equipment for this research.								
	Referenc	es						
ataille, M., & Bataille, P. (2008). Extraction of proteins from shrimp processing waste. Jour	urnal Of Chemical Technology And Biotechnology	ogy. Biotechnology, 33	(4), 203-208.					
jellouli, M., López-Caballero, M., Arancibia, M., Karam, N., & Martínez-Alvarez, (<i>Ilorization</i> , 11(6), 2491-2505.	O. (2019). Antioxidant and Antimicrobial En	nhancement by Reacti	on of Protein Hyd	lrolysates Derived	from Shrimp By-F	Products with Glucosamine. Waste And Biomass		
g P., Li J., Wang H., Xu Z., (2020). Biomass-Based Activated Carbon and Activators: Preparation of Activated Carbon from Corncob by Chemical Activation with Biomass Pyrolysis Liquids, American Chemical Society, 5 (37), 24064-24072.								
Y.S., McKay G., (1999). Pseudo-second order model for sorption processes, <i>Process Bioc</i> arthi, S., Sangeetha, R., Arumugam, K., Karthika, T., & Vimala, S. (2022). Removal of a arkin P., IR and Raman Spectroscopy, Principles and spectral interpretation, Elsevier edition	<i>chemistry</i> , 34(5), 451-465. Tmethylene blue dye using shrimp shell chitin f n, USA, 2011.	from industrial effluent	s. Materials Today	v: Proceedings, 66(4	(4),1945-1950.			
u, J., Yang, X., Liu, H., Jia, X., & Bao, Y. (2021). Mixed biochar obtained by the co-pyroly	lysis of shrimp shell with corn straw: Co-pyrol	lysis characteristics and	l its adsorption cap	ability. <i>Chemosphe</i>	ere, 282, 131116.			
aspolli Galletti A.M., D'Alessio A., Licursi D., Antonetti C., Valentini G., Galia A., Di N	Nasso N.N. (2015). Midinfrared FT-IR as a Too	ol for Monitoring Herba	aceous Biomass Co	omposition and Its	Conversion to Furf	ural, Journal of Spectroscopy 1, 1-12.		