

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

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ABSTRACT

The intensive production of shrimp by-products from processing industries has increased significantly in recent years. The continuous discarding of shrimp waste has a negative effect on the environment. The shrimp waste contains several bioactive compounds with high added value while they can also be converted to useful materials with new properties. Therefore, a shrimp by-product utilization strategy would lead to the development of innovative products, e.g., the production of adsorbents via pyrolysis reducing the quantities of wastes in the environment. The purpose of this research is the production and characterization of carbonaceous materials derived from shrimp by-product. Specifically, two different types of shrimps *Pleoticus mullieri* (SPM) and *Litopenaeus vannamei* (SLV) were separated into shells (SPMS, SLVS), and tails (SPMT, SLVT). The adsorption properties of the materials were investigated, and they were characterized through the FTIR analysis. The results have shown that the carbonaceous materials presented the maximum adsorption percentage according to the order: SPMS>SLVT>SLVS>SPMT. The FT-IR spectra have shown a broad-band at 1634-1638 cm⁻¹ which may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The pseudo-first order (Lagergren), the pseudo-second order, the Elovich and Power models were applied to study the kinetics of the adsorption process while the intraparticle diffusion model was used to determine the diffusion mechanism. According to the results, 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 all models, it seems that pseudo-second order fits well for all adsorbents indicating that chemisorption is the prevailing step.

Keywords: shrimp biomass, methylene blue adsorption, carbonization, FTIR analysis, kinetic models.

INTRODUCTION

In recent years, there has been a rapid increase in shrimp consumption. With the appropriate raw shrimp processing, the removed non-edible biomass, e.g., heads, shells, and tails, is equivalent to 50% of the total shrimp biomass (Heu et al., 2003). Therefore, the continuous increase in seafood industry waste, is a major problem not only for the industrial sector but also for the environment (Sila et al., 2014). 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 process (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.

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. After their transportation to the laboratory, the frozen shrimps were thawed smoothly at room temperature. 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 in a drying oven separately at 100°C for 96h. The dried waste was fully crushed by a blender, grounded by a mortar, sieved up to 200µm, and then stored in a shady place at 20°C. Finally, the specimens were then carbonized in an oven under an inert atmosphere and the temperature rise rate was 5°C/min. The carbonaceous materials were weighted before and after the carbonization process. The discoloring abilities of the carbonaceous materials were also determined. Methylene blue dye (MB) was produced in a solution of 0.032g/L. More specifically, 0.015g of each adsorbent were mixed with 15mL of dye solution and placed in test tubes in a proportion of 1.0g of adsorbent/L of dye. Then, the samples were stirred at 240 rpm for 12h at 20°C and then were centrifuged for 5 min

at 7000 rpm. The procedure was repeated until the samples have completely discolored. The absorbance of each sample was measured in the visible spectrophotometer ONDA V-10 Plus spectrophotometer ($\lambda = 664 \text{ nm}$). The above procedure was repeated three times for each sample. IR spectra were determined for the carbonized biomass before and after methylene blue adsorption. An Agilent Cary 630 FTIR spectroscope, equipped with an ATR accessory, was used with Microlab software. All measurements were performed on the same day at 25°C . The spectra were measured in the region from 400 to 4000 cm^{-1} . The diamond ATR sensor was cleaned with ethyl alcohol or acetone before each sample measurements. The kinetic study of MB adsorption on carbonaceous adsorbents was also examined with the application of five different models, i.e., pseudo-first order, pseudo-second order, Elovich and Intraparticle diffusion model. The equations of the five models are described in Table 1.

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

Intraparticle diffusion model	$q_t = K_D t^{1/2} + Z$	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 ($\text{mg g}^{-1} \text{min}^{-1/2}$), Z the constant related to the thickness of the boundary layer (mg g^{-1}), K_{SE} the rate constant of pseudo second order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), 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 ($\text{mg g}^{-1} \text{min}^{-1}$), p is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}), n is the order of the physical phenomenon (e.g. adsorption) and a is the initial rate of the power function ($\text{mg g}^{-1} \text{min}^{-n}$)

RESULTS AND DISCUSSION

The weight loss percentage of each carbonaceous material produced by the two different species of shrimp waste after the pyrolysis process is shown in Fig.1a. It seems that SPMT presents the highest weight loss while SPMS the lowest. The weight loss increased significantly on the materials according to the order: SPMT (67.6%) > SLVT (62.8%) > SLVS (61.6%) > SPMS (58.0%).

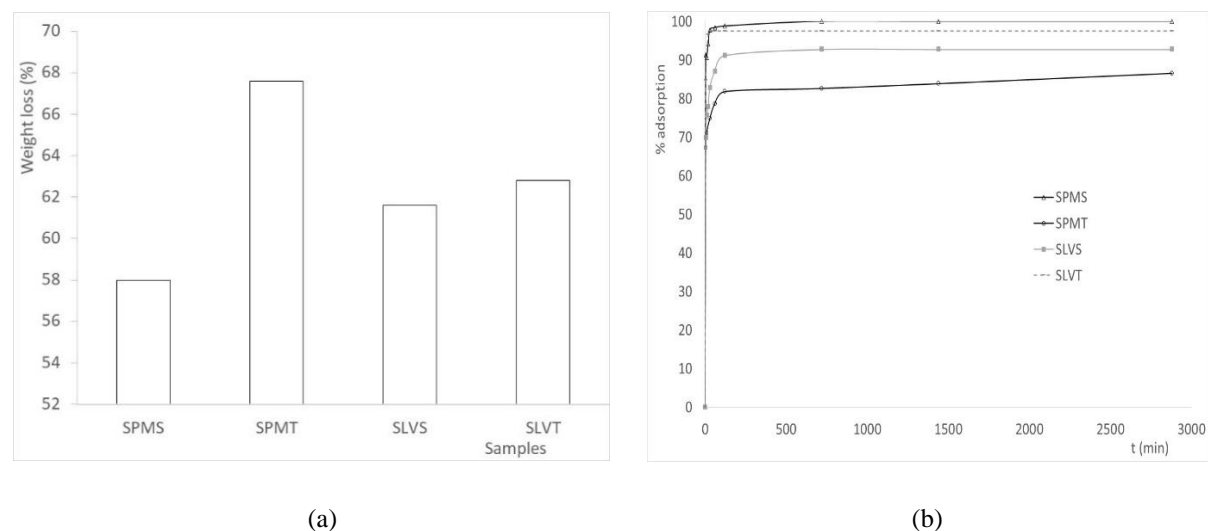


Figure 1: (a) Percentage of weight loss for each sample after carbonization and (b) MB adsorption percentage from aqueous solution on carbonaceous materials in a proportion of adsorbent to adsorbate solution equal to 1.0 g/L .

The results have shown that shrimp waste tails reduce significantly their weight compared to shells. According to Fig.1b, 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 of MB. All the other carbonaceous materials derived from shrimp species *Litopenaeus vannamei* (SLV) presented intermediate values of MB adsorption percentage from aqueous solutions. Moreover, the concentration of MB dye in the solution (Fig.2a) decreases according to the order: SPMT>SLVS>SLVT>SPMS. According to Fig.2a, the highest reduction of MB concentration in the solution belongs to SPMS, while the same material also presents the highest percentage of MB adsorption (31.99 mg/g) as it seems from Fig.2b. Therefore, the carbonized shrimp shell of *Pleoticus muelleri* adsorbs quicker and higher amounts of MB dye in comparison with all the other carbonized materials. The MB adsorption in equilibrium reaches after 20 to 30 min for all carbonaceous materials.

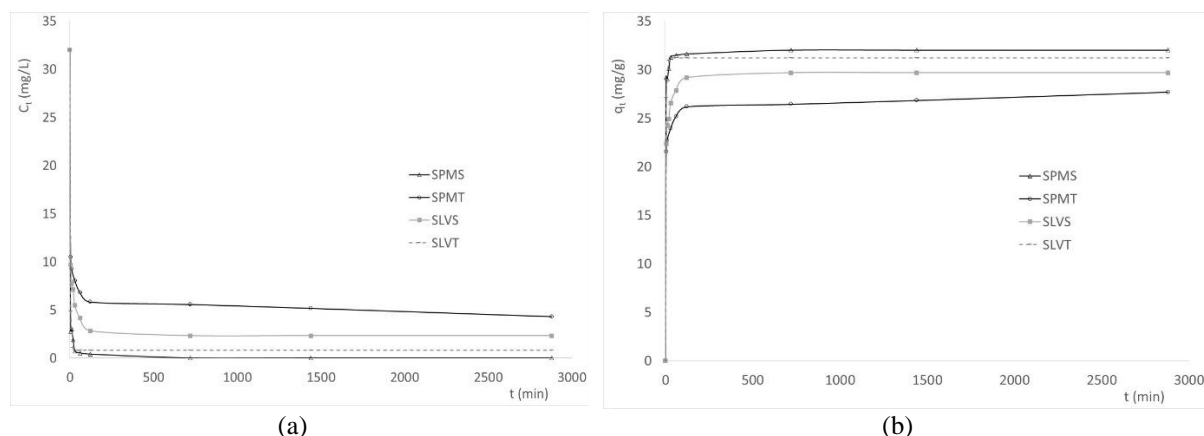


Figure 2: (a) The concentration of MB in the solution (mg/L) versus time and (b) MB adsorption per gram of adsorbent versus time for the four different types of shrimp's carbonaceous materials (SPMS, SPMT, SLVS, SLVT) in a proportion of adsorbent to adsorbate solution equal to 1.0/1.0 g/L

The IR spectra of the materials (Fig.3) show a broad band around 3250-3270 cm^{-1} corresponding to O-H stretching vibrations, observed in samples that have absorbed methylene blue. The low peak at 3730-3740 cm^{-1} corresponds to free -OH groups. Moreover, the peaks at 1638-1634 cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The bands at 1405-1395 cm^{-1} is due mainly to the asymmetric deformations of C-H bonds, while the peak at 2372-2314 cm^{-1} is due mainly to stretching vibrations of C-N or O-C-O. The peak at 872-870 cm^{-1} can be attributed to the out-of-plane bending vibration of C-H in the aromatic ring and 1216-1211 cm^{-1} corresponds to C-O stretching (Raspolti et al., 2015, Feng et al., 2020). The bands at 1088 and 1022 cm^{-1} involves in-plane movement of the ring carbons and the substituents (Larkin et al., 2011).

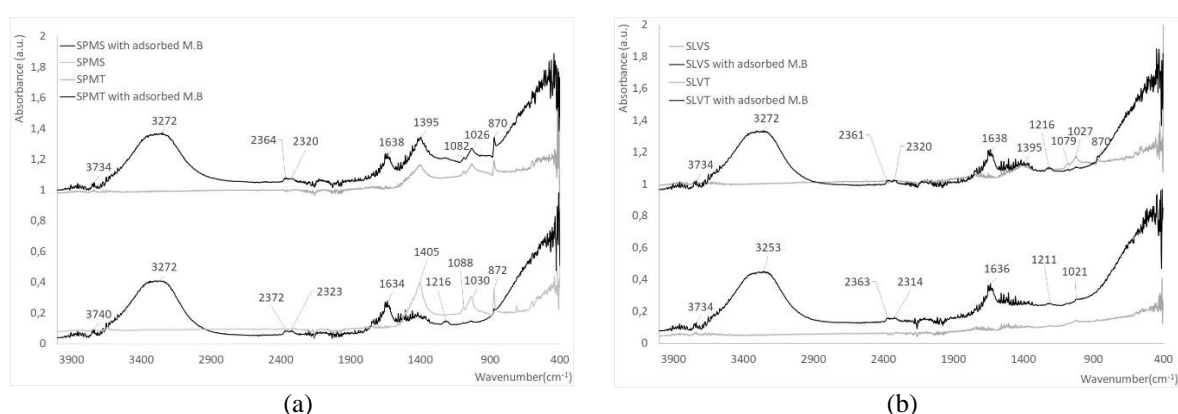


Figure 3: IR spectra of the carbonized biomass before and after MB adsorption using Agilent Cary 630 FTIR with the diamond ATR accessory for (a) *Pleoticus mullieri* species (SPM) and (b) *Litopenaeus vannamei* (SLV)

The pseudo-first order (Lagergren), the pseudo-second order, the Elovich and Power models were applied to study the kinetics of the adsorption process while the intraparticle diffusion model was used to determine the diffusion mechanism. According to the results (Table 1), 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 all models, 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, resulting to the rejection of these models to the description of MB adsorption on adsorbents derived from shrimp by-products. Similar results were also presented to other studies (Ho and McKay, 1999).

Table 1: Kinetic parameters of the five different kinetic models, i.e., Intraparticle diffusion model, pseudo-second order, power, Lagergren, Elovich and Power in a proportion of adsorbent to adsorbate solution equal to 1.0 gL⁻¹

Material code	q _{e,exp}	Intraparticle		Pseudo-second order			Lagergren			Elovich			Power		
		K _D	R ²	K _{SE}	q _{e,theor}	R ²	K _L	q _{e,theor}	R ²	ln (mp)/p	1/p	R ²	α	n	R ²
SPMS	31.99	1.98	0.57	9.73x10 ⁻⁴	32.05	1.00	2.60x10 ⁻²	4.60	0.55	28.87	0.46	0.75	28.90	1.50x10 ⁻²	0.74
SPMT	27.70	0.74	0.58	0.13x10 ⁻⁴	27.62	1.00	0.07x10 ⁻²	4.30	0.39	20.86	0.89	0.92	22.44	2.74x10 ⁻²	0.40
SLVS	29.68	0.84	0.56	0.11x10 ⁻⁴	29.76	1.00	2.70x10 ⁻²	10.28	0.84	22.03	1.12	0.84	22.28	4.21x10 ⁻²	0.83
SLVT	31.20	0.90	0.51	0.10x10 ⁻⁴	31.25	1.00	0.22x10 ⁻²	21.21	0.96	28.52	0.43	0.44	28.48	1.45x10 ⁻²	0.44

CONCLUSIONS

-The adsorption capacity of MB decreases according to the order: SPMS>SLVT>SLVS>SPMT while the weight loss decreases according to the order SPMT > SLVT > SLVS > SPMS. The lowest weight loss of the carbonaceous material SPMS leads to the highest MB adsorption.

-According to IR analysis, the peaks at 1636cm⁻¹ may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB indicating the adsorption of MB on carbonaceous materials.

-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.

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