Removal of organic compounds using carbonaceous materials derived from sea urchin by-products

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ABSTRACT

In recent years, there has been a rapid increase in edible sea urchin consumption. The seafood processing industry produces high amounts of sea urchin by-products, consisting usually of shells, spines, and viscera. These processing wastes are continuously deposited in the soil, and the sea, causing environmental degradation. The chemical composition of sea urchins contains valuable bioactive ingredients that can be used in a wide range of applications. Consequently, the prospect of exploitation of sea urchin shells, spines, and viscera contributes to the circular economy with the production of new innovative products used for environmental decontamination. The purpose of this research is the removal of organic compounds from water bodies using carbonaceous materials derived from sea urchin by-products. Sea urchin waste was separated into shells (SUSH) and spines (SUSP). The adsorption properties of the carbonaceous materials were investigated with the removal of methylene blue (MB) dye from aqueous solutions. Moreover, the materials were characterized through the FTIR method. The results have shown that the carbonaceous materials pyrolyzed at 800°C presented the maximum MB adsorption percentage according to the order: S.U.S.P.>S.U.S.H. The maximum percentage of MB adsorption is equal to 94.2% when the adsorbent to adsorbate ratio is equal to 1.0 gL^{-1} of MB. The FT-IR spectra of the materials show a peak at 1647 cm^{-1}, which may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB, indicating the adsorption of MB on carbonaceous materials. 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 and all adsorbent-to-adsorbate ratios, indicating that chemisorption is the prevailing step.

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

INTRODUCTION

In Mediterranean countries, sea urchins are flavor agents and ingredients in many dishes. During the raw sea urchin processing, the gonads are removed because they are culinary delicacies, while simultaneously high amounts of sea urchin wastes are produced (Castaldi et al., 2012), consisting of shells, spines and viscera (Bacenetti et al., 2021). Over than 80% of the biomass consist of waste particularly for the case of the green sea urchin. (Mamelona et al., 2010). The exploitation of sea urchin by-products constitutes a practice of waste deposit reduction and probably an environmental degradation reduction (Zilia et al., 2021). The pyrolysis process is a processing method for the valorization of sea urchin waste with the production of innovative materials, e.g., adsorbent materials, for the removal of organic compounds, which are toxic for the environment. Toxic pollutants, such as organic dyes, polyphenolic compounds, and heavy metals, can be removed from wastewaters, potable water, and groundwaters through different methods, i.e., filtration, liquid extraction, biological treatment, chemical oxidation. The above methods have many disadvantages such as insufficient capacities, slow reaction rates, and low selectivity (Yao et al., 2017). Adsorption is a widely used method because carbonaceous adsorbents have a large surface area, high adsorption ability, high purity, and easy availability. In the present study, new adsorptive materials are produced from sea urchin by-products through a physical carbonization process. The materials are characterized through FTIR analysis. Methylene blue (MB) adsorption experiments are conducted at two different adsorbent-to-solution ratios equal to 1.0 and 10 gL^{-1}. MB adsorption kinetics are also studied.

EXPERIMENTAL

Sea urchins were caught in the port of Myrina in Lemnos. After their transportation to the laboratory, the raw sea urchins were rinsed with running water and then they were separated to shells (S.U.S.H) and spines (S.U.S.P). Sea urchin waste biomass was dried in an oven for 72 hours. The dried waste biomass was crushed by blender, grounded by a mortar, sieved up to 300μm and then stored in a shady place at 15°C. The specimens were

carbonized in an horizontal cylindrical tube furnace under continuous flow of nitrogen. The produced carbonaceous materials were weighted before and after carbonization and then stored in the shade at 15°C. The discoloring abilities of carbonaceous materials were also determined. Methylene blue dye (MB) was used in a concetration of 0.032gL^{-1}, while the proportion of each carbonaceous material to MB solution rate was equal to 1.0 and 10 gL^{-1}. IR spectra were determined before and after methylene blue adsorption on the carbonized wastes using Agilent Cary 630 FTIR instrument. The kinetic study of MB adsorption on carbonaceous adsorbents was also examined with the application of five different models, i.e., pseudo-first order (Lagergren), pseudo-second order, Elovich, Power and Intraparticle diffusion model as it seems in Table 1.

Table 1: Kinetic equations of five different models, i.e., pseudo-first order (Lagergren), pseudo-second order, Elovich, Power 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 (mg g^{-1} min$^{-1/2}$), $t_{1/2}$, the time to reach 50% of the adsorbed amount, 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 AND DISCUSSION

The percentage of the weight loss of each waste after the carbonization process is equal to 53% for the spines (S.U.S.P) and 52% for the shells (S.U.S.H), indicating that the two parts of sea urchin present similar weight losses after the pyrolysis process.

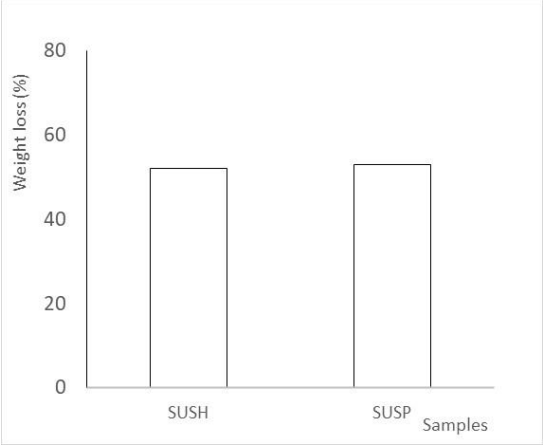
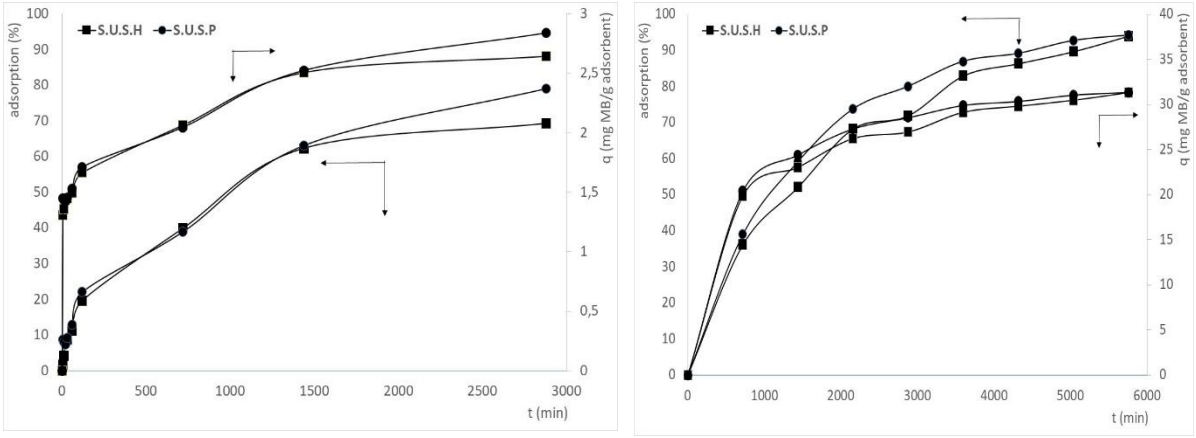


Figure 1: Percentage of weight loss for each sample after carbonization

According to Fig.2a, the increase in MB adsorption on carbonaceous materials follows the order: S.U.S.P>S.U.S.H. The results have shown that the carbonaceous material derived from sea urchin spines (S.U.S.P) has a maximum percentage of MB adsorption equal to 94.2% compared to shells S.U.S.H (93.96%), when the adsorbent to adsorbate rate is equal to 1.0 gL^{-1} of MB (Fig.2b). MB adsorption results on carbonized materials (79.09% for S.U.S.P and 69.26% for S.U.S.H.) are also presented to the adsorbent to adsorbate rate equal to 10 gL^{-1} (Fig.2a). Therefore, the carbonized spines adsorb quicker and higher amounts of MB dye in comparison with carbonized shells. Comparing the adsorption behavior of the two materials, i.e., S.U.S.P, S.U.S.H, in different ratios of adsorbent to adsorbate, it seems that the lowest ratio (1g/L) needs more time so as MB adsorption to reach

at equilibrium. Moreover, Fig.2a,b show that the carbonaceous material S.U.S.P has the maximum MB adsorption in equilibrium equal to 31.35 mg M.B/g adsorbent compared to all the other materials.



(a) (b)

Figure 2: MB adsorption percentage and MB adsorption per gram of adsorbent versus time from aqueous solution on carbonaceous materials in a proportion of adsorbent to adsorbate solution equal to (a) 10 g/L and (b) 1.0 g/L

According to Fig.3, the highest reduction of MB concentration in the solution belongs to SUSP in a proportion of 1.0g of adsorbent/L of adsorbate, while the lowest reduction of MB concentration in the solution belongs to SUSH in a proportion of 10g of adsorbent/L of adsorbate. As a conclusion, the carbonized sea urchin spines (S.U.S.P) adsorb quicker and higher amounts of MB dye in comparison with all the other carbonized materials.

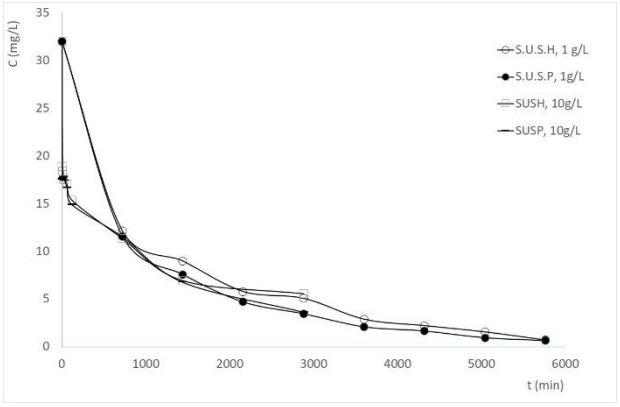


Figure 3: The concentration of MB in the solution (mg/L) versus time for the different types of carbonaceous materials (SUSH, SUSP) in two different proportions of adsorbent to adsorbate solution equal to 1 and 10 g/L.

The IR spectra of the materials (Fig.4) show a broad band around 3308-3350 cm^{-1} corresponding to O-H stretching vibrations, observed in samples that have absorbed methylene blue. The low peak at 3738 and 3630 cm^{-1} corresponds to free -OH groups. Moreover, the peaks at 1647cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB. The bands at 1395-1397 cm^{-1} is due mainly to the asymmetric deformations of C–H bonds, while the peak at 2301-2372 cm^{-1} is due mainly to stretching vibrations of C-N or O-C-O. The peak at 872 cm^{-1} could be attributed to the out-of-plane bending vibration of C–H in the aromatic ring and 1216 cm^{-1} corresponds to C-O stretching (Raspolli et al., 2015, Feng et al., 2020).

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. Power and Elovich kinetic models also present high correlation coefficient factors, r^2, for both SUSP and SUSH materials only in the proportion of adsorbent to adsorbate solution equal to 1.0 g/L. All the other models 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).

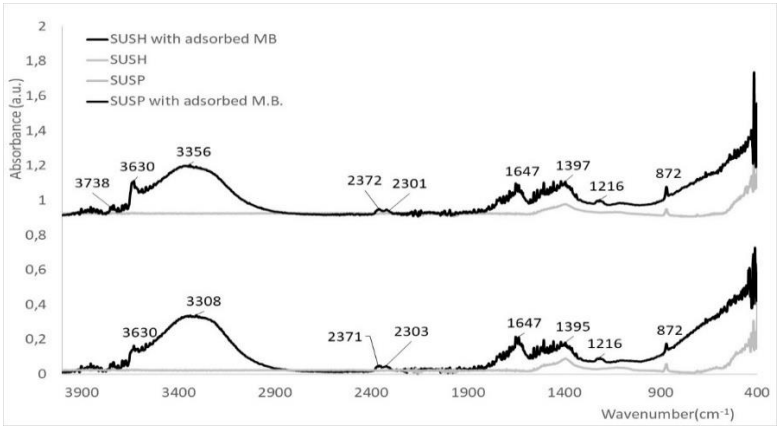


Figure 4: IR spectra of the carbonized biomass before and after MB adsorption using Agilent Cary 630 FTIR with the diamond ATR accessory.

Table 1: Kinetic parameters of the five different kinetic models, i.e., Intraparticle diffusion model, pseudo-second order, Lagergren, Elovich and Power in different proportions of adsorbent to adsorbate solution (w/v) in g/L.

Material code	w/v	$q_{e,exp}$	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	m	p	R^2	α	n	R^2
SUSH	1	31.31	0.37	0.89	$4.19x10^{-5}$	34.72	1.00	$6.53x10^{-4}$	23.63	0.95	0.26	0.17	0.98	4.72	0.22	0.98
SUSP	1	31.35	0.37	0.86	$5.38x10^{-5}$	34.28	1.00	$9.21x10^{-4}$	25.55	0.95	0.39	0.19	0.98	5.60	0.20	0.97
SUSH	10	2.64	0.03	0.70	$7.58x10^{-3}$	2.64	1.00	$1.57x10^{-3}$	1.43	0.90	8.11	4.62	0.92	1.01	0.12	0.96
SUSP	10	2.84	0.04	0.71	$5.50x10^{-3}$	2.81	1.00	$1.09x10^{-3}$	1.56	0.83	9.63	4.57	0.87	1.06	0.11	0.90

CONCLUSIONS

-The sea urchin biomass can be converted to carbonaceous materials via a pyrolysis process under an inert atmosphere, e.g., nitrogen atmosphere
- Sea urchin spines and shells present similar weight losses after the pyrolysis process
-The adsorption capacity of MB increases according to the order: S.U.S.P>S.U.S.H
-According to kinetic studies, the adsorption of dye on carbonaceous materials can be best described by the pseudo-second order kinetic model indicating that the prevailing mechanism is chemisorption
-According to IR analysis, the peaks at $1647cm^{-1}$ may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB indicating the adsorption of MB on carbonaceous materials.

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