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

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Introduction

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 (Bacenetti et al., 2021). 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 (Bacenetti et al., 2021, 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 (Zilia et al., 2021, Yao et al., 2017). 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 and then was crushed by blender, grounded by a mortar, sieved up to 300μm and 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 the carbonization process. The discoloring abilities of carbonaceous materials were also determined using methylene blue dye (MB) solution. The carbonized wastes were characterized by FTIR analysis using an 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.

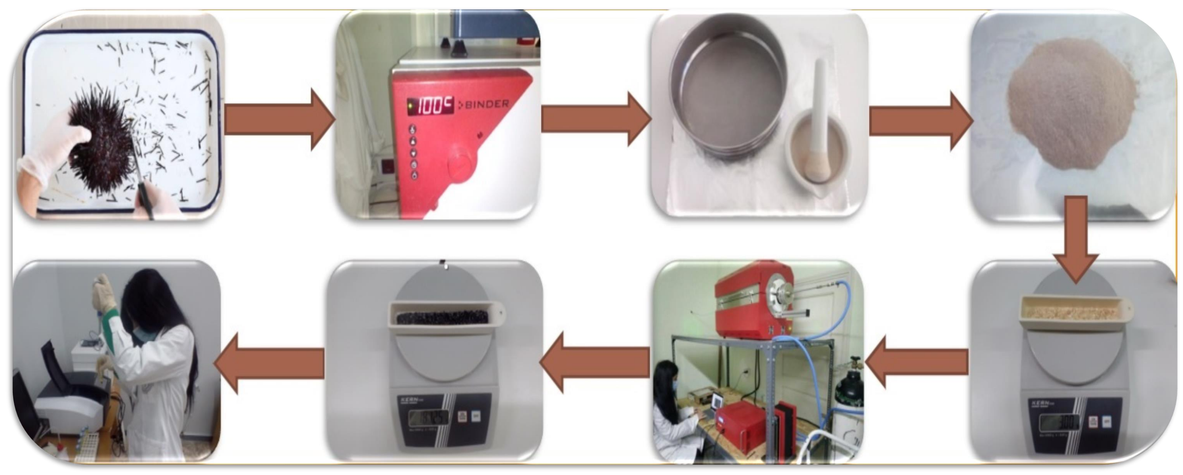


Fig. 1: Flow chart for the production of adsorbents through the pyrolysis process

Table 1: Kinetic equations of five different models, i.e., 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 & Discussion

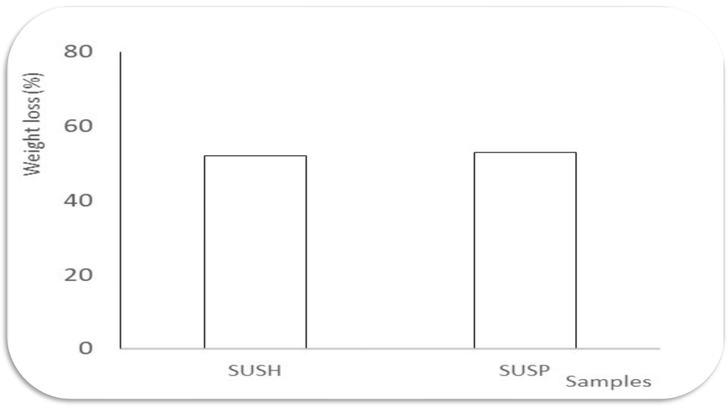
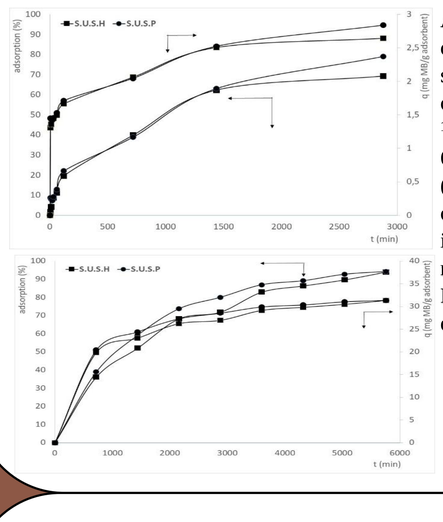


Fig 2: Percentage of weight loss for each sample after carbonization.

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.



According to Fig.3a, 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.3b). 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.3a). 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 (1.0g/L) needs more time so as MB adsorption to reach at equilibrium. Moreover, Fig.3a,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.

Fig 3: 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 and (b) 1.0 g/L

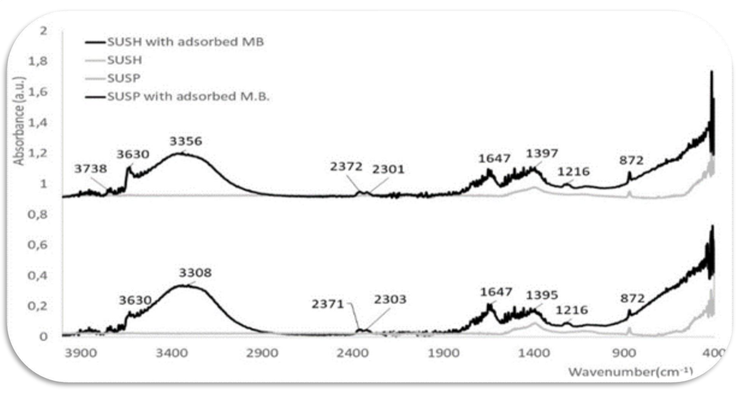


Fig.4: IR spectra of the carbonized biomass before and after MB adsorption using Agilent Cary 630 FTIR with the diamond ATR accessory.

Comparing the FTIR spectra of the adsorbents before and after MB adsorption (Fig. 4), it seems that the peaks at 1647 cm^{-1} may be attributed to C=C stretching "in plane" vibrations of the aromatic ring of MB (Raspolli et al., 2015, Feng et al., 2020).

Table 2: Kinetic parameters of pseudo-second order model in two different proportions of adsorbent to adsorbate solution (w/v) in gL^{-1}

Material code	w/v	$q_{e,\,exper.}$	Pseudo-second order		
			K_{SE}	$q_{e,\,theor.}$	R^2
SUSH	1	31.31	$4.19x10^{-5}$	34.72	1.00
SUSP	1	31.35	$5.38x10^{-5}$	34.28	1.00
SUSH	10	2.64	$7.58x10^{-3}$	2.64	1.00
SUSP	10	2.84	$5.50x10^{-3}$	2.81	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.

Conclusions

- ❑ The sea urchin biomass can be converted to carbonaceous materials via a pyrolysis process under an inert atmosphere.
- ❑ The adsorption capacity of MB increases according to the order: S.U.S.P>S.U.S.H,
- ❑ 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.
- ❑ According to kinetic studies, the adsorption of dye on carbonaceous materials can be best described by the pseudo-second order model indicating that the prevailing mechanism is chemisorption.

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