Development of A New Biosorbent Based on The Extract Residue of Marine Alga Sargassum Vulgare: Application in Biosorption of Volatile Organic Compounds

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Abstract—**The objective of this study is the valorization of a sub-product of marine alga; it is the extract residue of the marine alga Sargassum vulgare, which represents more than 80% of the weight of the raw material. It is a natural residue that we could turn into biosorbent under the effect of chemical activation with phosphoric acid which allows the development of a large pore in the activated material. To optimize the conditions for elaboration of our biosorbent, experimental design was applied to reduce the number of experiment trials needed to evaluate   some parameters (percentage of phosphoric acid, temperature and time of activation) and their   effects on the responses (capacity of biosorption of methylene blue, yield biosorbent). The product obtained under the optimal conditions has good textural and structural properties and development of surface functions. The application of optimized biosorbent in the treatment of gaseous effluents, has revealed its efficiency and significant biosorption properties towards some volatile organic compounds i .e. the toluene, the cyclohexane and the ethylbenzene.**

Index Terms— Biosorbent, Marine alga, Sargassum vulgare, characterisation, Biosorption, Volatile organic compounds.

I. INTRODUCTION

Volatile organic compounds (VOCs) are one of the families of the more common pollutants present in numerous industrial gaseous effluents. VOCs are known as one of the main

contributing to the formation of photochemical ozone and secondary organic aerosol (SOA), which would have the harmful consequence of healthy and serious environmental

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problems. They are therefore harmful or carcinogenic chemicals, their emissions have become the most rigorous environmental challenges in many industrial processes [1]-[3]. Reduction techniques of VOCs can be divided into two categories: destructive techniques (thermal oxidation and catalytic oxidation), which remove undesirable compounds, and recovery techniques (adsorption, absorption, and condensation) allowing their recovery [4]. Generally the methods (especially condensation) other than the adsorption are effective when VOCs concentrations are relatively high (> 1%). Therefore, the adsorption has been effective for low concentrations (ppm) [5]. This explains the growing interest in the development of highly efficient industrial adsorbents for the treatment of VOCs laden gas[6]. The objective of this study is the valorization of the part not extractible of marine alga by the development of a new biosorbent, optimization of conditions for its preparation, their characterization, and its application in the biosorption of volatile organic compounds.

II. MATERIALS AND METHOD

A. Biomass and chemical modification

The algae used in this study were collected from the Dar Bouaaza beach (Casablanca), Morocco in June 2011. Prior to extraction, the marine algae were identified, washed with running water and with deionized water. The washed biomass was oven-dried at 60 °C for 24 h, ground using an electric grinder, and extracted by methanol In order to eliminate the maximum of the extractable organic matter. The extract residues of the algae were washed with double distilled water, dried at 110 °C for 24 h, ground and reduced to a particle size between 1 and 2 mm, the obtained material was mixed with phosphoric acid ($H3PO4$), with a weight ratio of phosphric acid/ obtained material equal to 1/1. The mixture was dried overnight at 120 °C. The activated product has subsequently undergone heat treatment in air. The domains of variation of activation temperature, activation time and percentage of chemical activated agent were defined on the univariate analysis. To optimize the conditions for the elaboration of our biosorbent, the methodology of experimental design was used to reduce the number of experimental trials necessary for evaluation of the parameters studied (percentage of phosphoric acid, activation temperature and activation time) and their effects on the responses (biosorption capacity of methylene blue and yield biosorbent). The optimised biosorbent was obtained using 225°C activation temperature, 150 min activation time and 70% of chemical activating

agent, resulting in 66.14% of mass yield and 93.77 % of methylene blue biosorption capacity [7]. The optimised biosorbent was washed with distilled water until all acid was eliminated, dried, ground and sifted to obtain a powder with a particle size capable of passing through a 100µm sieve; it was finally kept in a hermetic bottle for subsequent uses.Final Stage

B. Physico-chemical characteristics of the biosorbent

Porosity and pore volume

The porosity and pore volume of the biosorbent were given by pycnometry. In order to determine the real density (ρ_s), water was chosen since it can penetrate in porous space [8]. Whereas, for the apparent density (ρ_p), mercury was chosen since it does not penetrate in the porous network. The porosity (χ) and pore volume (V_P) can be calculated by following equation:

$$X = \frac{\rho_s - \rho_p}{\rho_s} \times 100 \quad (1)$$

$$V_P(g/cm^3) = \frac{1}{\rho_p} - \frac{1}{\rho_s} = \frac{\chi}{\rho_p} \quad (2)$$

Surface area evaluation

The specific surface area of the biosorbent was estimated by the methylene blue (MB) biosorption method. MB stock solution 1000 mg/L was prepared by dissolving 1 g of MB in 1000 mL of deionized water. In a series of 250 mL glass bottles were placed successively 100 mL of MB solutions with initial concentration varying between 100 and 1000 mg/L and a biosorbent dose of 4 g/L. The bottles were capped and shaken for 24 h in a thermostatic bath at 25°C until biosorption equilibrium was established. Samples were taken and centrifuged at 4000 rpm and the supernatant was analyzed by measuring the absorbance at 664 nm, using a UV–visible spectrophotometer [9]. The amount of MB biosorbed q (mg/g biosorbent) was calculated by using the equation:

$$q = (C_0 - C_e)\frac{V}{m} \quad (3)$$

where C_o and C_e are the initial and equilibrium MB concentrations, respectively (mg/L), V is the total volume of the suspension (L), and m the biosorbent dose (g).

The plot of 1/q versus $1/C_e$ for the biosorption of MB on the biosorbent gave the saturation biosorption amount, determined from the slope of the plot. The MB molecule has a parallelepiped shape and can be regarded as a rectangular volume with dimensions $17 \times 7.6 \times 3.25$ Å. Previous research reported that, generally, for monolayer biosorption 2.45 m^2 can be taken as the occupying area for 1 mg MB. The specific area of the biosorbent was calculated by using the equation:

$$S = 2,45 \times Q_m \quad (4)$$

Iodine number

The iodine number (mg/g of biosorbent) was evaluated using the procedure proposed by the Standard Test Method (ASTM D 4607-86). The biosorbent (approximately 0.3–0.6 g) was placed in a 250 mL dry Erlenmeyer flask, and was fully wetted with 10 mL HCl 5% (in weight). The mixture was then boiled for 30 s and finally cooled. Then 100 mL of iodine solution (0.1 M) was poured into the flask, and the mixture was vigorously shaken for 30 s. After a quick filtration, 50 mL of the solution was titrated with sodium thiosulfate (0.1 M) until the solution became pale yellow. Two milliliters of starch indicator solution (1 g/L) were added, and the titration was continued with sodium thiosulfate until the solution became colorless. The concentration of iodine in the solution was thus calculated from the total volume of sodium thiosulfate used.

pH of contact

The measurement of pH of contact can quickly evaluate the acidity or basicity of a biosorbent. It was carried out and measured as follows: 50 mg of the biosorbent was placed in a 250 ml vessel and 100 ml of deionised water was added. This mixture was agitated for 24 h and filtered. The pH of residual solution was measured using pH-metter [10].

pH Point of zero charge (pHPZC)

The pH of zero point of charge (pHzpc) was determined by adding a known amount of the biosorbent (0.1 g) to a series of bottles that contained 50 mL of deionised water. Before adding the biosorbent, the pH of the solutions was adjusted to be in the range of 1.0–9.0 by the addition of either 0.1 M HCl or 0.1 M NaOH. These bottles were then rotated for 1 h in a shaker and pH values were measured at the end of the test. The pH of the suspensions is represented as a function of the initial pH of the solutions. The curve obtained theoretically cross the bisector of axes at the point of zero charge [11].

Fourier transform infrared (FTIR) spectroscopy

FTIR was principally employed as a qualitative technique for the assessment of the chemical structure of biosorbent. The FTIR spectra of the resulting biosorbent were recorded between 400 and 4000 cm^{-1} in a spectrometer type Perkin-Elmer 783.

Surface functional groups

The well-known Boehm's method allows modeling the principal acidic oxygenated functions of the biosorbent such as carboxylic acids, lactones, and phenols using bases of increasing strength as NaHCO$_3$, Na$_2$CO$_3$ and NaOH, respectively. Then, the total basicity is given by titration by HCl [12]- [13].

X-Ray diffraction

The X-Ray diffraction patterns were obtained using a PANalytical diffractometer equipped with a CuKα radiation (45 kV, 40 mA) at a step size of 0.06° between 5 and 90°.

Surface morphology

Scanning Electron Microscopy (SEM) was employed to visualize the external morphology. In the present work, the raw material and prepared biosorbent were analyzed by this technique using Environmental Scanning Electron Microscope (ESEM) (Mark FEI Quanta 200) to see the effect

of chemical activation with phosphoric acid on the structure of the raw material.

C. Experimental biosorption of VOCs

The biosorption study of VOCs is performed by "Headspace" in Static mode. It is an extraction device that works in tandem with a gas chromatography (GC) and which is reserved for the analysis of volatile compounds present in a non chromatographiable matrix [14]- [16].
The studied VOCs are toluene, cyclohexane and ethylbenzene.
A mass of 50 mg of the biosorbent was introduced into a pillbox of 20 mL. After the liquid was added using a micropipette. The pillbox was subsequently sealed by a septum. The studied VOCs were diluted in ethanol (10000 ppm).The samples were placed in thermal equilibrium for 24 hours at the temperature of 25 °C prior to analysis by gas chromatography. The analysis by gas chromatography gives a peak corresponding to each VOC and the area of each peak is a function of the amount of the respective VOCs.
The reducing volatility (RV) of VOCs was calculated using the equation below.

$$RV(\%) = \frac{1 - SA_{AC}}{SA_0} \times 100 \qquad (4)$$

Where SA_{AC} is the air surface of (biosorbent + VOCs) and SA_0 is the air surface of VOCs.

III.   RESULTS AND DISCUSSION

A. Characterization of the biosorbent

Physical characteristics

Surface area, porosity, pore volume and iodine number are characteristic parameters of the performance of the biosorbent.

The specific surface area of the biosorbent was estimated using the methylene blue biosorption method. The initial points on the isotherm plot of q versus C_e for the biosorption of MB on the biosorbent lie on the y-axis since the biosorbent at low initial solute concentration (100–200 mg/L) biosorbed all MB present in the solution (Fig. 1a). The plot of C_e/q versus C_e for the biosorption of MB on the biosorbent for initial MB solution concentrations ranging from 300 to 1000 mg/L at 25 °C gave a straight line with correlation coefficient 0.999 (Fig. 1b). The saturation biosorption amount was determined from the slope of the plot ($Q_m = 125$ mg/g). The specific surface area of the biosorbent was calculated as 306.25 m²/g.
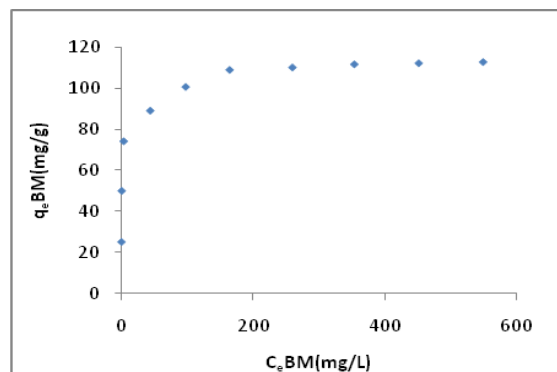

Fig. 1a. Biosorption isotherm of methylene blue on the biosorbent
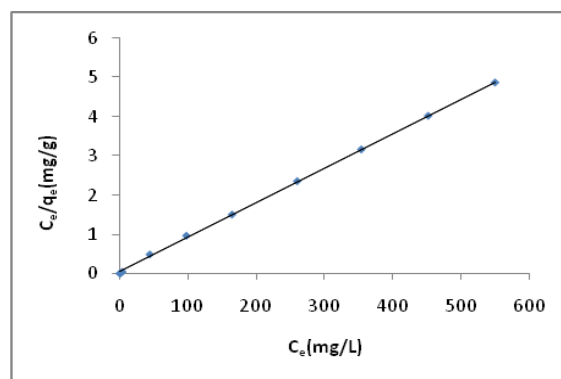

Fig. 1b. linear plot of langmuir isotherm for the biosorption of methylene blue on the biosorbent

The values of various physical parameters determined for the prepared adsorbent are regrouped in table 1.

Table 1. Physical parameters of the biosorbent

Physical parameters	Value
Estimated specific surface area (m²/g)	306
Pore volume (cm³/g)	0.88
Prosity (%)	69
Iodine number (mg/g)	846

The analysis of results presented in Table .1, can show that the developed biosorbent present a high iodine number which reveals their microporous structure.

The observation of the SEM image of the raw material   (Fig. 2a) shows that the grains are not homogeneous with almost total absence of porosity. The external surfaces of the prepared biosorbent (Fig. 2b) show large cavities and are very irregular, indicating that the porosity of the material was produced by attack of the reagent (H_3PO_4) during activation.
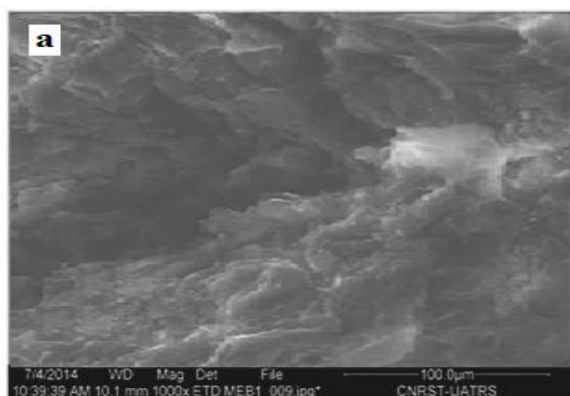
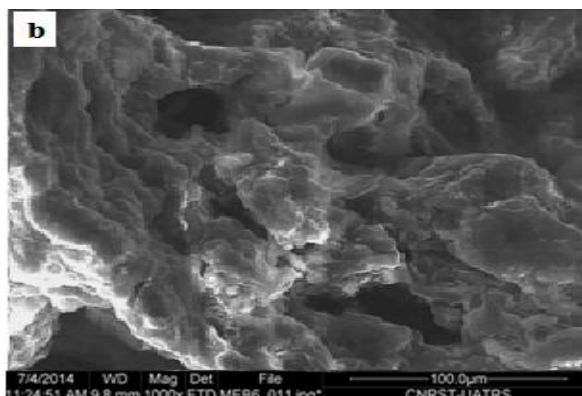Fig. 2a. SEM images of raw material

Fig. 2b. SEM images of biosorbent

Chemical characteristics

FTIR spectroscopic analysis: In this work, infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the biosorbent (figure not shown). A wide absorption band at 3200–3600 cm^{-1} with a maximum at about 3400 cm^{-1} is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl groups [17]. The absorption band at 2990 cm^{-1} is assigned to the stretching vibrations of aliphatic CH, CH_2, and CH_3 side chain groups of the aromatic nuclei. The absorption peaks at 2350 and 2330 cm^{-1} appeared for the biosorbent is possibly attributed to stretching [18]. The FTIR spectrum of the biosorbent contains absorbance peaks at 1600 and 1700 cm^{-1} which are the characteristics of C=O in quinone [19] and carboxylic acid structure respectively. The medium absorption band at 1400 cm^{-1} shows an aromatic ring of the biosorbent. The bands at 1200–1000 cm^{-1} have been assigned to C–O stretching vibrations in alcohols and phenols confirming the OH group in the biosorbent. The biosorbent contains –OH and C=O functional groups which could be involved in chemical bonding and may be responsible for the biosorption [20]. The oxygen of each carbonyl and hydroxyl group is considered a strong Lewis base because of the presence of nonbonding electron pairs. The oxygen base makes coordination bonds with the metal ions (which are Lewis acids).

Oxygen functional groups: The identification and quantification of the surface oxygen groups in the biosorbent was done by means of the point of zero charge and Boehm titration. The results are detailed in table 2.

The results show that the biosorbent produced by chemical activation is characterized by an acidic surface. The pH of the biosorbent was measured as 4.75. This result confirmed the Boehm analysis.

X-Ray Diffraction Analysis: The X-Ray Diffraction pattern of the biosorbent (figure not shown) exhibit broad peaks and absence of a sharp peak that revealed predominantly amorphous structure, which is an advantageous property for well-defined biosorbents [21]. However, the occurrence of broad peak around 24° showed sign of formation of a crystalline carbonaceous structure, resulting in better layer alignment [22].

Table 2. Chemical parameters of the biosorbent from Boehm method, pH, and Point of zero charge.

Chemical parameters	Value
Total of acid functions	1.34
Carboxylic (–COOH)	0.73
Lactones (–COO–)	0
Phenol (–OH)	0.61
Total of basic functions	0.295
pH	4.75
pH_{PZC}	4.25

B. Biosorption of the biosorbent

Reducing volatility of VOCs

The results of the reducing volatility of toluene, cyclohexane and ethylbenzene by the biosorbent are shown in table 3. The results show that the capacity of the biosorbent to fix the cyclohexane and the ethylbenzene is significant in comparison with toluene. Which indicates a high affinity of our biosorbent against theses molecules.

Table 3. Reducing volatility of VOCs

VOC	Reducing volatility (%)
Toluene	36
Cyclohexane	83
Ethylbenzene	73

Adsorption isotherms of cyclohexane and etylbenzene

The study of biosorption isotherms of cyclohexane and etylbenzene is based on their great affinities with the biosorbent. The Fig. 3 shows the biosorption isotherms of biosorbent at the temperature of 25 °C and at different initial amounts of cyclohexane and ethylbenzene.
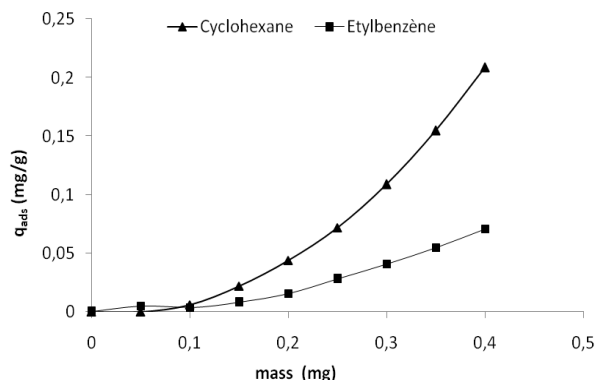
Fig.3. Biosorption isotherms of cyclohexane and ethylbenzene by the biosorbent at 25 °C

The biosorption isotherms of cyclohexane and ethylbenzene by the biosorbent are of type II of B.E.T classification, which generally corresponds to the multilayer biosorption on non microporous surfaces or a combination of type I and type II isotherms (Filling micropores followed by a multilayer biosorption on an external surface).

IV. CONCLUSION

In this study, we developed a new biosorbent from the extract residue of the marine alga *Sargassum vulgare* by chemical activation with phosphoric acid. The characterization of biosorbent showed that it has the very developed textural and structural properties with the presence of different functional groups (carboxylic, hydroxyl and lactone) and a porous structure on the surface of the biosorbent. The remarkable retention of cyclohexane and ethylbenzene indicates a high affinity of these VOCs against the biosorbent, which shows the possibility of using this biosorbent in the treatment of gaseous effluents, charged with VOCs.

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