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Adsorptive Removal of 2-Nitrophenol and 2-Chlorophenol by Cross-Linked Algae from Aqueous Solutions

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Abstract: The use of the cross-linked marine seaweeds Lessonia nigrescens Bory and Macrocystis integrifolia Bory to remove 2-nitrophenol and 2-chlorophenol from aqueous solutions at room temperature was investigated. The effect of the initial pH, adsorbent dose, and initial concentration of the pollutant were evaluated in batch experiments. The mathematical adsorption models of Langmuir and Freundlich show a mixed adsorptive mechanism of both phenolic compounds by the algae. The calculated parameters demonstrate a high adsorbent to pollutant affinity ratio, indicating the potential effectiveness of these marine seaweeds in the removal of these phenolic compounds from diluted aqueous solutions.

Keywords: 2-chlorophenol, 2-nitrophenol, adsorption isotherms, cross-linkage, marine algae

INTRODUCTION

The contamination of aquatic sources by organic and inorganic substances has always been a universal concern. Among common organic substances, phenols are undesirable industrial by-products and are one of the most dangerous (1). Phenols, their derivatives and the organic compounds with two condensed rings belong to the most recurrent and

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harmful contaminants in the plastics, dyes, and paper industries (2,3). The biodegradation of humic acids, tanines, and lignines also produce phenols under normal conditions. These compounds are toxic and pose a possible carcinogenic effect in humans which has not yet been completely understood. For this reason, a substantial number of phenols have been cited by the European Community Directive and the U.S. Environmental Protection Agency (EPA) (4,5). The concentration of these phenolic compounds established in potable water should not exceed $10\,\mu g\,L^{-1}$ according to the E.C. Directive 75/440/EEC (6). A very small concentration of phenolics can cause bad odors, particularly when the phenol contaminated aquatic systems are chlorinated for disinfection (7).

The isomers of nitrophenol are water soluble and moderately acidic in water, a product of their dissociation. 2-nitrophenol and 4-nitrophenol act as intermediates in the synthesis of phosphorilated pesticides and some pharmaceutical products. The primary sources of nitrophenols are benzene and oil refineries, charcoal mines and the plastics industry (8).

Chlorophenols are typically by-products of the paper industry, produced during the bleaching step, as well as in the preparation of antiseptics and pesticides. Moreover, they are skin permeable weak acids and rapidly absorbed by the human digestive system. The intoxication by chlorophenols causes breathing acceleration and nauseas in humans (9).

These phenolic compounds are generally eliminated by means of conventional techniques such as coagulation, solvent extraction (2), adsorption with activated charcoal (10–12), ionic exchange resins (13), photocatalytic degradation in suspensions of titanium oxide (14), oxidation with hydrogen peroxide (15), biodegradation (16,17), among others. Unfortunately, these technologies exhibit low efficiency in small contaminant concentrations and represent a big economic investment for developing countries, producing in some cases toxic residues that need later treatments.

For several decades, biotechnology has devoted a lot of effort to solving the problem of environmental pollution through the development of clean technologies for the removal of organic and inorganic contaminants. Biosorption has become a cheap and efficient tool, easily applicable in the detoxification of residual waters from mines and waters polluted with heavy metals (18) showing positive results. Commonly used biosorbents include marine seaweeds (19,20), edible mushrooms (21), yeast (22), and others (23–25). These biosorbents have also shown a high affinity towards organic pollutants.

This current research proposes the use of cross-linked brown marine seaweeds for the removal of phenolic compounds, taking 2-nitrophenol (2-NP) and 2-chlorophenol (2-CP) as model compounds. Cross-linked marine algae have previously demonstrated a high adsorption of phenols and derivatives (26) by several research groups that also utilized eggshells, chicken feathers, fungus, dried sewage sludge, etc. for the same purpose (3,27–31) but very few have coherently explained the obtained equilibrium parameters. Moreover, the effect of initial pH as a crucial step in the adsorption of organic compounds has not been completely investigated in previous studies. Our laboratory has determined the acid-base properties of brown marine seaweeds and other adsorbents by potentiometric titrations (32,33); these results will be utilized in the present work in order to analyze the effect of the pH on the adsorption as well.

EXPERIMENTAL

Chemicals and Solutions

Stock solutions were prepared dissolving 1 g of the phenolic compound (2-NP and 2-CP of analytical grade purity obtained from MERCK) in 1 L of deionized water. Different solutions were prepared by dissolution of the stocks to the desired concentrations. All the dilutions were made with type-I water purified by reverse osmosis using a Barnstead/Thermolyne (Dubuque IA) D2714 purifier, which provide water with a conductivity of 18 mΩ. The pH of each solution was adjusted to the required value with aliquots of 0.1 N HCl and 0.1 N NaOH upon contact with the adsorbent. No significant changes were observed in the initial pH once the equilibrium was reached, a constant pH during the experiments was assumed.

Pre-Treatment of the Adsorbent

The marine seaweeds Lessonia nigrescens Bory (S1) and Macrocystis integrifolia Bory (S2) were collected from the beaches of Tacna and Marcona in Peru, respectively, to a distance approximately 200 m from the shore. The algae were washed with abundant potable water, taken to the laboratory for their taxonomic identification and kept under refrigeration. Then, the seaweeds were washed with type-I water, dried at room temperature, ground, and separated according to their particle diameter by sieving.

Both seaweeds were cross-linked by suspending 2.5 g of particle diameter between 150 and 212 μm in 100 mL of a 0.2 M solution of $CaCl_2$, keeping a 2–3 W/V ratio of adsorbent mass and cross-linker volume; shaken at 175 rpm during 24 h by using a orbital shaker INNOVA 2100. The product was vacuum-filtered and washed with type-I water to remove any excess of $CaCl_2$. Finally, the algae were dried at 60°C and stored under refrigeration until their use.

Characterization of Adsorbent

The specific surface area of both cross-linked algae was measured by means of the methylene blue adsorption method at room temperature. The calculation was made assuming a value of 108 $(\text{Å})^2$ for the ionic cross-sectional area of methylene blue (34).

In order to analyze the thermal stability and detect possible impurities, thermal analysis (TGA) of the cross-linked algae was carried out with a thermogravimetric analyzer Perkin Elmer TGA7 at a heating rate of $5^\circ\text{C}\,\text{min}^{-1}$ up to 1000°C.

Infrared spectra of natural and modified algal biomass were recorded on a Perkin Elmer 1600 infrared spectrometer in order to identify the binding groups present in the surface of the algae and verify the absence of chemical modification due to the cross-linkage. Disks of finely ground powder of each dried sample combined with potassium bromide were prepared less than 24 h prior to recording.

Adsorption Experiments

Duplicated batch experiments were carried out by mixing variable masses of cross-linked algae S1 and S2 with 100 mL of a phenolic solution of 2-NP and 2-CP of variable concentrations at room temperature, under orbital agitation of 200 rpm during 24 h. The mixtures were filtered and the residual concentration of phenolic compounds was analyzed by using a UV-vis spectrophotometer SHIMADZU model UV-mini 1240 at wavelengths of 274 and 276 nm for 2-NP and 2-CP, respectively.

Effect of Initial pH

The effect of initial pH on the adsorption of both phenolic compounds was studied. The pH value of a solution of $100\,\text{mg}\,\text{L}^{-1}$ of the phenolic compounds was adjusted to a range between 2 and 10. Finally, 0.1 g of cross-linked adsorbent S1 and S2 were added to each.

Adsorption Isotherms and Effect of Biomass Dose

Solutions of different concentrations of phenolic compound were prepared with the pH adjusted to the optimum value as determined in the previous section then a variable mass of cross-linked seaweed was added. The same procedure was carried out for both seaweeds and phenolic compounds.

Data Analysis

The amount of adsorbed phenolic compound is expressed as Adsorption Capacity (q, g g^{-1}) and Adsorption Percentage (%ADS) calculated as follows:

$$q = \frac{(C_i - C_f)^* V}{m} \qquad (1)$$

$$\%ADS = \frac{(C_i - C_f)^* 100}{C_i} \qquad (2)$$

where m is the mass of adsorbent expressed in g, V is the volume of solution in L and C_i and C_f are the initial and at the equilibrium concentrations, respectively expressed in mg L^{-1}.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

A specific surface area of 1512 and 820 $m^2 g^{-1}$ for the algae S1 and S2 respectively was determined using the methylene blue method. These values are in agreement with the results found by Rubin et al. (34) in which values around 300 $m^2 g^{-1}$ were obtained for algal biomass sieved in the size pore range from 0.5 to 1 mm (five fold larger the size used in the present work). Other adsorbents were also analysed with this method, observing inferior surface areas: pre-treated cotton fibers around 35 $m^2 g^{-1}$ (35) and clays within the range of 118–782 $m^2 g^{-1}$ (36). We believe that the "egg-box" conformation of algae (18,19) is responsible for their higher surface area compared to the conventional cellulose composition of cotton fibers. As for the natural clays, even though they present a considerable surface area due to their intrinsic inner channelling nevertheless, their hydrophilicity plays an important role in the reduction of the adsorption of organic molecules such as methylene blue (36). We also believe the use of methylene blue on the surface area measurement of algae is more accurate than the BET method based on nitrogen adsorption and desorption isotherms where lower surface areas are usually found. The discrepancy may be the result of a different sorption mechanism for nitrogen and dye molecules since in the water-wet state (methylene blue method) the algae are swollen and there is a water filled porous structure (34).

The data corresponding to the thermogravimetric analysis (TGA) for the samples of S1 and S2 are presented in Fig 1. The results show a very stable structure up to 1000°C, only observing a loss of mass

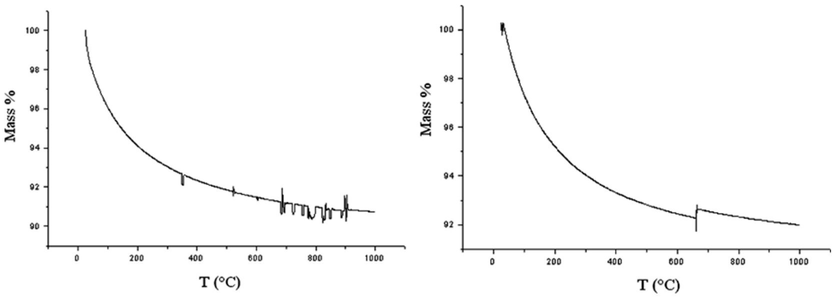

Figure 1. Thermogravimetric curves of cross-linked S1 (left) and S2 (right) algae.

percentage around 8% and 5% (S1 and S2 respectively) up to 250°C attributed to water elimination as explained by previous studies (22). The cross-linked algae do not undergo any oxidative decomposition or volatilization of organic matter within this range of temperature as do other biosorbents (22,25). This proves the enhancement of the mechanical properties of natural algae by cross-linking the polysaccharic chains of alginates with calcium, forming a rigid structure resistant to heat and oxidants.

The FTIR spectra of both native and cross-linked S1 and S2 algae are shown in Figs. 2 and 3. Both seaweeds show no substantial changes in the IR absorption before and after the cross-linkage with $CaCl_2$, elucidating no chemical modification of the adsorptive active sites on

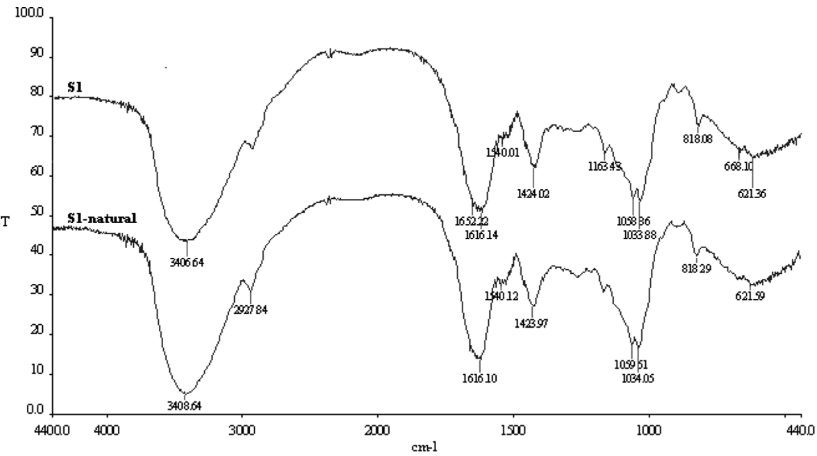

Figure 2. FTIR spectra of Lessonia nigrescens Bory before (S1-natural) and after (S1) cross-linkage with $CaCl_2$.

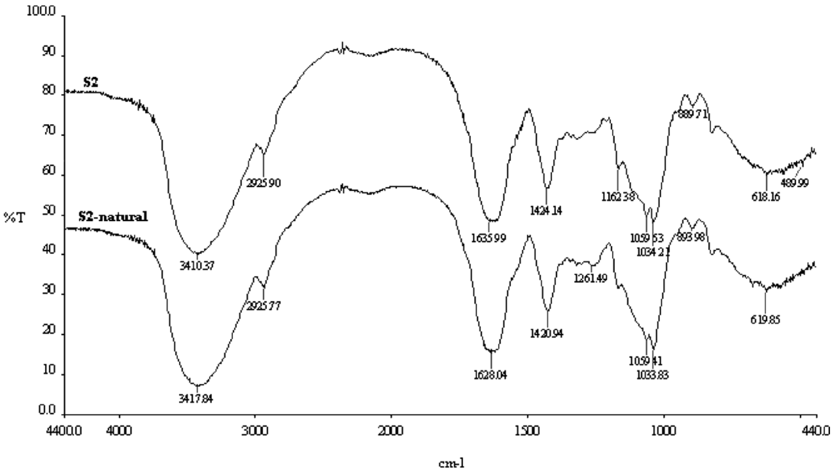

Figure 3. FTIR spectra of Macrocystis integrifolia Bory before (S2-natural) and after (S2) cross-linkage with $CaCl_2$.

the algae upon addition of the cross-linker. As seaweeds were reported to mainly contain carboxyl, sulfonate, and hydroxyl groups as well as proteins in their structure (20), the FTIR spectra is highly complex. In spite of this high complex nature, several distinctive features typical of brown seaweeds are seen. The peaks corresponding to 1035 cm^{-1} (sugar region), 1430 and 1635 cm^{-1} (carboxyl and protein region), 820 and 1160 cm^{-1} (sulfonate region) and the broad peaks between 3000 and 3600 cm^{-1} (–OH and –NH groups and hydrogen bonding) are all present in the IR spectra of both algae (20,37,38).

Effect of Initial pH

The dependence of the adsorption of contaminants by biosorbents on the solution pH is widely known, since pH not only affects the aqueous chemistry of the pollutant but also the degree of ionization of the adsorptive sites on the adsorbent surface (19,21). In the case of phenolic compounds such as 2-NP and 2-CP with pK_a values of 7.23 and 8.48, respectively (39,40), the degree of ionization practically depends on the experimental pH.

As expected, 2-NP is more acidic than 2-CP due to the strong delocalization of electrons from the hydroxyl group towards the nitro group by induction and resonance. Although 2-CP also presents both effects, the resonance contribution is not as effective as the one given in 2-NP. These phenolic compounds, compared from the heavy metals, can be adsorbed not only by electrostatic interactions, but also by Van der Waals forces in their neutral state. Consequently, the non-electrostatic interactions will be maximized with the decrease of the pH, due to the total protonation of phenols and adsorption sites.

Regarding the adsorbents, the algae S1 and S2 have been previously studied by our laboratory, based on their acid-base properties (32), showing high concentrations of the acidic group, in the range of 2.84–4.1 mmol per gram of seaweed and pK_a values of 3.13 and 2.83 for S1 and S2, respectively. Therefore, the surfaces of both algae will be negatively charged at pH values below the phenols' pK_a and in their neutral state above the same value.

Figures 4 and 5 show the effect of pH on the adsorption of 2-NP and 2-CP by both marine algae. For 2-NP, the alga S1 shows a higher adsorption percentage of 7.1% at pH 3, whereas the alga S2 reached 6.5% at pH 4. On the other hand, the maximum adsorption of 2-CP was around 14% with the S2 at pH 2 and 5.5% at pH 3 with the alga S1.

From the results, we can conclude that the maximum adsorption of 2-NP by both seaweeds is given at pH values higher than their pK_a, at

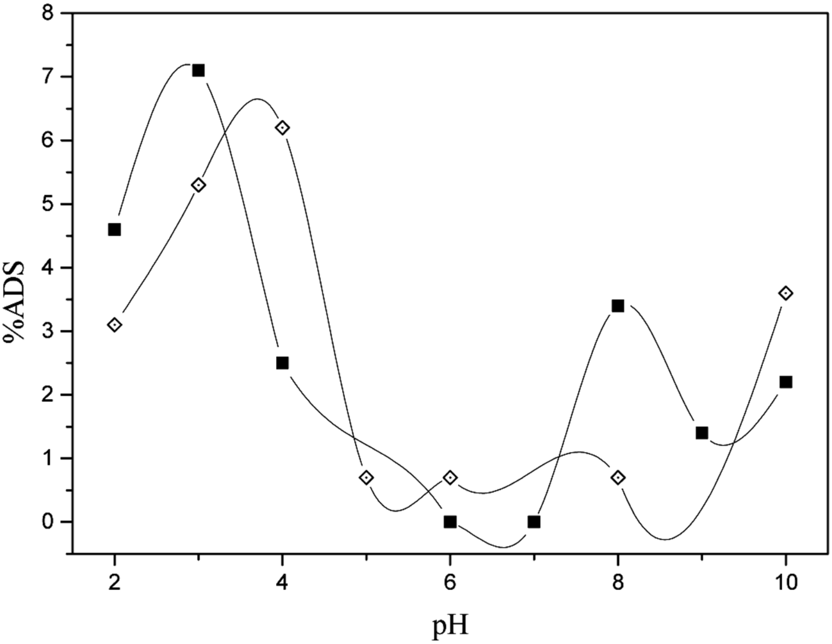

Figure 4. Effect of initial pH on the 2-NP adsorption by (■) S1 and (◇) S2.

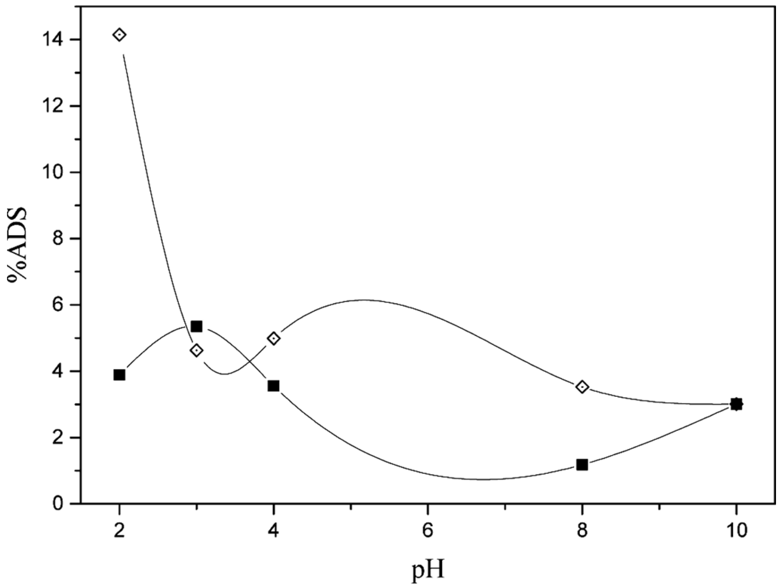

Figure 5. Effect of initial pH on the 2-CP adsorption by (■) S1 and (◇) S2.

which the adsorbent surface is negatively charged almost in its totality. Moreover, 2-NP is a type of phenol that is not equally polarized along the entire molecule, the negative charge is principally located on the nitro group ($-NO_2$) whereas the positive charge is distributed on the entire aromatic ring surface by resonance. Therefore, 2-NP will be better adsorbed in negatively charged environments, which is the reason why the maximum adsorption is reported at pH 3 and 4 for algae S1 and S2, respectively. These optimum pH values are below the ionization constants of alginates of these algae, as reported elsewhere (32).

At higher pH values a higher adsorption capacity may be expected, but the existence of other chemical species in the marina algae such as proteins and lipids, alter the acid-base equilibrium (20, 38) that may in turn alter the adsorption of 2-NP. Also, at pH values below to 7.23, 2-NP is deprotonated and would generate electrostatic repulsion with the negatively charged alginates, reducing even more the contact between the adsorbent and the pollutant.

As previously mentioned 2-CP does not have a distribution of electron density as expansive as 2-NP, therefore, 2-CP will have more affinity towards neutral environments; that is to say at pH values which alginate are neutral or protonated. For this reason, maximum adsorption is seen at pH values of 2 and 3 for the seaweeds S2 and S1, respectively.

Effect of the Adsorbent Dose

Figures 6 and 7 show the effect of different doses of algae on the adsorption of two different initial concentrations of 2-NP and 2-CP at the optimum pH observed in the previous section. From the results, we observe that the use of 0.125 g of alga S1 is sufficient to reach the highest adsorption percentage of 50 mg L^{-1} of 2-NP, utilizing more adsorbent does not cause any considerable increase in the adsorption. This could be understood as the saturation of the adsorbent surface under these experimental conditions. Rubin et al. (26) studied the adsorption of phenolic compounds by the brown marine seaweed Sargassum muticum, observing that 0.5 g of the alga levelled off the adsorption percentage. They consider that the plateau observed in the adsorption at high biomass concentrations is a consequence of partial aggregation of the algae in solution that reduces the number of available adsorption sites. For the alga S2, more than 0.375 g is required to saturate the surface, since an increasing adsorption is seen with larger amounts of adsorbent used within this range of mass.

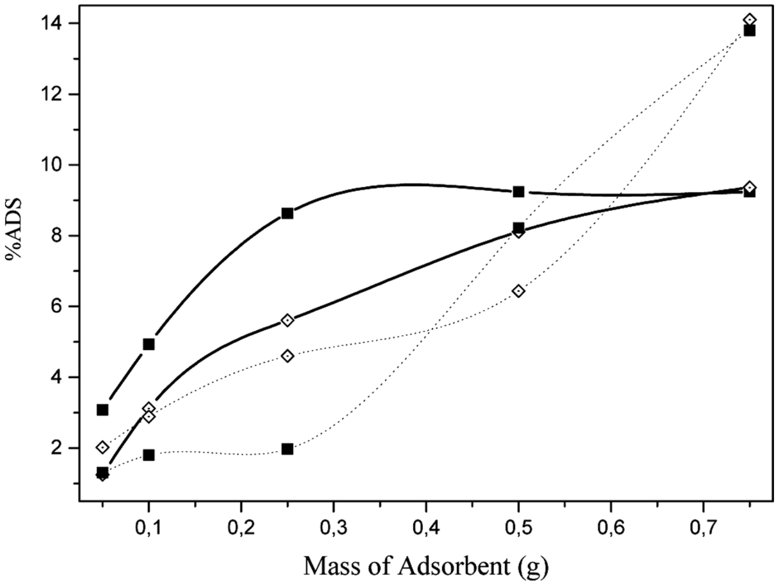

Figure 6. Effect of the mass of adsorbent on the 2-NP adsorption by (■) S1 and (◇) S2 at initial concentrations of 2-NP: 50 mg L^{-1} (solid line) and 200 mg L^{-1} (dotted line).

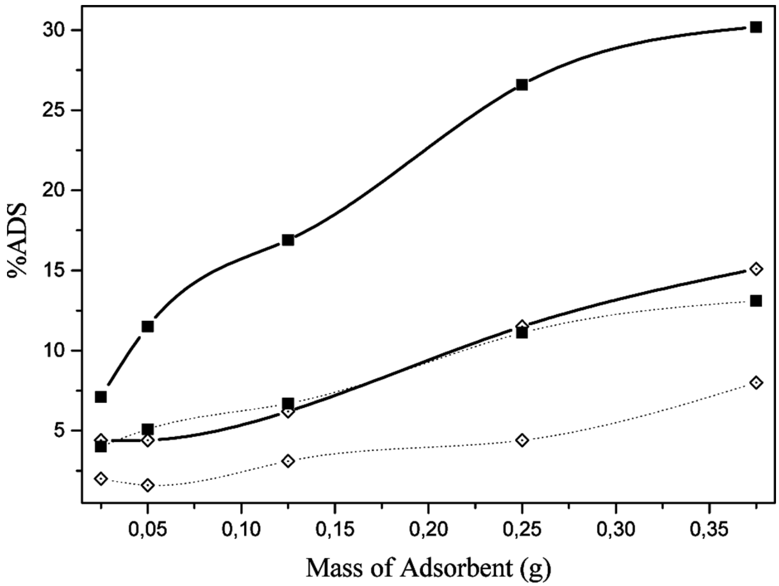

Figure 7. Effect of the mass of adsorbent on the 2-CP adsorption by (■) S1 and (◇) S2 at initial concentrations of 2-CP: 50 mg L^{-1}(solid line) and 200 mg L^{-1} (dotted line).

A gradual saturation of the surfaces of both is alga observed for both concentrations of 2-CP with the use of 0.375 g of both seaweeds. The use of more adsorbent doses would not generate substantial change in the adsorption percentage.

Adsorption Isotherms

The adsorption of 2-NP and 2-CP were analysed using the models given by Langmuir and Freundlich. Langmuir theory assumes uniform adsorption energy on the surface of the adsorbent, where the migration of the pollutant among neighboring active sites is restricted. The linear form of the Langmuir isotherm is calculated as follows:

$$1/q = 1/q_{max} + 1/(b^{*}q_{max}*C_f) \qquad (3)$$

where q_{max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and to the adsorption energy, respectively. The constant q_{max} represents the total number of available adsorption sites for one adsorbent. The constant b is important for the comparison of the adsorption efficiency between two different adsorbents under the same experimental conditions. A higher b constant represents a higher adsorbent/pollutant affinity. Figure 8 shows the lineal regression analysis for the Langmuir models of both marine seaweeds for 2-NP and 2-CP. The corresponding calculated Langmuir constants q_{max} and b are shown in Table 1.

The same adsorption results for both phenolic compounds were also analysed by the model of Freundlich, whose logarithmic expression is given by equation (4):

$$\ln\ q = \ln K + (1/n)^{*} \ln C_f \tag{4}$$

where K and 1/ n are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. Figure 9 shows the lineal regression analysis for the model of Freundlich of both marine algae for 2-NP and 2-CP. The calculated Freundlich constants K and n are shown in Table 1 as well.

From the equilibrium results, the alga S1 shows the highest adsorption capacity ($q_{max} = 167.5\,mg\,g^{-1}$) for 2-NP, adjusted to both adsorption theories of Langmuir and Freundlich, suggesting a mixed adsorptive mechanism. The alga S2 also shows a good affinity towards 2-NP, but apparently with a higher tendency to the Langmuir rather than

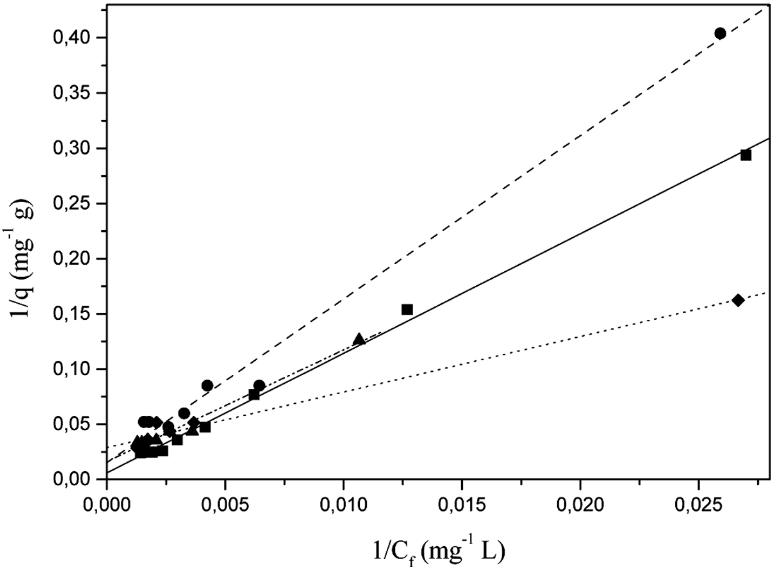

Figure 8. Linearized Langmuir isotherms obtained from 2-NP adsorption by S1 (■) and S2 (•) and 2-CP adsorption by S1 (◆) and S2 (▲).

Table 1. Values of the calculated constants in the Langmuir and Freundlich models

		Lessonia nigrescens Bory (S1)		Macroscystis integrifolia Bory (S2)	
Model	Coefficients	2-NP	2-CP	2-NP	2-CP
Langmuir	q_{max}(mg g^{-1})	167.504	61.275	65.317	34.614
	b (L mg^{-1})	0.00055	0.00161	0.00103	0.00574
	R^2	0.997	0.983	0.989	0.979
Freundlich	K	0.089	0.0925	0.149	0.722
	n	1.008	1.072	1.234	2.366
	R^2	0.997	0.946	0.935	0.996

Freundlich adsorption model. According to the Freundlich n value (n = 1 and 1.2 for S1 and S2, respectively), both marine seaweeds possess a high affinity towards 2-NP. Other adsorption studies of 2-NP with bentonites (41), show lower adsorption capacities than the ones reported in this work, with q_{max} near 38.5 mg g^{-1} and n = 0.088, which demonstrates a lower affinity between bentonite and 2-NP. On the other hand,

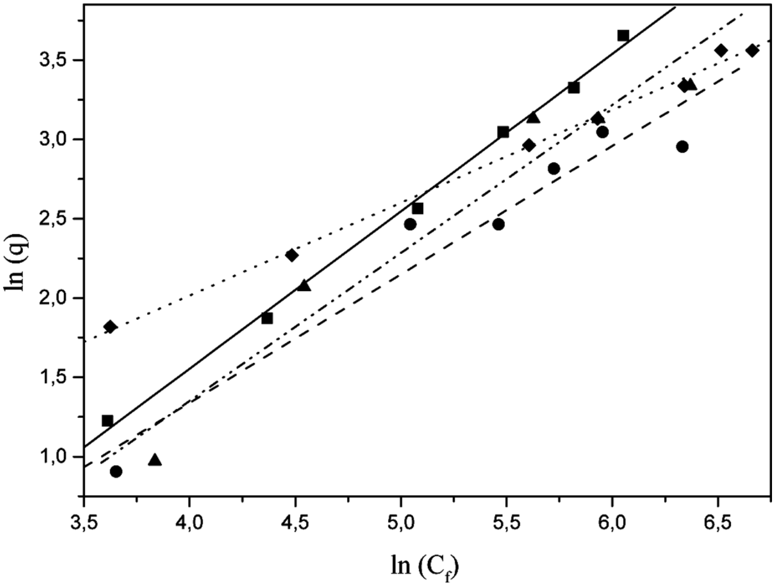

Figure 9. Linearized Freundlich isotherms obtained from 2-NP adsorption by S1 (■) and S2 (●) and 2-CP adsorption by S1 (◆) and S2 (▲).

biosorption studies with lignines (8) also report lower q_{max} values near $11.93\,mg\,g^{-1}$, considering the Langmuir adsorption model.

The alga S1 also presents a maximum adsorption capacity q_{max} of $61.28\,mg\,g^{-1}$ with 2-CP, mainly described by the Langmuir model, whereas alga S2 obeys both adsorption theories and possesses a high affinity with 2-CP as concluded from its K and n values (Table 1), according to the Freundlich theory. Other adsorbents like rice husks show equilibrium constants with values below the ones observed by S1 and S2 (1). Chan and Fu adsorbed 2-CP by using cationic starch, obtaining q_{max} values of $1.72\,mg\,g^{-1}$, according to the Langmuir model (42). Recently, Xialoli and Youcai determined that aged-refuse also adsorbs 2-CP under Freundlich model reaching K and n values of 0.042 and 1.22, respectively (43).

CONCLUSIONS

The present work demonstrates the marine algae Lessonia nigrescens Bory (S1) and Macrocystis integrifolia Bory (S2), cross-linked with $CaCl_2$, can potentially be used as adsorbents of organic molecules such as 2-nitrophenol (2-NP) and 2-chlorophenol (2-CP) from aqueous solutions at room temperature. The cross-linkage with $CaCl_2$ enhances the algae mechanical properties and shows no chemical alteration on their surfaces, evidenced by TGA and FTIR analysis, respectively. The pH shows a strong effect on the adsorption capacity of both algae and phenolic compounds, reporting a maximum percentage adsorption at pH 3 and 4 for 2-NP and pH 3 and 2 for 2-CP by using S1 and S2, respectively. These results are in agreement with the acid-base properties of the algae as previously observed (32), correlating the ionization constants of the functional groups on the surface of the adsorbent with the pH at which the maximum adsorption is observed. The adsorbent dose was studied as well, showing a higher adsorption with increasing amount of adsorbent until the saturation of the adsorbent surface. Such saturation was observed in the adsorption of $50\,mg\,L^{-1}$ of 2-NP by S1, requiring only 0.125 g for reaching the saturation of its surface. The excess adsorbent did not cause any substantial increase on the adsorption. Finally, the mathematical models of Langmuir and Freundlich were applied, proposing a mixed adsorptive mechanism for both phenols and adsorbents. The calculated parameters from the adsorption isotherms demonstrate an interesting adsorbent/pollutant affinity and a higher maximum adsorption capacity than the one reported in the available literature explaining their applicability for phenol-containing real solutions.

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