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Effect of pH on phenol biosorption by marine seaweeds

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Abstract

Biosorption of phenol by the marine seaweeds *Lessonia nigrescens Bory* and *Macrocystis integrifolia Bory* was investigated as a function of initial solution pH, showing a higher adsorption percentage at pH 10 with values between 10% and 35%, respectively. The apparent ionization constants of the algae were determined by means of the Katchalsky's theory, obtaining values close to 3.0 for both seaweeds. From the results, a strong adsorption dependence on pH is proposed at the level of the phenol's aqueous chemistry driven purely by a polar mechanism that involves the formation of hydrogen bonds with the hydroxyl groups that are spatially arranged in the polysaccharic chains that form the seaweed structure. This study shows that both marine algae are potential biosorbents in their application for the removal of phenol and derivatives from residual waters.

Keywords: Marine seaweeds; Phenol; pH; Hydrogen bond; Biosorption

1. Introduction

Phenols and derivatives are long half-life pollutants frequently found in industrial effluents. Phenolic compounds are widely used for the commercial production of a variety of resins such as: epoxic resins, phenolic resins, adhesives and polyamides for numerous applications. On the other hand, chlorophenols are extensively used as fungicides, herbicides, insecticides as well as for pharmaceutical applications, wood preservants, glues, paints, vegetable fibers and tannery [1,2]. Chlorophenols can be formed by the degradation of chlorinated pesticides, from the reaction of water with the phenols present in the environment and during the incineration of organic material in the presence of chlorine. This creates an even more dangerous contamination [3]. In general, phenolic compounds in potable water emit an unpleasant odor and flavor in concentrations as low as 5 μg/l and are poisonous to aquatic life, plants and human as a product of the bio-concentration. Ingestion of phenols in concentrations from 10 to 240 mg/l for long periods causes mouth irritation, diarrhea, excretion of dark urine and vision problems. The lethal phenol concentration in blood ranges approximately from 4.7 to 130 mg/l [4]. Due to their toxicity, the polynuclear aromatic and phenolic compounds were two classes of compounds widely perennial and classified by the Environmental Protection Agency (EPA) in 1984 as high level pollutants [5]. In this regard, the World Health Organization (WHO) followed the EPA's lead the same year by establishing the maximum level of phenol concentration allowable in drinking water at 1 μg/l.

With the purpose of keeping the drinking water within the permissible limits for its consumption, different methods of purification have been developed for its treatment, for example: sedimentation, precipitation, osmosis, ultra-centrifugation, micro-filtration, etc. Adsorption in activated charcoal is a method commonly used to remove phenolic compounds [6], but due to its high cost, its application is increasingly prohibited. Consequently, considerable research has been devoted to optimizing the removal techniques for phenol and derivatives from aqueous solutions.

Today, biotechnological processes have attracted the attention of the scientific community for their variety of purification techniques for environmental decontamination [7,8]. Among them, biosorption has already tackled the problem of phenolic compounds removal from aquatic sources, using a variety of biomasses and obtaining positive results.

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In the present work the use of brown marine algae that have been successfully used like adsorbents of heavy metals [9–11] is proposed. This biomass also shows a high efficiency in the elimination of methylene blue and other textile dyes [12,13]. Other studies have been conducted using adsorbents such as rice husk, eggshell, chitosan, chicken feathers, etc. [14–17]. But very few have established a mechanism coherent to the results [18], furthermore none of these have developed the role of the pH in the removal capacity of pollutants. Recent studies have elucidated the acid–base properties of marine algae [19] and fungi [20] in the adsorption of heavy metals, but their application to the elimination of phenols still remains unfinished.

2. Materials and methods

2.1. Reagents and solutions

Salts and reagents were of analytical grade obtained from MERCK. The solutions were prepared with type-I water purified by reverse osmosis using a Barnstead/Thermolyne (Dubuque IA) D2714 purifier, which provides water with a conductivity of 18 mΩ. The titrant was valued with potassium biphtalate. During the titration and equilibrium assays the pH was controlled by means of a Chem-Cadet 5986-25 potentiometer from Cole Parmer; the conductance of the solution was controlled as well, to confirm abrupt changes in pH.

2.2. Adsorbent preparation

The marine seaweeds *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2) were collected from the beaches of Tacna and Marcona in Peru, respectively, to an approximated distance of 200 m of the border. The seaweeds were washed with abundant potable water in order to eliminate solid particles and then, taken to the laboratory for their taxonomic identification and kept under refrigeration. Prior to their preparation, the seaweeds were washed with abundant type-I water, dried at room temperature, ground and separated in different sizes by means of sieves reaching particle sizes of ($d_1 < 75$ μm) and ($75 > d_2 > 106$ μm). A portion of the algae were suspended in 0.1N HCl under constant agitation during 1 h with the purpose of protonating all their active sites, then vacuum-filtered and rinsed with water type I to eliminate the excess acid. Finally, the algae were dried in the stove at 60 °C during 24 h and stored in hermetic plastic bottles, cooled until their use for the titration (sizes d_1 and d_2). For equilibrium assays, 2.5 g of seaweed (size d_1) was suspended in 100 ml of a solution 0.2 M of $CaCl_2$, shaked at 175 rpm during 24 h using an orbital agitator INNOVA 2100. Then, the seaweeds were vacuum-filtered, washed with type-I water, dried at 60 °C and finally stored in plastic bottles until their later use.

2.3. Potentiometric titration

1 g of HCl pre-treated seaweed (size d_2) was added to 100 ml of a solution 0.1N KCl, with the purpose of maintaining a stable ionic strength during all the titration. The initial solution pH of the protonated biomass was around 2.4 in both cases and titrated down to 2 by adding 200–300 μl of 6N HCl. The suspension was titrated with 0.25852N KOH within the interval of pH 2 to approximately 13. Each titration was made by duplicates at 25 °C using a constant temperature bath, keeping the container under nitrogen bubbling to maintain an inert atmosphere. The particle size d_1 of both seaweeds were titrated in the same way to analyze the effect of particle size on the titration.

2.4. Equilibrium assays

To correctly determine the effect of pH on the steady state, a constant mass of 100 mg were added to 100 ml of a 100 mg/l solution of phenol. The pH was adjusted to a range between 2 and 10, by using diluted solutions of HCl and NaOH.

The batch phenol biosorption was carried out in duplicate at room temperature under orbital agitation at 200 rpm during 24 h. The samples were filtered, diluted and their concentration was determined by using a UV–vis SHIMADZU UV-mini 1240 spectrometer at 510 nm of the colored product obtained by the reaction of phenol with 4-amino-antipyrine which reaches sensitivity as high as 100 μg/l.

2.5. Fourier transform infra-red spectroscopy

The type of binding groups present in the surface of the adsorbents was identified by FTIR analysis using a PerkinElmer 1600 infra-red spectrometer with a pellet of powered potassium bromide and dried algae.

2.6. Analytical procedure

In order to only compare the efficiency of both seaweeds considering the effect of the pH, the amount of adsorbed phenol by the algae is expressed as adsorption percentage by means of Eq. (1):

$$\%\mathrm{ADS} = \frac{(C_\mathrm{i} - C_\mathrm{f}) \times 100}{C_\mathrm{i}} \quad (1)$$

where C_i and C_f stand for phenol concentration in solution at initial and at the equilibrium, respectively, which is expressed in mg/l.

3. Results and discussion

3.1. Adsorbent's acid–base properties

Previous studies have determined that environmental polluting agents are mostly attracted to specific functional groups present in marine seaweed [10] and in other biosorbents [21] such as carboxyl and sulphonic acids and phosphates, under the form of alginates, fucoidans and phosphorylated proteins whose values of pK_a are 3.5–4.5, 1–2 and 3–4, respectively [10,22].

Figs. 1 and 2 empirically show points of equivalence near pH 7, which can be understood as the ionization of diverse functional groups that have different chemical properties present in both marine algae. Certain acidic behavior in the range of

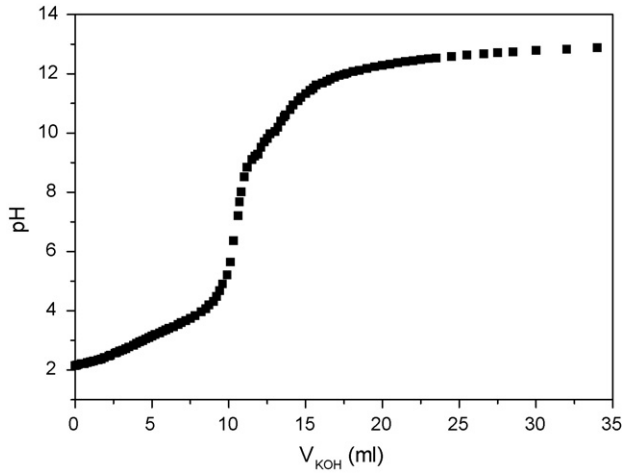

Fig. 1. Titration curve of *Lessonia nigrescens Bory* (A1) in 0.1N KCl at 25 °C.

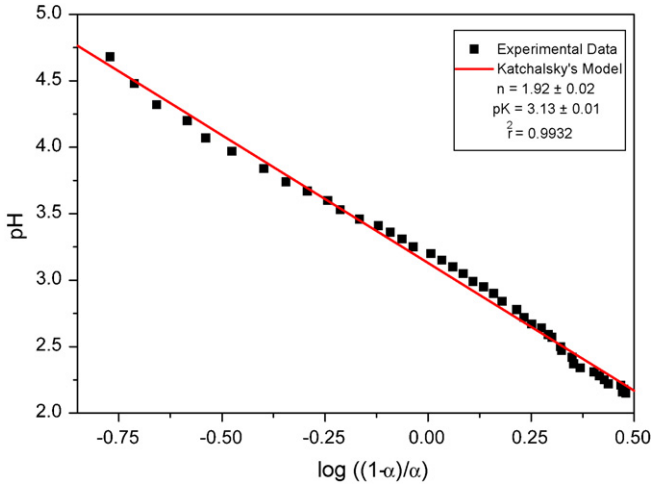

Fig. 3. Lineal regression analysis of Katchalsky's model in the titration of *Lessonia nigrescens Bory* (A1).

pH 10–11 for A1 could even be argued to be due to a slight deviation of the curve in this rank of pH (Fig. 1). Although both titration curves show similar equivalence points under equal work conditions, nevertheless A2 shows a better curve resolution (Fig. 2). This demonstrates a greater concentration of acidic groups that regulate their acid–base equilibrium, whereas in the case of A1, it could even display other groups like proteins and phosphorylated compounds that alter its equilibrium.

In order to understand the removal of phenol from aqueous solutions by means of mathematical models, the apparent ionization constant (pK_a) of both marine seaweeds and the total concentration of acidic groups expressed like carboxyl groups were determined. These algae have previously shown a high capacity of heavy metal adsorption [23,24].

The total concentration of carboxyl groups by gram of marine seaweed $[carboxyl]_t$ can be calculated in mmol/g taking into account the volume from the consumed titrant to reach the point of equivalence (V_q) of the potentiometric titration curve using a mass of adsorbent w. Eq. (2) summarizes it by means of the expression:

$$[\text{carboxyl}]_t = \frac{V_q\,[\text{base}]}{w} \tag{2}$$

According to the results, A1 presents 2.84 mmol/g whereas A2 reached a concentration of 4.1 mmol/g. The studies of Navarro et al. [20] showed concentrations near 1 mmol/g for edible mushrooms and Rey-Castro et al. [25] reported comparable values to ours for other varieties of marine seaweeds of 2 mmol/g. Katchalsky et al. [26] demonstrated that the titration curve of polyacid can be described by Eq. (3), based on constants n and pK:

$$\text{pH} = pK - n \log \frac{(1-\alpha)}{\alpha} \tag{3}$$

where α represents the degree of dissociation defined in Eq. (4) and n is an empirical constant, whose acceptable value is greater but close to one. Eq. (4) is summarized by means of the following expression:

$$\alpha = \frac{[\text{carboxylate}]}{(C_i V_i)/(V_i + V_b)} \tag{4}$$

where V_b represents the volume of base used in the titration and C_i is the initial concentration of acidic groups calculated in a similar form from Eq. (2), but referred to the volume of the dissolution, where now V_i (initial volume in ml) replaces the mass w. The variable [carboxylate] can be calculated by means of the charge balance of Eq. (5), where C_b represents the titrant concentration and $[H^+]$ the concentration of hydronium ions in the solution, calculated from the pH.

$$[\text{carboxylate}] = [H^+] + \frac{(V_b C_b)}{(V_i + V_b)} - \frac{K_w}{[H^+]} \tag{5}$$

After linear regression analysis pH versus $\log(1-\alpha)/\alpha$, the values of pK and n in both marine algae were calculated as shown in Figs. 3 and 4 with an acceptable coefficient of linear correlation. The same analysis with both seaweeds of particle size d_1 was performed, obtaining similar results (data not shown).

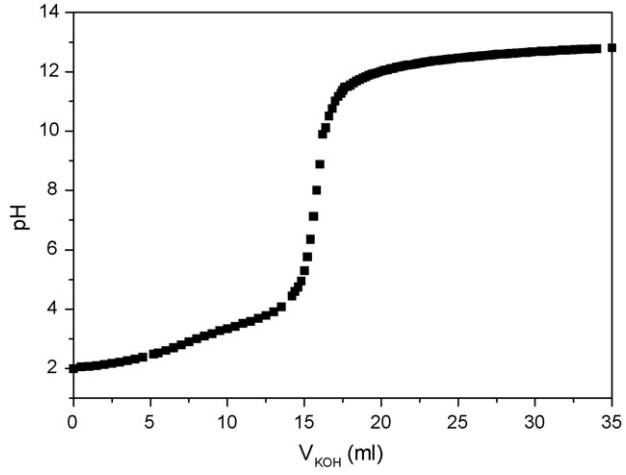

Fig. 2. Titration curve of *Macrocystis integrifolia Bory* (A2) in 0.1N KCl at 25 °C.

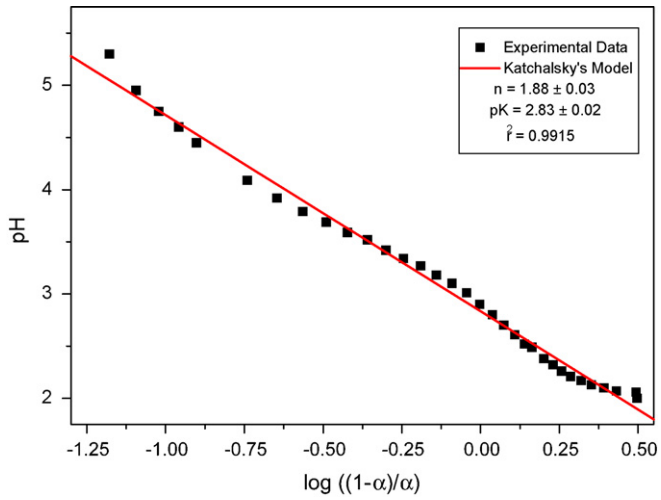

Fig. 4. Lineal regression analysis of Katchalsky's model in the titration of *Macrocystis integrifolia Bory* (A2).

For each seaweed, a pK_a within the range of 2.8–3.1 was observed, where A2 reports greater acidity (pK_a 2.83) and also a greater concentration of carboxyl groups by gram of biomass, that indicates that it not only contains ionizable acidic groups at low pH values, but that its surface is sufficiently populated with these carboxyl groups in comparison to A1, representing only 69% of A2 and has a pK_a of 3.13. These values are in complete agreement with the results reported by Chojnacka et al. [27] within the range 2.06–3.09 for the algae *Spirulina* sp.

Due to its lower pK_a, A2 might present a higher fucoidans concentration in its structure, whereas A1 possibly has a higher concentration of alginates and/or higher protein content that not only increases the pK_a values, but also alter the titration curve resolution. The ionization constants for both algae agree with the average pK_a of the functional groups present in their structures such as polyalginates and fucoidans and ratify the high adsorption capacity involving heavy metals at pH values greater than 2–3 [28,29] and methylene blue [30].

Table 1
Stretching frequencies observed in A1 and A2 FTIR spectra

Wavenumber (cm^{-1})	Assignment	References
3410	–OH, –NH stretching	[10]
1634	C═O stretch of COOH	[32]
1425	Symmetric C═O	[33]
1160	Symmetric $–SO_3$ stretching	[32]
1033	C–O alcohol	[10]
817	S═O stretch	[32]

3.2. FTIR analysis of biomass

FTIR spectroscopy offers excellent information on the nature of the bonds present on biomasses surface and allows the determination of different functionalities. Several chemical groups have been proposed to be responsible for the adsorption of contaminants. Among them, carboxyl, sulfonate, hydroxyl and amino groups are the most important in seaweeds [10,31]. The infra-red spectra of the cross-linked algae A1 and A2 is shown in Fig. 5. Both biomasses display a very similar spectroscopic profile, which suggests the presence of equal chemical groups on their composition. The main stretching frequencies observed by various references and the sources of these stretches are listed on Table 1. These results confirm the presence of acidic groups other than alginates, containing sulfonate groups (fucoidans).

3.3. Equilibrium assays

It is widely known that heavy metal adsorption by biosorbents strongly depends on the solution pH, since pH not only affects the metallic ion availability in solution but also the ionization of active sites on the adsorbent surface [34,35]. In the case of phenol (p$K_a \sim 10$), unlike metallic ions, the existence of two types of phenol–biosorbent interactions is postulated: one electrostatic (like metallic ions) due to the ionizable hydroxyl group and other hydrophobic thanks to the aromatic ring that phenol presents in its structure. As expected, the strength of the

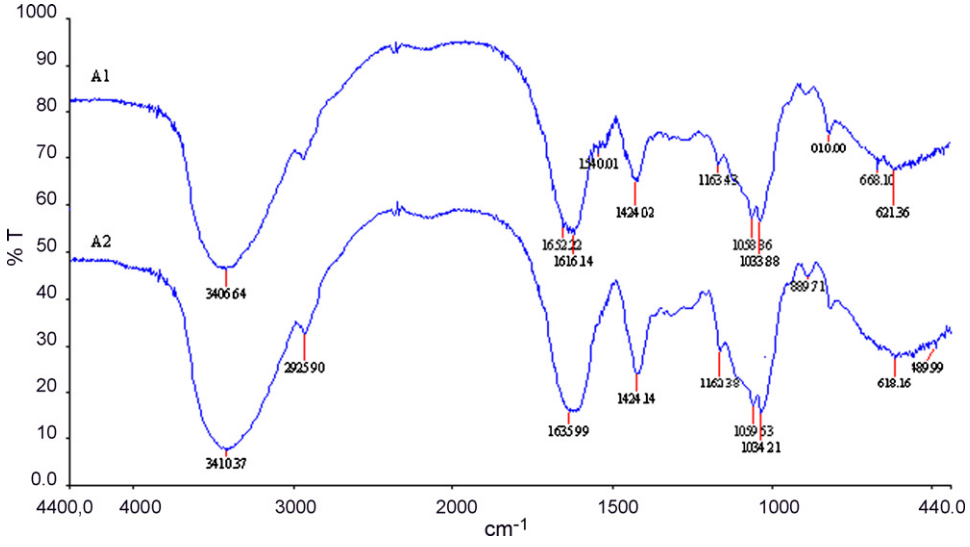

Fig. 5. FTIR spectra of cross-linked biomass of *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2).

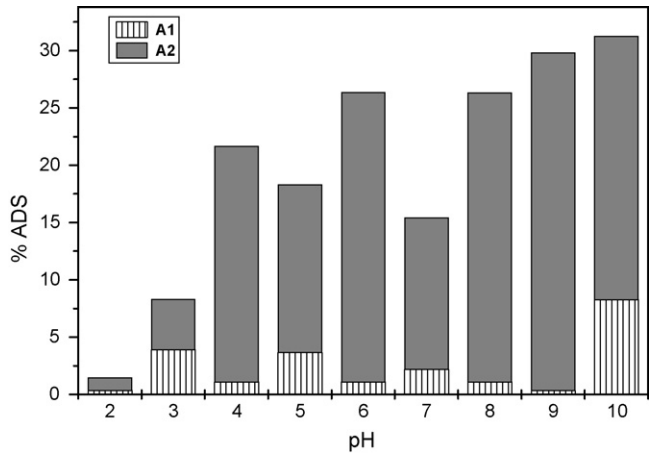

Fig. 6. pH effect on the adsorption percentage of phenol by both seaweeds. Initial phenol concentration: 100 mg/l, adsorbent mass: 100 mg with particle size d_1 at 25 °C.

hydrophobic interactions will be stronger as long as the hydroxyl group remains protonated (neutral) and this happens at pH values lower than 10. Consequently, the electrostatic interactions are proportionally maximized with increasing pH.

Fig. 6 shows the effect of pH on the adsorption of phenol for both marine seaweeds. A clear difference in the percentage of adsorption between both adsorbents is observed, being A2 the one that presents a maximum adsorption percentage near 35% at pH 10.

The seaweed A1 shows almost no adsorption capacity at low pH values, whereas it reaches up to 10% at pH 10. A2 also undergoes a gradual increase in the adsorption percentage with the increase of pH. Navarro et al. [36] elucidated the effect of pH on the biosorption of divalent cations under two points of view: chemical ion speciation in aqueous solution and the ionic state of the biosorbent's surface, like the two determining factors in heavy metal adsorption. On the other hand, the potentiometric titration results are in agreement with the theory of Katchalsky, showing that the surfaces of both seaweeds are negatively charged at pH values greater than 2.8. Nevertheless radical changes on adsorption around pH 2–3 in both seaweeds are not observed, rather a gradual increase in the adsorption percentage at greater pH values, which corresponds with the gradual deprotonation of phenol, rather than the ionization of the adsorbent's surface. In this respect, it is clearly established the importance of the chemical state of phenol over the chemical state of the adsorbent's surface.

Contradictorily, the adsorption percentage is increased with pH, which would imply the presence of the phenoxide anion and alginates in the same solution. Therefore, the carboxyl groups would not be responsible for the adsorption of phenol in marine seaweeds, due to the repulsion of their negative charges at pH where maximum adsorption occurs. The adsorption could be due to the numerous hydroxyl groups that remain protonated during the experimental conditions and posses a strong dipole O–H able to form three hydrogen bonds, which are strengthened if the other molecule is also charged, like phenol is at high pH values. This kind of adsorption has also been discussed by other research groups with a diversity of biosorbents [37,38].

This raises a question: can any polyhydroxylated compound adsorb phenol? The answer is no. Other research groups have studied the properties of other biosorbents rich in carbohydrates such as chicken feathers, paper-mill by-products, etc. and low adsorption capacities were observed [2,15,39]. The alginates in the marine seaweed have singular geometric distributions that differentiate them from the other polysaccharides. The alginates are polymers of guluronic (G) and manuronic acid (M), which are randomly alternated in the polysaccharic chain, co-existing sequences MM, GG, GM and MG as shown in Fig. 7. Particularly, it has been demonstrated that sequence GG is vital for the biosorption of heavy metals [11,40] because of its concave form that allows the formation of chelates. In addition, with the purpose of stabilizing the ionizable groups, the carboxyl group are always located in equatorial positions in the polysaccharide. This leaves the hydroxyl groups alone in the axial position, in which it could adsorb phenol by means of the proposed hydrogen bonds.

The adsorption of phenol could not occur by means of the sequence GG, as in the case of metallic ions since the great size and hydrophobicity of the aromatic ring would not be compatible with the available space nor with the polarity of the hydroxyl groups that are around.

The difference in adsorption percentages between both seaweeds is quite obvious, although both present high concentrations of alginates, nevertheless A2 presents a greater adsorption capacity (almost 35%). As explained in the previous section, the functional groups present in these seaweeds, are not in the same concentration. A greater amount of proteins in A1 is proposed, which would increase the repulsion of charges in the surface or could also be associated with the greater number of sequences GG in the polysaccharic chains that constitute their structure and that would be weak active sites for phenol.

Finally, Fig. 6 also stands out that the hydrophobic interaction phenol–adsorbent is very weak for A1, since at pH lower than the biosorbent's pK_a (neutral surface of the biosorbent), an adsorption percentage near zero was observed.

The biosorption of phenol by means of marine seaweed is a field that needs more meticulous study, allowing the opportunity to optimize its use and to elucidate the real mechanism. So far, a

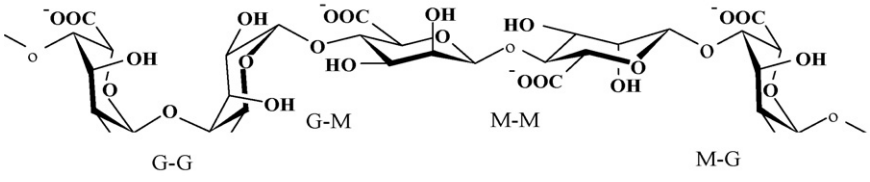

Fig. 7. Primary sequence of polyalginate.

mechanism very different from the one involving metallic ions has been postulated.

Future studies would include the effect of the temperature on the adsorption capacity, the released and absorbed enthalpy of the process would allow us to confirm the presence of hydrogen bonds between phenol and adsorbent, and elaborate isotherms of adsorption to verify a possible adsorption by multilayers, which is common in a system composed of low polarity compounds such as phenol and the preparation of mixtures metallic ion/phenol to verify if their adsorption is synergistic, antagonistic, indifferent or additive.

4. Conclusions

The use of marine seaweed *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2), for the adsorption of phenol was demonstrated to strongly depend on pH. The apparent ionization constants of both seaweeds were determined, considering the theory of Katchalsky, obtaining values of 3.13 and 2.83 for A1 and A2, respectively. The equilibrium assays reveal a greater adsorption percentage at pH near 10, when added with the ionization constants shows evidence that pH acts exclusively in the chemistry of phenol in aqueous solution, but not in the chemical state of the surface of the adsorbent. In addition, a maximum adsorption percentage was reached at pH 10 of 10% and 35% after A1 and A2, respectively. From the results, a purely polar adsorption mechanism rather than an electrostatic adsorption is proposed for phenol onto the surface of marine seaweeds by the formation of hydrogen bonds with the hydroxyl groups of the polysaccharides that form algae's structure, such as alginates that strengthen this adsorption thanks to its particular geometry. The present work elucidates that the studied algae are potential biosorbents for their application in the removal of phenol and derivatives as the result of industrial waste.

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