Research Article

Chemistry in Sustainability and Chemistry of Sustainability: Waste of use of Fishing Industry for Removal of Waste Textile Industry

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Abstract

One of the negative consequences related to socioeconomic development in recent centuries has been the rise of environmental contamination. In light of this, human has sought to implement actions in all spheres (social, economic and cultural) aiming to minimize the impact on the environment. Concern about the pollution of bodies of water and industrial wastewater treatment is the biggest worry in this regard. Among various treatment methods highlights the adsorption solid phase, by being very efficient and economically feasible. The use of chitosan as an adsorbent makes the process more ecologically interesting, once chitosan is also retrieved from waste. In this study we evaluate the adsorption process of the bromothymol blue dye by the chitosan. The parameters that influence the sorption process were studied (pH, ionic strength, adsorbent mass and dye initial concentration), and the process thermodynamics.

Introduction

It is inevitable not to recognize the benefits of scientific and technological advances in the quality of human life; likewise, it's impossible doesn't notice and recognize the effects of human activity on the environment and its serious consequences. In this context the term "sustainable development", first presented in 1987 has been adopted by many countries to assist in raising awareness of this problem [1].

This expression refers to activities aimed at reducing the amount of waste from production processes; it also relates to the search for viable economically alternatives of reuse and/or recycling of such waste. Considering this focus, powerful tool and special role is applied by Chemistry science.

Although wide and varied with regard to sustainability, a sector that has been highlighted in this scenario is the contamination of water bodies by discharging effluents from industrial processes [2,3].

According to current estimates, the textile industry works with an amount close to 100,000 different types of dyes used in the various stages of the industrial process; during the production process, the release of this material in the environmental has its inherent consequences. This effluent presents, in general, different types of dyes in wide ranges of concentrations, leading to several problems to the ecosystem [4-7].

Another highly-generating activity waste is the fishing industry. The cultivation of shrimp in captivity is one of the ways that cause significant environmental impacts. In this case, the product to be marketed, it is peeled and has its head removed, and this residue (on the order of tons) is disposed, becoming an environmental problem [8,9].

In order to minimize toxic effects of dyes to the environment and humanity, and to comply with all aspects of sustainability, it has been increasingly common (and in many countries is required) that industries treat their industrial wastewater before the release into the environment.

The effluent treatment with the aim of removal of dyes are usually classified as physical (such as filtration, sedimentation and sorption), physicochemical (such as coagulation, flotation separation or sedimentation) and biological (such as biodegradation and bioremediation) [10].

A very common way to reduce the concentration of dyes found in bodies of water is the solid phase extraction process. This process is currently one of the best cost-benefit relations between the physical processes, to be linked to low costs, high removal and, in some cases, it is not a destructive method (in this case, the adsorption enables recovery without decomposition of the dye) [11].

The literature is rich and varied in approaches in which the use of renewable sorbent is an interesting remediation strategy and wastewater treatment; in this sense, more recent studies point
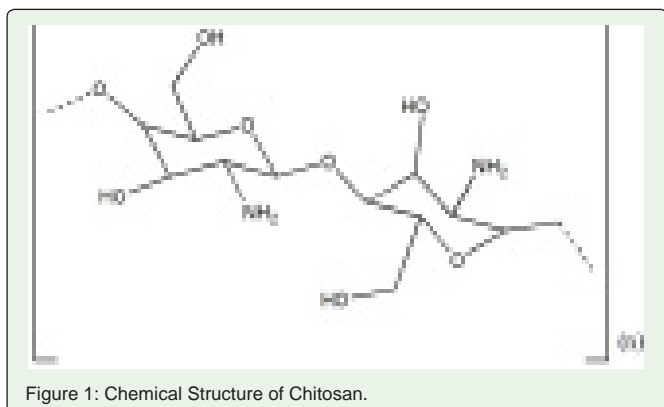
Figure 1: Chemical Structure of Chitosan.

to the use of derivatives of shrimp peel as chitosan (Figure 1), for solid phase extraction process, in order to extract some species of environmental interest. [12-18].

The shrimp peel is basically composed of chitin, through deacetylation of the acetamido groups produces another biopolymer chitosan. [19] This conversion improves considerably the sorption properties of the polymer, so that chitosan presents a straight chain polyamine with reactive groups amino and hydroxyl [5].

Although represented as a homopolymer, the chitosan is a copolymer composed of repeating units mainly β (l → 4) -2-amino-2-deoxy-D-glucose and β (l → 4) -2-acetylamino-2 deoxy-D-glucose of chitin, where this ratio varies according to the degree of deacetylation. [20] To be considered chitosan the product of the deacetylation must present degree of deacetylation higher than 50-60% [15].

Among the advantages of chitosan applying as well as solid phase that highlight its biodegradability, it is high sorption capacity and chelating, due to the presence of the hydroxyl and amino groups. Moreover, the load that the polymer may be adjusted depending on the solution pH, which allows improvements in its sorptive capacity. This adjustment normally occurs in the pH range between 5 and 9 (beyond this range the material is solubilized) [21].

In this work it studied the use of chitosan particles aimed at removing bromothymol blue present in aqueous solutions. The use of chitosan, then, is an advantageous alternative implementation for a material hitherto regarded as waste.

The bromothymol blue (Figure 2) belongs to the class of synthetic organic dyes, sulfophthaleines, it was chosen as model species to simulate contamination in water bodies from the textile industry [22].

The bromothymol blue is a species when in solution has halochromic property. In other words, an aqueous solution of bromothymol blue changes color depending on the pH, therefore, one of the most common applications of such dye is a pH indicator.

In the water it behaves like a weak organic acid having pKa 17.1. In aqueous solution, exhibits a yellow color when pH is below 6.0 and blue coloration when pH is greater than 7.6.

The color change of the acid for basic or basic for acid happens in certain pH ranges, called tracks or turning intervals, for the bromothymol blue is 6.0 to 7.6. When the pH is within the turning range the coexisting species contribute equivalently, forming an intermediate color, green.

The eviction of this irregular form of dye causes the change in water quality and a serious imbalance in the aquatic ecosystem. Once this has not biodegradable and colored species when found in natural water decreases the transparency of the water and the penetration of solar radiation, which modifies the photosynthetic activity and the solubility of gases scheme [4].

The studies of the thermodynamic focus were performed using univariate analysis, assessing different parameters influencing the removal process (pH of the aqueous phase, chitosan mass, ionic strength of the solution, contact time, process temperature) results were exploited for interpreting phenomenon according to the main models of isotherms, Freundlich and Langmuir.

Materials and Methods

Reagents and solutions

All the solutions used were prepared by direct dilution of the respective analytical grade reagents in ultrapure water (18.2 mΩcm) obtained by ultra purification system Elga Classic Plus.

The chitosan used was obtained from Sigma-Aldrich, prepared by washing with 500 mL of deionized water and subjected to drying in oven Brasdonto model 3 at 50° C for 40 min.

The stock solution of bromothymol blue (8.01×10^{-4} mol L^{-1}) was prepared. This solution was stored in an amber glass vial protected from light. The dye solutions employed in sorption experiments was prepared daily from appropriate dilutions of the stock solution.

The stock solution of Britton-Robinson buffer (4.0×10^{-2} mol L^{-1}) was prepared by adding 2.30 mL of glacial acetic acid, 2.30 ml phosphoric acid and 2,472 g of boric acid in volumetric flask of 100.0 mL, it swelled with ultrapure water. The pH was adjusted to pH: 6, 7, 8 and 9 using NaOH 6 mol L^{-1}.

The solutions used had their pH adjusted using appropriate dilutions of this buffer.

Instrumentation

Initially, the sorption tests were conducted in batch mode at room temperature (25°C) with constant stirring using a horizontal shaker MRII Roller Mixer Biomixer.
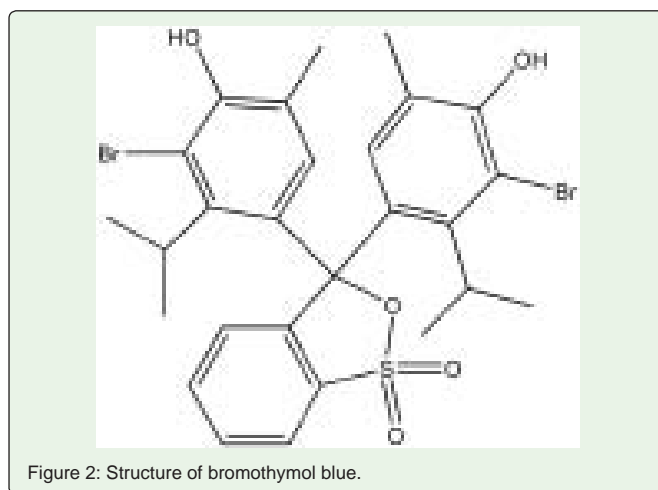

Figure 2: Structure of bromothymol blue.

At the end of agitation, the tubes containing the solutions for evaluation were centrifuged for phase separation prior to spectrophotometric analyses using an Eppendorf Centrifuge model 5804 with centrifuge capacity of up to 5000 rpm.

The weight of the adsorbent solid and reagents used for the preparation of the solutions was performed using an analytical scale Shimadzu model AUY 220(Sao Paulo, Brazil) with a capacity of 220g and accuracy of 0.1 mg. The pH measurements of solutions were carried out by a pH meter model DM 22 of Digimed (São Paulo, Brazil) with a combined electrode glass.

The monitoring of the concentrations of dye solutions during the adsorption step was conducted by an Agilent Cary 60 UV–visspectrophotometer (Agilent, USA) by means of spectrometric measurements in the 400-800 nm region. During the measures the solutions were conditioned in glass cuvettes with an optical path of 1 cm.

The thermodynamic study was conducted by immersing the samples in a water bath, controlled temperature and under stirring using a mechanical stirrer Novatecnica.

Sorption procedure

The dye sorption study was conducted in batch mode at room temperature and with constant stirring of 110 rpm, it using dispersions of particles of chitosan in bromothymol blue dye solutions. The influence of different parameters such as adsorbent mass, pH of the aqueous phase, contact time, initial dye concentration and ionic strength (adjusted by addition of NaCl) in the sorption process, it was evaluated using univariate analysis.

The solutions to be analyzed were prepared as follows: an specific amount of the mass of biopolymer was weighed and transferred to a 50 ml polyethylene tube and to this was added 1.0 ml of dyestuff stock solution (8.01×10^{-4} mol L^{-1}) and 2 ml of Britton-Robinson buffer (4.0×10^{-4} mol L^{-1}), and completing the volume up to 50 mL with ultrapure water. Each mixture was stirred for a time of 60 minutes at 110 rpm stirring speed, this stirring period was divided into stages, every 5 min stirring the mixture was stopped, the solution was centrifuged at 5000 rpm for 4 minutes and then an aliquot of supernatant was removed so that the molecular absorption spectrum could be recorded and used to calculate the removal efficiency. At the end of the spectrophotometric measurement, the aliquot was returned to the original flask containing the remaining mixture.

The analytical curves were constructed using a bromothymol blue solution at concentrations of 8.01×10^{-6} to 3.20×10^{-5} mol L^{-1} by adjusting the pH to 6.0 with Britton-Robinson buffer (4.0×10^{-4} mol L^{-1}). It was appropriate transferred in volumes of stock solution of bromothymol blue for volumetric flasks 5.0 ml, in which it was added 400 μL of buffer solutions used for the construction of curves. The volumetric flask was then swelled with deionized water. The experiment was performed in triplicate.

The removal efficiency was calculated by Equation 1, in which E is the removal efficiency in percent, C0 is the initial concentration of the dye and Ct is the concentration of the dye at certain time.

$$E\left(\%\right) = \frac{\left(C_0 - C_t\right)}{C_0} \times 100$$

Thermodynamic study

The construction of the sorption isotherms was necessary a strict temperatures control. The system by stirring was adapted so that the polyethylene tube containing the mixture (solution phase + solid) stay immersed in a water bath.

The temperatures studied were 25°C, 35°C, 45°C and 55°C. For this study 100 mg of chitosan masses were employed, followed by 100 μL of bromothymol blue (3.20×10^{-6} mol L^{-1}), 2 ml of Britton-Robinson buffer (4.0×10^{-4} mol L^{-1}) pH 6.0, and ultrapure water to adjust final volume of 25 mL.

The mixture was stirred for 120 minutes at 220 rpm of stirring speed, the agitation was stopped at each interval of 20 min, the solution was centrifuged at 5000 rpm for 4 minutes for the removal of an aliquot from the supernatant and obtaining the spectrum of molecular absorption. At the end of the measure, the aliquot was returned to the mixture.

Results and Discussion

Preliminary studies

Initially some preliminary experiments were realized to obtain the fundamental spectroscopic characteristics of the dye in the solution study. The molecular absorption spectra in the visible region to the dye solutions at the concentration of 3.20×10^{-5} mol L^{-1} prepared in the pH range between 6.0 and 9.0 (Figure 3) showed λ_{max} at 615 nm in accordance to that described by Meyer (2014).

The calibration curve was constructed using solutions with concentrations between 1.60×10^{-6} and 4.80×10^{-5} mol L^{-1} at pH 6.0, the signals was monitored employing λ_{max} for bromothymol blue. Under these conditions, we found a linear relation between absorbance and concentration ($Abs = 24159 C_{AB} + 0.0611$, $r^2 = 0.99$), which allowed to calculate process efficiency.

The concentration of 3.2×10^{-5} mol L^{-1} was chosen to be applied this work once it sufficiently reached a high value of concentration and absorbance (0.8), allowing, as the sorption occurs the measured signals are still within a range of proportionality between signal and concentration (linear range Lambert-Beer).
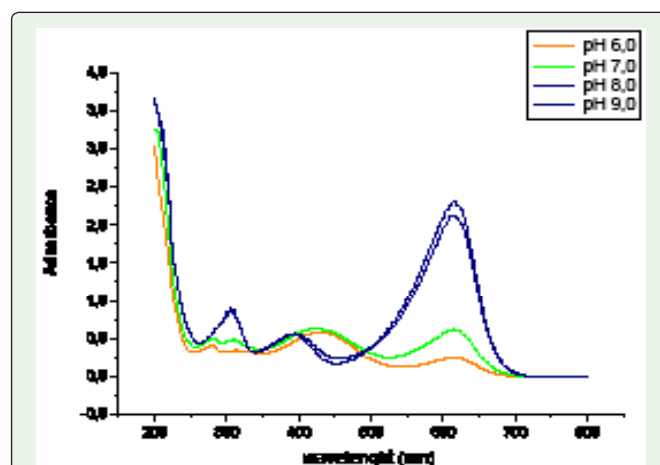

Figure 3: Adsorption spectra un the uv-visible region of bromothymol blu dye in water at pH 6,0 ; 7,0; 8,0 and 9,0.
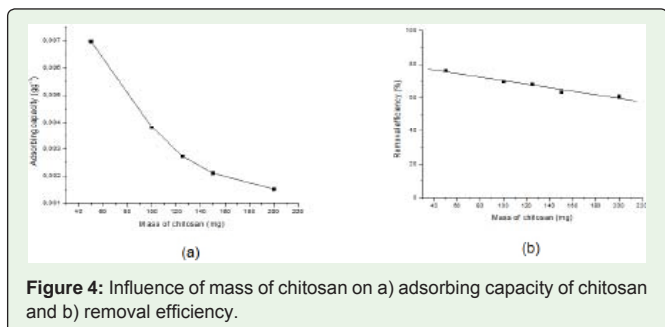
Figure 4: Influence of mass of chitosan on a) adsorbing capacity of chitosan and b) removal efficiency.

Evaluation of process variables

The process of sorption using chitosan as a solid phase is associated the physicochemical characteristics of the sorbent and sorvato and the process variables. The next items presented will be a discussion on the mass of the influence of the sorbent, initial solution pH, ionic strength and the initial concentration of the dye.

Study of the adsorbent mass influence on the adsorption of the dye: The study of the influence of the mass of chitosan in the sorption process was conducted by a variation between 50 and 200 mg of chitosan, for an initial fixed concentration of 3.2×10^{-5} mol L^{-1} of bromothymol blue dye at pH 6.0. The removal efficiency according to chitosan adsorbent mass is illustrated in (Figure 4).

It observed increase in removal efficiency resulting from the reduction of the adsorbent mass range applied. The highest efficiency was obtained in the mass of 50 mg which showed about 76.4% removal of the dye for chitosan.

The sorption capacity at equilibrium (q), expressed in g sorbed material per g of adsorbent was evaluated and the result is illustrated in (Figure 2b).

Crini (2008) describes that this effect can be attributed to overlapping or aggregation of adsorption sites, resulting in a decrease of the total surface available for adsorption of the colorant and an increase in the diffusion throughout the process.

Once sorption is a surface phenomenon, the increase in sorbent weight does not cause a proportionate increase in the amount of sites for adsorption, thus resulting in an absolute increase of sites, but a relative reduction in free sites for adsorption.

Study of the influence of initial pH on the adsorption of the dye solution: The effect of initial pH on bromothymol blue removal percentage using chitosan as adsorbents was evaluated by varying the starting pH of the solution in the range of 6.0 to 9.0, because the chitosan is solubilised pH ≤ 5.5 and pH > 9.0 is dissolved.

In (Figure 5) shows the solution removal efficiency behavior as a function of the initial pH.

According to the literature, adsorption of anionic dyes by chitosan is mainly mechanism by electrostatic interactions. [23,24]

Chitosan has a pKa around 6.3. That value depends on the mass, degree of deacetylation of this aminopolysaccharide and ionic strength of the solution. In an acidic ambience, protonation occurs at the amino grouping, generating positive charges on the surface of chitosan, which facilitates the electrostatic interactions with anionic dyes.

The bromothymol blue is an anionic dye that has in its structure a sulfonic grouping and two hydroxyls. That, when placed in contact with water behaves as a weak acid and its deprotonation enable a rearrangement of internal connections resulting in the formation of a SO_3^- group and at greater stability of the molecule *via* conjugated system. The SO_3^- group formed enables the interaction of this with cationic groups.

It was observed that increasing the initial pH decreased the sorption of the dye; it was caused by a reduced protonation of its amino groups. At alkaline pH the glycoside units of the adsorbent again show hydrogen interactions between monomer units of the same chain lowering its reactivity.

At pH 7, about 50% of the total amino groups protonated and remain theoretically available for sorption of the dye, with 100% of bromothymol blue, in the conditions are deprotonated. Thereby, coexistence of protonated amino groups of the dye and anionic species in solution to allow sorption, although in smaller amount.

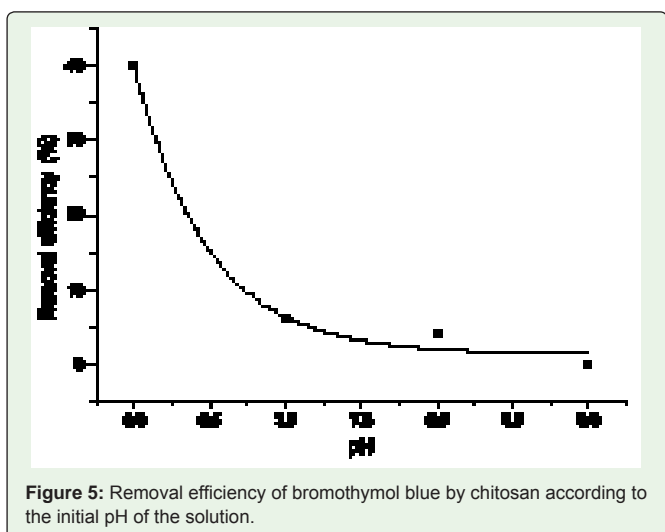**Figure 5:** Removal efficiency of bromothymol blue by chitosan according to the initial pH of the solution.
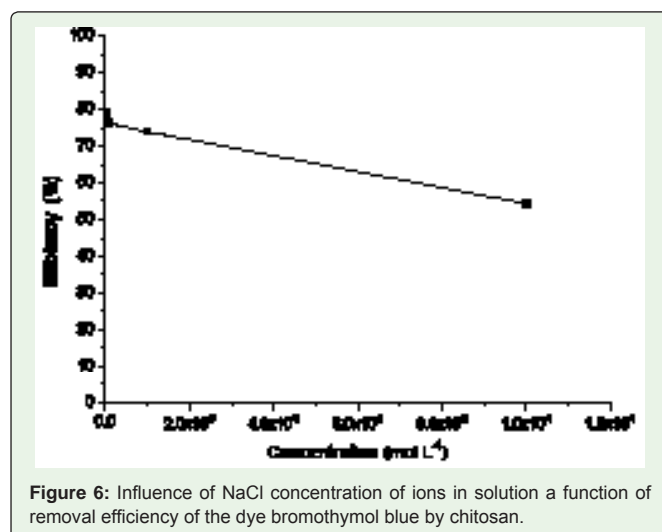

Figure 6: Influence of NaCl concentration of ions in solution a function of removal efficiency of the dye bromothymol blue by chitosan.

As the pH decreases, the protonation of the amine together with increases efficiency.

Therefore, in the pH range studied the dye will always present a negative charge. Once the sorbent has a positive charge in acidic and neutral solutions, the sorption of the dye can be explained by the electrostatic attraction between the sulfonic acid group present in the dye and protonated amino groups.

The highest percentage retention was observed at pH 6.0, of 40%. For the remaining studies, the initial pH of the solution was set at pH 6.0.

The influence of ionic strength on the adsorption of the dye: In this study, the influence of ionic strength on sorption of bromothymol blue by chitosan was evaluated by adding sodium chloride solution. The same was varied in the range of 1.0×10^{-4} to 1.0×10^{-1} mol L^{-1}. In (Figure 6) it can be seen that as the ionic strength increases, the removal efficiency decreases.

As expected, the dye sorption being electrostatic mechanism of the chitosan, the presence of other ionic species from the salt (Na^+, Cl^-) and buffer solution (PO_4^{3-}, BO_4^{3-}, $CH_3CO_2^-$, H^+, K^+) may interact with the dye and with chitosan, reducing the electrostatic attraction between them and consequently reducing the sorption.

The dye under negative charge (in the experimental conditions), this can be surrounded by positive species, while positive sites of the chitosan can attract negative species. This effect results in a reduction of the electrostatic interaction force between the positive sites of the chitosan and the anionic dye.

This behavior, observed in this study, was also described by Chiou, et al. [25], in their study of the adsorption of the RR 189 in chitosan beads, where it was observed that the presence of NaCl in the solution decreases the adsorption capacity and suggested that the addition of NaCl to reduce the electrostatic interaction between dye and chitosan.

Influence of the initial concentration of bromothymol blue in the adsorption: For the evaluation the concentration effect of this was varied between 8.0×10^{-6} mol L^{-1} to 6.4×10^{-5} mol L^{-1}. Figure 7 illustrates the behavior of chitosan removal efficiency as a function of the initial concentration bromothymol blue solution.
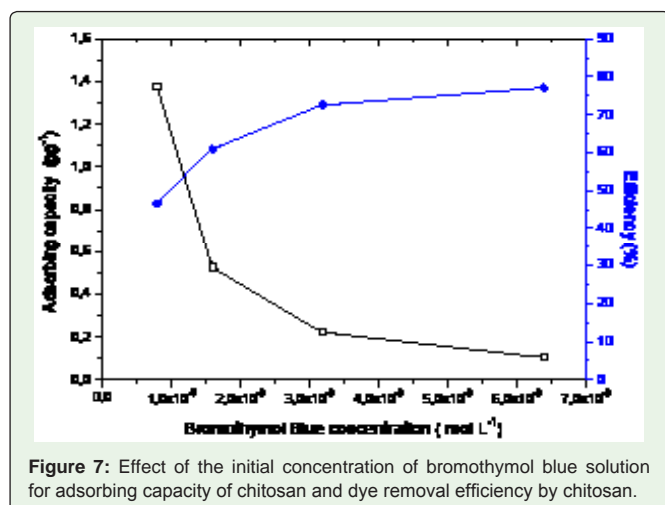

Figure 7: Effect of the initial concentration of bromothymol blue solution for adsorbing capacity of chitosan and dye removal efficiency by chitosan.

The profile of the curve obtained allows us to observe that the increase in dye initial concentration results in increased removal of dye by chitosan, but for higher concentrations of 3.2×10^{-5} mol L^{-1} removal efficiency remains practically constant with removal percentage of about 75%.

At lower initial concentrations of dye sorption on chitosan it is very intense and rapidly reaches equilibrium. This observation indicates the possibility of forming a monolayer of molecules on the external interface of chitosan [25].

The influence of increased dye initial concentration of chitosan in the adsorption capacity was also studied. The behavior of chitosan sorption capacity as a function of the initial concentration of dye can be seen in (Figure 7).

Analyzing the graph given "q" as a function of the initial concentration of bromothymol blue, a linear trend is noted, in increasing adsorption capacity of the adsorbent with the rise of the initial dye concentration.

This phenomenon is explained by the large number of active sites on the chitosan in relation dye mass. It would be necessary to further increase the dye concentration to reach the point of saturation sorption capacity of chitosan. To continue his studies, he was chosen dye concentration of 3.2×10^{-5} mol L^{-1}.

Study of the influence of temperature on the adsorption process of bromothymol blue: Another crucial aspect to be evaluated is the influence of temperature on the sorption process. This can interfere in the speed of reaction, the solubility of sorvato, the sorption capacity of the sorbent, among others. Determining the enthalpy (ΔH_{sor}), entropy (ΔS_{sor}) and Gibbs free energy (ΔG_{sor}) help us understand the spontaneity of the system under study.

For this study was used the pre-established standard conditions in the studies discussed above. The dye concentration was fixed at 3.2×10^{-5} mol L^{-1}, the mass of adsorbent used was 100 mg, pH and ionic strength of the solution (expressed in buffer concentration) was fixed in 6.0 and 4.0×10^{-2} mol L^{-1}, respectively with the temperature varying in the range of 25 to 55° C. Figure 8 illustrates the behavior of chitosan capacity and removal efficiency a function of temperature variation.

In this study was observed that the increase of 25° C to 55° C caused a 20% decrease of the adsorption capacity of chitosan.

Khattri, et al. [26] observed the same temperature effect on the sorption of the crystal violet dye in sawdust. The results indicated that the temperature rise promotes a reduction in the maximum sorption capacity of the sorbent. This behavior was explained by the relation of dependence of the solubility and chemical potential the sorvato with temperature, since with increasing temperature the solubility of sorvato increases, the chemical potential increases and both effects (solubility and temperature) working in the same direction in the chemical balance, causing reduction in sorption.

Determination of thermodynamic properties: The thermodynamic properties of ΔH and ΔS sorption were calculated through the employment of Equation 2 and are represented in (Table 1):

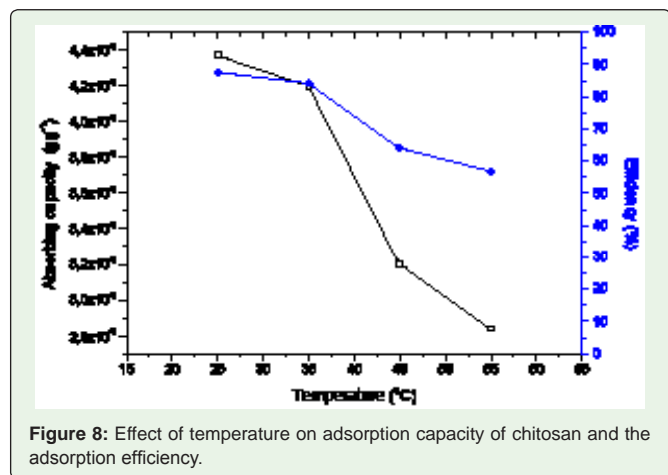$$\ln Kd = \frac{\Delta S}{R} + \frac{\Delta H}{RT}$$

Figure 8: Effect of temperature on adsorption capacity of chitosan and the adsorption efficiency.

In which R is the general gas constant (8.314 J K $^{-1}$ mol $^{-1}$) T is temperature (in Kelvin) and K_d is the distribution coefficient, which can be obtained from the ratio between sorption capacity (g g $^{-1}$) on the concentration in the liquid phase at equilibrium sorvato (g L^{-1}). The values for DH and Ds were calculated from the linear and angular coefficients, respectively, of the resulting straight ln K_d chart versus 1 / T. The Gibbs free energy was determined according to equation 3 below:

$$\Delta G = \Delta H + T \Delta S$$

The negative value of DH confirms the exothermic nature of the sorption process. The negative value of Ds indicates that the disorder in the solid-liquid interface during the process decreased, confirming the spontaneous formation of the adsorption layer. The negative values DH and Ds suggest that the enthalpy contributed more than entropy to obtain negative values of ΔG. Furthermore, the increase of ΔG due to the increase in temperature indicates that the sorption occurs more easily at low temperatures and is a strong indication that the conclusion of (Figure 8) is correct, so that the temperature raises disadvantage sorption.

Thermodynamic equilibrium

Considering that the models of the sorption isotherms are fundamentals to providing information about the properties of the sorbent surface and the affinity of the sorbent by sorvato, the equilibrium studies are extremely important to achieve a better understanding of adsorptive properties of a certain sorbent.

To conduct such studies was applied Langmuir and Freundlich, respectively, using the corresponding linearized equations for each
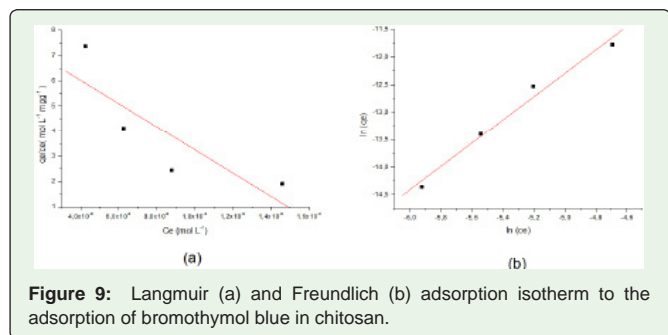

Figure 9: Langmuir (a) and Freundlich (b) adsorption isotherm to the adsorption of bromothymol blue in chitosan.

Table 1: Values of thermodynamic parameters.

Thermodynamic properties		Temperature (K)			
		298	308	318	328
ΔH(kJxmol^{-1})	-49.490	-	-	-	-
ΔS (kJ x K^{-1}x mol^{-1})	-0.107	-	-	-	-
ΔG(kJ x mol^{-1})	-	-17.587	-16.516	-15.446	-14.375

of these models. The Langmuir and Freundlich was adjusted to the experimental data, where the graphical representation of c_e/q_e in function of c_e and ln q_e in function of ln c_e, it is depicted in (Figure 9).

By the linearization of the models it was possible to obtain the respective parameters and through analysis of the values of linear coefficients (R^2) acquired for both models, the identification of the isotherm model that best represents the data of this study was performed.

The parameters obtained by applying those models to the experimental results are presented in (Table 2). The model that best fit to the results was the model of Freundlich isotherm.

The use of KF sorption coefficient allows identifying the adsorption capacity in balance for chitosan and KF obtained equal to 5.594 g g^{-1}. The parameter 1/n is the surface heterogeneity factor, thereby evaluating the degree of heterogeneity of sorption energy sites. Thus as more different of 1 is the parameter value, most heterogeneous is energy in the surface of the sorbent.

Therefore, it can be inferred that this is further evidence supporting the proposed mechanism of adsorption by electrostatic attraction, and also that the process may occur through the formation of multiple layers.

In this case, the formation of multiple layers can occur since the sorption mechanism is electrostatic. As these interactions are weak and long reach, the dye molecules will be attracted by the sorbent and other dye molecules through intermolecular interactions dipole-dipole and thus multiple layers are formed.

Finally, as experimental data are suited best to Freundlich model, according to literature, it is concluded that sorption dye bromothymol blue by this sorbent is reversible (physical adsorption) and exotherm as proposed in the previous section.

Conclusion

Through execution this work it was found to be possible to develop an analytical methodology using chitosan particles as solid phase, to retain the dye bromothymol blue from aqueous solution.

Table 2: Parameters for the Langmuir and Freundlich for absorption of bromothymol blue in chitosan.

Models	Parameters	Values
Langmuir	K_L (g g^{-1})	-5836.06
	1/q$_{max}$	-2.1833 x10^{-5}
	R^2	0.6992
Freundlich	1/n	2.114
	K_F (g g^{-1})	5.594
	R^2	0.9933

The chitosan showed an excellent performance as cationic adsorbent, with 69.75% efficiency in removing the dye to the solid phase at room temperature. Although the studies have been conducted with commercial chitosan, the same results are obtained with chitosan obtained by deacetylation, simple treatment of the waste from the shrimp industry with dilute acetic acid.

Thus, the use of chitosan for this purpose is an excellent tool to keep the industrial activities in a sustainable manner, since this is an alternative implementation to solve two environmental problems: the accumulation of residue from the shrimp and contamination of industrial effluents.

According to the studies performed using univariate analysis, it was observed that the increase of the mass of adsorbent, pH and ionic strength influence negatively the dye removal efficiency of the adsorbent. The increase of the initial dye concentration increases the removal efficiency and the adsorption capacity considerably.

In the equilibrium condition the best isotherm adjusted to the results obtained in the study was the Freundlich isotherm. As described in the model of the Freundlich isotherm adsorption process seems to involve the formation of multilayer and adsorption by electrostatic interactions. As those assumptions reaffirmed in the calculations of enthalpy, adsorption entropy and Gibbs free energy for the process.

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