



## Chitosan films modified with glow discharge plasma in aqueous solution of pyrrole and its evaluation in the removal of red dye no. 2

### Películas de quitosano modificadas con plasma de descarga luminiscente en solución acuosa de pirrol y su evaluación en la remoción del colorante rojo no. 2

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Received: December 24, 2019; Accepted: January 6, 2020

#### Abstract

In this work, the elasticity, morphology and chemical structure of chitosan(C)-glycerol(G)-EDGE films, treated with glow discharge plasma (GDP) of pyrrole for the removal of red dye No. 2, were studied. The treatment of the films with plasma was accomplished supplying 1.57 kV voltage, a current of 0.74 A, and a frequency of 5.54 kHz. The exposure times of the films to the plasma were 20, 40 and 60 min and a mass of 15 mg of film were used. The stress-strain results for untreated films was 2.6 N with an elongation of 17 mm, while for the treated film was 66 N with an elongation of 6 mm. The film, treated for 40 minutes at pH of 5, showed the highest adsorption capacity at  $q_e = 770$  mg/g. The morphology of the film before its treatment showed a smooth surface; after treatment, some pores were observed, produced by the impact of pyrrole ions on the surface of the film. The hydroxyl -OH functional groups that belongs to the chitosan decreased after plasma treatment, and the presence of the N-H, C-N and C=C groups, produced by the polymerization of pyrrole in the chitosan polymer matrix.

**Keywords:** Thin film chitosan-glycerol-polypyrrole, azo dyes, adsorption, glow discharge plasma.

#### Resumen

En este trabajo se presenta un estudio sobre la elasticidad, morfología y estructura química de películas de quitosano-glicerol-EDGE tratado con plasma de descarga luminosa (GDP) en presencia de pirrol para la eliminación del colorante rojo No. 2. El tratamiento de las películas con plasma se realizó suministrando un voltaje de 1.57 kV, una corriente de 0.74 A, y una frecuencia de 5.54 kHz. Los tiempos de exposición de las películas al plasma fueron 20, 40 y 60 min. y una masa de 15 mg de película fueron utilizados. Los resultados de la prueba de esfuerzo-deformación para las películas no tratadas fue de 2.6 N con un alargamiento de 17 mm, mientras que para la película tratada fue de 66 N con un alargamiento de 6 mm. La película que mostró mayor capacidad de adsorción de colorante fue la tratada durante 40 minutos con una  $q_e = 770$  mg/g a pH de 5. La morfología de la película antes del tratamiento mostró una superficie lisa; después del tratamiento, se observaron poros, producidos por el impacto de los iones de pirrol en la superficie de la película. Los grupos funcionales hidroxilo -OH que pertenecen al quitosano disminuyeron después del tratamiento por plasma, y se presentó la aparición de los grupos N-H, C-N y C=C, producidos por la polimerización del pirrol en la matriz polimérica de quitosano.

**Palabras clave:** Películas quitosano-glicerol-polipirrol, colorantes azoicos, adsorción.

## 1 Introduction

Currently, one of the main worldwide problems is the environment pollution, mainly on water because of the industrial development and primarily those that uses “azo” dyes in their processes to give a different appearance to their product (Arango-Ruíz *et al.*, 2009; Dotto *et al.*, 2015). Although azo dyes are not

toxic, most of them have a nitrogen-nitrogen (N=N) double bond, whose fragmentation pattern results in the release of aromatic amines, which possess high toxicity when they are put in contact with water (Vakili *et al.*, 2014; Hadi *et al.*, 2014).

Industries, that generate this type of pollution during their dyeing processes, dump between 15 to 50% of the dye into water streams, causing significant effects on the biological activity of species; mainly, in the aquatic flora and fauna (Robinson *et al.*, 2001).

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<https://doi.org/10.24275/rmiq/IA893>

issn-e: 2395-8472

Other problems due to water pollution are: decrease of dissolved oxygen, eutrophication, formation of recalcitrant and toxic compounds to cells, as well as the obstruction of the passage of light altering the processes of biological metabolism that cause destruction of aquatic communities present in the ecosystem (Epps *et al.*, 2001; Ravi Kumar *et al.*, 2000; Chen *et al.*, 2009), which brings major problems to aquatic life.

Synthetic dyes are highly soluble in water, and are used to color textiles, food, flowers, medicines, among others. This type of pollutant is resistant to degradation by physical and conventional chemical methods (Crini *et al.*, 2008; Rêgo *et al.*, 2013; Dotto *et al.*, 2013). Nowadays, numerous materials are used for the removal of such pollutants, including some ecological bioadsorbent materials, i.e. fungi or bacterial biomass and biopolymers, which are obtained in large quantities from natural sources (Arago Ruíz *et al.*, 2009). There are very different methods to remove polluted wastewater from effluents, among them: Fenton's reagent, ozonation, photochemical processes, electrochemical oxidation, membrane filtration, irradiation, activated carbon adsorption, ultrafiltration, electrocoagulation etc. (Dotto *et al.*, 2014; Dotto *et al.*, 2011). In the case for the treatment of colored wastewater, a mixture of different processes is used to obtain water with a specific quality at moderate costs. Removal of dye traces is difficult, and it shows a high rate of pollution in the aquatic environment (Horrocks *et al.*, 2000; Guibal *et al.*, 2003). Among the physicochemical removal dye adsorption techniques, the easiest design is the most frequently used, which is simple to operate and is flexible (Dotto *et al.*, 2017; Casey *et al.*, 2015). Adsorption can be carried out in two ways: the first is based on contact mixing and stirring (batch), and the second on percolation column (Kyzas *et al.*, 2014). The adsorption process consists of the interaction between solute and adsorbent (Jawad *et al.*, 2017), where the magnitude of the process depends largely on the nature of the solid and molecules that are being adsorbed, as well as the concentration, temperature, and exposure time (Goncalves *et al.*, 2017; Huang *et al.*, 2017). The treatment with activated carbon is one of the most used and considered by the Environmental Protection Agency (EPA) as one of the best technologies for dyes removal (Apul *et al.*, 2015). Nevertheless, its high cost has led to the search for other alternatives such as adsorbent materials, namely, chitosan (Arango Ruíz *et al.*, 2009; Dotto *et al.*, 2011; Guibal *et al.*, 2003). The application

of adsorption processes in effluents has resulted in the obtainment of treated water with better quality, becoming an alternative for the treatment of polluted water, especially whether it has a low-cost adsorbent (Arango Ruíz *et al.*, 2009; Dotto *et al.*, 2014).

On the other side, chitosan is a natural polysaccharide derived from chitin, the second most abundant natural biopolymer, after cellulose (No *et al.*, 1995). Chitosan is biodegradable and it is widely studied as a bioadsorbent because of its great capacity to remove heavy metals and dyes from aqueous solutions (Esquerdo *et al.*, 2014). Moreover, chitosan is soluble in acidic media, and the amino groups are protonated at a pH value of 3 causing the breaking off the polymer chains (Velásquez *et al.*, 2003; Gerente *et al.*, 2007). For this reason, chitosan is modified by some cross-linking reactions to avoid its dissolution at low pH values and has been used to remove wastewater dyes (Chiou *et al.*, 2006; Ravi Kumar, 2000; Guibal *et al.*, 2005).

On the other side, pyrrole (Py) is an organic compound that promotes biocompatibility and is capable of conducting electrical current (Paosawatyanong *et al.*, 2010). It has the ability to form polymeric matrices in the form of thin films or surface coatings that has brought numerous applications to scientific advances in the development of new materials. The adsorption capacity of polypyrrole and its composition is recently studied for its use in the adsorption of food dyes from aqueous solutions such as, congo red, acid red and methylene blue, among other artificial dyes (Ansari *et al.*, 2006). Plasma is a quasi-neutral gas of charged and neutral particles, which shows collective properties. It plays an important role in the processing of polymeric materials, semiconductor manufacturing, among others (Yasuda, H., 1985 and Yang *et al.*, 2011). Plasma applied under thermal conditions generates electrons, ions and high energy radicals, which generates new reaction fields, this leads to the oxidation of effective organic compounds for homogeneous and heterogeneous reactions (Wahyudiono *et al.*, 2012). In recent years, interest in plasma discharges in liquids has grown due to their potential applications in various areas of technology such as biological, environmental, medical, material treatment, among others (Yang *et al.*, 2011). For these reasons, the main purpose of this work is the synthesis of chitosan (C-G-EDGE) films with the incorporation of polypyrrole (PPy), through its exposure to glow discharge plasma, in aqueous solution. Finally, the effect of PPy on the mechanical,

morphological and structural properties of chitosan films and its potential in the adsorption of red azo dye No. 2 was investigated.

## 2 Materials and methods

### 2.1 Chemicals

Chitosan was obtained from American-Aliments (deacetylation degree of 85%), while glycerol was acquired from Sigma-Aldrich (purity 99.5%), and, ethylene glycol diglycidyl ether EDGE of Tokyo Chemical Industry Co. LTD (50% technical grade). Distilled water was used throughout this study. Other chemicals were of laboratory reagent grade and used without further purification.

### 2.2 Film synthesis

Chitosan-Glycerol-EDGE-PPy (C-G-EDGE-PPy) films were obtained by the dissolution of chitosan in acetic acid at 1.5% (v/v) for 240 min until a homogeneous solution was achieved. During its dissolution, glycerol was incorporated at different concentrations, 2.4, 3, 3.6, 4.3 and 5% (w/v), to determine the characteristics of the chitosan matrix, since it acts as a plasticizer which confers elasticity properties to films. The cross-linking was carried out by evaluating different concentrations: 0.8, 0.15, 0.16, 0.31 and 0.36% (v/v) of ethylene glycol diglycidyl ether cross-linked agent to determine the appropriate concentration to be used. This process was carried out for 5 h, at a controlled temperature of 20 °C, with a constant stirring of 200 rpm, in a two-necked flask under nitrogen atmosphere, to avoid oxidation of the polymer. Subsequently, the solution was poured into Plexiglass boxes of 12.5×26cm, dried in a muffle at 45 °C for 24 h, by the evaporation of solvent method until a constant weight was reached (Núñez-Gastélum *et al.*, 2019). Films were washed for several cycles until a constant pH value was obtained; then, they were placed in hermetically sealed containers to avoid pollution. The treatment of the glow discharge plasma films in aqueous pyrrole solution was carried out in a Pyrex cylindrical reactor, with a supply voltage of 1.57 kV and a current value of 0.74 A, with a working frequency of 5.4 KHz. Films were treated with glow discharge plasma in an aqueous pyrrole solution, with a concentration of 0.05 M, and different times of 20, 40 and 60 min, and at atmospheric pressure. The films

for treatment were placed between the anode and the cathode of the reactor.

### 2.3 Absorption studies

The adsorption tests of red dye No. 2 were carried out in aqueous solution at a concentration of 250 mg/L, with 15 mg of untreated and treated films for 40 min, volume of 10 mL of red dye No. 2, in a magnetic stirrer with a stirring speed of 200 rpm. Effect of pH tests (2 to 7) were performed at temperatures of 30 °C and for 72 h, to determine which of them reach the maximum adsorption capacity.

Kinetics was performed with films treated for 40 min, with a pH of 5 and temperatures of 10, 30 and 50 °C to determine the speed and time in which the equilibrium between adsorbate and adsorbent is reached. On the other hand, adsorption isotherms were carried out at temperatures of 10, 30 and 50 °C, using dye concentrations of 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L, mass of 15 mg of the treated films for 40 min, the Langmuir and Freundlich models that described the possible adsorption mechanism were used.

### 2.4 Characterization

The morphology of films was analyzed by means of scanning electron microscopy (SEM) employing a JEOL JSM-6610LV-w / HP xw4600 microscope, the sample was fixed on a copper sample holder applying a voltage of 20kV and magnification of 1500x. The analysis and identification of the functional groups of films was performed using Fourier transform infrared spectroscopy (FTIR) with a Varian 640 IR device in a spectral range of 4000 to 400  $\text{cm}^{-1}$  with 80 scans and a resolution of 4  $\text{cm}^{-1}$ . Mechanical stress-strain properties of C-G-EDGE and C-G-EDGE-PPy films were evaluated in triplicate with the universal SHIMADZU machine, under the norm EN ISO 527-3, established conditions for mechanical stress-strain tests of polymeric materials in shape of thin films (Method *et al.*, 2009; Malaysia *et al.*, 2012; Norma EN ISO 1997; Ziani *et al.*, 2008), under the following characteristics: the thickness of the specimens was lesser than 1 mm, width of 2 cm, length of 15 cm, applying a 50 N load with a displacement of 2 mm/min. The thickness of films was measured with Mitutoyo brand measuring instrument capable of measuring up to one micron thickness.

### 3 Results and discussion

The stability of C-G-EDGE-PPy films was achieved with a concentration of the EDGE cross-linked of 0.15% v/v; in the case of concentrations lower than 0.15% v/v, films became rough and tended to roll easily in contact with water; while at concentration higher than 0.15% v/v, at the first contact with water they became very brittle. The concentration of the used glycerol was 3.6% (w/v) which gave better flexibility to films. The concentration of the employed pyrrole was 0.05 M; the best time of treatment was 40 min for the C-G-EDGE films. Lastly, by means of GDP, the increasing amount of pyrrole ions, the amino groups in the polymer chain, as well as the properties of adsorption of red No. 2 on the film, were studied.

#### 3.1 SEM Analysis

Figure 1a shows the morphology of the uncrosslinked and untreated chitosan film, where a homogeneous and smooth surface can be observed (Feng *et al.*, 2015). On the other hand, Figure 1b shows the micrograph of the chitosan film cross-linked with EDGE, where some pores can be observed on the surface, which can be attributed to the modification of the polymer structure due to the concentration of the crosslinker.

As for the films C-G-EDGE treated with GDP in aqueous pyrrole solution, Figure 1c shows a porous surface, with an average pore size of 1.36 nm, corresponding to the classification of microporous

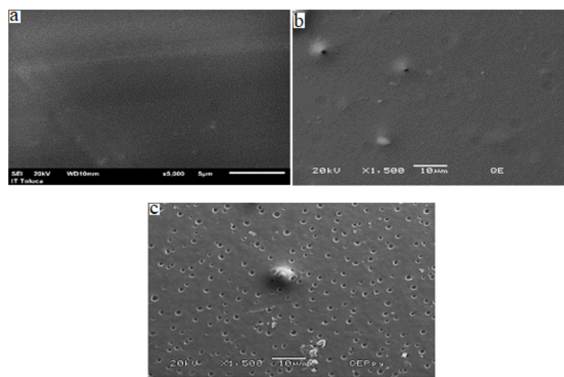


Fig. 1. Scanning electron micrographs (SEM) of a) chitosan, b) C-G-EDGE untreated film and c) C-G-EDGE-PPy treated film with GDP at 1500x, and 20 kV.

material, according to the IUPAC classification, with a surface area of 92.9 m<sup>2</sup>/g. These characteristics, in the polymeric structure of the treated films, are adequate and provide excellent properties for adequate adsorption capacity of red dye No. 2. Pores formation in the film treated with GDP was mainly due to the impact of the pyrrole ions; which are accelerated by the high energy of the electric field formed between the cathode and the anode of the reactor.

#### 3.2 FTIR analysis

This analysis allowed to identify the functional groups of chitosan samples. Figure 2 shows the difference between the FTIR spectra of the untreated C-G-EDGE film (Figure 2a) and the GDP modified C-G-EDGE-PPy film with pyrrole (Figure 2b).

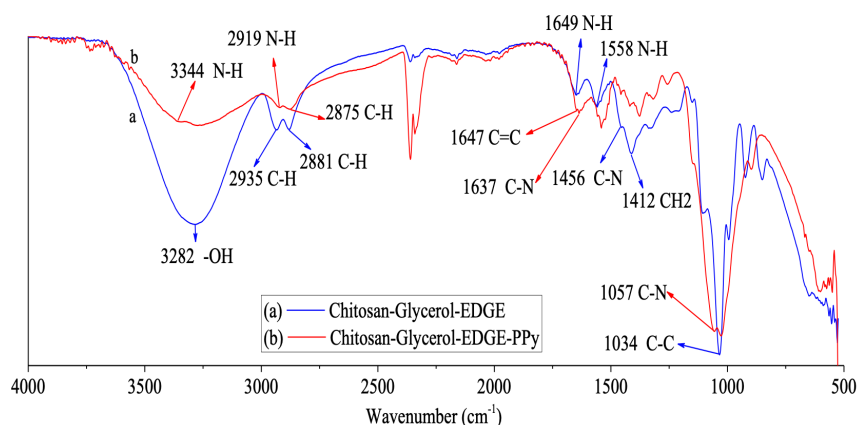


Fig. 2. FTIR spectra of the C-G-EDGE and C-G-EDGE-PPy films.

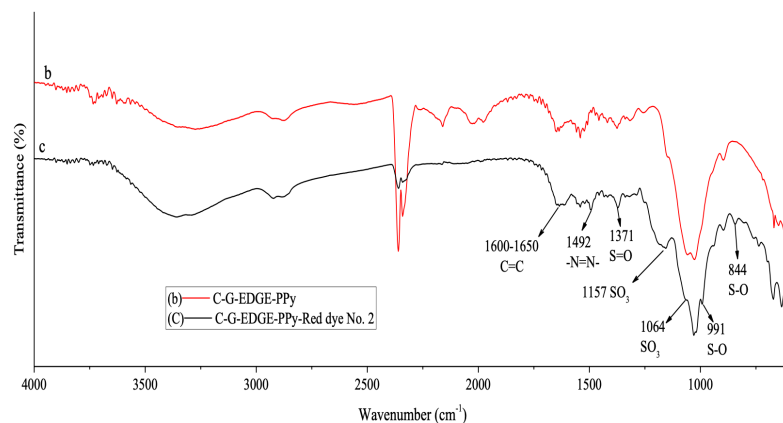


Fig. 3. FTIR spectra of C-G-EDGE-PPy films after adsorption of red dye No. 2.

A change in the gap of  $3600\text{--}3250\text{ cm}^{-1}$  is observed, due to the decrease of the hydroxyl groups ( $\text{--OH}$ ) during the treatment of GDP. After its treatment, the spectrum changed due to the incorporation of pyrrole in the film structure, with observed peaks at:  $3344\text{ cm}^{-1}$  ( $\text{N--H}$ );  $2919$  and  $2875\text{ cm}^{-1}$  ( $\text{C--H}$ ),  $2360$  and  $1647\text{ cm}^{-1}$  ( $\text{C=C}$ ),  $1637$  and  $1057\text{ cm}^{-1}$  ( $\text{C--N}$ ), which correspond to the functional groups of the aromatic ring of pyrrole. Peaks between  $3600\text{--}3250\text{ cm}^{-1}$  ( $\text{--OH}$  and  $\text{N--H}$ ) as reported by (Núñez-Gastélum *et al.*, 2019),  $1700\text{--}1600\text{ cm}^{-1}$  ( $\text{N--H}$ ),  $1420\text{--}1381\text{ cm}^{-1}$  ( $\text{CH}_2$  and  $\text{CH}$ ),  $1250\text{--}1000\text{ cm}^{-1}$  are due to vibrations of ( $\text{C--O--C}$ ) as reported by (Pérez-Escobedo *et al.*, 2010); while peaks at  $1637\text{ cm}^{-1}$  ( $\text{--NH}$ ),  $1377\text{ cm}^{-1}$  ( $\text{--CH}_2$ ) and  $1421\text{ cm}^{-1}$  ( $\text{--CH}_3$ ), corresponded to the untreated film (Coates, 2000). The  $\text{N--H}$  bond (between  $1700$  and  $1600\text{ cm}^{-1}$ ) is related to the amide I vibration,  $\text{CH}_2$  ( $1420\text{ cm}^{-1}$ ) and  $\text{CH}$  ( $1381\text{ cm}^{-1}$ ),  $\text{C--O--C}$  between ( $1250$  and  $1000\text{ cm}^{-1}$ ) corresponded to the chitosan.

The possible interactions between the red dye No. 2 and the film were investigated from the FTIR analysis; Figure 3c shows the spectrum of the C-G-EDGE-PPy film after the adsorption of the dye. Finally, a band at  $1371\text{ cm}^{-1}$  is observed that belongs to the  $\text{S=O}$  bond of the sulfonate group, and between  $1600\text{--}1650\text{ cm}^{-1}$ , the  $\text{C=C}$  bonds of the benzene aromatic ring, while the amino group  $\text{--N=N--}$  it is observed in  $1492\text{ cm}^{-1}$ , the symphonic group  $\text{SO}_3$  is observed in  $1157$  and  $1064\text{ cm}^{-1}$  and the  $\text{S--O}$  bonds are observed in  $991$  and  $844\text{ cm}^{-1}$ , which belongs to the red dye No. 2, that are interacting with the adsorbent, as observed (Vasquez-Ortega *et al.*, 2014; González -Torres *et al.*, 2014), (Figure 3).

### 3.3 Strain-stress characterization

Chitosan-glycerol-EDGE films showed a  $17\text{ mm}$  elongation with  $2.6\text{ N}$  breaking strength, compared to chitosan-glycerol-EDGE-polypyrrole films with a  $66\text{ N}$  breaking strength and  $6\text{ mm}$  elongation, decreasing its elongation capacity by  $62.7\%$ , which indicates lower elasticity (Bautista-años *et al.*, 2018). One of the functions of pyrrole is to make the films exhibit greater resistance to breakage, which was achieved by the incorporation of the mentioned polymer.

### 3.4 Adsorption tests of Red No. 2 dye

The adsorption capacities of the dye were  $815$ ,  $800$ ,  $830$  and  $1074\text{ mg/g}$  for the treated and untreated films, respectively at a pH value of 2. The main advantage of the modified films with pyrrole plasma was an increase in its adsorption capacity at pH values between 4 and 6, with respect to the untreated films; moreover, pyrrole plasma treatment increased the strength to rupture of the C-G-EDGE films. Figure 4 shows the adsorption capacity for the treated films at 20, 40, 60 min, and for the untreated films.

The adsorption capacity of the films treated for 40 min was  $770\text{ mg/g}$ , meanwhile for the treated films at 60 min, it was  $756\text{ mg/g}$  and the treated for 20 min had an adsorption capacity of  $681\text{ mg/g}$  with a pH value of 5; therefore, it was proposed to work with the treated films for 40 min, since they had a higher adsorption capacity and the cost of plasma treatment is reduced. It should be noted that industrial wastes, and especially industries using azo dyes such as Red No. 2, discharge their wastes with pH values from 4 to 7; for this reason, new materials that could satisfy these conditions are investigated (Epps *et al.*, 2001).



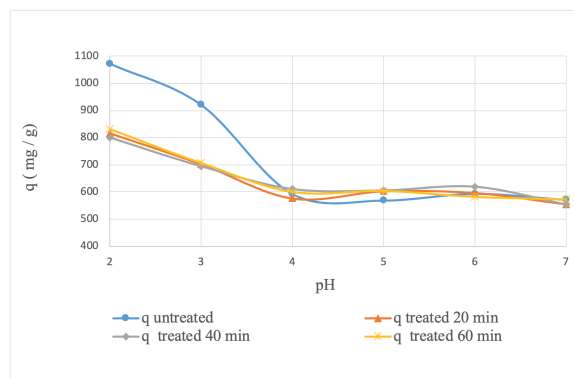


Fig. 4. Comparison of the adsorption capacity of the four obtained materials.

### 3.5 Adsorption kinetics

The adsorption kinetics of the red dye No. 2 was performed with films treated for 40 min with pyrrole plasma (CG-EDGE-PPy). From the obtained results, it is observed that as the temperature in the solution increased, the time in which the equilibrium was reached decreased, as shown in Figure 5.

The kinetic models of pseudo-first order (Lagergren) and pseudo-second order (Ho and McKay) were used to determine the mechanism of adsorption, the speed and the time in which the balance between adsorbate and adsorbent was reached. From the experimental data a correlation coefficient  $R^2 = 0.89$  was obtained for the pseudo-first order model, while for the second order model the achieved correlation coefficient was  $R^2 = 0.98$ , which indicates a better fit to the experimental data for this last model, which is attributed to processes that involve a possible mechanism of chemisorption, due to the formation of chemical bonds between the adsorbate and the adsorbent in a heterogeneous surface that can involve different energies of activation and its peculiarity to estimate the load in equilibrium (Aksu *et al.*, 2008; Zheng *et al.*, 2010).

This was due to the fact that the temperature of the solution was increased; therefore, the vibration speed of molecules increased as well, which resulted in pores opened for the polymer. This led to a better dye diffusion through the pores; thus, to the saturation of the active sites of the adsorbent. The average adsorption capacity at 10 °C was 609.74 mg/g; at 30 °C, it was 742.81 mg/g; finally, at 50 °C, it was 762.16 mg/g, (Dotto *et al.*, 2013; Feng *et al.*, 2015).

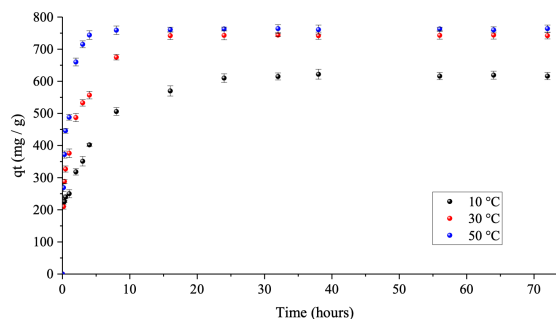


Fig. 5. Effect of the temperature on the adsorption kinetics of red dye No. 2.

### 3.6 Adsorption isotherms

The adsorption isotherm was carried out with films treated for 40 min with plasma in pyrrole solution (C-G-EDGE-PPy) observed that as the concentration of the red dye No. 2 increased as well as the temperature in the solution the adsorption capacity increased, while the time to reach the equilibrium decreased. This shows that films have active sites available for the adsorption of the dye, and there is a high affinity between the dye molecules and the surface of the films.

Figure 6 shows the effect of temperature on the adsorption process; it is observed that at a temperature of 30 °C the adsorption capacity was  $q_e = 757$  mg/g; meanwhile, at 10 °C, it was  $q_e = 681$  mg/g and at 50 °C, it was  $q_e = 743$  mg/g. From this set of results, it can be seen that the adsorption capacity slightly decreased, this was due to a greater solubility of the dye molecules in the solvent when the temperature increased. The greater movement of the particles resulted in the interaction forces between the solute and the solvent being stronger than between the solute and the adsorbent (Feng *et al.*, 2015); therefore, there is a greater difficulty of interaction between them.

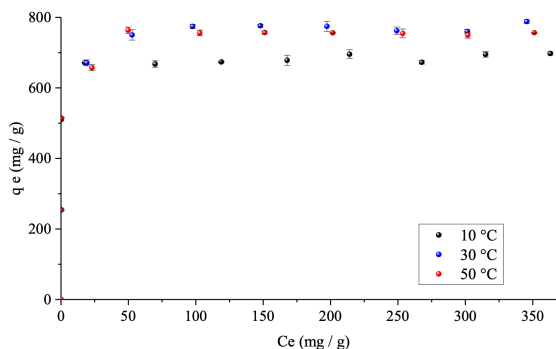


Fig. 6. Effect of the temperature in the adsorption capacity of red dye No. 2.

It is noteworthy that Feng *et al.* (2015) obtained an adsorption capacity of 40.65 mg/g with a mass of 100 mg and a dye concentration of 200 mg/L; on the other hand, (Dotto *et al.*, 2013), obtained an adsorption capacity of 194.6 mg/g, with a mass of 50 mg and a dye concentration of 100 mg/L. Therefore, we could verify that the treated films with plasma, in aqueous pyrrole solution, have higher adsorption capacity compared to the aforementioned works.

Finally, the affinity between the adsorbate and the adsorbent gave rise to the attraction of the adsorbate towards the adsorbent polymer matrix until an equilibrium was reached. Mathematical models describing this mechanism are adsorption isotherms, which relate the amount of dye removed, and remains in solution when the equilibrium is reached at a constant temperature. The determined isotherm model that best fitted the experimental data on the equilibrium time between adsorbate and adsorbent were the Langmuir and Freundlich models from the obtained correlation coefficients  $R^2$ . A correlation coefficient  $R^2=0.82$  was obtained for the Langmuir model, while for the Freundlich model, it was  $R^2=0.94$ , which is a sign that the chemisorption process could be the predominant one.

## Conclusions

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In this work, films of C-G-EDGE and C-G-EDGE-PPy were obtained, showing that films treated with glow discharge plasma, in aqueous pyrrole solution, increased their breaking strain from 5 to 66 N. The treatment of chitosan films in aqueous pyrrole solution, with glow discharge plasma, improved their adsorption capacities at pH values between 4 and 6, for red dye No. 2. The adsorption capacity at a pH value of 2 for the untreated films was 1074 mg/g, meanwhile for the treated films it was 830 mg/g. SEM results showed that the treatment of the film with glow discharge plasma increased their porosity, while the untreated film presented a homogeneous and smooth surface. Finally, the treatment for 40 min with glow discharge plasma in aqueous solution pyrrole was an efficient technique to give higher resistance to chitosan films used for the adsorption of azo dyes from pollution water at pH from 5.

## Acknowledgements

Juan Nabor Balderas Gutiérrez is grateful to the National Council of Science and Technology (CONACYT) for his scholarship.

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