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# IMPACT OF CORONA TREATED ACTIVATED CARBON IN ANIONIC AND CATIONIC DYE ADSORPTION

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**ABSTRACT:** Dye degradation is a significant topic in environmental science, since dyes can bring several problems to the environment. Activated carbon (AC) is an important material used as adsorbent of these hazardous substances, but need to be improved especially into specific substances. This paper aimed to evaluate the impact of activated carbon surface modified by corona treatment (electric discharge) on adsorption of different dyes. Activated carbons were treated by corona treatment to cause surface modification, modifying exposure time to treatment (2, 5, 8 and 10 minutes). Evaluation of adsorption was performed by adsorption isotherms and kinetic adsorption. Dyes differed in their charge (anionic or cationic) and molecular weight. Dyes used were Methylene Blue (cationic) and Congo Red (anionic). Surface area and Scanning Electron Microscopy (SEM) were also conducted. Surface chemistry was impacted by corona treatment and interfered in dye adsorption. There was decrease of dye adsorption for both dyes according to time exposure. However, the decrease of Methylene Blue (25%) was higher than Congo Red (14%), suggesting that either charge or molecule weight interfere in the adsorption isotherms. In kinetic adsorption, there was no difference between treatments, although there was a difference in adsorption equilibrium. SEM showed that surface was impacted (pore destruction) by corona treatment. Furthermore, estimated surface area was strongly impacted by the treatment, reducing with the increase of time exposure. Thus, textural properties might have contributed to reduce adsorption capacity of both dyes and play a higher role than chemical properties.

# IMPACTO DE CARVÕES ATIVADOS TRATADOS COM DESCARGA CORONA NA ADSORÇÃO DE CORANTES CATIÔNICOS E ANIÔNICOS

**RESUMO:** A degradação de corantes é um importante tópico nas ciências ambientais, já que os corantes podem trazer diversos problemas para o meio ambiente. O carvão ativado é um importante material usado como adsorvente dessas substâncias causadoras dos mais diversos danos, mas precisam ser melhoradas especialmente quando envolve substâncias específicas. Este manuscrito tem como objetivo avaliar o impacto da superfície de carvões ativados modificados pelo tratamento corona (descarga elétrica) na adsorção de diferentes corantes. Os carvões ativados foram tratados pelo tratamento corona para promover a modificação na superfície, modificando os tempos de exposição ao tratamento (2, 5, 8 e 10 minutos). A avaliação da adsorção foi realizada pelas isotermas de adsorção e velocidade de adsorção. Os corantes diferiram pelas suas cargas (aniônico e catiônico) e massa molecular. Os corantes utilizados foram o Azul de Metileno (catiônico) e o Vermelho Congo (aniônico). A área superficial e a microscopia eletrônica de varredura (MEV) também foram realizadas. A superfície química foi impactada pelo tratamento corona e interferiu na adsorção dos corantes. Houve decréscimo na adsorção dos corantes para ambos de acordo com o tempo de exposição. No entanto, o decréscimo de Azul de Metileno (25%) foi maior que para o Vermelho Congo (14%), sugerindo que a carga ou a massa molecular interferiram na isoterma de adsorção. Na velocidade de adsorção, não houve nenhuma diferença entre os tratamentos, embora houve diferença no equilíbrio da adsorção. A análise MEV mostrou que a superfície foi impactada (destruição dos poros) pelo tratamento corona. Além disso, a área superficial estimada foi fortemente impactada pelo tratamento, reduzindo com o aumento do tempo de exposição. Assim, a propriedades texturais pode ter contribuído para a redução na capacidade de adsorção de ambos corantes, desempenhando papel de maior importância comparado com as propriedades químicas.

#### INTRODUCTION

Dyes are colored substances that are used in several industries for many applications imparting permanent color to their products. Dyes are essential, especially to textile industries, which use their properties to color many fabrics (GUARATINI; ZANONI, 1999). However, the indiscriminate use of these substances and the lack of well-treated waste generated by these industries are a huge problem for the environment. Dyes may disturb the environment, especially the water environment. Dyes are toxic to micro-organisms, may decrease oxygenation, prevent light penetration through the water surface and significantly impact aquatic ecosystem. Dyes can also cause visual pollution (GOTTLIEB et al., 2003).

Water pollution is one of the issues of most concern in environmental science. Governmental control, severe legislation and effluent treatment have contributed to decrease this problem (ROBINSON et al., 2001). Dye pollution reduction has been exhaustively studied for several years, yet, currently new technologies have been developed to perform and improve dye degradation, making the environment cleaner and reducing pollution. The main and new methods to reduce dye pollution involve activated carbon (GHAEDI et al., 2012), surface modified activated carbons (MOHAMMED et al., 2015), nanoadsorbents (KYZAS; MATIS, 2015), agricultural adsorbent waste (PELÁEZ-CID et al., 2013), other adsorbents (YAVUZ; SAKA, 2013), ozonation (CASTRO et al., 2016), irradiation (HERNÁNDEZ-URESTI et al., 2011), photocatalics (MAHMOODI, 2013), plasma discharge (JIANG et al., 2014), biological methods (KANAGARA] et al., 2014) and others.

Activated carbons have a key role in reducing dye pollution. Activated carbons are used as adsorbents for many dyes and other substances. The main characteristics which impact adsorption are the high surface area, porosity and surface chemistry. Also, dye properties have an important influence on the activated carbon adsorption process (ACEVEDO et al., 2015).

Dyes properties directly affect adsorption capacity. The main dye characteristics which can impact adsorption capacity are polarity, molar mass, molecular size, acidity, basicity, molecular charge and the relationship among these properties and the surface structure of adsorbents. Moreover, some factors can influence adsorption capacity such as pH, dye concentration, adsorbent dosage, contact time and temperature (SALLEH et al., 2011). Different surface chemistries of activated carbons impact the adsorption capacity of anionic and cationic dyes. Equilibrium

isotherms and other adsorption process are impacted by the relationship of different dye groups and surface chemistry. Thus, surface chemistry and dye properties play an important role in dye adsorption (FARIA et al., 2004).

Molecule charge is one of the most studied properties in the adsorption process. Basically, the molecule charge can be anionic or cationic. An anionic dye has a negative charge and a cationic dye has a positive charge (WAN NGAH et al., 2011). Dye charges directly interact with adsorbent surface chemistry. Surface chemistry could be different depending on surface modification and its surface functional groups, which have different properties (SHAFEEYAN et al., 2010). Thus, the relationship between molecule charge and adsorbent surface chemistry impacts the adsorption capacity of specific molecules differently.

Corona treatment is an electric discharge that is applied to some material to cause surface modification and changes in materials properties. This treatment is used in polymers, rubber, aluminum sheets and other carbonaceous materials. Corona treatment is a treatment that promotes surface oxidation thought the ionization of gases  $(O_3, O_2)$  by electric discharge, causing covalent chemical reactions on the surface which changes some materials properties (STEPCZYŃSKA, 2015).

Corona treatment can be a surface modification technique which changes surface structure and impacts dye adsorption process. Therefore, this study aimed to evaluate the impact of corona treatment on the adsorption process of anionic and cationic dyes.

### **MATERIAL AND METHODS**

### **Surface modification**

In this study a powdered commercial activated carbon was used. This activated carbon was used because their large adsorption capacity. The activated carbon was from Alphacarbo Company.

Corona treatment was used to cause surface modification (oxidation) of activated carbons. The corona equipment was from Plasma Tech - Corona Brazil (Figure I), Model PT-I, 0.5 kW power, 220 V and frequency of 60 Hz. Activated carbon were submitted to corona discharge (high frequency and voltage) at four different exposures times. Treatment one (TI) was the standard, without treatment (virgin activated carbon). The other treatments (T2, T3, T4 and T5) varied exposure time 2, 5, 8 and 10 minutes respectively. Head height was established at 4.5 cm. An aluminum box was used to reduce material losses during treatment, since agitation was high during treatment.



FIGURE I Corona treatment scheme.

## **Adsorption isotherms**

Adsorption isotherms are the most common way to evaluate solid adsorption capacity. The evaluation of activated carbon adsorption capacity was performed using two kinds of dyes (Figure 2): one with negative charge (anionic) and other with positive charge (cationic). The anionic dye was Congo Red and cationic dye was Methylene Blue.

FIGURE 2 Dye molecules used in activated carbon adsorption tests A-Congo Red (anionic) B-Methylene Blue (cationic)

The activated in 10mg carbons (treated and nontreated) were weighed. After, 10 mL solutions at different concentration (25, 50, 100, 200, 400, 800, 1000 mg·L<sup>-1</sup>) for Methylene Blue and (10, 25, 50, 75, 100, 200, and 400 mg·L<sup>-1</sup>) for Congo Red were added to obtain the adsorption isotherms. The aliquots were kept under agitation for 24 hours at 200 rpm at room temperature in a Certomat MO II orbital shaker. The materials were centrifuged and the determination of equilibrium concentration was performed by UV-visible analysis on a Biospectro SP-22 UV spectrophotometer in wavelengths of 665 nm for Methylene Blue and 500 nm for Congo Red.

The dye solutions were prepared by weighing an exact quantity of dye, being dissolved in distilled water to prepare a 1000 mg·L<sup>-1</sup> stock solution, which were diluted according to concentration. Solutions preparation and

concentration determination to obtain the adsorption isotherms were performed at room temperature (22.5°C) and pH 3.7 – 4.2 for Methylene Blue and room temperature (20°C) and pH (6.5-7) for Congo Red. The pH was measured by a PG1800 digital pH meter.

Calibration curves were adjusted according to known dye solution concentrations. The amount of dye adsorbed per unit mass of activated carbon (mg·g·l) was calculated according to Equation I. Where:  $C_0$  (mg·L·l) = initial dye concentration;  $C_{eq}$  (mg·L·l) = equilibrium concentration; V (L) = solution volume;m (g) = adsorbent mass.

$$q_{eq} = ((C_o - C_{eq}) \cdot V) \cdot m^{-1}$$
 [1]

## **Adsorption kinetics**

Kinetics studies allow determining the time necessary to attain adsorption equilibrium. These studies are important to determine adsorption efficiency.

Methylene Blue and Congo Red were also used as adsorbent. For each treatment 5 mg of activated carbon were weighed together with 5 mL of adsorbates at a concentration of 50 mg·L<sup>-1</sup> for Methylene Blue and 25 mg·L<sup>-1</sup> for Congo Red. In time intervals (5, 10, 15, 30, 60, 120, 240, 360, 720 and 1440 minutes), aliquots were removed, centrifuged and their concentrations were determined, using wavelengths of 665 nm for Methylene Blue and 500 nm for Congo Red. Absorbance readings were performed on a Biospectro SP-22 UV spectrophotometer.

# Scanning electron microscopy (SEM)

Treated and non-treated activated carbon samples were submitted to surface microscopy analysis to observe the changes occurred in the structure of the materials. The analysis was performed on an Evo40 LEO XVP (25 kV) equipment. An aluminum support was coated with aluminum foil. Samples were held on double-sided carbon tape attached to aluminum support and then covered by a thin layer of gold.

#### **Estimated surface area**

It is possible to estimate surface area of solid materials using the Methylene Blue model molecule, when it is not possible to use BET methodology. Estimated surface area uses molecular properties, such as diameter, in order to obtain a consistent result. The Methylene Blue molecules have important properties which enable them to be used as estimators of the surface area of activated carbons.

Using the surface area of a Methylene Blue molecule it is possible to estimate surface area through Equation 2. Where:  $S_{BM}(m^2 \cdot g^1) = Activated$  carbon area accessible to Methylene Blue;  $S_{BM}^{\circ} = Methylene$  Blue surface area; qm  $(mg \cdot g^1) = Maximum$  adsorption capacity of Methylene Blue.

$$S_{BM} = 1000 \cdot S_{BM}^{o} \cdot q_{m}$$
 [2]

#### **RESULTS AND DISCUSSION**

Surface modifications of many materials are impacted by corona treatment. Electric discharge with high frequency and voltage supplied by corona treatment provoke surface modification through the ionization of gases located between surface material and corona equipment. This ionization promotes liberation of photons and electrons causing chemical reactions and oxidation in materials surface. Different chemical reactions lead to material surface different properties, since new structures in surface are formed. Wettability, acidity, basicity, polarity, reactivity, chemical and textural properties are the main properties impacted by corona treatment.

Surface chemistry of treated AC was strongly affected by the corona treatment. Comparing to nontreated AC, there was a tendency towards increasing acidity, Oxygen content, Carboxyl acid and O/C ratio. There was a tendency of decreasing Carbon content, lactone and phenol groups. The differences are related to time exposure. Thus, surface modification was performed on activated carbon and resulted in different properties that could impact the adsorption process (PEGO, 2016).

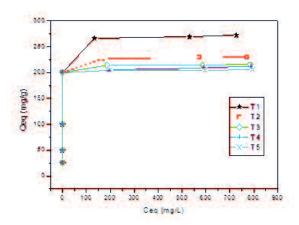
#### **Adsorption isotherms**

Adsorption isotherms were performed aiming to evaluate adsorption capacity and better understand dye adsorption process. Adsorption isotherms demonstrated the activated carbon capacity to adsorb a particular substance (dye) at equilibrium.

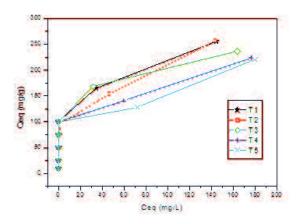
Figure 3 and 4 show adsorption isotherms of Methylene Blue and Congo Red dyes, respectively. According to these Figures, there was a dye adsorption decrease with increased of time exposure to the corona treatment. Thus, generally, for these dyes, corona treatment does not improve adsorption capacity of the activated carbons.

### Methylene Blue adsorption

Adsorption isotherms of the Methylene Blue dye (cationic) on activated carbons is shown in Figure 3. According to this Figure, there was a decrease in



**FIGURE 3** Adsorption isotherm of Methylene Blue in the different treatments (10 mg de AC; 10 mL solution; pH= 3.7 - 4.2; 200 rpm; concentration 25-1000 ppm; Room temperature= 22.5 °C).



**FIGURE 4** Adsorption isotherm of Congo Red in the different treatments (10 mg of AC; 10 mL solution; pH= 6.5-7; 200 rpm; concentration 10-400 ppm; Room temperature= 20 °C).

adsorption capacity of the activated carbons with the increase of time exposure to corona treatment. This decrease is approximately 25% less, comparing non-treated AC and the AC which had the highest exposure time and the lowest Qeq.

Therefore, the treatment that obtained higher adsorption capacity was non-treated AC (TI), with Qeq of 272.2 mg·g<sup>-1</sup>. After 24 hours, all treatments reached equilibrium adsorption. Qeq values for T2, T3, T4 and T5 treatments were respectively 230.2; 215.3; 211.4 and 205.1 mg·g<sup>-1</sup>.

This reduction could be explained by the fact of activated carbon surface treatment and other substances, which use similar surface modification processes such as corona treatment, most often need special conditions, like: specific atmosphere, different pressure conditions

PEGO et al.

and reactors. These characteristics provide alterations in its properties or even protection in activated carbon structure. Plasma surface modification and other physical surface modifications methods are similar to corona treatment. Generally, these treatments expose materials to extreme conditions, causing damages or changes in their structure.

Reduction of activated carbon adsorption can also be related to adsorbate properties, the intrinsic relation between adsorbent-adsorbate and to the change occurred to porosity and textural characteristic caused by agitation and high temperatures due to electric discharge.

It is possible to infer that surface characteristics like acidity and basicity impact adsorption capacity. There are some studies demonstrating that Methylene Blue adsorption is potentiated in more basic surface (WANG et al., 2005)methylene blue, from aqueous solutions onto as-received activated carbons and acidtreated carbons was investigated. The physical and surface chemical properties of the activated carbons were characterized using BET-N2 adsorption, X-ray photoelectron spectroscopy (XPS. Therefore, surfaces which have large number of acidic groups, generally, are not ideal for Blue Methylene. Treated activated carbons have higher acidity and were related to time exposure, culminating in the adsorption capacity decrease. Thus, this may suggest that higher exposure time had higher acidity and consequently lower adsorption capacity for Methylene Blue.

The adsorption capacity behavior caused by other similar surface treatments (plasma discharge) is different depending on factors that may impact adsorption. Some authors have increased adsorption capacity due to treatment compared to virgin activated carbons (CHE et al., 2013; QU et al., 2013). However, other authors reported that electric discharge had a negative impact on adsorption capacity. They attributed this to destruction of surface functional groups (HAO et al., 2009; JI et al., 2013). The adsorption capacity behavior especially depends on methodology employed aiming to cause the surface modification, since many factors can impact adsorption capacity.

## Congo red adsorption

Adsorption isotherm of Congo red dye (anionic) on activated carbons is showed in Figure 4. According to the Figure 4, as well as Methylene Blue adsorption, there was a decrease in adsorption capacity due to the corona treatment exposure time. It was expected that adsorption capacity would be increased since there was an increase

of acidity. However, the decrease can be related to the decrease of surface area. Also, textural properties can play an important role on adsorption capacity. Thus, considering factors that impact adsorption, chemical properties was weaker than textural properties, as showed in surface area and pore structure, observed in the following topics.

The decrease is approximately of 14% comparing non-treated AC and the treatment that had higher exposure time and obtained the lowest Qeq value. Thus, the AC which showed higher adsorption capacity was non-treated AC (T1), with a Qeq of 256.2 mg·g·l. The Qeq values for T2, T3, T4 and T5 treatments were respectively of 256.1; 236.4; 223.6 and 220.3 mg·g·l. The higher adsorption capacity of these activated carbons may be due to their being commercial activated carbons.

According to these results, it is possible to infer that Congo Red adsorption was less impacted than Methylene Blue adsorption. This can be related to the reaction occurred between adsorbent and adsorbate, particularly in the influence of some variables such as pH and temperature. According to (YAVUZ; SAKA, 2013) pH has a high importance on the adsorption process and strongly impacts adsorption capacity.

Nonetheless, dye charge may have been responsible for adsorption differences between the two types of dyes. Methylene Blue, by having a positive charge, is more attracted to basic surfaces. The Congo red molecule, by having negative charge, is more attracted to acid surfaces.

#### **Adsorption kinetics**

Adsorption kinetics differs from adsorption isotherm. Adsorption kinetics shows adsorption efficiency and provides information about the velocity of the adsorption process.

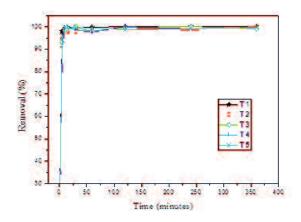
As in adsorption isotherms, for the adsorption kinetics study were used the same dyes. Figures 3 and 4 showed that there were no large differences in adsorption velocity. In addition, the differences occurred seem not to be correlated with time exposure. Yet, it is possible to observe that the adsorption kinetics of Congo Red showed fewer differences between treatments when compared to Methylene Blue kinetics. All treatments showed great initial dye adsorption speed. After a short time, reaction equilibrium was reached for both dyes.

#### Methylene Blue adsorption kinetics

Adsorption kinetics of Methylene Blue is presented in Figure 5. According to this Figure, there

were no significant differences in kinetic behavior for the treatments. It was not possible to relate kinetic behavior to increasing exposure time and all AC adsorbed approximately 100% of the dyes in a few minutes.

The initial Methylene Blue adsorption velocity for all treatments was very fast, reaching adsorption equilibrium after 16-18 minutes, indicating rapid filling of sites for all activated carbons.

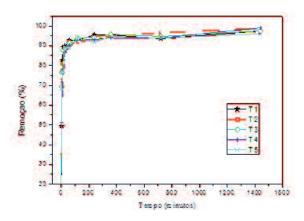


**FIGURE 5** Methylene Blue Adsorption Kinetic, 50 mg·L<sup>-1</sup> concentration (5 mg of AC and 5 mL of solution).

# Congo Red adsorption kinetics

Congo Red adsorption kinetic is presented in Figure 6. According to the Figure, as in the Methylene Blue adsorption kinetics there were no significant differences in kinetic behavior for the treatments. There was no pattern in the kinetic behavior according to increased corona treatment time exposure.

The adsorption kinetics of the Congo Red molecule by the activated carbons were less than those of Methylene Blue. Equilibrium adsorption was achieved after approximately 4 hours, with more than 95% dye removal. The differences between adsorption kinetics may be related to the different molecular properties, especially size and charge. The Congo Red molecule (696.68 g·mol-1) has molecular mass higher than the Methylene Blue molecule (356 g·mol-1). Furthermore, the molecules present opposite charges that interfere in adsorption kinetics until equilibrium is reached. Chowdhury et al. (2009)especially for the treatment of colored effluent generated from the dyeing and bleaching industries. Low cost adsorbents have gained attention over the decades as a means of achieving very high removal efficiencies to meet effluent discharge standards. The present article reports on batch investigations for color removal from aqueous solutions of Methylene Blue (MB observed differences between adsorption kinetics patterns; Methylene Blue obtained faster adsorption compared to Congo Red.



**FIGURE 6** Congo Red Adsorption kinetics, 25 mg·L<sup>-1</sup> concentration (5 mg of AC and 5 mL solution).

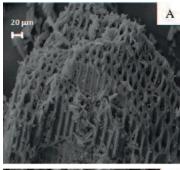
# Scanning electron microscopy (SEM)

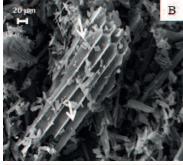
SEM analysis was performed in order to observe if the structure of the activated carbons was impact by the corona treatment, since the electric discharge decrease adsorption capacity of both dyes. Analyzing Figure 7, it is possible to observe that changes occurred in the AC structure with the increase of exposure time. It is believed that ruptures of the porous structures took place, making the surface more irregular and heterogeneous. Figure 7 shows internal pore structure, its regularity and sizes. According to this Figure, pores were damaged according to the time exposure. The pore destruction occurred both on the surface and the internal structure. Observing TI (Figure 7 A), the porous structure seems to be well arranged, being a large structure with regular and intact pores. On the other hand, T5 (Figure 7 E) had significant porous structure destruction.

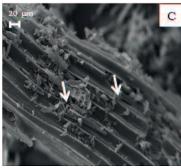
Porous structure destruction of activated carbons might be related to the temperature that is generated during treatment and agitation of AC inside the aluminum box. Electric discharge promotes agitation, requiring the use of an aluminum box. Material agitation was high due low particle size and lightweight material. Besides, high temperatures are generated by the equipment (high voltage and frequency). These factors may impact pore destruction of treatments. According to Yavuz and Saka (2013), high exposure times to corona treatment can destroy functional groups structure and porosity.

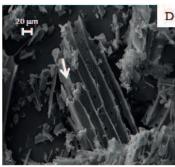
Some analysis of activated carbon surface using methods similar to the corona treatment is divergent regarding surface changes. Some author reported that these methods can cause destruction of pores and other benefit modifications. Thus, structural modifications are dependent on the methodology of the treatment that is applied to cause modifications. Che et al. (2013)

PEGO et al.









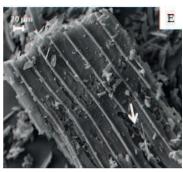


FIGURE 7 Electron micrographs (759 x) of non-treated AC TI (A) and treatments T2 (B), T3 (C), T4 (D) and T5 (E).

analyzing the surface of AC treated by plasma observed that the external surface was impacted on a microscale and became rough. In this regard, Ji et al. (2013) also working with the same treatment, found that the surface became irregular and heterogeneous. Vignesh et al. (2016) using specific conditions, via SEM analysis verified that plasma treatment does not cause structural damage on AC and it maintained the same dimensions and mass compared to non-treated activated carbon.

Thus, it is evident that the conditions under treatment are carried out have a huge influence on surface structure. Specific treatment conditions determine properties and morphology of the activated carbon surface. The main methods are the use of barriers, reactors, pressure conditions and specific atmospheres.

#### Estimated surface area

The activated carbon surface area was estimated using Methylene Blue adsorption. This is a simple and rapid method that provides important information on the structure of the adsorbent material. The estimated surface area is presented in Table I. According to this Table, the increased exposure time of each treatment decreased the estimated surface area of the activated carbon, which was completely dependent on the Methylene Blue adsorption capacity. The high temperature reached and agitation received by corona discharge may have caused the destruction of porous structures, negatively contributing to the surface area.

**TABLE I** Surface area estimated values according to treatments.

Treatment	Surface area (m²·g-1)
TI	525.34
T2	444.29
Т3	415.53
T4	408.00
T5	395.84

Surface modification using plasma discharge (similar treatment) can cause reduction of surface area and total pore volume. The reduction is conditioned due to the time exposure acting on the surface, adding new surface functional groups which can be allocated to pore entrances, causing a reduction in surface area. Furthermore, surface area reduction may be caused by factors inherent to surface modification, such as temperature, pressure, exposure (CHE et al., 2013).

## **CONCLUSION**

In this study the impact of corona treatment on the activated carbon adsorption process of anionic and cationic dyes was evaluated. Although the Corona treatment caused surface modification of activated carbon, this modification was not able to improve adsorption capacity of Methylene Blue and Congo Red, it not being possible to infer about other adsorbates. Higher exposure time resulted in lower adsorption capacities. Blue Methylene adsorption had Qeq of 272.2 mg·g<sup>-1</sup> (non-treated) and with the increase of exposure time had 230.2; 215.3; 211.4 and 205.1 mg·g<sup>-1</sup>, respectively. Congo Red adsorption had Qeq of 256.2 mg·g<sup>-1</sup> (non-treated) and with the increase of exposure time had 256.1; 236.4; 223.6 and 220.3 mg·g<sup>-1</sup>.

Kinetic adsorption was not different between treated and non-treated activated carbons for both dyes. However, Methylene Blue adsorption was faster than Congo Red, possibly due to differences in molecule size and charge.

Dye charges have an influence on dye adsorption, although this influence does not contribute to improve dye adsorption. Decreasing adsorption capacity may be related to decreasing surface area. The surface area decrease is due to porous structure ruptures, making the surface more irregular. Thus, surface chemistry was not the main factor involved in the adsorption process. Other factors may impact this, such as surface structure, porosity, surface area and dye properties.

#### **REFERENCES**

- ACEVEDO, B.; ROCHA, R. P.; PEREIRA, M. F. R.; FIGUEIREDO, J. L.; BARRIOCANAL, C. Adsorption of dyes by ACs prepared from waste tyre reinforcing fibre. Effect of texture, surface chemistry and pH. Journal of Colloid and Interface Science, v. 459, p. 189–198, 2015.
- CASTRO, F. D.; BASSIN, J. P.; DEZOTTI, M. Treatment of a simulated textile wastewater containing the Reactive Orange 16 azo dye by a combination of ozonation and moving-bed biofilm reactor: evaluating the performance, toxicity, and oxidation by-products. **Environmental Science and Pollution Research**, p. 1–10, 2016.
- CHE, Y.; ZHOU, J.; WANG, Z. Plasma Modification of Activated Carbon Fibers for Adsorption of SO2. **Plasma Science and Technology**, v. 15, n. 10, p. 1047, 2013.
- CHOWDHURY, A. K.; SARKAR, A. D.; BANDYOPADHYAY, A. Rice husk ash as a low cost adsorbent for the removal of Methylene Blue and Congo Red in aqueous phases. Clean Soil, Air, Water, v. 37, n. 7, p. 581–591, 2009.
- FARIA, P. C. C.; ÓRFÃO, J. J. M.; PEREIRA, M. F. R. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. **Water Research**, v. 38, n. 8, p. 2043–2052, 2004.
- GHAEDI, M.; TAVALLALI, H.; SHARIFI, M.; KOKHDAN, S. N.; ASGHARI, A. Preparation of low cost activated carbon from Myrtus communis and pomegranate and their efficient application for removal of Congo red from aqueous solution. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, v. 86, p. 107–114, 2012.

- GOTTLIEB, A.; SHAW, C.; SMITH, A.; WHEATLEY, A.; FORSYTHE, S. The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. Journal of Biotechnology, v. 101, n. 1, p. 49–56, 2003.
- GUARATINI, C. C. I.; ZANONI, V. B. Fixação do Corante A forma de fixação da molécula do corante a essas fibras geralmente é feita em solução aquosa e pode envolver basicamente. **Química Nova**, v. 23, n. 1, p. 71–78, 1999.
- HAO, X. L.; ZHANG, X. W.; LEI, L. C. Degradation characteristics of toxic contaminant with modified activated carbons in aqueous pulsed discharge plasma process. **Carbon**, v. 47, n. 1, p. 153–161, 2009.
- HERNÁNDEZ-URESTI, D. B.; MARTÍNEZ-DE LA CRUZ, A.; TORRES-MARTÍNEZ, L. M. Photocatalytic properties of PbMoO4 synthesized by co-precipitation method: organic dyes degradation under UV irradiation. **Research on Chemical Intermediates**, v. 38, n. 3–5, p. 817–828, 2011.
- JI, P.; QU, G.; LI, J. Effects of Dielectric Barrier Discharge Plasma Treatment on Pentachlorophenol Removal of Granular Activated Carbon. Plasma Science and Technology, v. 15, n. 10, p. 1059–1065, 2013.
- JIANG, B.; ZHENG, J.; QIU, S.; WU, M.; ZHANG, Q.; YAN, Z.; XUE, Q. Review on electrical discharge plasma technology for wastewater remediation. Chemical Engineering Journal, v. 236, p. 348–368, 2014.
- KANAGARAJ, J.; SENTHILVELAN, T.; PANDA, R. C. Degradation of azo dyes by laccase: biological method to reduce pollution load in dye wastewater. Clean Technologies and Environmental Policy, v. 17, n. 6, p. 1443–1456, 2014.
- KYZAS, G. Z.; MATIS, K. A. Nanoadsorbents for pollutants removal: A review. **Journal of Molecular Liquids**, v. 203, p. 159–168, 2015.
- MAHMOODI, N. M. Photocatalytic ozonation of dyes using multiwalled carbon nanotube. **Journal of Molecular Catalysis A: Chemical**, v. 366, p. 254–260, 2013.
- MOHAMMED, J.; NASRI, N. S.; AHMAD ZAINI, M. A.; HAMZA, U. D.; ANI, F. N. Adsorption of benzene and toluene onto KOH activated coconut shell based carbon treated with NH. **International Biodeterioration and Biodegradation**, v. 102, p. 245–255, 2015.
- PEGO, M. F. F. Modificação superficial de carvão ativado utilizando o tratamento corona. 2016. 78 p. Dissertação (Mestrado em Ciência e Tecnologia da Madeira)-Universidade Federal de Lavras, Lavras.
- PELÁEZ-CID, A. A.; VELÁZQUEZ-UGALDE, I.; HERRERA-GONZÁLEZ, A. M.; GARCÍA-SERRANO, J. Textile dyes removal from aqueous solution using Opuntia ficus-indica fruit waste as adsorbent and its characterization. **Journal of Environmental Management**, v. 130, p. 90–97, 2013.



- QU, G. Z.; LI, J.; LIANG, D. L.; HUANG, D. L.; QU, D.; HUANG, Y. M. Surface modification of a granular activated carbon by dielectric barrier discharge plasma and its effects on pentachlorophenol adsorption. **Journal of Electrostatics**, v. 71, n. 4, p. 689–694, 2013.
- ROBINSON, T.; MCMULLAN, G.; MARCHANT, R.; NIGAM, P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. **Bioresource Technology**, v. 77, n. 3, p. 247–255, 2001.
- SALLEH, M. A. M.; MAHMOUD, D. K.; KARIM, W. A. W. A.; IDRIS, A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. **Desalination**, v. 280, n. 1–3, p. 1–13, 2011.
- SHAFEEYAN, M. S.; DAUD, W. M. A. W.; HOUSHMAND, A.; SHAMIRI, A. A review on surface modification of activated carbon for carbon dioxide adsorption. **Journal of Analytical and Applied Pyrolysis**, v. 89, n. 2, p. 143–151, 2010.
- STEPCZYŃSKA, M. Analysis of the decay of some effects of modification of polylactide surface layers. **Polimery**, v. 60, n. 7, p. 462–467, 2015.

- VIGNESH, K.; VIJAYALAKSHMI, K. A.; KARTHIKEYAN, N. Impact of Plasma Surface Treatment on Bamboo Charcoal/Silver Nanocomposite. **Surface Review and Letters**, v. 23, n. 1, p. 1550089, 2016.
- WAN NGAH, W. S.; TEONG, L. C.; HANAFIAH, M. A. K. M. Adsorption of dyes and heavy metal ions by chitosan composites: A review. **Carbohydrate Polymers**, v. 83, n. 4, p. 1446–1456, 2011.
- WANG, S.; ZHU, Z. H.; COOMES, A.; HAGHSERESHT, F.; LU, G. Q. The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. **Journal of Colloid and Interface Science**, v. 284, n. 2, p. 440–446, 2005.
- YAVUZ, Ö.; SAKA, C. Surface modification with cold plasma application on kaolin and its effects on the adsorption of methylene blue. **Applied Clay Science**, v. 85, n. I, p. 96–102, 2013.