International Journal of Engineering & Scientific Research
Vol.5 Issue 1, January 2017,
ISSN: 2347-6532 Impact Factor: 5.900
Journal Homepage: http://www.ijmra.us, Email: editorijmie@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

ADSORPTION OF CONGO RED ON ACTIVATED CARBON MODIFIED BY PLASMA

AbdoulWahabou[*]

Abdoul Ntieche Rahman[**]

KouotouDaouda[***]

Abba Paltahe[****]

Abstract

The surface functional groups of a powdered activated carbon were modified by plasma to enhance its ability for the adsorption of dyes. The powdered activated carbon (PAC) used in this work was prepared from post-consumer plastic waste. It was modified by plasma using the post-discharge method for 10, 20 and 30 minutes. The surface functional groups analyses using Fourier transform infrared spectroscopy were performed on the original activated carbon sample and on the modified samples. Congo red adsorption experiments were carried out on thesesamples and the results obtained for the modified samples were compared against those relating to the original sample. The adsorption isotherms of all samples obey Langmuir model thus indicating monolayer coverage of Congo red onto the various samples. The maximum adsorption capacity of Congo red was 476.190 for the original PAC and reached 555.555 for the modified sample PAC10. Parameter n of Freundlich constant has a value

[*]Institute of Mines and Petroleum Industries, University of Maroua, P.O. Box 46, Maroua, Cameroon

[**]Higher Teachers' Training College, University of Maroua, P.O. Box 55, Maroua, Cameroon

[***]Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon

[****]Higher Teachers' Training College, University of Maroua, P.O. Box 55, Maroua, Cameroon

between 0.3246 and 0.466 thus characterizing a favorable adsorption of Congo red onto all the samples. Furthermore, the results show that PAC30, the sample treated for 30 minutes, has the greatest affinity towards Congo red.

Keywords:activated carbon;adsorption;Congo red;plasma;post-discharge.

1. Introduction

The contamination of waters by pollutants from various sources is a topical problem. Many industries (textile, paper, plastics, food and agriculture…) are large water consumers and use organic coloring agents (soluble dyes and pigments) to color their products. These synthetic dyes are both toxic and responsible for waters coloring. In textile industry, in particular, residuary waters are one of the most important sources of pollution for surface and underground waters, especially with regard to farming lands, fauna and flora [1, 2].

Textile industry waste constitutes a great nuisance for human health and environment. In fact, the various dyes used cause serious problems due to their stability and low biodegradability. Thus, it is necessary to treat this waste prior to its release in the water improvement network. Several physical, chemical and biological methods exist for the treatment and discoloring of polluted effluents namely coagulation, flocculation, biodegradation, membrane filtration, chemical oxidation, ozonation, ions exchange, electrochemical methods and adsorption …[3-5]. Adsorption technique which is the most favorable method for the elimination of dyes has become an analytical method of choice, very efficient and simple in its use [1-3, 6]. The adsorption treatment principle is to trap the dyes by a solid material named adsorbent. There exist in the literature several solid materials (clays, zeolites, activated alumina, mud, biomass, agricultural residues, industrial by-products and activated carbon …) that can be used in water discoloring processes [7].

Researches are oriented towards the utilization of low-cost adsorbents, locally available, biodegradable, manufactured from natural sources. Lately, activated carbons synthesized from agricultural residues have been largely used as adsorbents for the treatment of colored effluents due to their much extended porous structure, to their large specific surface area and to their great adsorption capacity [8, 9].

In this work, the surface functional groups of the activated carbon prepared from post-consumer plastics are plasma modified in order to adapt it to the adsorption of dyes. The powdered activated carbon sample is first treated by plasma using the post-discharge method. It is subsequently used to adsorb Congo red dye which is a coloring agent used in the textile industry. Freundlich, Langmuir I, Langmuir II, and Temkin isotherm models are used to determine the adsorption properties of the various samples and the properties of the modified samples are compared to those of the original sample.

1- Materials and Methods

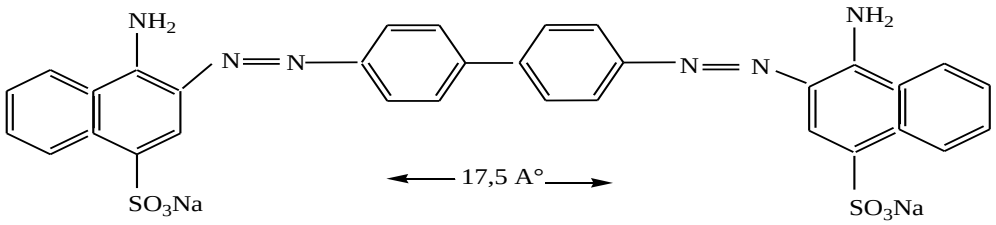
2.1- Adsorbent: The activated carbon is obtained by carbonization of the raw material in a cylindrical stainless steel reactor of 30 cm length and 5 cm diameter approximately. The reactor is fitted with a gas inlet and an exit for the various gas susceptible to be formed. The interior of the reactor is linked to a thermocouple for controlling the rate of temperature rise and the duration of the plateau at the final temperature. The experimental procedure is presented as follows: The post-consumer plastic bottle is washed and dried under sun for 24 hours. The plastic is next subdivided into small particles and is then kept in a drier at 110°C for 24 hours. The carbonization starts at ambient temperature (18°C) with an increase rate of 10°C/min to a temperature of 600°C. The carbonization process is stabilized by nitrogen atmosphere whose flow rate is approximately 100 mL/min. After a residence time of 3 hours at 600°C the nitrogen supply is cut-off and the carbonized material is allowed to cool down to the ambient temperature and is then kept in a desiccators. 5 to 6 grams of carbonized material are picked and placed in the stainless steel reactor, then the heating starts from ambient temperature (18°C) with a heating rate of 10°C/min to the final temperature of 850°C under steam atmosphere whose flow rate is 0.13 mL/min. After a residence time of 2 hours at this temperature, the steam supply is next cut-off and the sample is cooled down to the ambient temperature. The sample is next ground to yield the powdered activated carbon that is subsequently used in this work under the label «PAC» [8, 9].

Adsorption of N_2 is the standard procedure for the determination of the porosity and the specific surface area of activated carbon. Prior to adsorption, all the molecules susceptible to be present in the porous structure of the sample are eliminated through degassing under vacuum at an appropriate temperature for a definite period. In this work, the degassing process was carried out during 6 hours at 200°C. The adsorption-desorption isotherms were

obtained from liquid nitrogen at 77 K and under atmospheric pressure using **Micromeritics TriStar3000 V6.08** type apparatus.

2.2 Treatment of PAC by Plasma: The powdered activated carbon «PAC» is treated by plasma to modify the surface functional groups. The modification process was carried out by post-discharge which consisted in ionizing water by plasma in the first place. The activated carbon is next introduced in this water. The contact is maintained at time interval fixed respectively at 10, 20 and 30 min for each sample. The various samples are designated by PAC, PAC10, PAC20 and PAC30 respectively for the original sample and the samples treated for 10, 20 and 30 min.

Adsorbate: Congo red is a diazoic molecule, which is made up of twice the structure of azobenzene (figure 1). It is both an organic dye, which is no longer much used due to its toxicity, and a pH indicator.



Benzidine diazo-bis-1-naphtylamine-4-sulfonic acid

Figure 1: Structure of Congo red**[10].**

2.3- Adsorption procedure

The adsorption equilibrium studies were performed using isotherm technique. 600 mg of Congo red is weighed and introduced in a 2 liter volumetric flask. The flask is then filled with distilled water up to the calibrated mark. The solution is left under stirring for 12 hours and is then filtered to eliminate undissolved particles. A volume V of the parent solution is taken, put in a 100 mL volumetric flask and completed with distilled water to the calibrated mark. The solution so obtained is put in a bottle containing 10 mg of activated carbon which was kept beforehand in a drier at 110°C for 24 hours. Eight solutions of different concentrations are thus prepared by varying the volume V of the parent solution from 2.5 to 20 mL.Each solution was shaken vigorously using magnetic stirrer at the rate of 200 rpm at room temperature for 4 hours. At the end of the adsorption process, the solutions were filtered and the equilibrium concentrations were determined by spectrophotometric analysis.

The quantities of micropollutants adsorbed are calculated using the following equation:

$$Q_{ads} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where, C_0 and C_e are respectively the initial and equilibrium concentration (mg/L), of phenolic compounds in solution; V the volume (L), and *m* is the weight (g) of the adsorbent.

2.4- Identification of the surface functional groups by FT-IR method

The sample to be analyzed is mixed with a transparent KBr support, the whole is placed in a FT-IR apparatus where it is crossed through by an infrared beam. The infrared beam moves across the sample and the energy released by the latter is measured. The transmission T is defined as the fraction of light energy moving across the sample. At the entrance of the sample the intensity of light is I_0. It is equal to I on the other side of this same sample. Thus T = I/I_0. The percentage of transmission (transmittance) is defined as %T = 100 (I/I_0). The absorbance is therefore A = log (I_0/I).

3- Results and Discussion

The activated carbons were prepared by physical activation under inert atmosphere using post-consumer bottle in polyethylene terephthalate waste as precursors; the activated carbon obtained is designated by PAC. The characterization of the porous adsorbents was carried out using several methods. **Figure 2** shows that the adsorption-desorption isotherm of N_2 on the sample prepared is of type IV of IUPAC classification; a type characteristic of a system containing a mixed porous structure with predominance of the quantity of micropores. The results obtained by BET method are presented in **Table 1**.

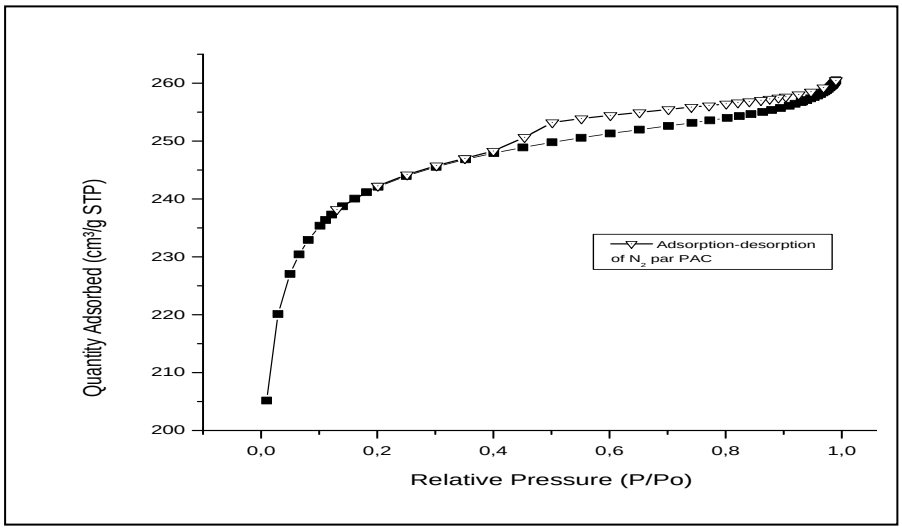


Figure 2: Adsorption-desorption isotherms of N_2 on the activated carbon (PAC) prepared by physical activation method obtain from post-consumer bottle in polyethylene terephthalate

Table1: Characteristics of activated carbon (PAC) obtained from post-consumer polyethylene terephthalate-made bottles and prepared by physical activation method

Activated carbon used	**Precursor**	**Specific surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (nm)**	**Iodine Index(I.I) (mg/mol)**	**Methylene blue Index (mg/mol)**
PAC	Plastic bottle	849.16	0.4018	1.8129	420	460

The texture of the activated carbon is not easy to define but the images (**Figure 3**) obtained by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) of the PAC sample prepared by activation suggest that the material is made up of a network of more or less spherical particles very interconnected.

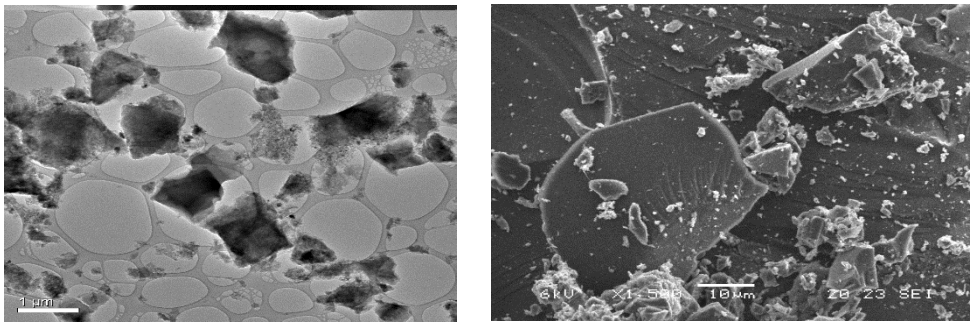


Figure 3: (a) Transmission electron microscope (TEM) and (b) Scanning electron microscope (SEM) images of the activated carbon PAC

3.1- Structural analysis by FTIR

The spectra of analysis by infrared spectroscopy of the various plasma-treated activated carbon samples are presented in **Figure 4**.

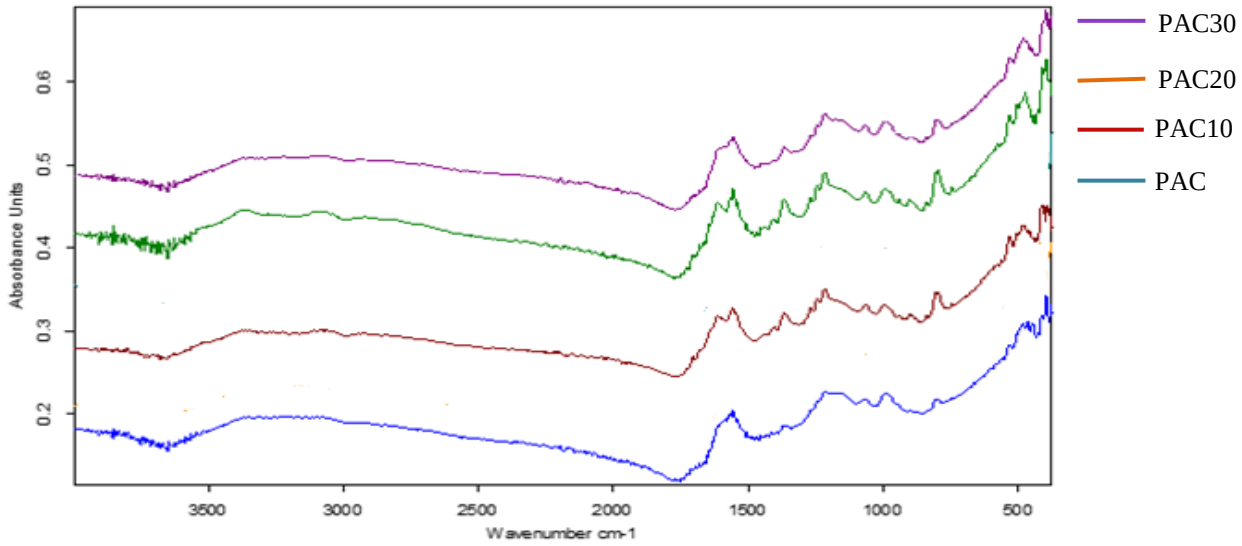


Figure 4: IR spectra of the samples PAC, PAC10, PAC20 and PAC30.

All the activated carbon samples absorb nearly at the same bands. The various spectra all show:

- a broad absorption band at around 3370-3680 cm^{-1} characteristic of –OH bond.
- a broad band around 1750 cm^{-1} which is ascribed to the stretching vibration of the C=O bond in carboxylic acids, anhydrides and lactones.
- a broad band between 1400 and 1620 cm^{-1} which can be due to the vibrations of aromatic rings C=C bonds.
- a band between 920 and 750 cm^{-1}which is ascribed to vibration absorption for out-of-plane deformation of C–H aromatic bonds. This region allows to take into account the substitutions on benzene rings and to evaluate the degree of condensation of aromatic rings [11].

It is to be noted that the various samples absorb with different intensities. The order of recorded intensities is: PAC30 >PAC20 >PAC>PAC10. This shows that the treatment of the activated carbon PAC by plasma has led to important modifications of surface functional groups.

3.2- Adsorption isotherms

The adsorption isotherm show the relationship between adsorbate at equilibrium with adsorbent at constant temperature. Figure 5 represents the adsorption isotherms of Congo red onto the original sample of activated carbon and the samples of activated carbon modified by plasma. It can be seen for all the samples that the number of available sites for further adsorption of Congo red reduces when the concentration increases. These isotherms are

concave downward at weak solution concentration, which indicates a decrease in free sites as long as the adsorption goes on. The isotherms correspond therefore to type-L isotherms indicating monolayer coverage onto microporous materials.

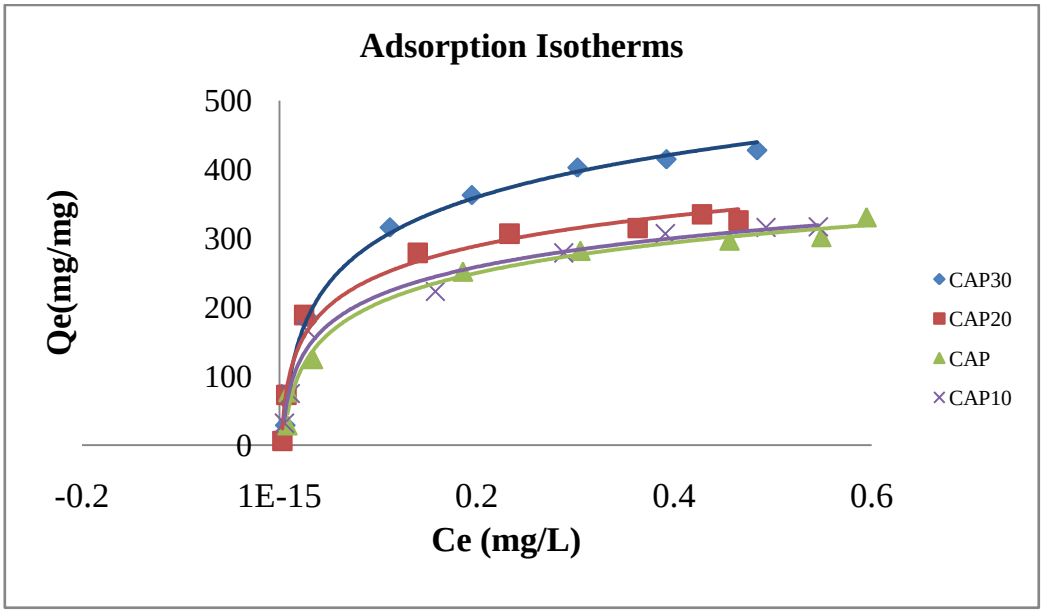


Figure 5: Adsorption isotherms of PAC, PAC10, PAC20 and PAC30

3.2- Linear transforms of the various adsorption isotherms models used

The various characteristic constants of adsorption for each model and each sample were obtained. All the constants inferred from the linear transforms of the different isotherms (figure 6 to figure 8) are found in table 2.

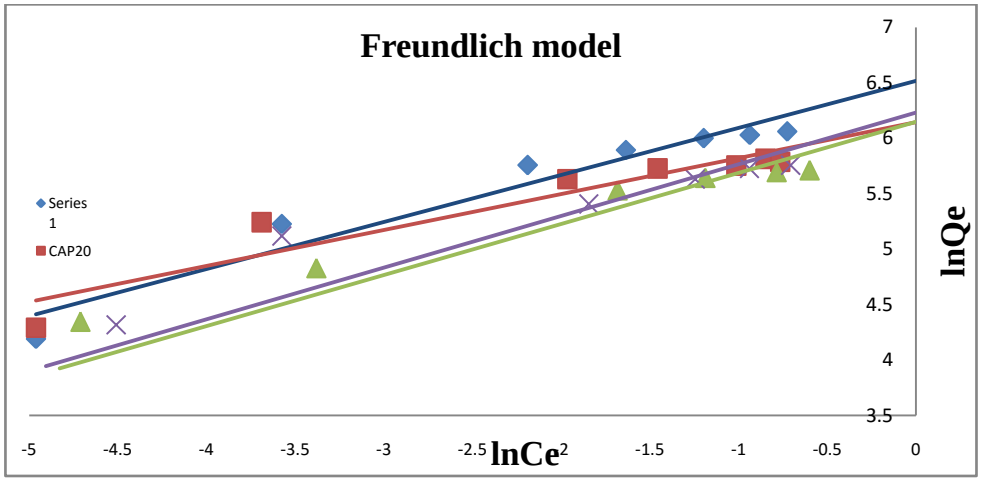


Figure 6: Freundlich linear tranform for the samples PAC, PAC10, PAC20 and PAC30

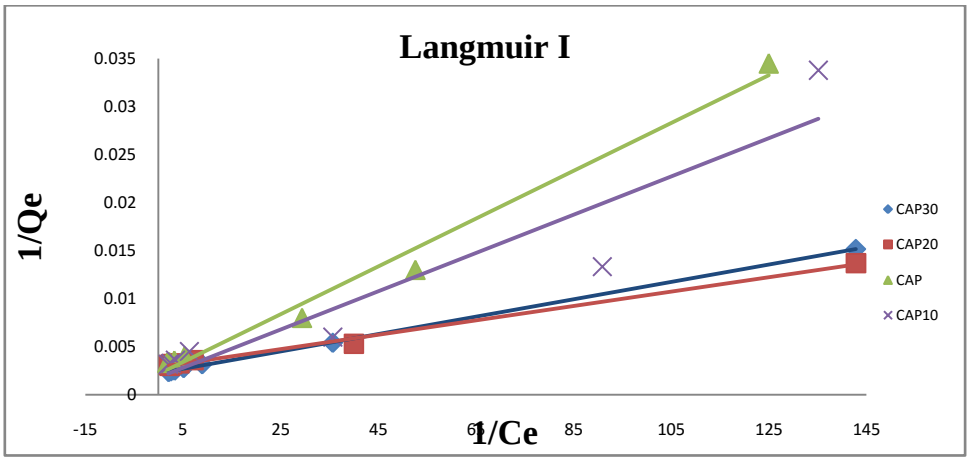


Figure 7: Langmuir I linear transform for the samples ***PAC, PAC10, PAC20 and PAC30***

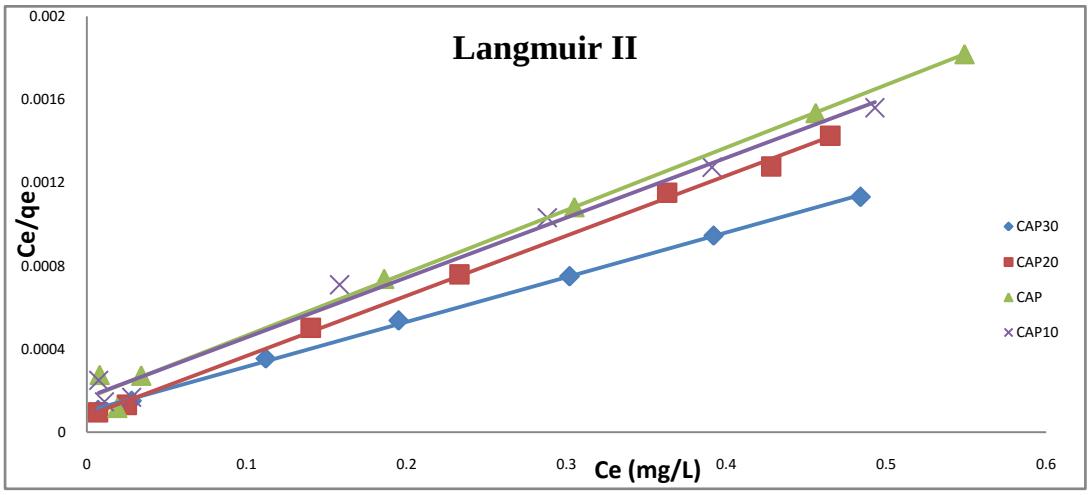


Figure 8: Langmuir II linear transform for the samples ***PAC, PAC10, PAC20 and PAC30***

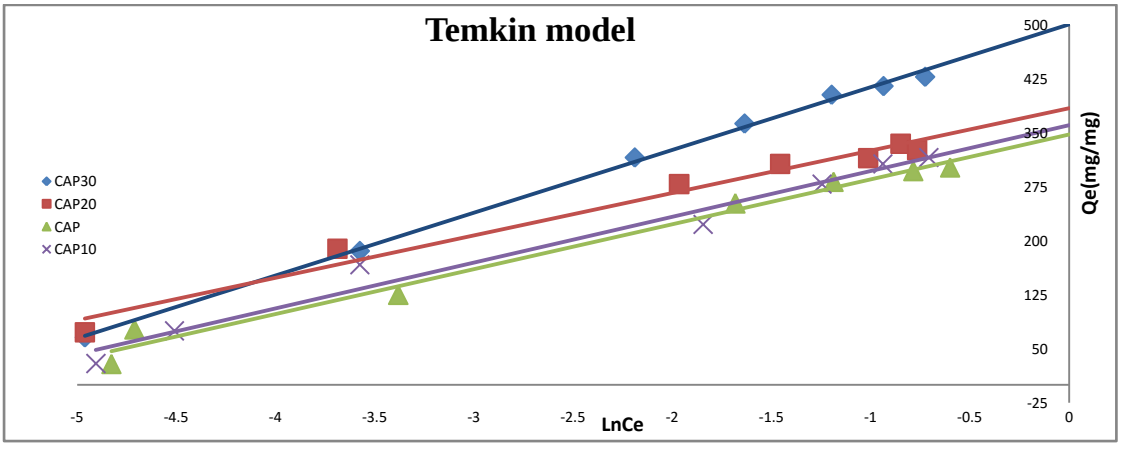


Figure 9: Temkin*linear transform for the samples***PAC, PAC10, PAC20 and PAC30**

Table 2:Correlation coefficient and adsorption parameters inferred from the various adsorption models

Samples	Freundlich model			Langmuir I model			Langmuir II model		
	R^2	n	K_F (mg/mg).(mg/L)$^{-n}$	R^2	q_m mg/mg	K_L L/mg	R^2	q_m mg/mg	K_L L/mg
PAC	0.8831	0.4603	466.706	0.9867	476.190	10.500	0.993	333.33	15.00
PAC10	0.8564	0.466	507.450	0.8909	555.555	9.000	0.9884	344.827	14.50
PAC20	0.8998	0.3246	466.426	0.9957	344.827	41.428	0.9984	344.827	36.25
PAC30	0.9411	0.424	675.261	0.9997	454.545	24.444	0.9992	476.190	21.00

Samples	Temkin model		
	R^2	B_T J.g/mmol^2	K_T L/mg
PAC	0.9847	62.366	264.509
PAC10	0.9747	63.636	289.414
PAC20	0.9767	58.853	683.884
PAC30	0.998	87.200	311.321

Freundlich equation is an empirical equation and is the most popular. It assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases as the sorption centers of the adsorbent are gradually occupied which correlated well with a highly heterogeneous surfaces having different chemical/physical properties [12]. For the various samples, the values of n are between 0.325 and 0.466 thus characterizing a favorable adsorption of Congo red onto the three plasma-modified activated carbons as well as onto the initial sample. Thus, the affinity of Congo red is highest for PAC20 and least for PAC10. The arrangement of Congo red affinity for the activated carbons is the following: PAC20>PAC30>PAC>PAC10. These values also show that the adsorbents present more and more heterogeneous texture. K_F values of the various samples are between 466.426 (mg/mg).$(mg/L)^{-n}$ and 675.261 (mg/mg).$(mg/L)^{-n}$ which indicates a high adsorption capacity of the samples, the order being PAC30>PAC10>PAC>PAC20.

Langmuir model assumes that the adsorption takes place onto homogeneous surface sites. Langmuir constant, K_L, is a measure of adsorption intensity. In fact, the greater K_L, the stronger the affinity between the adsorbent and the adsorbate is. It can be observed here that for all the samples K_L values (**Table 2**) are sufficiently high for Langmuir I as well as for Langmuir II. The adsorption of Congo red onto plasma-modified activated carbons is therefore favorable in the concentration range considered. The affinity of Congo red is greatest for PAC20 sample and least for PAC10 sample in terms of Langmuir I and Langmuir II models.

For Langmuir models, the greatest adsorption capacities are observed for samples PAC10 (q_m = 555.555mg/mg) in Langmuir I and PAC30 (q_m = 476.190 mg/mg) in Langmuir II and the smallest for samples PAC20 (q_m= 344.827mg/mg) in Langmuir I and PAC (q_m= 333.33mg/mg) in Langmuir II. The following arrangement is obtained: PAC10>PAC>PAC30>PAC20 (Langmuir I) and PAC30>PAC10=PAC>PAC20 (Langmuir II).

Furthermore, the correlation coefficient values for Langmuir I and Langmuir II models for all the samples except for sample PAC10 in Langmuir model I (R^2 = 0.8909) are greater

than 0.96. These models are therefore applicable for the description and analysis of the adsorption of Congo red onto plasma-modified activated carbon.

Temkin adsorption model can not only be used to explain the nature of adorbent-adsorbate interactions but is able to yield at the same time the information on the energies involved in the adsorption process. If Temkin constant B_T is positive then the adsorbent-adsorbate interactions are gravitational (attractive); otherwise they are repulsive [14]. For all the samples, the values of the constant are positive thus characterizing attractive interactions. It is to be noted that some activated carbon samples attract Congo red more and give rise to stronger Congo red-activated carbon bonds than others. Thus sample PAC30 with a value of B_T = 87.200 J.g/mmol^2 attracts Congo red most whereas sample PAC20 with B_T = 58.853 J.g/mmol^2 attracts Congo red least. The following arrangement is obtained: PAC30>PAC10>PAC>PAC20. This very arrangement is confirmed in Freundlich model as far as the adsorption capacities of the various samples are concerned.

The bond equilibrium constant K_T (L/mg) is a measure of the adsorbent-adsorbate bond energy. The greater K_T, the stronger the Congo red-activated carbon bond and the larger the heat released [15]. Thus, the strongest Congo red-activated carbon bond is obtained for PAC20 sample with K_T = 683.884 (L/mg) and the weakest for PAC with K_T = 264.509 (L/mg). The following arrangement is obtained: PAC20>PAC30>PAC10>PAC. This arrangement shows the positive impact of the modification of the functions at the surface of activated carbon by plasma for the sorption of organic dyes.

The correlation coefficient values of Temkin model for all the samples are greater than 0.96. This model is therefore applicable for the description and analysis of the adsorption of Congo red onto plasma-modified activated carbon.

4- Conclusions

The principal objective of this work was to modify by plasma the surface functional groups of an activated carbon prepared from post-consumer plastics in order to adapt it to the adsorption of dyes. Analysis of FT-IR spectra indicated that the surface functional groups of the activated carbon were effectively modified by plasma treatment, by increasing the quantities of functional groups at the surface of solid material. Adsorption tests of Congo red onto the investigated samples were conducted and the resulting adsorption isotherms

showed that CAP30 adsorbs better than the other samples. The surface modification by plasma has therefore enhanced the adsorption capacity of the samples so treated.

References :

[1] J.S.B. Cui, Dye Congo Red adsorptive decolorization by adsorbents obtained from Trametes pubescens pellets, Desalination and Water Treatment, 51 (2013) 13.

[2] S.X.F.Z. Tao Fenga, Application of cross-linked porous chitosan films for Congo red adsorption from aqueous solution, Desalination and Water Treatment, 20 (2013) 7.

[3] D.S.L. Sudipta Chatterjee, Min W. Lee, Seung H. Wooa, Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with nonionic or anionic surfactant, Bioresource Technology, 100 (2009) 7.

[4] Z.Q.J. Z.Wang, Y.Kong, and W.Shen, Comparative studies of Activated Carbon-attapulgite and Zeolite-attapulgite Composite Adsorbent on Congo Red Adsorption, Applied Mechanics and Materials, 33 (2010) 4.

[5] M.C.M.A.-F. Joana M. Diasa, Manuel F. Almeidaa,, M.S.-P. Jose´ Rivera-Utrillab, Waste materials for activated carbon preparation and its use in aqueous-phase treatment, Journal of Environmental Management, 85 (2007) 833–846.

[6] Z.Z.D.Y. Liu Dong, A Simple Method to Prepare Magnetic Modified Corncobs and its Application for Congo Red Adsorption, Journal of Dispersion Science and Technology, 37 (2015) 7.

[7] F.R.-R. Harry Marsh, Activated carbon book, Elsevier Science & Technology Books, (2006).

[8] A.B. Abdoul Ntieche Rahman, Isaac Beas Nongwe, Ketcha Joseph Mbadcam, Abdelrani Yaacoubi, Composite activated carbon from plastic waste and lignocellulosic waste materials, International Research Journal of Natural and Applied Sciences, 2 (2015) 12.

[9] L.B.B. Abdoul Ntieche Rahman, Abdelaziz Bacaoui and Ketcha Joseph Mbadcam, Modified Composite Activated Carbon Derived from Post-Consumer Plastics and Lignocellulosic Materials, American Chemical Science Journal, 3 (2013) 9.

[10] P.V.V.B. Venkat S. Mane, Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (Eucalyptus globulus) saw dust, Journal of the Taiwan Institute of Chemical Engineers, 44 (2013) 9.

[11] S.H. Fumitoshi Iyoda, Shuichi Arakawa, Baiju John, Masami Okamoto,, G.Y. Hidetomo Hayashi, Synthesis and adsorption characteristics of hollow spherical allophane nano-particles, ScienceDirect, 56 (2012) 77-83.

[12] A.M.R. Muhammad Shafiq, M. Yaseen, S. M. Mehdi and A. Hannan, Comparison of Freundlich and Langmuir adsorption equations for Boron adsorption on calcareous soils, J. Agric. Res., 46 (2008) 8.

[13] R.C. Bansal and M. Goyal, Activated carbon adsorption, Taylor & Francis Group, (2005).

[14] L.F.C. F. Rozada, A.I. Garc, J. Martın-Villacorta, M. Otero, Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems, Bioresource Technology, 87 (2003) 10.

[15] O.S. Mohd. Rafatullaha, Rokiah Hashima, Anees Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, Journal of Hazardous Materials 177 (2010) 11.