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Removal of Textile Dye Acid Green 1 from Wastewater by Activated Carbon

E. Mourid[1], M. Lakraimi[1*], E. El Khattabi[1], L. Benaziz[1], M. Berraho[2]
[1] Physical Chemistry of Materials Team, Cadi Ayyad University, Marrakech, Morocco.
[2] Laboratory of Biomolecular Chemistry, Cadi Ayyad University, Marrakech, Morocco.

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mlakraimi@yahoo.fr
+212633987819

Abstract

Activated carbon were used as the adsorbent, in this study, for the removal of textile dye acid green 1 (AG1) from aqueous solutions. Effects of various experimental parameters, such as adsorbent dose, contact time, initial dye concentration, and initial pH solution are studied. The removal of AG1 effluent is a rapid process. At pH 2 and at room temperature, the adsorption equilibrium is reached after 2 hours and the kinetics follow a pseudo-second order model. The adsorption isotherm is in good agreement with the Langmuir model, is of L-type. The adsorption of dye on the surface of activated carbon was done in monolayer. This mechanism has been confirmed by IR spectroscopy and Scanning Electron Microscopy. The removal of acid green 1 by activated carbon is total (100 %) at optimized conditions and the maximum adsorption capacity was reached 121.5 mg/g.

1. Introduction

Synthetic dyes are widely used in the textile industry and intensely colored substances used for the coloration of various substrates, and these compounds are extensively used in various industries, such as those producing textiles, foods, cosmetics and paper printing [1] and are generally resistant to biodegradation due to their xenobiotic nature. About 15% of these dyes are released in effluents during dyeing processes [2].

The colored from effluents of the textile industry cause serious environmental problems due to the structural variety of dyes and to the use of large amounts of water in the dyeing processes, that is why the color removal from industry or domestic effluents has drawn considerable attention in the last few years.

Biological, physical and chemical methods used for industrial textile wastewater treatment include microbial biodegradation, membrane filtration, oxidation and ozonation [3]. Conventional treatments are often disadvantageous to remove dyes owing to their high solubility and low biodegradability [4].

The use of adsorption on solid materials has been considered as a choice method for the removal of textile dyes [5]. It is an efficient and economical physical method which could allow a complete decolorization of the wastewater and possible reuse.

Commercial activated carbons are sophisticated in the sense that they are designed for a variety of applications.

Adsorption on activated carbon is currently widely used for the removal of different types of dyes, because of the high specific surface area and an adequate pore size distribution of this material. More groups of dyes such as acidic, alkaline, reactive, direct can be found in the environment. These compounds due to their chemical structure are characterized by high toxicity, mutagenicity and carcinogenic nature [6].

The main aim of the present study is investigation of a commercial activated carbon application for removal of Acid Green 1 (AG1) from aqueous solution.

2. Materials and methods

2.1. Adsorbent and adsorbate

This study was performed experimentally and in laboratory scale. In this research, the effect of adsorbent dose, contact time, initial dye concentration and initial pH are studied.

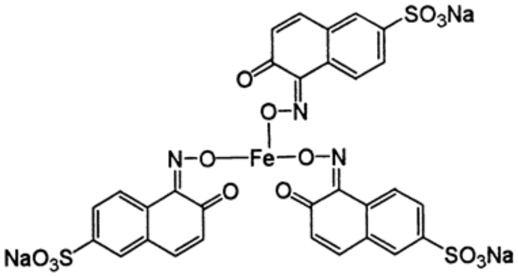
The stock solution was prepared by dissolving 200 mg of AG1 in 1L decarbonated water. For the present analyses, the dye solutions with different concentrations (10 to 200 mg/L) were prepared by diluting the stock solution in decarbonated water in 100 ml Erlenmeyer flasks. Stirring was done using a magnetic stirrer in static mode in closed flasks.

The AG1 quantity retained by activated carbon, Q, was calculated as the difference between initial and equilibrium (final) concentrations of the dye in solution (C_i and C_e, respectively) by mass of the adsorbent (m) in the volume of solution (V) using the following equation:

$$Q = (C_i - C_e).V/m$$

Acid Green 1 dye (AG1) was obtained commercially from DyStar. Some of the important physicochemical properties of AG1 are stated in Table 1.

Table 1: Chemical structure and characteristics of AG1.

Commercial Name	Acid Green 1
Systematic name	[Ferrate (3-), tris[5,6-dihydro-5-(hydroxyimino-kappa.N)-6-(oxo-kappa.O)-2-naphthalenesulfonato(2-)]-sodium (1:3)]
Synonyms	Basacid Green 970
Chemical structure	
Formula	$C_{30}H_{15}FeN_3Na_3O_{15}S_3$
Molecular weight	878.45 g/mol
Group	Nitroso
Solubility in H_2O	30 g/L
Use	Leather and fur dye, Biological stain, dyeing wool, nylon and paper
Toxicity	Toxic (contact with eyes may cause irritation)

The activated carbon (AC) used is a commercial product of coconut origin, in powder form and was obtained from Loba Chemie (Pharma Grade 7440-44-0 CAS), some of its properties are as follows: specific surface area 750 m^2/g, average pore size 6 Å, density varied of 1.8 to 2.1.

2.2. Analytical techniques

The supernatants were recovered and the residual dye concentration was determined by absorbance spectrum detection between 200 nm to 800 nm using the UV/Vis Jenway-6300 spectrophotometer. The maximum absorption of AG1 is obtained for a wavelength $\lambda_{max} = 650$ nm.

Absorbance IR spectra were recorded on a JASCO model FT/IR - 4600, at a resolution of 2 cm^{-1} and averaging over 100 scans, in the range 400–4000 cm^{-1}.

The Scanning Electron Microscopy (SEM) allows viewing the external morphology of materials. The principle of scanning is to scan the surface of the sample in successive rows and to transmit the sensor signal to a cathode ray tube whose scan is exactly synchronized with that of the incident beam. The scanning microscope use a very fine beam which scans the surface point by point of the sample. The observations are carried out at a voltage of 10 kV.

3. Results and discussion

3.1. Chemical stability study of activated carbon

The final pH values were plotted against the initial pH (Figure 1) shows the presence of buffer zone where the pH is almost quasi-constant. This zone characterizes the buffer power.

Calibration of the different initial pH values is done by adding a few drops of NaOH or HCl solutions.

The pH of the point of zero charge (pH_{pzc}) is the point where the curve final pH versus initial pH crosses the lines initial pH = final pH [7]. This point of intersection is pH_{pzc} equal 7.6.

The surface charge of AC is neutral at pH_{pzc}. At $pH < pH_{pzc}$, the AC surface has a net positive charge, while at $pH > pH_{pzc}$ the surface has a net negative charge [8].

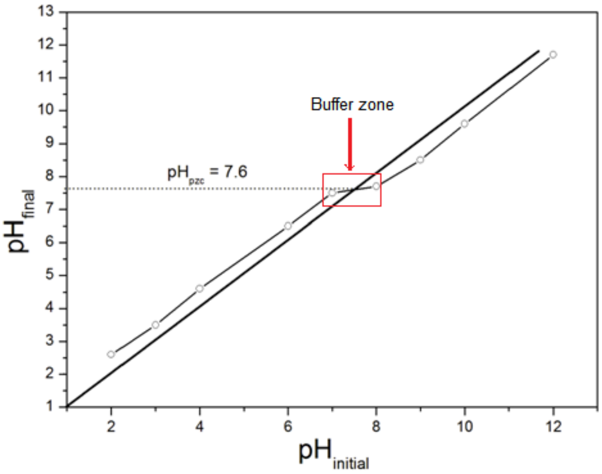


Figure 1: Determination of pH_{pzc} of activated carbon (t_c = 4 h, m_{AC} = 100 mg, and C_i = 100 mg/L).

3.2. Influencing factors

Preliminary adsorption experiments were conducted to determine the optimal conditions for the removal of AG1 by activated carbon regarding the initial pH, contact time (t_c), initial concentration (C_i) of adsorbate, the mass of AC (m_{AC}) and the mass ratio (AG1/AC).

3.2.1. Effect of initial pH

Adsorption is also affected by change in pH of the solution [9,10] as shown in Figure 2.

The pH is the important factor which controls the adsorption process at water-adsorbent interfaces. In this study the effect of initial pH was studied by performing the adsorption experiments at different pH ranging from 2 to 11.

It is shown that the AG1 adsorption is at its maximum in the pH 2. In this range of acid pH, the positive charge of the surface of the activated carbon increases, this causes an increase of the electrostatic attraction between the dye and the surface of the adsorbent. The adsorbed amount decreases when the pH increases by 4 to 11. Gradually, as the pH of solution increases, the number of negatively charged sites increases and the number of positively charged sites decreases and consequently there is a reduction in the interaction between AG1 ions and the surface of the activated carbon. For the optimization of the other factors influencing the retention, an optimum pH equal to 2 will be chosen subsequently.

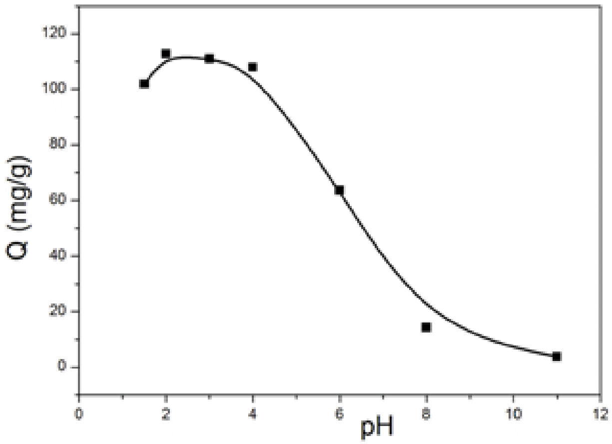


Figure 2: Effect of initial pH on AG1 removal efficiency (t_c = 4 h, m_{AC} = 100 mg, and C_i = 200 mg/L).

3.2.2. Effect of contact time

Figure 3 show the adsorption of AG1 onto activated carbon at different contact time for three initial concentrations of the dye.

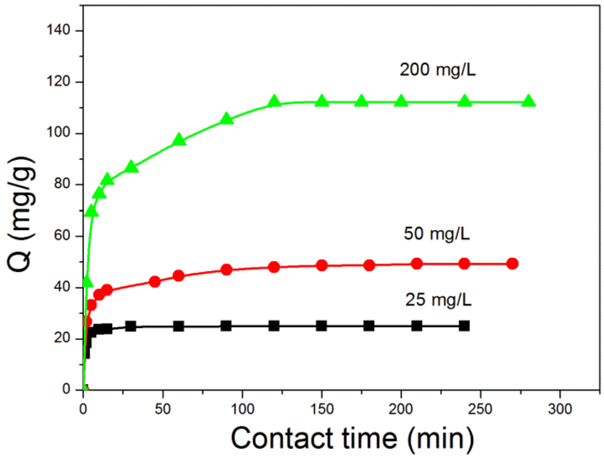


Figure 3: Effect of contact time on AG1 removal efficiency (pH = 2, m_{AC} = 100 mg).

The adsorption efficiency and the adsorption capacity increase with increase in agitation time. It is noted that the adsorption rate is fast at the beginning of the process and becomes slower during the stirring time and equilibrium is reached after 2 h.

3.3. Adsorption Kinetics (*Pseudo-first and pseudo-second order models)*

Several models can be used to express the mechanism of solute adsorption onto an adsorbent. In order to design a fast and effective model, investigations were made on adsorption rate. For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer, several kinetics models are used to test the experimental data. In this study, two kinetic models (the pseudo-first order and pseudo-second order) were used to fit the experimental data from the adsorption of AG1 dye onto activated carbon at pH 2 and initial dye concentration at 50 mg/L.

For the pseudo-first order model, a linear equation is obtained as follows [11]:

$$\mathbf{\log (q_e - q_t) = \log q_e - (k_1 /2.303).t}$$

where q_e (mg/g) and q_t (mg/g) are the sorption capacities at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the rate constant.

The pseudo-second order model is presented by following equation [12]:

$$\mathbf{t/q_t = 1 /k_2.q_e^2 + (1 /q_e)\ t}$$

where k_2 is the pseudo-second order rate constant of adsorption (g/mg/min).

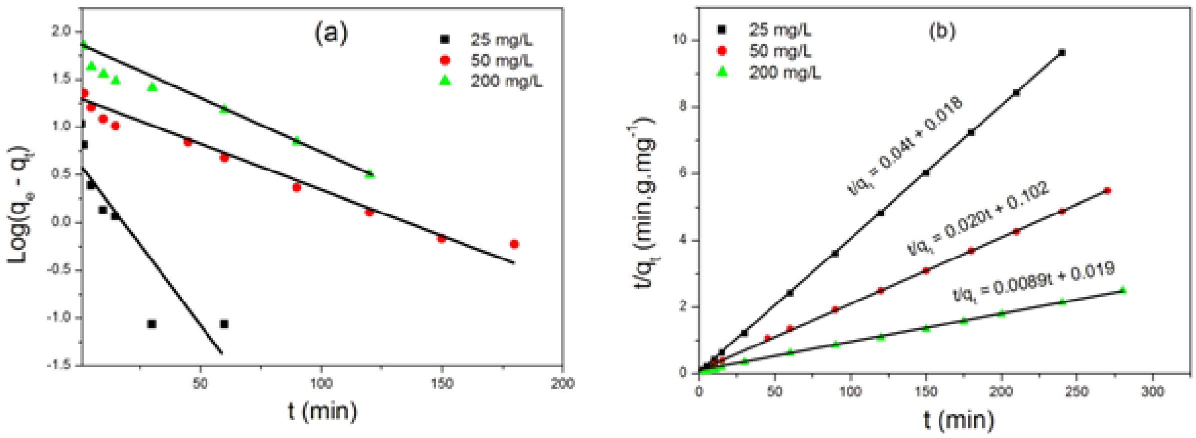


Figure 4: Pseudo-first order model (**a**) and pseudo-second order model (**b**) plots adsorption of AG1 onto activated carbon (m_{AC} = 100 mg and pH = 2).

The results linearization both models are summarized in Table 2. The correlation coefficient for the pseudo-second order equation is better than them for the pseudo-first order equation. It can be said that the AG1 retention kinetics by activated carbon is in good agreement with the model of the pseudo-second order.

Table 2: Adsorption kinetics describes the order and correlation coefficients for adsorption of AG1 dye on activated carbon.

	Pseudo-first order				**Pseudo-second order**			
C_0 (mg/L)	**k_1** (min^{-1})	**$q_{e}th$** (mg/g)	**$q_{e}exp$** (mg/g)	**R^2**	**k_2** (g/mg/min)	**$q_{e}th$** (mg/g)	**$q_{e}exp$** (mg/g)	**R^2**
25	0.078	4.508	24.914	0.793	0.088	25	24.914	0.999
50	0.0184	16.634	49.305	0.978	0.004	50.01	49.305	0.999
200	0.027	55.36	112.20	0.971	0.004	112.25	112.20	1

3.4. Intra-particle diffusion model

The adsorption process is a diffusive mass transfer process where the rate can be expressed in terms of the square root of time (t).

The intra-particle diffusion model is expressed as follows [13,14]:

$$\mathbf{q_t = k_i\, t^{1/2} + b}$$

where q_t is the fraction dye uptake (mg/g) at time **t**, **k_i** is the intra-particle diffusion rate constant (mg/g/min$^{1/2}$) and **b** is the intercept (mg/g). A plot of **q_t** versus **$t^{1/2}$** (Figure 5) will give **k_i** as slope and **b** as intercept.

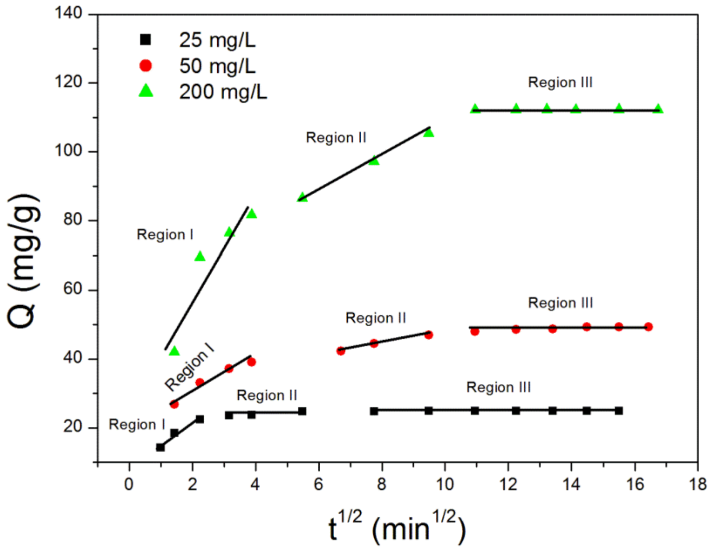


Figure 5: Intra-particle diffusion kinetics for adsorption of AG1 on activated carbon.

The intra-particle diffusion model for adsorption for AG1 on the activated carbon is shown in figure 5, and its shape is satisfactory to experimental data. From these results, it can be noted that the diffusion mechanism of the adsorption system is described by three distinct regions instead of a single linear over the whole domain, which implies that the process has more than one step.

If intra-particle diffusion is a speed control step, then the curve must be linear and must pass through the origin. These plots show three stages, starting with an initial part, followed by an intermediate linear part and ending with a plateau. The initial part may be due to an adsorbate (AG1) transfer on the external surface of the adsorbent (AC), the intermediate linear part is due to the intra-particle diffusion and the plateau to the equilibrium stage where the intraparticle diffusion begins at slowing down due to extremely low solute concentrations in the solution and saturation of the material sites [15].

So we can say that the transport of the dye molecules from the surface to the internal pores of the adsorbent (AC) is done by intraparticle diffusion.

These results are presented in Table 3.

Table 3: Intra-particle diffusion kinetics model constants and correlation coefficients for adsorption of AG1 on activated carbon.

	Region I			**Region II**			**Region III**		
C_0 (mg/L)	**k_{1P}** (mg/g/ $min^{1/2}$)	**R^2**	**b** (mg/g)	**k_{2P}** (mg/g/ $min^{1/2}$)	**R^2**	**b** (mg/g)	**k_{3P}** (mg/g/ $min^{1/2}$)	**R^2**	**b** (mg/g)
25	6.419	0.960	8.437	0.565	0.972	21.69	0.007	0.998	24.80
50	4.925	0.954	20.86	1.647	0.986	31.46	0.234	0.978	45.61
200	15.22	0.857	26.70	4.676	0.998	60.89	0.005	0.997	112.1

3.5. Study of adsorption isotherms

The adsorption isotherm indicates how the molecules are distributed between the liquid phase and solid phase when the adsorption reached the maximum**.**

Figure 6 displays the adsorption isotherms of AG1 onto 30, 60 and 100 mg of activated carbon. The dye adsorption isotherms on AC can be considered clearly as pure L-type, indicating that the interaction adsorbate-adsorbent is much stronger than solvent–sorbent at the adsorption sites. The profiles of these isotherms are typical of systems where the adsorbate is strongly attracted by the adsorbent, mainly by ion-ion interaction, which tends to reach a saturation value given by a quasi-plateau. These results again suggest that the AG1 anions are preferentially eliminated by AC.

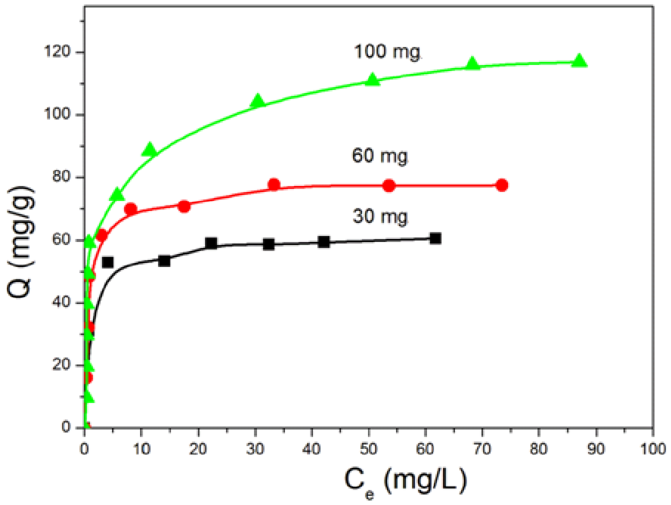


Figure 6: Adsorption isotherms for AG1 determined with three different adsorbent doses.

The adsorption of AG1 is proportional to the mass of activated carbon. The Q_m value increases when the activated carbon mass increases. An increase in adsorption with adsorbent dosage can be attributed to the increased surface area and the availability of more adsorption sites [16]. Figure 6 showed that AG1 dye adsorption increases to certain limit, and then it remains constant.

To determine the nature and mechanisms of adsorption, it is important to establish a correlation with the most appropriate theoretical models with the experimental curves.

***Freundlich isotherm**:*

It is used by assuming a heterogeneous surface of adsorbent with a non-uniform distribution of the adsorbate molecules on the surface. The Freundlich equation is presented in the linear form:

$$\mathbf{Ln\ q_e = Ln\ K_F + (1/n)\ ln\ C_e}$$

Where $\mathbf{K_F}$ is an indicator of the adsorption capacity (L/mg) and **n** is adsorption intensity.

Langmuir isotherm:

It is used to describe the monolayer adsorption of dye molecules that occurs on a completely homogeneous surface with negligible interaction between the adsorbed molecules. The data for adsorption of AG1 were treated according to the linear form of the Langmuir equation:

$$\mathbf{C_e/Q = (1/KQ_m) + C_e/Q_m}$$

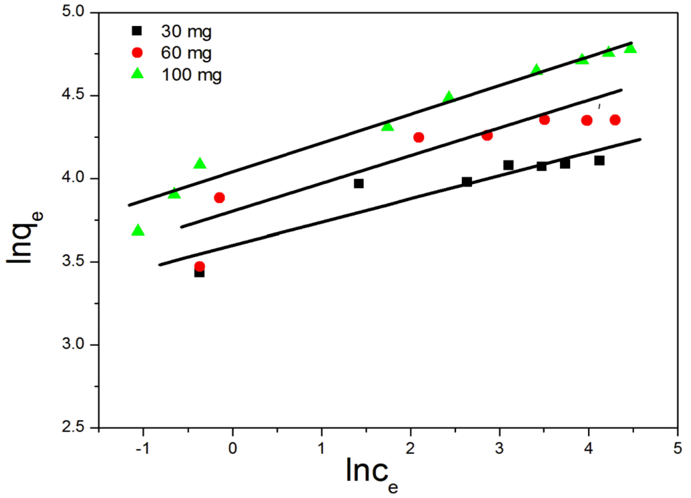


Figure 7: Freundlich adsorption isotherm plots for adsorption of AG1 onto activated carbon (m_{AC} = 30, 60, and 100 mg, pH = 2 and t_c = 2 h).

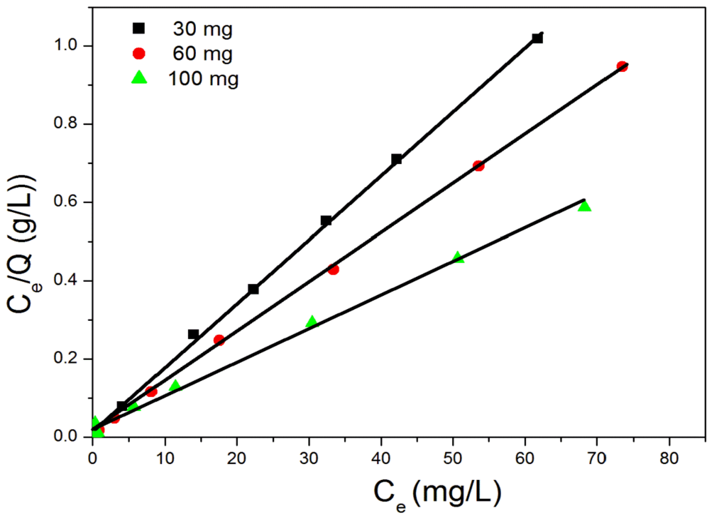


Figure 8: Langmuir adsorption isotherm plots for adsorption of AG1 onto activated carbon (m_{AC} = 30, 60 and 100 mg, pH = 2 and t_c = 2 h).

These isotherms had an appearance reminiscent of those of the Langmuir adsorption isotherms. They provide a satisfactory linearization of retained amount Q. This linearization was used to standardize the method of determining the maximum quantity Q_m. It also provides the affinity constant K, on which it is difficult to pronounce. In that order of size, the K values is at least comparable, suggesting that whatever the mass used of activated carbon, the type of interaction between adsorbent and adsorbate is the same.

Table 4 shows the comparison between the two models described above; the value of the correlation coefficient (R^2> 0.997) indicates that the Langmuir isotherm is the most suitable for describing the adsorption behavior of AG1, suggesting that the surface of the sorbent is homogeneous. The Q_m values increased from 61.31 to 121.5 mg/g with the increase in m_{AC} from 30 to 100 mg (Table 4).

3.6. Effect of mass ratio AG1/AC

The percentage removal of the AG1 dye varies in the same direction with the mass of activated carbon (Figure 9). The removal is almost complete, reaches 100%, for a mass ratio varying between 0.025 and 0.05 which requires a small AG1/AC mass ratio corresponding to a high mass of activated carbon. In the relatively large range of ratios between 0.066 and 0.266, the percentage of removal decreases when the mass of activated carbon decreases, it reaches 22.97% for a mass ratio equal to 0.266.

Table 4: Langmuir and Freundlich isotherms model constants and correlation coefficients for adsorption of AG1 on activated carbon.

	Langmuir isotherm			**Freundlich isotherm**		
m_{AC} (mg)	**Q_m** (mg/g)	**K** (L/mg)	**R^2**	**K_f** (mg/g)	**n**	**R^2**
30	61.31	0.895	0.999	35.873	7,194	0.852
60	78.74	0.968	0.999	35.445	4,385	0.734
100	121.5	0.421	0.997	55.146	5.649	0.906

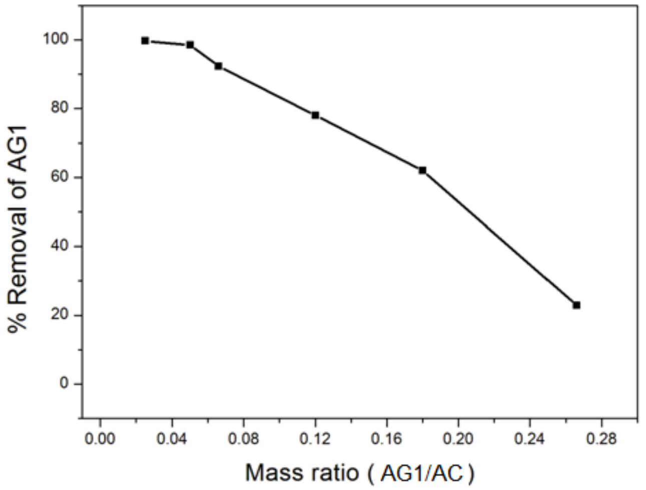


Figure 9: Effect of mass ratio AG1/AC on AG1 removal percentage.

3.7. Characterization of activated carbon before and after adsorption of AG1

3.7.1. Study by Scanning Electron Microscopy

The SEM images of AC before and after adsorption are shown in figure 10. The adsorbent has a porous surface, pores of different sizes and shapes are observed [17,18].

The clearly visible macro-pores facilitate the easy diffusion of more AG1 molecules into this porous structure and are also adsorbed onto the surface of the adsorbent (Figure 10). After adsorption, we note that there are no pores and that the surface has become almost smooth. The structure of the adsorbent is therefore modified [19], which clearly shows that the AG1 ions are adsorbed on the activated carbon and confirms the results obtained by infrared spectroscopy.

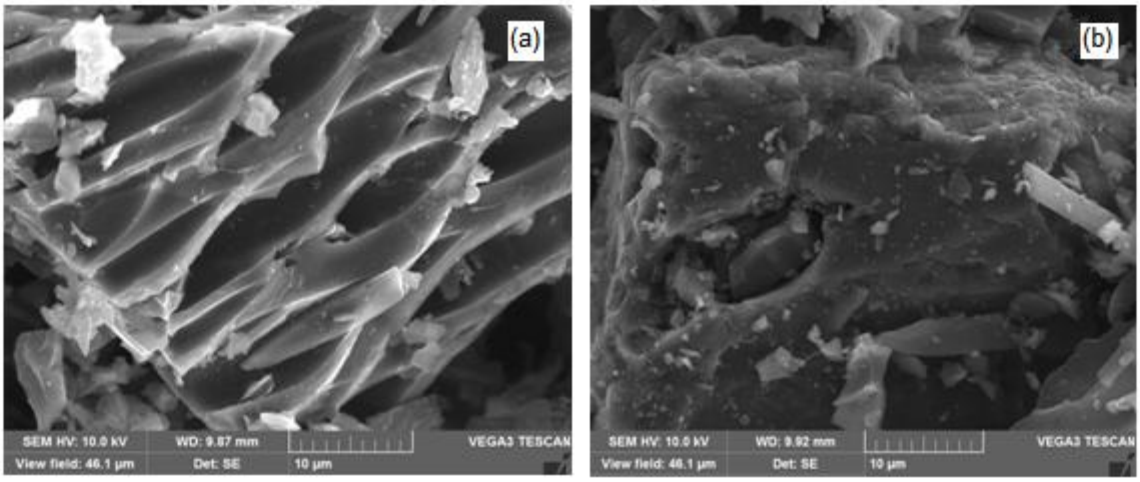


Figure 10: SEM photographs of AC before (a) and after adsorption (b).

3.7.2. Study by Infrared spectroscopy

The IR spectra characteristic of AC before and after adsorption of AG1 are shown in figure 11. The FT-IR spectra of the activated carbon after adsorption showed the characteristic bands at 3445 cm^{-1} due to O-H stretching, peaks at 2852 and 2920 cm^{-1} represents the C–H stretching, peaks at 2374 cm^{-1} represents the C-C stretching, the absorption band at 1564 cm^{-1} are assigned to the stretching vibrations of C=C in an aromatic ring and of N=O stretching, peaks at 1630.5 cm^{-1}represents the C=O stretching [20-22], the large absorption band at 1067.5 cm^{-1} is assigned to the stretching vibration of C-N and represents the S=O stretching. Absorption band at 475.8 cm^{-1} is corresponding to Fe-O stretching vibration [23,24].

The presence of the Fe-O band confirms the adsorption of AG1 dye on the activated carbon because the iron atom exists in the AG1 ion.

The vibration bands at 3433.4, 2370.3, 2287.1, 1703.2, 1560.3, 1045 and 597.6 cm^{-1} before adsorption are shifted respectively to 3445, 2374, 2287.3, 1709.7, 1564.2, 1067.5 and 605.8 cm^{-1} after adsorption. This result indicates that the functional groups of the AG1 dye well affect the absorption process [25,26].

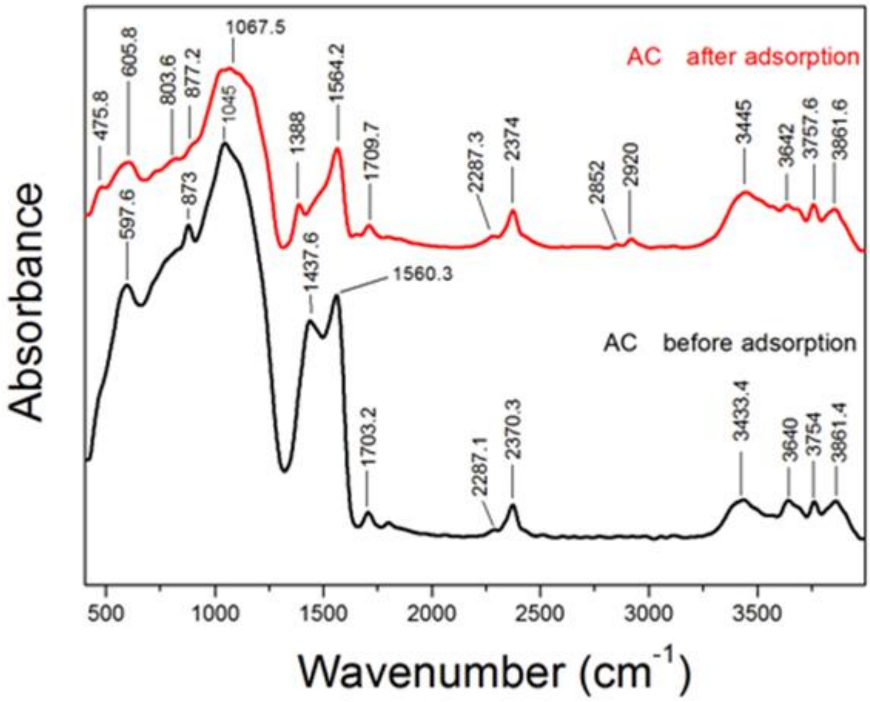


Figure 11: FTIR spectra of activated carbon before and after adsorption of AG1.

Conclusion

The requirement of life leads to a development of the global industry which causes an increase of the contamination of the water by organic pollutants such as the textile dyes and thus poses serious environmental problems.

For this, the activated carbon was used as a potential adsorbent for the removal of the Acid Green1 textile dye from an aqueous solution. The adsorption of Acid Green 1 on AC gave the expected results. It is relatively fast and reaches its equilibrium after 2 h. The adsorption capacity increases in the acid solutions but decreases in the basic solutions with an optimum pH of 2. This is favored by the existence of positive charges on the surface of our material in an acid medium. It has also been found that the adsorption kinetics follows the pseudo-second order model which. The intraparticle diffusion model informed us about the possibility of diffusion of AG1 in the pores of our material (AC).

The different equilibrium isotherms follow the Langmuir model involving an adsorption of AG1 in monolayer with an adsorption capacity which reaches 121.5 mg/g in the concentration domains used for dyeing. This material (activated carbon) has been shown to be effective for the total removal (100%) of such pollutants (dyes) and that the removal of AG1 was confirmed by the results of SEM and IR spectroscopy.

References

1. Arulkumar M., Sathishkumar P., Palvannan T., *J. Hazard. Mater.* 186 (2011) 827-834.
2. Bangash F., Manaf A., *J. Chem. Soc. Pak.* 28 (2011) 20-26.
3. Forgacs E., Cserhatia T., Oros G., *Environ. Int*. 30 (2004) 953-971.
4. Robinson T., McMullan G., Marchant R., Nigam P., *Bioresour. Technol*. 77 (2001) 247-255.
5. Crini G., *Bioresour. Technol*. 97(9) (2006) 1061-1085.
6. Wawrzkiewicz M., *Przemysł Chemiczny* 91(1) (2012) 45-52.
7. Faria P.C, Orfao J.J., Pereira M.F. *Water Research* 38 (2004) 2043-2052.
8. Al-Degs Y., Khraisheh M., Allen S., Ahmad M. *Water Research* 34 (2000) 927-935.
9. Iqbal M.J., Hussain M., *J. Chem. Soc. Pak.* 15(1) (1993) 7-10.
10. Iqbal M.J., Hussain M., *J. Chem. Soc. Pak*. 15(1**)** (1993) 93-97.
11. Ho Y.S., McKay G., *Water Res.* 34 (2000) 735-742.
12. Okeola F.O., Odebunmi E.O., *Adv. Nat. Appl. Sci.* 4 (2010) 281-288.
13. Cheung W.H., Szeto Y.S., McKay G. *Technol.* 98 (2007) 2897-2904.
14. Kang D.J., Yu X.L., Tong S.R., Ge M.F., Zuo J.C., Cao C.Y., Song W.G. *Chem. Eng. J.* 228 (2013) 731-740.
15. Namasivayam C., Kavitha D., *Dyes and Pigments*, 54 (2002) 47-58.
16. Daifullah A.A.M., Yakout S.M., Elreefy S.A., *J. Hazard. Mater*. 147(2007) 633-643.
17. Rahman M.S., Islam M.R., *Chem. Eng. J. 149* (2009) 273-280.
18. Fettouche S., Tahiri M., Madhouni R., Cherkaoui O., *J. Mater. Environ. Sci*. 6(1) (2015) 129-137.
19. Vijayakumar G., Tamilarasan R., Dharmendirakumar M., *J. Mater. Environ. Sci.* 3(1) (2012) 157-170.
20. Pouchert C.J. (1975) The aldrich library of infrared spectra, 2nd Edition. Aldrich Chemical Co., Milwaukee, Wisc. 1576 pp.
21. Pavia D.L., Lampman G.M., Kriz G.S., Introduction to spectroscopy, Harcourt Brace College Publishers, Orlando, 1996.
22. Rubino F.M., *J. Chromatogr. B Biomed. Sci. Appl*. 764(1-2) (2001) 217-254.
23. Ahmed M.A., El-Katori E.E., Gharni Z.H., *J. Alloy. Compd.* 553 (2013) 19-29.
24. Chirila L., Tutulea D.M., Sibiescu D., Rosca I., Cretescu I., Cailean A., Butnaru R., *Rev. Chim. (Bucharest)*, 62(5) (2011) 499-503.
25. Sun D., Zhang Z., Wang M., Wu Y., *Am. J. Anal. Chem.* 4 (2013) 17-26.
26. Gupta V.K., Rastogi A., *J. Hazard. Mater*. 163 (2009) 396-402.

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