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Discoloration of Azo Dye Solutions by Adsorption on Activated Carbon Prepared from the Cryogenic Grinding of Used Tires

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This present work reports a study about the adsorption of cationic dye (Methylene blue) by activated carbon prepared from the cryogenic grinding of used tires. Characterization of the obtained activated carbon by chemical analysis, FTIR and SEM, was studied and resumed that the activated carbon was mesoporous. The effect of various experimental parameters such as contact time, solution pH, adsorbent dose and dye concentration, on the dye adsorption uptake on the activated carbon has been investigated using batch adsorption experiments. According to the experiments results, it was shown, that equilibrium was achieved in less than 114 min. The effect of pH investigated for values ranging from 2 to 11, showed maximum adsorption for pH 11. The equilibrium adsorption isotherms models of Langmuir, Freundlich and Dubinin-Radushkevich, were tested for the quantitative description of the dye adsorption. The Langmuir isotherm provided the best fit for dye adsorption onto the prepared activated carbon and the maximum adsorption capacity was found to be 30.21 $mg.g^{-1}$. The results show that the produced activated carbon from used tire is an alternative low-cost adsorbent for removing dyes from solutions.

1. Introduction

Dyes are recalcitrant molecules, which are difficult to degrade biologically. With the increasing use of a wide variety of dyes, pollution by dyes wastewater is becoming increasingly alarming. Most of the dyes decompose to give out hazardous products, such as carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen chlorides and can reduce light penetration photosynthesis (Gupta et al., 2011). Moreover dyes itself are toxic to some organism. Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia and hypertension (Pathania et al., 2013). Color removal, in particular, has recently become a major scientific interest. The typical dyestuff treatment include physical and chemical methods, such as coagulation/flocculation, adsorption, ozonation, sodium hypochlorite treatment, photochemical decolourization, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation, these methods are not very successfully due to suffering from many restrictions (Sulak et al., 2007). Among all of these methods, adsorption has been preferred due to its cheapness and the high-quality of the treated effluents especially for well-designed sorption processes (Qadeer, 2007). However, despite its inherent advantages, adsorption using activated carbon remains an expensive process. This fact has incited a growing interest into the production of low-cost alternatives to activated carbons (Zuorro et al., 2013). Taking into account the problems related to the worn tires in Algeria (air and visual Pollution) we propose in our article to develop the worn tires into activated carbon which will be used thereafter for the adsorption of the dyes (Trouzine et al., 2011). The aim of the present work was to investigate the potential feasibility of activated carbon prepared from used tyres with cryogenic grinding for the adsorption of Methylene Blue. The effect of various parameters such as contact time, initial pH, adsorbent dose and initial concentration of dye was investigated. The experimental adsorption data were modeled using the conventional isotherm equations including Langmuir, Freundlich, and Dubinin-Radushkevich isotherms.

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2. Materials and methods

2.1 Preparation of activated carbon

For the production of the activated carbon, we use fractions of tires powder sized between 0.063 cm and 0.2 cm obtained from cryogenic grinding. The impregnation with phosphoric acid (20 %) was performed for about one hour. Then the mixture was placed in an oven at 110 °C for 2 h. 5 grams of dried and impregnated powder is placed in a stainless steel tubular reactor and then introduced in a muffle furnace for activation. After that we proceeded to the carbonisation at inert atmosphere of nitrogen at 110 °C for 24 h and stored on hermetic bottle for subsequent use.

2.2 Adsorbate

Methylene blue was chosen as the adsorbate, due to its extensive use in the textile industry. It contains one –N N– (azo), it's physico-chemical properties are presented in Table 1.

Table 1: Physico-chemical properties of dye Methylene Blue

Molecular formula	$C_{16}H18N_3SCl$
IUPAC name	3.7-bis(Dimethylamino)-phenothiazin-5-ium chloride
Molar weight ($g.mol^{-1}$)	319.85
λ_{max}(nm)	663

2.3 Adsorption experiments

Batch adsorption experiments were performed at ambient temperature using 50 mL glass bottles containing a given mass of activated carbon and 10 mL of the dye solution. The initial concentration of the dye was varied from 10 to 100 $mg.L^{-1}$, depending on the experimental conditions. The glass bottles were agitated in orbital shaker (Wise Shake) for three hours and then centrifugated at 7000 rpm for 30 min. The sample was collected and diluted before analysis using UV-visible spectrophotometer (Model Specot 200 plus) at 663 nm. The equilibrium adsorption capacity and the yield of adsorption were calculated respectively by Eq. (1) and (2):

$$q_e = (C_0 - C_e)\, V/m \qquad (1)$$

$$Re\ (\%) = [(C_o - C_e)/ C_o\ ]*100 \qquad (2)$$

where, m is the mass of adsorbent (g), V is the volume of the solution (L), Co is the initial concentration of dye ($mg.L^{-1}$) and q_e is the dye quantity adsorbed at equilibrium (mg of dye/g of adsorbent).

2.4 Calculation of adsorption isotherms parameters

The tests concerning the study of the adsorption equilibrium were carried out for dye concentrations of 10 $mg.L^{-1}$ to 100 $mg.L^{-1}$. During adsorption, a rapid equilibrium is established between the quantity of dye adsorbed on the adsorbent (q_e) and dye remaining in solution (C_e). The isotherms data were characterized by the Langmuir (3) and Freundlich (4) equations:

$$q_e = q_{max}\, bC_e / (1+bC_e) \qquad (3)$$

$$q_e = K_F\, C_e^n \qquad (4)$$

where (b, q_{max}) and (K_F, n) are empirical constants of Langmuir and Freundlich isotherms, respectively, that will be calculated from the linear forms of the equations (3) and (4) :

$$1/q_e = (1/q_{max}b).1/C_e + 1/q_{max} \qquad (5)$$

$$\ln q_e = \ln K_F + n \ln C_e \qquad (6)$$

Dubinin-Radushkevih (D-R) model is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$q_e = q_{max} \exp([-B[RT)\, Ln(1+1/C_e)]^2)] \qquad (7)$$

where B is a constant related to the adsorption energy, R (8.314 J.mol^{-1}.K^{-1}) is the gas constant, and T (K) is the absolute temperature. The constant B (mol^2 .kJ^{-2}) gives the mean free energy E (kJ.mol^{-1}) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = 1/(2.B)^{0.5} \quad (8)$$

This parameter gives information about chemical or physical adsorption. The magnitude of E between 8 and 16 kJ.mol^{-1} indicates that the biosorption process follows chemical ion-exchange, while for the values of E< 8 kJ.mol^{-1}, the biosorption process is of a physical nature. The linear form of this model is expressed by :

$$Lnq_e = lnq_{max} - B.\varepsilon^2 \quad (9)$$

Where

$$\varepsilon = RT\ Ln(1+1/C_e) \quad (10)$$

3. Results and discussions

3.1 Characterisation of activated carbon

SEM micrograph of activated carbon obtained from cryogenic grinding of used tires, clearly indicate the surface texture and porosity of the rubber tire adsorbent. Carbon being the prominent component indicates the carbonaceous nature which in turn imparts porosity observed in the SEM results. SEM micrograph was processed and segmented and illustrated in Figure 1.

The Infrared Spectroscopy spectra of the activated carbon which is illustrated in Figure 2, indicates the presence of a prominent band at region of 3590-3650 cm^{-1}, 2850-3000 cm^{-1}, 1670-1640 cm^{-1}, 1640-1550cm^{-1}, 1070-1150 cm^{-1}, 720-725 cm^{-1} and 675-725 cm^{-1} which can be inferred to the presence of functions normally detected on this type of products such as hydroxyl acids, carboxyl acids, the aromatic rings or bands corresponding to C-H bonds. All results of the characterisation were presented in our previously paper (Belgacem et al., 2013).

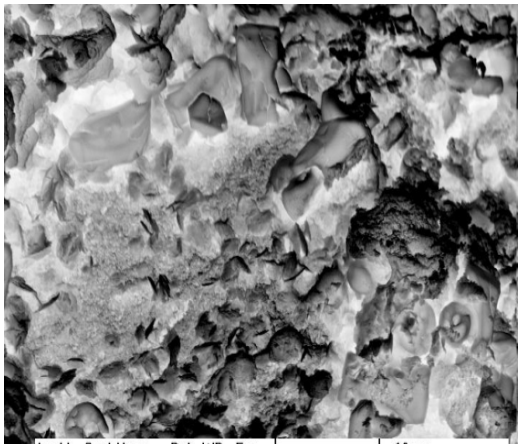

Figure 1: SEM micrograph of activated carbon obtained after processing and segmentation

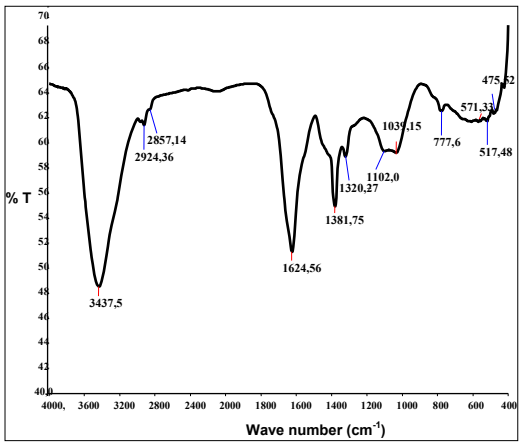

Figure 2: Transmittance FTIR spectra of activated carbon

3.2 Effect of operating parameters

3.2.1 Effect of contact time

Figure 3 indicates that the sorption increased with increasing contact time initially and became almost constant after 114 min of contact. From the plots, it is evident that for the investigated initial concentrations of MB, maximum adsorption rate of 93 % is achieved almost in 114 min of contact. A further increase in

the contact time has a negligible effect on the rate of MB adsorption. The rate of dye removal is higher in the beginning due to a larger surface area of the sawdust being available for dye adsorption. Same results were reported by Pathania et al. (2013)

3.2.2 Effect of solution pH

The pH factor is very important in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. The effect of pH on the MB removal by activated carbon resulting from the cryogenic grinding of the tire was investigated over the pH range from 2 to 11. The results were presented in Figure 4. It has been revealed that the MB removal was increased from 86 to 93 % as pH varies from 2 to 11. At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged (Özcan et al., 2007). It resulted in higher force of attraction between cationic MB and negatively charged adsorbent surface ultimately leading to higher MB adsorption (*Gupta and* Pathania, 2014).

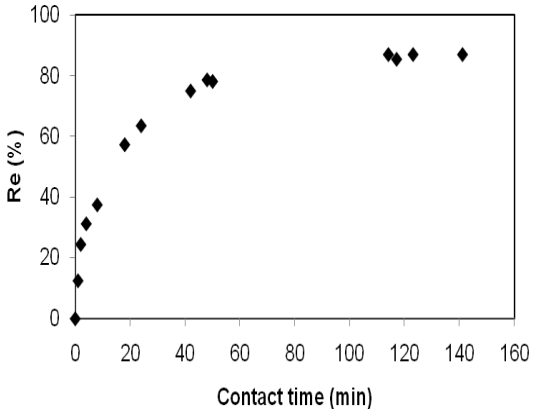

Figure 3: Kinetic of MB sorption on activated carbon (initial MB concentration: 5 mg.L^{-1}, pH: 6, AC concentration: 1 g L^{-1}, T: 25°C)

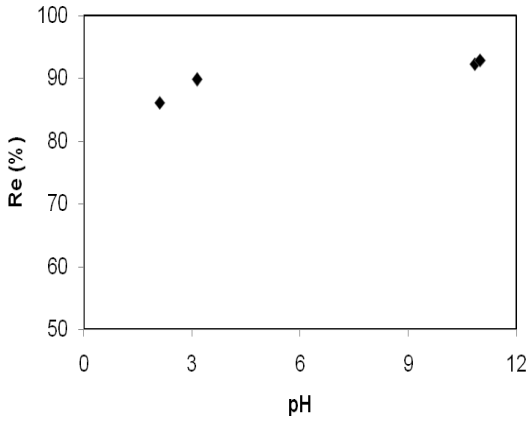

Figure 4: Effect of initial pH on sorption of MB by Activated carbon (initial MB concentration: 5 mg.L^{-1}, Activated carbon concentration:1g.L^{-1},T: 25°C)

3.2.3 Effect of activated carbon dosage

Study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of dye to be adsorbed with a minimum dosage. The results of the effect of adsorbent dose on the removal of Methylene Blue by the activated carbon are shown on Figure 5. They indicate that dye removal efficiency increased with the adsorbent dosage. This is due to the availability of more binding sites as the dose of biosorbent increases (Okeola et al.., 2012*).* However the removal will grow up to certain limit and then remains constant, the limit in each case is still related to the effect of adsorbate on adsorption. This will be attributed to metal concentration shortage in solution (Fourest and Roux, 1992).

3.2.4 Effect of initial dye concentration

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. Figure 5 shows the progress of the MB removal with different initial MB concentrations. It is clear that the Yield of MB adsorption increased from 62 % to 96 % as the Methylene blue concentration was increased from 5 mg.L^{-1} to 40 mg.L^{-1}. The increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration (Bulut and AydIn, 2006). Though, further increase in dye concentration, don't affect the adsorption yield. This will be attributed to the saturation of adsorption sites on the adsorbent surface (Eren and Acar, 2006).

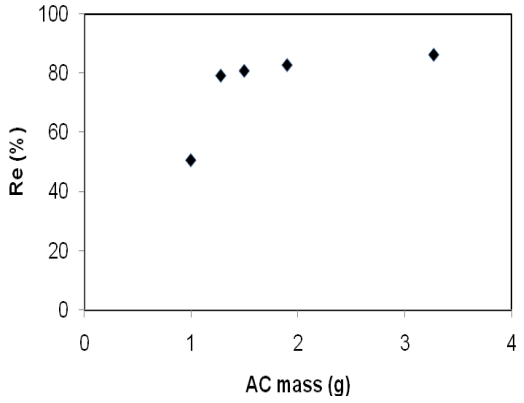

Figure 5: Effect of AC dosage on MB sorption on activated carbon (initial MB concentration: 5 mg L^{-1}, pH: 6, T: 25°C)

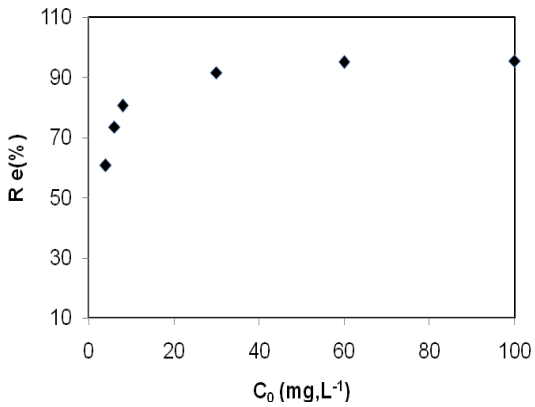

Figure 6: Effect of initial MB concentration on MB sorption on activated carbon (AC dosage: 1 g.L^{-1}, pH: 6, T: 25°C)

3.2.5 Adsorption isotherms

The adsorption capacity of the obtained activated carbon for MB can be determined by measuring equilibrium isotherms. Adsorption isotherm plays a crucial role in the predictive modelling procedures for the analysis and design of an adsorption system. Thus, the correlation of the equilibrium data by either theoretical or empirical equations is essential to practical operation (Poots et al., 1976). Adsorption isotherms were analysed according to the linear form of Langmuir, Freundlich and Dubinin-Radushkevich isotherms, Table 2 displays the results of the calculated isotherm constants.

Table 2. Isotherm constants for Methylene Blue adsorption onto activated carbon

Langmuir			Freundlich			Dubinin-Radushkevich			
q_{max} ($mg.g^{-1}$)	b ($L.mg^{-1}$)	R^2	K_F	n	R^2	q_{max} ($mg.g^{-1}$)	B ($mol^2.J^{-2}$)	E ($kJ.mol^{-1}$)	R^2
30.21	0.19	0.94	5.466	1.92	0.605	23.178	$4.,3.10^{-7}$	1.07	0.69

The experimental results are well represented by the Langmuir model, with higher value of correlation coefficient. The maximum adsorption capacity estimated by means of the Langmuir model was 30.21 $mg.g^{-1}$, namely higher than the maximum adsorption capacities reported for some other adsorbents in the available literature and collected in Table 3.

Table 3. Maximum capacity of MB adsorption on some adsorbents

	q_{max} ($mg.g^{-1}$)	References
AC prepared from waste tyre rubber	49.0	(San Miguel et al., 2002)
AC prepared from Delonix Regia pods (flame-tree-pods)	25.1	(Ho et al., 2009)
Cross linked poly(4-vinylpyridine /crotonic acid)	19.96	(Coşkun, 2011)
AC prepared from Wheat shell	16.56	(Ghaedi et al., 2013)
AC prepared from cryogenic grinding of uses tires	30.21	Present study

4. Conclusions

Liquid phase adsorption process was employed in this study and adsorption isotherms were used to investigate adsorption capacity and ability of the activated carbon prepared from the cryogenic grinding of used tire to remove Methylene Blue from aqueous solutions. Effects of the experimental conditions on the performance of the adsorbent were investigated. According to the experiments results, it was shown, that equilibrium was achieved in less than 114 min. The effect of pH investigated for values ranging from 2 to 11, showed maximum adsorption of MB on the activated carbon for pH 11. The equilibrium adsorption isotherms models of Langmuir, Freundlich and Dubinin-Radushkevich, were tested for the quantitative description of the dye adsorption. The Langmuir isotherm provided the best fit for dye adsorption onto the prepared activated carbon and the maximum adsorption capacity was found to be 30.21 $mg.g^{-1}$.

References

Belgacem A., Belmedani M., Rebiai R., Hadoun H., 2013, Characterization, Analysis and Comparison of Activated Carbons Issued from the Cryogenic and Ambient Grinding of Used Tyres, Chemical Engineering Transactions 32, 1705-1710 DOI: 10.3303/CET1332285.

Bulut Y., AydIn H., 2006, kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination 194? 259–267.

Coşkun R., 2011, Removal of cationic dye from aqueous solution by adsorption onto crosslinked poly(4-vinylpyridine/crotonic acid) and its N-oxide derivative, Polymer Bulletin, 67(1) 125-140.

Eren Z., Acar F.N., 2006, Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies, Desalination 194, 1–10.

Fourest E., Roux J.C., 1992, Heavy metal biosorption by fungal mycelia by-product: mechanism and influence of pH, Appl. Microbiol. Biotechnol. 31, 399-403.

Ghaedi M., Ghaedi A.M., Hossain pour M., Ansari A., Habibi M.H., Asghari A.R., 2013, Least-square vector (LS-VM):Method for modeling of MB dye adsorption using copper oxide leaded on activated carbon: Kinetics and isotherms study, J. of Industrial and Engineering Chemistry, In Press

Gupta V. K., Gupta B., Rastogi A., Agarwal S., Nayak A., 2011, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113, Journal of Hazardous Materials, 186(1) 891-901.

Gupta V. K., Pathania D., Singh P., Kumar A., Rathore B. S., 2014, Adsorptional removal of methylene blue by guar gum–cerium (IV) tungstate hybrid cationic exchanger, Carbohydrate Polymers, 101(0) 684-691.

Ho Y.S., Malarvizhi R., Sulochana N., 2009, Equilibrium isotherm stusy of MB adsorption onto activated carbon prepared from Delonix Regia pods, J. of Env. Prot. Sci. 3, 111-116.

Okeola O.F, Odebunmi E.O., Ameen O.M., 2012, Comparison Of Sorption Capacity And Surface Area Of Activated Carbon Prepared From Jatropha Curcas Fruit Pericarp And Seed Coat, Bull. Chem. Soc. Ethiop. 26 (2) 171-180.

Özcan A., Ömeroglu Ç., Erdogan Y., Özcan A.S., 2007, Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19, J. Hazard.Mater. 140, 173–179.

Pathania D., Sharma S., Singh P., 2013, Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast, Arabian Journal of Chemistry(0).

Poots V. J. P., McKay G., Healy J. J., 1976, The removal of acid dye from effluent using natural adsorbent Wood. Water Research, 10(12) 1067-1070.

Qadeer R., 2007, Adsorption behavior of ruthenium ions on activated charcoal from nirtic acid medium, Colloids Surf. A: Physicochem. Eng. Aspects 293, 217–223.

San Miguel G., Fowler G.D., Sollars C.J., 2002, Adsorption of organic compounds from solution by activated carbons produced from waste tyre rubber, Separation Science and Technology 37(3) 663-676.

Sulak M.T, Demirbas E., Kobya M., 2007, Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran, J. Biores. Technol. 98, 2590–2598.

Trouzine H., Asroun A., Asroun N., Belabdelouhab F.2011. Problématique des pneumatiques usagés en Algérie, Revue Juin 2011 « Nature & Technologie ». n° 05, pp 28- 35

Zuorro A., Lavecchia R., Medici F., Piga L., 2013, Spent tea leaves as a potential low-cost adsorbent for the removal of azo dyes from wastewater, Chemical Engineering Transactions 32, 19-24, DOI: 10.3303/CET1332004.