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ADSORPTIVE REMOVAL OF METHYLENE BLUE (MB) FROM WATER USING CARBON NANOPARTICLES PREPARED FROM DATE PITS

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Abstract

Recently, carbon nanostructures have played a crucial role in many vital aspects of nanoscience and nanotechnology; this can be attributed to their unique characteristics and potential applicability in a variety of fields. On the other hand, date pits have a relatively limited number of usages, which can be extended by the proposed new usage of date pits for synthesizing carbon nanoparticles. The present study provides a feasible method for synthesizing carbon nanoparticles (87.76 nm) through nitric acid reflux method using date pits as a carbon source, so as to maximize the value of the date pits. In addition, the current study evaluates the efficiency of the prepared carbon nanoparticles (CNPs) for adsorptive removal of (Methylene Blue (MB) from waste water. In addition, parameters affecting that adsorption were also studied. The MB dye removed by the CNPs was depending on contact time, pH and concentration of dye. The optimum conditions for removal of MB dye by CNPs were; contact time of 15 hrs, at pH 7 and an adsorbent dose of 0.01 g. In this study the data fit Langmuir model and the maximum adsorption capacity was found to be 97.65 mgg^{-1}. Adsorption of MB onto CNPs followed pseudo second order kinetics. These results indicated that carbon nanoparticles may be an attractive candidate for removal of MB from wastewater.

Keywords: Date pits; carbon nanoparticles; nanotechnology; methylene blue; adsorptive removal.

Introduction

In the last few years, a growing interest was oriented toward carbon-based nanostructures because of their potential applications in many fields as a result of their unique physical and chemical properties (Nicolas *et al.*, 2002). In this regard, several investigations were done on the potential uses of carbon nanoparticles in electronic materials (Kato & Ishibashi, 2008), medical imaging (Ya-Ping *et al.*, 2006), drug delivery (Sunghoon *et al.,* 2008 & Yonghui *et al.,* 2004) and many other applications. In addition, carbon nanoparticles have an advantage of being biocompatible and chemically inert (RAY *et al.*, 2009; Chi-Cheng *et al.*, 2007; Koichi *et al.*, 2002; Michael *et al.*, 2002 & Kong *et al.*, 2005), which makes it more benefit for medical and biological applications. On the other hand, several methods were developed to prepare carbon nanostructures such as chemical vapor deposition, arc-discharge, and plasma radiation (Xianglei *et al.*, 2005 & Alexandrou *et al.*, 2004); however, these methods are mostly restricted by the solid state strategies that can tolerate high levels of both energy and temperature, furthermore, their prerequisite for extreme conditions may impose many limitations in terms of large-scale and economical production since they require extreme conditions. These broad applications and limitations of preparation methods are encouraging many researches worldwide to develop simpler and faster methods for preparing carbon nanostructures (Kang *et al.*, 2003; Michael *et al.*, 2007 & S.C. *et al.*, 2009).

On the other hand, date palm is considered one of the most important fruit crops all over the world, particularly in the Middle East. The global production of dates reached 7600315 tons per year. In this context, Egypt occupies the fore among all other date-producers, with an annual production of 1465030 tons (F.A.O., 2014); among them 6-12% are pits (Barreveld, 1993).

(MB) is a cationic dye that has numerous applications in chemistry, medical science and dyeing industries. Methylene blue dye is an organic dye belonging to the phenothiazine family; its long term exposure can make vomiting, nausea, anemia and hypertension (Foo, 2012 & Hameed, 2009). Methylene blue is used in manufacture of paper and other materials such as nylons and polyesters. It is mainly used for coloring blast, paper, leather, cotton, silk, and wool. Based on its wide-range applicability for coloring various industrial materials, there is a dire need for eliminating it from aqueous media (Royer *et al.*, 2009).

There are numerous methods for removal of dyes from wastewaters such as, coagulation and flocculation, degradation, photocatalytic ozonation, photocatalytic oxidation (Sima & Hasal, 2013), Fenton process, electrochemical degradation, biological treatment. But, all these methods produced other byproducts that require continuous monitoring and identification, besides most of them are expensive (Forgacs *et al.*, 2004).

In this paper, we report for the first time the use of date palm pits for preparing carbon nanoparticles through nitric acid reflux method and its usage for removal of the methylene blue dye, this method has the advantages of being relatively easy, inexpensive and ecofriendly.

Materials and Methods

Materials

Nitric acid and methylene blue, analytical grade of purity, were obtained from Sigma-Aldrich Company (China).

Preparation of carbon nanoparticles

Firstly, date's pits, Sewi cultivar, were washed well using the tap water, then the pits dried at 100 °C for 24 h. Then, carbon nanoparticles were prepared from the dried pits through the nitric acid reflux method (Ray *et al.*, 2009), in which the dried pits were pulverized well in mortar and pestle; after that, 5.0 g of the pulverized pits was mixed with 100 mL of 5M nitric acid in 250 mL flask, then refluxed at 100 °C for 12 h under stirring. The black solution was cooled and centrifuged at 500 rpm for 10 min to separate out unreacted carbons. The light brownish supernatant was then collected and centrifuged again at 4000 rpm for 10 min; the black precipitate was collected, washed from the excess nitric acid with deionized water and dried in drier at 60 °C over night. the dried carbon nanoparticles were collected for further characterization.

Characterization of carbon nanoparticles

Carbon nanoparticles were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS).

In this regard, Infrared spectroscopy is considering one of the most important qualitative techniques that are used to characterize the surface functional groups in carbons (Moreno- Castilla *et al.*, 2000). In our study, we used FTIR in order to investigate the functional groups on which the methylene blue will be adsorbed. Thus, FTIR was done using FTIR spectrophotometer (Jasco 4100, range 400 – 4000 cm^{-1}) on the prepared carbon nanoparticles.

Furthermore, TEM was done using the transmission electron microscope (Tecnai G20, Super twin, double tilt, FEI, Netherland) of prepared carbon nanoparticles and DLS was done using DLS Instrument (Zetasizer nano series (Nano ZS), Malvern, UK) to detect particle size distribution and zeta potential of the prepared carbon nanoparticles.

Adsorption of methylene blue onto carbon nanoparticles

Methylene blue is the targeted pollutant in this work. 1.0 g of MB powder was dissolved to produce 1000 ppm MB stock solution. 0.01g of CNPs and equal volumes of methylene blue solutions at varying concentration (50-800 mg/L) were shaken in a thermostatic shaker at the desired temperature with shaking speed of 175 rpm for 15 hours. The equilibrium concentration of methylene blue was examined spectrophotometrically. The concentration of MB was calculated by UV–Vis spectrophotometer at 664 nm. Adsorbed amount at equilibrium, qe (mg/g) was calculated using Eq (1)

$$q_e = \frac{(C_0 - C_e)V}{W} \quad ...(1)$$

As, C_o and C_e are the initial and equilibrium liquid phase concentration of MB (mg/L). V is the volume of solution (L), and W is the weight of adsorbent used (g)

Effect of pH was determined at different pH between 2 and 12 at constant initial MB concentration of 500 mg/L.

Effect of time determined by using 0.01 g of carbon nano particles with 50 mL of MB at 500 mg/L. The concentration of MB is detected as (C_t); adsorption capacity at a time t, q_t (mg/g) was determined using Eq (2)

$$q_t = \frac{(C_0 - C_t)V}{W} \quad ...(2)$$

Where C_t (mg/L) is defined as liquid-phase concentration of adsorbate at time t

Results and Discussion

Characterization of carbon nano particles

FTIR of carbon nanoparticles is shown in Figure (1). The black color of carbons enables them to absorb radiation in a range of 360-800 nm. FTIR spectrum is obtained as result of reaction of various types of surface functional groups with the absorbed wavelengths (Matos *et al.*, 2011) From Figure (1), it's clear that the spectrum`s peaks indicate to the presence of O-H stretching vibrations at 3754.73 and 3420.14 cm-^{1}; C-H asymmetric stretching at 2920 cm^{-1}; O=C=O stretching at 2375 cm^{-1}; C=O stretching at 1637.27 cm^{-1}; C-H bending at 1382.71 cm^{-1}; C-O stretching at 1334.5 cm^{-1} and C-H bending at 776.208 cm^{-1}. Among these functional groups, it was proved that O-H, C-H, C=O, and C-O are involved in adsorbing methylene blue (Liu *et al.*, 2018). The abundance of these three functional groups in the prepared carbon nanoparticles enhances its efficiency in adsorbing methylene blue.

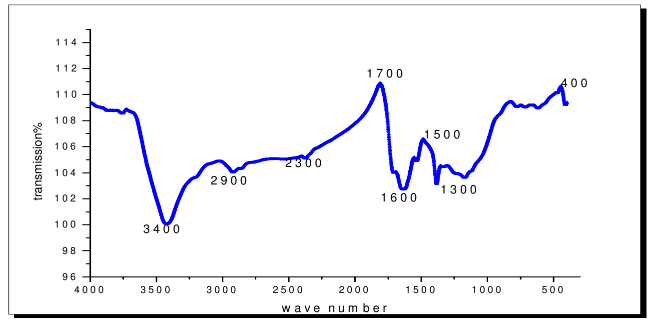

Fig. 1 : FTIR spectrum of carbon nanoparticles showing the functional groups of the prepared nanoparticles.

TEM micrograph of carbon nanoparticles is shown in Figure (2), it revealed that irregular shape of the prepared carbon nanoparticles, some of nanoparticles show a nearly spherical shape, while the other showed polygonal shapes.

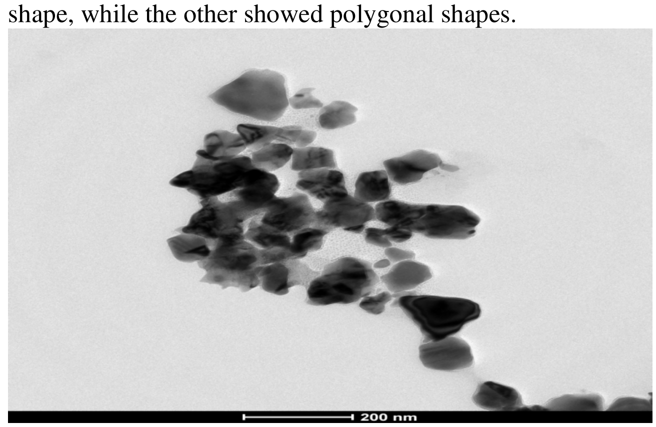

Fig. 2 : Transmission electron micrographs of the prepared carbon nanoparticles show a nearly spherical shape of the prepared nanoparticles.

Size distribution by using DLS indicated that carbon nanoparticles have particle size at 87.76 nm, as seen in Figure (3).

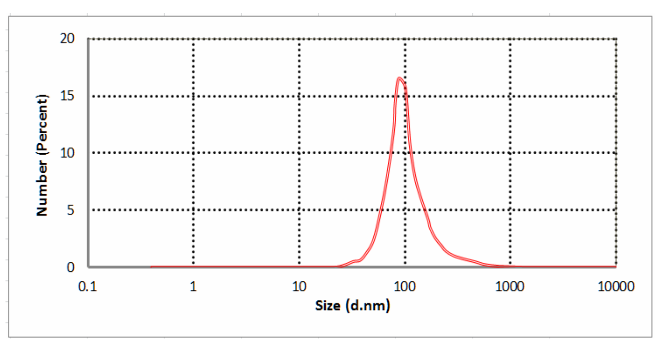

Fig. 3 : Size distribution by number using Dynamic Light Scattering for the prepared carbon nanoparticles.

Also, the prepared carbon nanoparticles showed a positive zeta potential at about +30 mV, as shown in figure (4). This means that the prepared carbon nanoparticles have a moderate stability (Hanaor *et al.*, 2012)

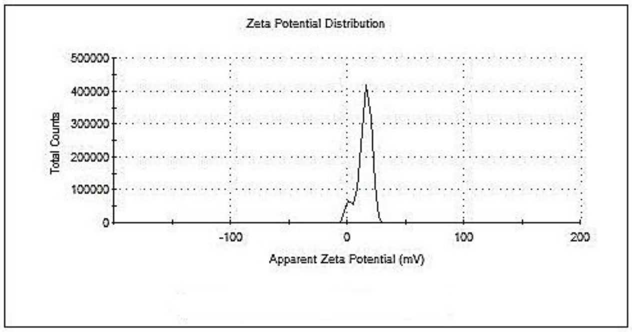

Fig. 4 : Zeta potential of the prepared carbon nanoparticles as measured using Dynamic Light Scattering, showing its positive zeta potential at about +30 mV.

Adsorption of Methylene blue

(i) Adsorption isotherm

The purpose of carrying out the batch adsorption isotherm is to describe the relation between amount adsorbed and the adsorbate concentration remains in the solution. The adsorption isotherms of MB onto carbon nanoparticles at 25 °C, and pH of 7 are presented in Figure (5). The Langmuir equation is represented as (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_e} \qquad ...(3)$$

Where q_e is the amount adsorbed at equilibrium time (mg/g), Ce is the equilibrium concentration of methylene blue (mg/L), q_m is the maximum adsorption capacity (mg/g), and b is known by Langmuir constant (L/mg) and it is related to the heat of adsorption. If we plot Ce/qe versus Ce for methylene blue carbon nanoparticles, we obtained straight line with a slope = 1/qm and an intercept = 1/ bqm, as shown in Figure (5B). Also, RL is known as separation factor which indicated in equation (4).

$$R_L = \frac{1}{1 + bC_0} \qquad ...(4)$$

Here, Co is the highest initial solute concentration. The RL value indicated if the adsorption is unfavorable (RL >1), linear (RL=1), favorable (0< RL<1), or irreversible ((RL= 0).

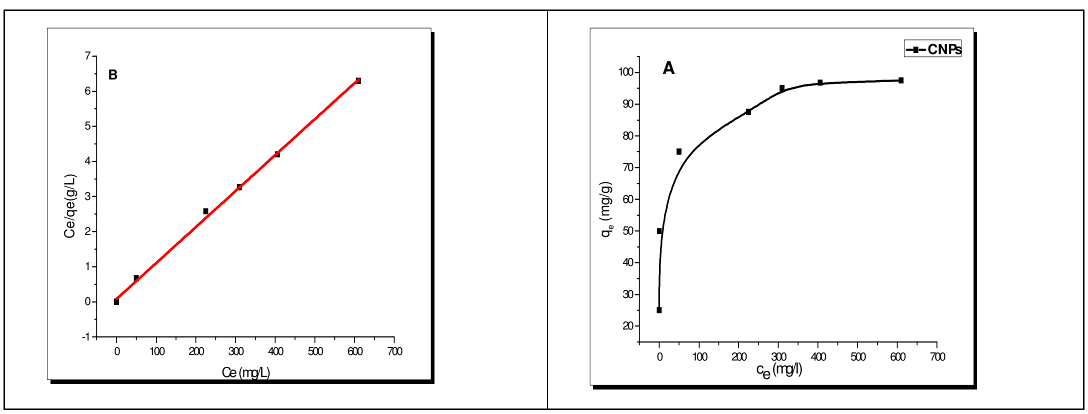

Fig. 5 : Adsorption isotherms and Langmuir plots for methylene blue adsorption on carbon nanoparticle at Ci =50–800 mg/L, pH= 7, adsorbent dosage=0.01 g/L, and 25 °C

The analyzed data will be listed in Table (1) showing that the correlation coefficient, R^2 in case of applying Langmuir model was 0.998 and dimensionless separation factor (R_L) as represented in Eq. (4) lies between 0-1 so adsorption process will be favorable and obey Langmuir.

Table 1: Langmuir parameter for adsorption of MB onto investigated carbon nano particles .

Sample	Langmuir parameters			
	q_{max} (mg/g)	b (L /mg)	R^2	R_L
CNPs	97.65	0.12166	0.998	0.1388

(ii) Effect of pH

The pH is an important factor that effect on removal of MB onto CNPs. Figure (6) indicated that the adsorption of MB is very high at acidic medium till pH 7, and then starts to decrease. This is attributed to MB gives positive charge ions when dissolved in water, so positive charge in acidic medium tends to oppose the adsorption of the cationic adsorbate. As pH increased the negative charge occurs in the surface, so the electrostatic attraction between positive charge of dye and negative charge of adsorbent occurs (Abd *et al.*, 2009 & Malik, 2003). At higher pH the zwitterion of methylene blue is formed methylene blue formed (dimer) and becomes unable to enter into the pore structure of the carbon nano particles surface.

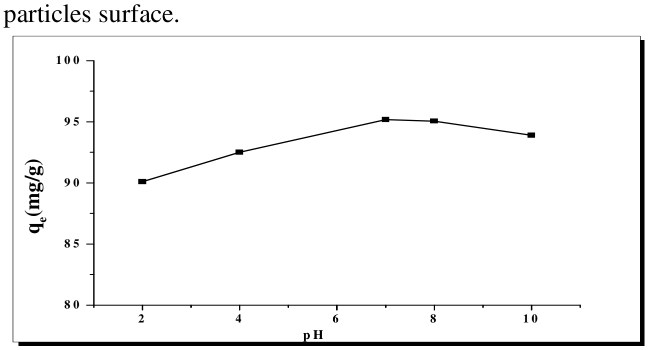

Fig. 6 : Effect of pH on adsorption of methylene blue using carbon nanoparticles

(iii) Effect of time on adsorption

The adsorptions of the methylene blue by carbon nano particles were studied at various time intervals (0.25- 25 h). Figure (7) Showed that the adsorption of MB was fast at the first, after that it slowed with time until the equilibrium happened. This due to large number of vacant sites which able to adsorbed MB at the first time (Hassan *et al*., 2014a & Hassan *et al*., 2014b) till a constant value at about 15 h (equilibrium time) after that active sites have been saturated, leads to a decrease in adsorption rate. To investigate the kinetics and mechanism of MB adsorption on carbon nano particles Pseudo-first (Eq. 5) and pseudo-second (Eq. 6) order equations were used to fit the kinetics process.

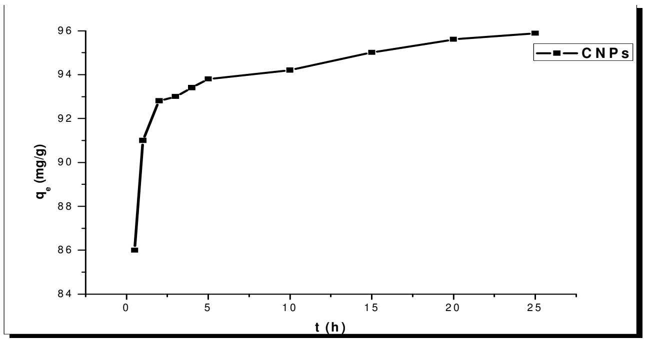

Fig. 7 : Kinetic adsorption curves of MB at 25 °C onto carbon nano particles

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2}.303t \qquad ...(5)$$

Where q_e is the equilibrium adsorbed amount (mg/g), q_t is the amount adsorbed in time t (mg/g), K_1 is the pseudo-first-order rate constant (g/mg. min) and t is the time in minute. Linearized form of the PSO can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e^2} t \qquad ...(6)$$

Where K_2 is the pseudo second order rate constant (g/mg. min)

Figure (8) depicts the application of linear PFO and linear pseudo second order kinetics model. Upon analysis of Table 2 one can concluded that the adsorption follow pseudo–second order kinetics model based on: (i) Correlation coefficient R2 for PSO is 0.9999 indicating the good applicability of PSO linearized form. On the other hand R2 for PFO is very low which equal 0.42503 (ii) Calculated q_e (mg/ g) from PSO model are closer to qm (mg/g) calculated from Langmuir adsorption model while that calculated from PFO is very high.

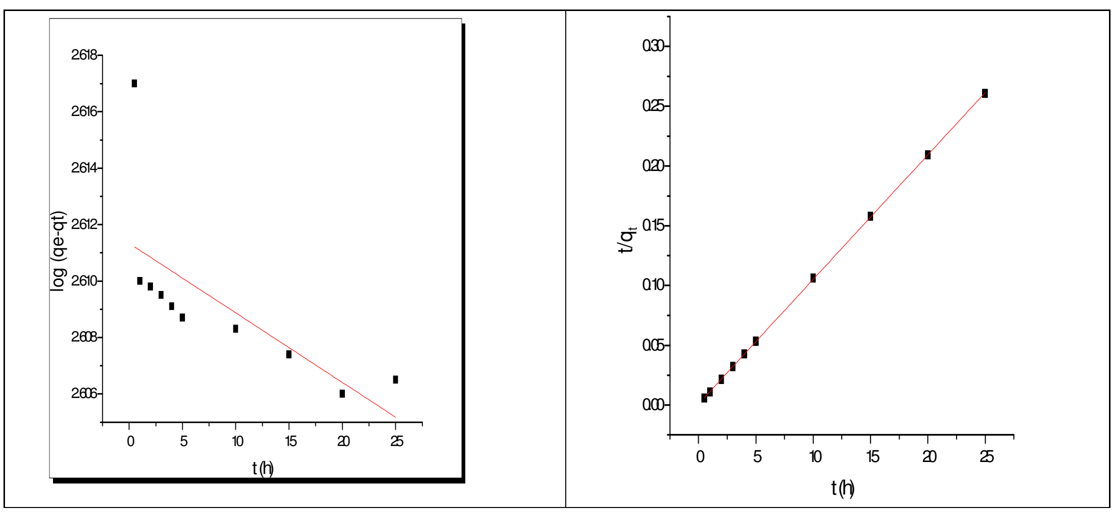

Fig. 8 : Pseudo–first order and Pseudo–second order kinetic model for removal of MB onto carbon nano particles

Table 2: Parameter of PFO and PSO kinetics model for removal of MB onto carbon nano particles

Sample	qm (mg/g)	PFO Kinetic model			PSO Kinetic model		
		qe (mg/g)	K1 (h^{-1})	R^2	qe (mg/g)	K2 (g/ mg h)	R2
CNPs	97.6	408.9	5.657	0.42503	95.96	0.10647	0.9999

Conclusively, the prepared carbon nanoparticles exhibit a good adsorption capacity compared with other adsorbents that can exhibit higher or lower capacities, as shown in table [3].

Table 3 : Adsorption capacity of the prepared carbon nanoparticles compared with some of the other adsorbents.

Adsorbent	q_{max} (mg/g)	References
Commercial activated carbon	980.3	(Kannan *et al*., 2001)
Activated carbon from Waste cotton activated with H_3PO_4	344.82	(Ekrami *et al*., 2016)
Activated carbon from Watermelon rind activated with $ZnCl_2$	231.48	(Uner *et al*., 2016)
Activated carbon from Macadamia nut endocarp activated with $ZnCl_2$	194.7	(Junior *et al*., 2014)

Carbon nanoparticles prepared from date palm pits	**97.6**	**this study**
Sewage sludge from an agri-food industry	87	(Otero *et al*., 2003)
Charcoal	62.7	(Banat *et al*., 2007)
Rice husk	28	(Mckay *et al*., 1986)
Humic acid	15.82	(Inam *et al*., 2018)
Coarse grinded wheat straw	3.82	(Batzias *et al*., 2009)

Conclusion

Carbon nanoparticles were prepared from date palm pits using nitric acid. The optimum condition for removal of MB was confirmed at pH7 and equilibrium time 15 h. Maximum adsorption capacities were found to be 97.6 mg/g at 25 ^{o}C. The adsorption of MB onto carbon nanoparticles follow pseudo-second order kinetic model with correlation coefficients reached to 0.9999.

References

Abd El-Latif, M.M. and Ibrahim, A.M. (2009). Adsorption, kinetic and equilibrium studies on removal of basic dye from aqueous solutions using hydrolyzed oak sawdust. *Desalination and Water Treatment*, *6*(1-3): 252-268.

Alexandrou, I.; Kiely, C.J.; Papworth, A.J. and Amaratunga, G.A.J. (2004). Formation and subsequent inclusion of fullerene-like nanoparticles in nanocomposite carbon thin films. Carbon, 42(8-9): 1651-1656.

Banat, F.; Al-Asheh, S.; Al-Ahmad, R. and Bni-Khalid, F. (2007). Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal. Bioresource Technology, 98(16): 3017-3025.

Barreveld, W.H. (1993). "Date palm products, agricultural services bulletin No 101" food and agriculture organization of the United Nations Pome, 216.

Batzias, F.; Sidiras, D.; Schroeder, E. and Weber, C. (2009). Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed-bed systems. Chemical Engineering Journal, 148(2-3): 459-472.

Cahalan, M.D.; Parker, I.; Wei, S.H. and Miller, M.J. (2002). Two-photon tissue imaging: seeing the immune system in a fresh light. Nature Reviews Immunology, 2(11): 872.

Ekrami, E.; Dadashian, F. and Arami, M. (2016). Adsorption of methylene blue by waste cotton activated carbon: equilibrium, kinetics, and thermodynamic studies. Desalination and Water Treatment, 57(15): 7098-7108.

F.A.O (2014). Dates Statistics 2014. Food and agriculture organization of the United Nations.

Foo, K.Y. (2012). Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K_2CO_3 activation. Bioresour. Technol., 104: 679–686

Forgacs, E.; Cserhati, T. and Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. Environment international, 30(7): 953-971.

Fu, C.C.; Lee, H.Y.; Chen, K.; Lim, T.S.; Wu, H.Y.; Lin, P.K. and Fann, W. (2007). Characterization and application of single fluorescent nanodiamonds as cellular biomarkers. Proceedings of the National Academy of Sciences, 104(3): 727-732.

Hameed, B.H. (2009). Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. Journal of hazardous materials, 161(2-3): 753-759.

Hanaor, D.; Michelazzi, M.; Leonelli, C. and Sorrell, C.C. (2012). The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO_2. Journal of the European Ceramic Society, 32(1): 235-244.

Hassan, A.F.; Abdel-Mohsen, A.M. and Elhadidy, H. (2014a). Adsorption of arsenic by activated carbon, calcium alginate and their composite beads. International journal of biological macromolecules, 68: 125-130.

Hassan, A.F.; Abdel-Mohsen, A.M. and Fouda, M.M. (2014). Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption. Carbohydrate polymers, 102: 192-198.

Inam, E.; Udo, O.O.; Edet, J.B.; Etim, U.J. and Offiong, N.O. (2018). Adsorption of Methylene Blue from Aqueous Solution by Humic Acid Extracted from Freshwater River Humus. J. Mater. Environ. Sci, 9(4): 1324-1334.

Junior, O.P.; Cazetta, A.L.; Gomes, R.C.; Barizão, É.O.; Souza, I.P.; Martins, A.C. and Almeida, V.C. (2014). Synthesis of $ZnCl_2$-activated carbon from macadamia nut endocarp (*Macadamia integrifolia*) by microwave-assisted pyrolysis: optimization using RSM and methylene blue adsorption. Journal of Analytical and Applied Pyrolysis, 105: 166-176.

Kang, Z.; Wang, E.; Gao, L.; Lian, S.; Jiang, M.; Hu, C. and Xu, L. (2003). One-step water-assisted synthesis of high-quality carbon nanotubes directly from graphite. Journal of the American Chemical Society, 125(45): 13652-13653.

Kannan, N. and Sundaram, M.M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. Dyes and pigments, 51(1): 25-40.

Kato, M. and Ishibashi, M. (2008). Carbon nanoparticle composite actuators. In Journal of Physics: Conference Series, 127(1): IOP Publishing.

Katz, M.J.; Kaluarachchi, H.; Batchelor, R.J.; Bokov, A.A.; Ye, Z.G. and Leznoff, D.B. (2007). Highly birefringent materials designed using coordination polymer synthetic methodology. Angewandte Chemie International Edition, 46(46): 8804-8807.

Keller, N.; Maksimova, N.I.; Roddatis, V.V.; Schur, M.; Mestl, G.; Butenko, Y.V. and Schlögl, R. (2002). The catalytic use of onion-like carbon materials for styrene synthesis by oxidative dehydrogenation of ethylbenzene. Angewandte Chemie International Edition, 41(11): 1885-1888.

Kim, S.; Shibata, E.; Sergiienko, R. and Nakamura, T. (2008). Purification and separation of carbon nanocapsules as a magnetic carrier for drug delivery systems. Carbon, 46(12): 1523-1529.

Kong, X.L.; Huang, L.C.L.; Hsu, C.M.; Chen, W.H.; Han, C.C. and Chang, H.C. (2005). High-affinity capture of proteins by diamond nanoparticles for mass spectrometric analysis. Analytical chemistry, 77(1): 259-265.

Kong, X.; Huang, L.L.; Liau, S.C.V.; Han, C.C. and Chang, H.C. (2005). Polylysine-coated diamond nanocrystals for MALDI-TOF mass analysis of DNA oligonucleotides. Analytical chemistry, 77(13): 4273-4277.

Langmuir, I. (1918). The Adsorption of gases on plane surface of glass, mica and platinum. J Am Chem Soc., 40(9): 1361–403.

Liu, L.; Fan, S. and Li, Y. (2018). Removal behavior of methylene blue from aqueous solution by tea waste: kinetics, isotherms and mechanism. International journal of environmental research and public health, 15(7): 1321.

Ma, Y.; Manolache, S.; Denes, F.S.; Thamm, D.H.; Kurzman, I.D. and Vail, D.M. (2004). Plasma synthesis of carbon magnetic nanoparticles and immobilization of doxorubicin for targeted drug delivery. Journal of Biomaterials Science, Polymer Edition, 15(8): 1033-1049.

Malik, P.K. (2003). Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes and pigments, 56(3): 239-249.

Matos, J.; Nahas, C.; Rojas, L. and Rosales, M. (2011). Synthesis and characterization of activated carbon from sawdust of Algarroba wood. 1. Physical activation and pyrolysis. Journal of hazardous materials, 196: 360-369.

McKay, G.G.R.P.R.; Ramprasad, G. and Mowli, P.P. (1986). Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials. Water, Air, and Soil Pollution, 29(3): 273-283.

Moreno-Castilla, C.; López-Ramón, M.V. and Carrasco-Marın, F. (2000). Changes in surface chemistry of activated carbons by wet oxidation. Carbon, 38(14): 1995-2001.

Otero, M.; Rozada, F.; Calvo, L.F.; Garcıa, A.I. and Moran, A. (2003). Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges. Biochemical Engineering Journal, 15(1): 59-68.

Ray, S.C.; Saha, A.; Jana, N.R. and Sarkar, R. (2009). Fluorescent carbon nanoparticles: synthesis, characterization, and bioimaging application. The Journal of Physical Chemistry C, 113(43): 18546-18551.

Ray, S.C.; Saha, A.; Jana, N.R. and Sarkar, R. (2009). Fluorescent carbon nanoparticles: synthesis, characterization, and bioimaging application. The Journal of Physical Chemistry C, 113(43): 18546-18551.

Ray, S.C.; Saha, A.; Jana, N.R. and Sarkar, R. (2009). Fluorescent carbon nanoparticles: synthesis, characterization, and bioimaging application. The Journal of Physical Chemistry C, 113(43): 18546-18551.

Royer, B.; Cardoso, N.F.; Lima, E.C.; Macedo, T.R. and Airoldi, C. (2009). Sodic and acidic crystalline lamellar magadiite adsorbents for the removal of methylene blue from aqueous solutions: Kinetic and equilibrium studies. Separation Science and Technology, 45(1): 129-141.

Šíma, J. and Hasal, P. (2013). Photocatalytic degradation of textile dyes in a TiO_2/UV system. Chemical Engineering, 32: 79-84.

Sun, Y.P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K.S.; Pathak, P. and Luo, P.G. (2006). Quantum-sized carbon dots for bright and colorful photoluminescence. Journal of the American Chemical Society, 128(24): 7756-7757.

Üner, O.; Geçgel, Ü. and Bayrak, Y. (2016). Adsorption of methylene blue by an efficient activated carbon prepared from *Citrullus lanatus* rind: kinetic, isotherm, thermodynamic, and mechanism analysis. Water, Air, & Soil Pollution, 227(7): 247.

Ushizawa, K.; Sato, Y.; Mitsumori, T.; Machinami, T.; Ueda, T. and Ando, T. (2002). Covalent immobilization of DNA on diamond and its verification by diffuse reflectance infrared spectroscopy. Chemical Physics Letters, 351(1-2): 105-108.