Palm Fronds Activated Carbon for the Removal of Brilliant Green Dye from Wastewater

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Abstract

Investigational studies were carried out to adsorb toxic brilliant green dye from aqueous medium using palm fronds activated carbon. The effects of initial dye concentration, contact time were studied for the adsorption of brilliant green in batch mode. The adsorption kinetic has been described by first-order, pseudo-second-order, Elovich's and intra-particle diffusion models. It was observed that the rate of dye adsorption follows pseudo-first-order model for the studied dye concentration range. The adsorption reached equilibrium after 150 minutes of contact. Adsorption isotherms were also used to fit the experimental data. It was found that the adsorption of brilliant green on palm frond activated carbon follows the Langmuir and Temkin adsorption isotherm models. The maximum adsorption capacity was found to be 45.45 mg.g^{-1}.

Keywords: *Brilliant green dye; Adsorption; Palm frond; Activated carbon; Kinetics; equilibrium*

1. Introduction

Among the several methods usually employed for wastewater treatment, the adsorption process is usually considered a best treatment method. Adsorption with the suitable choice of adsorbent offers an efficient as well as cheap water treatment process. In the recent years, the use of activated carbon prepared from locally available agricultural wastes has emerged as an eco-friendly adsorbent for wastewater treatment. Activated carbon (AC) is a type of carbonaceous materials with some excellent properties such as large specific areas, nontoxicity, high porosity, and the ability of their surface to contain different functional groups [1].

Activated carbons are usually produced by either physical and/or chemical activation method. The chemical activation is more preferred as it needs lower activation temperature and gives higher yield compared with the physical activation [2]. For alkaline chemical activation potassium or sodium hydroxides are often used. Although sodium hydroxide (NaOH) is more advantageous as it is cheaper, more environment-friendly and less corrosive than potassium hydroxide, this makes it suitable over KOH for several industrial applications [3].

A great amount of synthetic dyes is being discharged into water effluents as a result of several industrial processes. Dyes in water, even at very low concentration are highly unwanted. Dyes in water prevent the appropriate entrance of sunlight; delay photosynthesis; hinder the growth of aquatic biota and affect the solubility of gases within the water bodies and most severely they can cause the production of poisonous carcinogenic products [4].

There are several types of synthetic dyes used in industry among which we are concerned in the present work with brilliant green dye. It is an organic , cationic dye that belongs to the family of tri-phenyl methane and which is widely used as biological stain, dermatological agent, veterinary medicine, and an additive to poultry feed to inhibit propagation of mold, intestinal parasites, and fungus [5]. Brilliant green dye has been reported to be toxic for humans, it causes irritation to the gastrointestinal tract, nausea and vomiting, irritation to the respiratory tract and irritation to skin [6].

The removal of dyes from water effluents is thus an important issue and the use of an appropriate treatment method must be considered. Several techniques are available for treatment of wastewater such as adsorption, chemical coagulation, electro coagulation, membrane separation, biological methods such as fungal and microbial decolourization [4].

In the present work, we investigate the possible use of palm fronds as a precursor material for the preparation of activated carbon and the applicability of this activated carbon as adsorbent for brilliant green dye removal from wastewater.

2. Experimental

Palm fronds were obtained from Agricultural Research Center (ARC) in Egypt. The fronds were washed to remove any dirt and then oven dried overnight at 105°C. The fronds were then heated (transferred to ash) in a muffle furnace for 4 hrs at 500°C. The activation process was done using NaOH at an impregnation ratio of 1:1 (ash : NaOH). The activation steps used were as previously reported by [7] with little modification. The resulting activated carbon was assigned PFAC. The functional groups of PFAC were determined using Fourier Transformation infrared technique by a Perkin-Elmer FT-IR 1650 spectrophotometer with working range (200-4000 cm^{-1}).

Brilliant green dye (BG) was obtained from Sigma-Aldrich. Chemical formula: C27H34N2O4S Mwt: 482.62. The structure of BG is illustrated in Fig. 1. An accurately weighed quantity of the dye was dissolved in deionized water to prepare a stock solution (1000 mg/l). Experimental solutions of the desired concentrations were obtained by diluting the stock solution with deionized water.
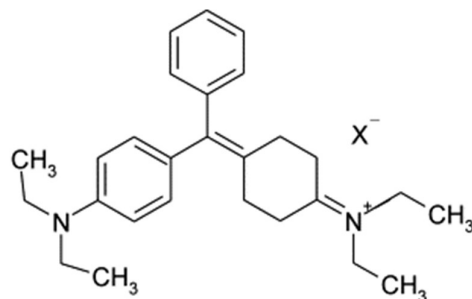

Figure1. Molecular structure of Brilliant Green.

2.1 Analytical measurements

Concentrations of dyes were determined by finding out the absorbance at the characteristic wavelength using a double beam UV/VIS spectrophotometer (SPECORD 250 plus, Analytik Jena). A standard solution of the dye was taken and the absorbance was determined at different wavelengths by scanning absorbance versus wavelength and the λmax corresponding to maximum absorbance was found to be λ= 638 nm. This wavelength was used for determining the concentration of the dye solution during the adsorption experiments.

2.2 Adsorption experiments

Batch experiments were performed at different contact time (30, 45, 60, 90, 120,150 and 180 min.) and different initial concentrations of BG (25 to 125 mg/l). The experiments were performed at room temperature. At the beginning of each experiment 25 ml of dye solution was mixed with (0.04g) of PFAC. The tubes were shacked for the pre-determined contact time and at the end of each experiment the adsorbent was separated from the solution by filtration. And the adsorption capacity (q) was calculated as follows.

$$q(mg/g) = (C_f - C_i) \times V/W \tag{1}$$

where, C_f (mg/l) is the remaining concentration of dye in solution after adsorption, C_i (mg/l) is the initial dye concentration, V (L) is the volume of solution used in the experiment and W(g) is the adsorbent weight.

3. Results and discussion

3.1. Adsorbent Characterization

The FTIR spectrum of PFAC is shown in figure 2. The spectrum shows five characteristic bands at positions 3442.31 are assigned to O-H stretching mode of hydroxyl groups, the strong bands at 1092.48 and1058.73 cm^{-1} may be due to C–O group [8], 796.45 cm^{-1}occurs probably due to the aromatic C-H bond and that at 469.582 cm^{-1} could be due to the C-C bending vibrations of normal alkenes. Thus the FTIR results have confirmed the presence of functional group that could offer potential adsorption sites [9]. A broad peak observed at 1629 cm^{-1}, before absorption, is assigned to the aromatic C–C ring stretch [10].
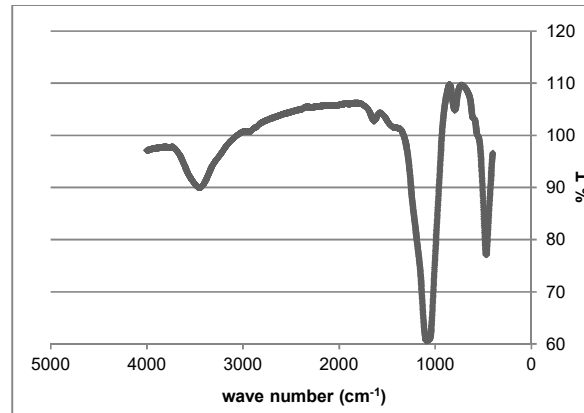

Figure 2. FTIR for Palm frond activated carbon (PFAC).

3.2. Effect of contact time and dye concentration on adsorption

Equilibrium time is one of the most important parameters in the design of economical wastewater treatment systems [11]. Figure 3 shows the variation of dye removal percentage in response to contact time. It is observed that at low contact time the removal percentage is usually small and then it starts to rapidly increase before reaching its equilibrium. The adsorption of BG by PFAC reached 85% after 150 minutes and remained almost unchanged thereafter. According to Mane and Babu (2011) at the start of contact time, there is a large number of vacant surface sites available for adsorption, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases[12].

The effect of initial BG dye concentration on its removal percentage by PFAC is shown in Figure 4. It is observed that the removal percentage decreased from 90.88 to 60.56% by increasing the dye concentration from 25 to 125mg/l, respectively. The percent removal of dye decreases with increase in initial concentration because of the fact that with increase in dye concentration, there will be increased competition for the active adsorption sites [13].
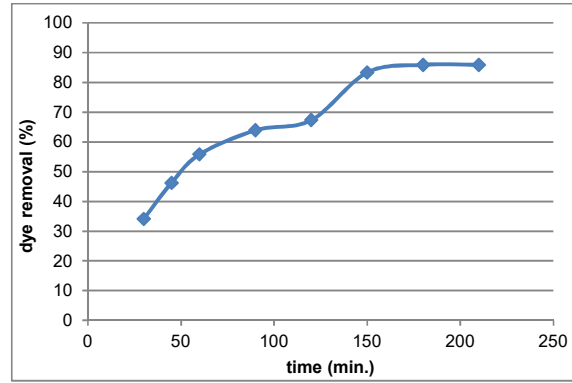
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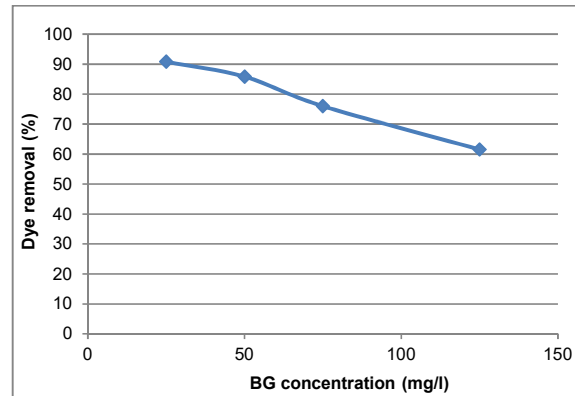Figure 3. Effect of contact time on BG removal.

Figure 4. Effect of BG concentration on its removal.

3.3. Adsorption kinetics and mechanism

In order to investigate the adsorption of brilliant green on the surface of palm fronds activated carbon, different kinetic models are used to examine the controlling mechanism of adsorption process. The pseudo-first-order kinetic model, pseudo-second-order kinetic model and Elovich's model were investigated to find the best fitted model for the experimental data.

The linear form of Lagergren's first order rate equation [14] is as follows.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

where q_e is the amount of dye adsorbed onto the adsorbent at equilibrium (mg/g), q_t is the amount of dye adsorbed onto the adsorbent at any time t (mg/g), and K_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of $\ln(q_e - q_t)$ against t.

The linearized form of the pseudo-second-order model as given by [15] is

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \tag{3}$$

where K_2 (g mg^{-1}min^{-1}) is the rate constant of the pseudo-second-order adsorption, q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g), and q_t is the amount of dye adsorbed on the adsorbent at any time, t (mg/g). K_2 (gmg^{-1}min^{-1}) can be calculated from the slope and intercept of the plot of t/q_t against t.

The Elovich's equation [16] is expressed as

$$q_t = (1/b) \ln(a \times b) + (1/b) \ln(t) \tag{4}$$

where a and b are the constants for this model obtained from the slope and intercept of the linear plot of q_t versus $\ln(t)$.

Figures (5, 6 and 7) gives plots of Lagergren's first order, pseudo-second-order and Elovich's models respectively. The parameters calculated from each model are listed in Table (1).
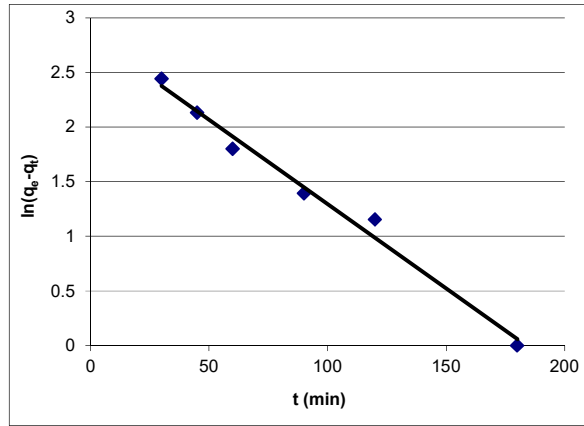
Figure 5. Lagergren's first order plots for the removal of Brilliant Green (BG) by PFAC.
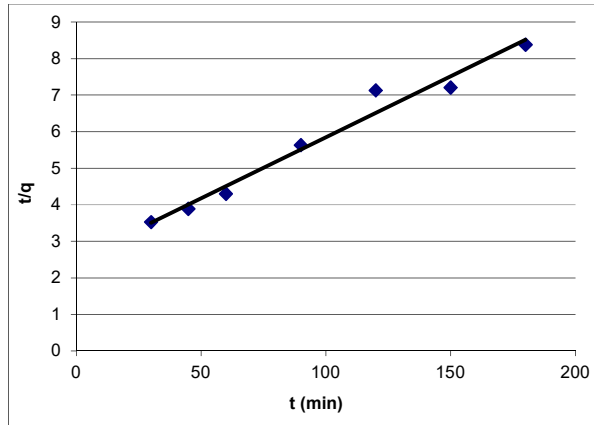
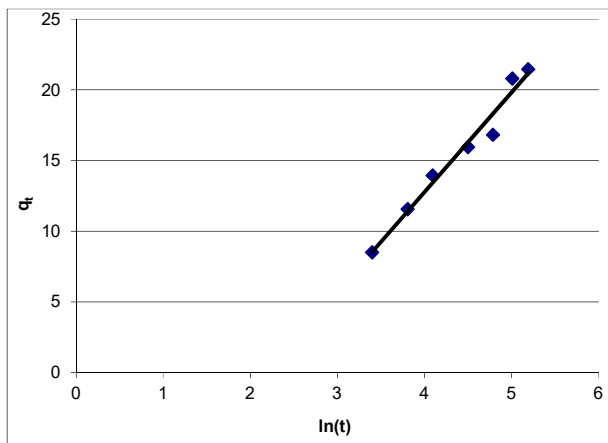Figure 6. pseudo-second-order plots for the removal of brilliant green (BG) by PFAC.

Figure 7. Elovich's plots for the removal of brilliant green (BG) by PFAC.

Table 1. Kinetic parameters for the removal of Brilliant Green (BG) by PFAC.

Lagergen first order			pseudo second order			Elovich			Intra-particle diffusion			$q_{exp.}$
R_2	K	q_e	R_2	K_2	q_e	R_2	a	b	R_2	K_{id}	C	20.0
0.986	0.0169	18.33	0.973	4.415	30.03	0.973	7.34×10^{-4}	0.513	0.9695	1.571	0.76	

The kinetic parameters and the determination coefficient (R_2) from the three kinetic models' equations are calculated and the results are shown in Table 1. The results showed that the determination coefficient for the first-order kinetic equation is greater than the coefficients of the two other models. Also the adsorption capacity calculated by the model is close to that determined by experiment ($q_{exp.}$). This indicates that adsorption of brilliant green dye onto the PFAC is best represented with a pseudo-first-order kinetic model. Shirsath et al. [6] have interpreted the pseudo-first order equation in terms of the kinetic process governed by the rate of first-order reversible reaction, in which the rate of sorption process in independent of the adsorbed amount present on the surface at a given time. These results suggested that a physical adsorption might be involved in the adsorption process [17].

The adsorption of BG by PFAC was also studied from mechanism point. In this respect, the Intraparticle diffusion model was applied to investigate whether the adsorption process was controlled by diffusion in the adsorbent particles and consecutive diffusion in the bulk of the solution [18].

The intra-particle diffusion equation [19] can be written as

$$q_t = K_{id} t^{1/2} + C \qquad (5)$$

where q_t is the amount of dye adsorbed onto the adsorbent at time t (mg/g), C is the intercept, and K_{id} is the intra-particle diffusion rate constant (mg g^{-1} min^{-1}).
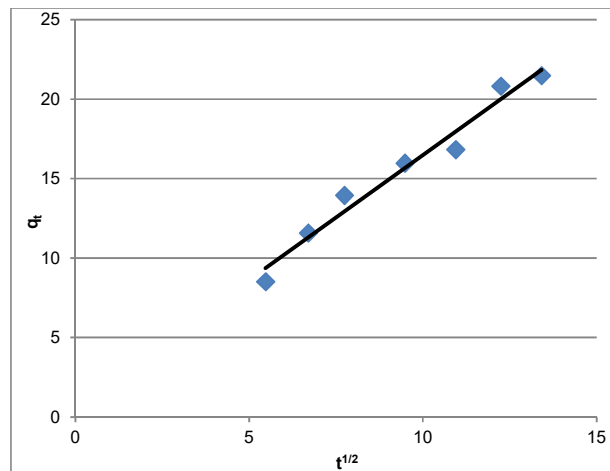

Figure 8. intra-particle diffusion plot for the removal of brilliant green (BG) by PFAC.

Figure (8) shows the plot of qt versus $t^{1/2}$ for the adsorption of BG onto PFAC with slope = 0.1571 mg g^{-1} min^{-1} and an intercept = 0.76 corresponding to the intra-particle diffusion rate constant (K_{id}) and the thickness of the boundary layer (C), respectively. It can be seen that the plot gives one straight line indicating that the adsorption mechanism follows the intraparticle diffusion process. The value of C gives an idea about the thickness of boundary layer i.e. the larger the intercept the greater is the boundary layer effect. The deviation of straight line from the origin may be because of the difference in the rate of mass transfer in the initial and final stages of adsorption[18].

3.4. Adsorption equilibrium

The equilibrium modeling of brilliant green dye removal by PFAC was further assessed by applying the Langmuir, Freundlich and Temkin models to the experimental data.

The Langmuir isotherm is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface. The equation of Langmuir isotherm [20] is represented as below.

$$C_e/q_e = 1/b_L\ q_0 + C_e/q_0 \tag{6}$$

where C_e (mg/L) and q_e (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively, and q_0 (mg/g) and b (L/mg) are the Langmuir isotherm constants.

The Freundlich isotherm model is an exponential equation that applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a mono layer. The Freundlich model [21] is given as

$$Log(q) = log(K_f)+ 1/n\ log(C_e) \tag{7}$$

where K_f (mg/g(L/g)1/n) is the Freundlich constant related to the bonding energy, and n is the heterogeneity factor. n is a measure of the deviation from linearity of the adsorption. It indicates the degree of non-linearity between solution concentration and adsorption.

The Temkin isotherm assumes that a decrease in the adsorption heat is linear and that the adsorption is characterized by a uniform distribution of binding energies. The Temkin linear form of isotherm is given by equation [22]:

$$q_e = a_t + b_t\ ln(C_e) \tag{8}$$

where b_t and a_t represent isotherm constant related to the adsorption capacity of the adsorbent.

Figures (9,10 and 11) gives plots of the Langmuir, Freundlich and Temkin models, respectively. The parameters calculated from each model are listed in table (2).
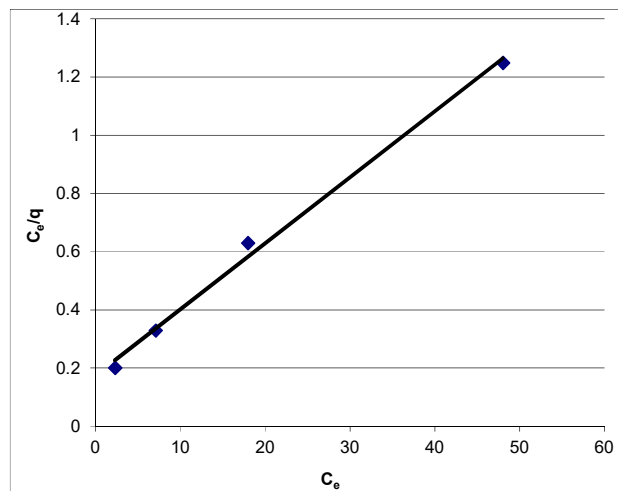

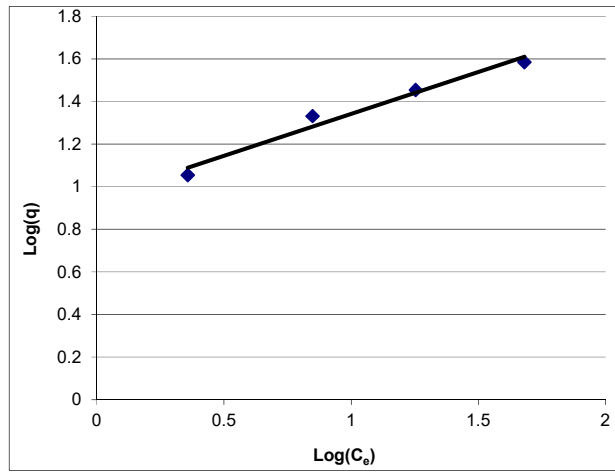Figure 9. Langmuir plots for the removal of Brilliant Green (BG) by PFAC.

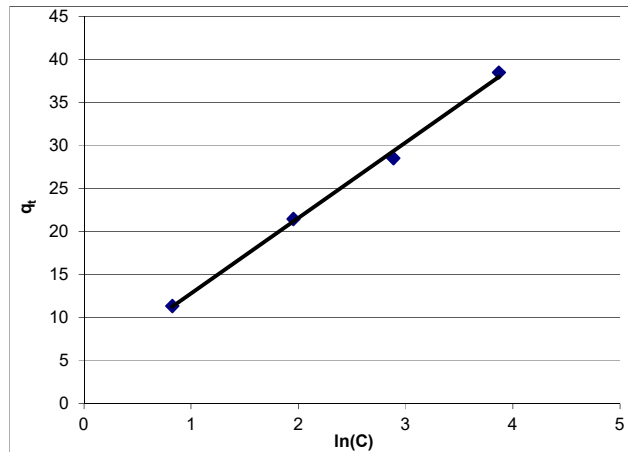Figure 10. Freundlich plots for the removal of Brilliant Green (BG) by PFAC.

Figure 11. Temkin plots for the removal of Brilliant Green (BG) by PFAC.

Table 2. Isotherm parameters for removal of Brilliant Green (BG) by PFAC.

Langmuir model			Freundlich model			Temkin isotherm		
R_2	b_L	q_m	R_2	$1/n$	K_f	R_2	a_t	b_t
0.9951	0.126	45.45	0.9715	0.39	8.87	0.9974	4.032	8.774

The correlation coefficients for the Langmuir, Freundlich and Temkin models as shown in Table (2) are all greater than (0.95). The adsorption equilibrium study indicated that the data of the adsorption of brilliant green onto PFAC best fitted the Temkin and Langmuir adsorption models ($R_2 > 0.99$).

In Table (2), the Langmuir maximum capacity (q_m), was obtained as 45.45 mg.g^{-1} and Langmuir constant, b_L, which indicated sorption energy, was found to be 0.126 L.mg^{-1}. The value of $1/n$ less than 1 in the Freundlich model indicate the favorable nature of adsorption of BG on PFAC under the studied conditions [23].

The suitability of the Temkin model for fitting the data of BG adsorption onto PFAC suggests adsorbent-adsorbate interactions which causes a decrease in the heat of adsorption of all the molecules in the layer to decrease linearly with coverage, and that the adsorption is

characterized by a uniform distribution of the binding energies up to some maximum binding energy [24]. Also, the good fitting of adsorption data with Langmuir equation, indicates that surface energies of PFAC were uniform. Langmuir model assumes uniform energies of adsorption onto the surface of adsorbent with no transmigration of adsorbate in the plane of the surface, and the adsorbed molecules have no interaction [25].

4. Conclusion

Activated carbon prepared from palm frond may be used as a less expensive adsorbent for the removal of brilliant green dye. The adsorption has been investigated with respect to contact time and initial dye concentration. The percentage removal attained equilibrium after 150 minutes and decreased by increasing the initial dye concentrations from 25 to 125mg/l. Adsorption kinetic followed the pseudo-first-order kinetics. The equilibrium data are analyzed using Langmuir, Freundlich and Tempkin isotherm equations. The results showed that the experimental data were best described by Langmuir and Temkin models.

References

[1] F. Pumpkin, T. Occidentalis and H.F. Seed, Preparation and Characterization of Activated Carbon From, Journal of Chemistry, vol 1. pp. 39–50, 2012.

[2] N.T. Abdel-Ghani, G. a. El-Chaghaby and E.M. Zahran, Pentachlorophenol (PCP) adsorption from aqueous solution by activated carbons prepared from corn wastes, Int. J. Environ. Sci. Technol., vol 12, pp. 211–222, 2015.

[3] N. Byamba-Ochir, W.G. Shim, M.S. Balathanigaimani and H. Moon, Highly porous activated carbons prepared from carbon rich Mongolian anthracite by direct NaOH activation, Appl. Surf. Sci., vol 379, pp. 331–337, 2016.

[4] A.F. Ali, A.S. Kovo and S.A. Adetunji, Methylene Blue and Brilliant Green Dyes Removal from Aqueous Solution Using Agricultural Wastes Activated Carbon, J. of Encapsulation and Adsorption Sciences, vol 7, pp. 95–107, 2017.

[5] O.S. Esan, O.N. Abiola, O. Owoyomi, C.O. Aboluwoye and M.O. Osundiya, Adsorption of Brilliant Green onto Luffa Cylindrical Sponge: Equilibrium, Kinetics, and Thermodynamic Studies, ISRN Phys. Chem. vol 2014, pp. 1–12, 2014.

[6] S.R. Shirsath, A.P. Patil, R. Patil, J.B. Naik, P.R. Gogate and S.H. Sonawane, Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study, Ultrason. Sonochem., vol 20, pp. 914–923, 2013.

[7] N.T. Abdel-Ghani, G.A. El-Chaghaby and F.S. Helal, Simultaneous removal of aluminum, iron, copper, zinc, and lead from aqueous solution using raw and chemically treated African beech wood sawdust, Desalin. Water Treat., vol 51, pp. 3558–3575, 2013.

[8] E.M. Soliman, S.A. Ahmed and A.A. Fadl, Reactivity of sugar cane bagasse as a natural solid phase extractor for selective removal of Fe(III) and heavy-metal ions from natural water samples, Arab. J. Chem., vol 4, pp. 63–70, 2011.

[9] V. Balakrishnan, S. Arivoli, A.S. Begum and A.J. Ahamed, Studies on the adsorption mechanism of Cu(II) ions by a new activated carbon, J. Chem. Pharm. Res., vol 2, pp. 176–190, 2010.

[10] E.S. Ribeiro, Removal of Brilliant Green Dye from Aqueous Solutions Using Home Made Activated Carbons, Clean Soil and Air, vol 38, pp. 521–532, 2010.

[11] M. Ghaedi, H. Hossainian, M. Montazerozohori, A. Shokrollahi, F. Shojaipour, M. Soylak, et al., A novel acorn based adsorbent for the removal of brilliant green, Desalination. vol 281, pp. 226–233, 2011.

[12] V.S. Mane and P.V.V. Babu, Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust, Desalination. vol 273, pp. 321–329, 2011.

[13] B.K. Nandi, A. Goswami and M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater., vol 161, pp. 387–395, 2009.

[14] S.Y. Lagergren, Zur Theorie der sogenannten Adsorption gelöster Stoffe, 1898. http://books.google.com.eg/books/about/Zur_Theorie_der_sogenannten_Adsorption_g.html?id=L PUlHQAACAAJ&pgis=1 (accessed January 2, 2014).

[15] Y. Ho and G. McKay, Pseudo-second order model for sorption processes, Process Biochem. vol 34, pp. 451–465, 1999.

[16] Y.B. Zeldovich, The oxidation of nitrogen in combustion and explosions, Acta Physicochim. URSS. vol 21, pp. 577–628, 1946.

[17] X. Liu and L. Zhang, Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies, Powder Technol. vol 277, pp. 112–119, 2015.

[18] M. Ahmaruzzaman and S. Laxmi Gayatri, Batch adsorption of 4-nitrophenol by acid activated jute stick char: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J., vol 158, pp. 173–180, 2010.

[19] J. Weber Jr and J. C. Morris, Kinetics of Adsorption on Carbon from Solution, J. Sanit. Eng. Div., vol 89, pp. 31–60, 1963. http://cedb.asce.org/cgi/WWWdisplay.cgi?13042 (accessed January 2, 2014).

[20] I. Langmuir, The Adsorption of Gases on Plane Surgaces of Glass, Mica and Platinum, J. Am. Chem. Soc., vol 40, 1361–1403, 1918.

[21] H. Freundlich, Über die Absorption in Lösungen, Zeitschrift für Physikalische Chemie, 1906. http://books.google.com.eg/books/about/Über_die_Absorption_in_Lösungen.html?id=rPuGGwA ACAAJ&pgis=1 (accessed January 2, 2014).

[22] M.J. Temkin and V. Pyzhev, Recent Modifications to Langmuir Isotherms, Acta Phys. Chem., vol 12, pp. 217–222,1940.
http://www.ljemail.org/reference/ReferencesPapers.aspx?ReferenceID=148986 (accessed July 23, 2015).

[23] V. Rawat, P. Rai, R.K. Gautam and M.C. Chattopadhyaya, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green Dye from aqueous solution by Oplismenus frumentaceus husk, J. Indian Chem. Soc., vol 90, pp. 577–583, 2013.

[24] N.T. Abdel-Ghani, E.S.A. Rawash and G.A. El-Chaghaby, Equilibrium and kinetic study for the adsorption of p-nitrophenol from wastewater using olive cake based activated carbon, Glob. J. Environ. Sci. Manag., vol 2, pp. 11–18, 2016.

[25] D. Tang, Z. Zheng, K. Lin, J. Luan and J. Zhang, Adsorption of p-nitrophenol from aqueous solutions onto activated carbon fiber, J. Hazard. Mater. vol 143, pp. 49–56, 2007.