

Original article

Low-Cost Carbon Biochar for Removing Methylene Blue from Its Aqueous Solution

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Abstract

Environmentally, water pollution is considered the most important issue because of its hazard to humans, animals, and aquatic. The importance and necessity of water is because its presence determines the existence and health of these living forms of life. However, humans were not able to treat the environment (Water) well because of the human population increment and extensive human agricultural and industrial activities, particularly in regions close to water resources. Industries dealing with the use of dyes, such as textile ones, have water effluents as wastewater when thrown to the rivers and seas can pose a serious environmental problem as it causes harm to the biota of the receptor water. This study examines the efficiency of the Biochar (BC) obtained from date stones (DS) in the removal of a basic dye model called Methylene blue (MB) from its aqueous solution. A batch mode system was used, and experiments were run to assess the effects of BCDS adsorbent dose (30-100 mg), pH (3-9), contact time (0-30 min), and MB initial concentrations (5-30 mg/l). The sorption exhibited high efficiency for MB adsorption, and the equilibrium state could be achieved in 30 minutes for the different MB initial concentrations. MB uptake was proven to increase with the increase in BCDS dose, pH, contact time, and MB initial concentration. Therefore, BCDS has the potential to be used as a local, abundant, low-cost, eco-friendly adsorbent for the removal of MB from aqueous solutions.

Keywords. Methylene Blue, Date Stones, Adsorption, Batch Mode.

Introduction

Pollution is one of the problems usually faced by both humans and the environment, especially after the technological development associated with contemporary life. All forms of pollution, either air, sand, or water, happen as a result of existing harmful organic or inorganic substances, or as a result of concentration fluctuation of main constituents in their original environment, more than their natural fractions. Pollutions usually happen either by the interference of humans or by the action of natural phenomena. Water pollution is one of the most important and dangerous environmental topics because of the importance and necessity of water to all living forms of life, whose presence determines their existence and normal, healthy life. However, human was not able to treat the environment well as a result of the human population increment and their extensive activities, such as agriculture or industrial fields, especially in regions close to water resources.

Water purification has become a problem facing a number of researchers and environmental protection foundations. It was found that the most water contaminants are those chemicals applied in many industries; dyes used in textile manufactories and the manufacturing of paints and printing inks are one big example [1]. Dyes are soluble organic compounds in a water medium [2]. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade [3]. Dyes and their degradation products may be carcinogens and toxins if these effluents are treated inefficiently before discharging to the streams; they could bring problems to human health and animals [4] and are not limited to themselves but also may be passed on to future generations by the way of genetic mutations, birth defects, and inherited diseases [5].

Methylene blue (MB) is selected as a model dye compound in order to evaluate the capacity of the adsorbent for the removal of MB basic dye from its aqueous solution. MB is widely used in textile manufactories for dyeing of cotton and silk, and also in the manufacturing of paints and printing inks [6]. The external exposure to MB can cause skin irritation and constant eye burns in humans and animals. Whereas, on inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, and mental confusion [7]. The dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [8]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

Rivers, seas, and even underground water can be polluted by the random and irresponsible activities of leather and textile tanning, plastics, paper, cosmetics, paint-making industries, represented in the discharging of their highly colored waste liquids. The discharge of colored liquid wastes into receptor water, such as rivers and seas, affects not only their aesthetic nature but also the transmission of light, thus upsetting the bio-aquatic processes within the receptors. The colored liquids of these industries' effluents are mainly produced from the utilization of dyes and pigments. Hence, it is environmentally very important to remove the synthetic dyestuff from the wastewater before discharging it into any natural receptor waters

[9]. In general, several difficulties are encountered in the removal of dyes from wastewater. By design, dyes are highly stable molecules, made to resist degradation by light, chemicals, biologicals, and other exposures. Dyes vary widely in chemical composition. Basic dyes are considered one of the more problematic classes of dye, which are considered toxic colorants. As a result, improved or cost-effective technologies are required to remove them from textile effluents [10]. A number of treatment processes for the removal of dyes from wastewater are in practice. They comprise the following: microbial degradation [11], electrochemical degradation [12], advanced oxidation processes [13], and cation exchange membranes [14]. However, each of these processes aforementioned has its merits and limitations in application.

Among these processes, adsorption currently appears to be the best in order to remove colours from wastewater [15]. Adsorption using activated carbon obtained from agricultural by-products/wastes such as cherry stones [16], palm ash [17], and pommel peels [18] is an inexpensive adsorbent, easily available and handled, and simply operated [19]. Date stones can represent a good example of a low-cost adsorbent; it is an agricultural by-product/waste found in abundance at the manufactories of date pastes and juices, particularly in Libya, where their fruitful trees are widely planted. Libya is considered one of the major countries engaged in taking care and cultivating date trees that the number of these trees cultivated and distributed in many regions of the country at many regions particularly at the oases were estimated to be around 5.0 million trees (5.6% of trees cultivated worldwide), and 60% of this estimate is considered fruitful and produces 0.1 MT of a variety of dates annually [20]. In the present study, carbon Biochar (BC) obtained from date stones was studied to evaluate its efficiency in the adsorption of MB from aqueous solutions. Batch mode experiments were conducted to determine the factors affecting the MB adsorption process.

Methods

Materials

MB was obtained commercially from B.D.H. Chemicals Ltd., England, while precursors used for the production of BC were date stones collected from a few local manufactories of date pastes and juices in Tripoli city in Libya.

Preparation of BCDS Adsorbents

The step-by-step preparation method of BCDS can be illustrated as follows: Half a kilo (0.5 kg) of date stone precursor was collected from one of the national factories located in Emselata city in the north northwest of Libya. For washing date stones, they were boiled in water a few times till they appeared clean on the outside. Initially, sun drying was employed on stones for one day. Next, stones were dried in an oven at 110 °C overnight. Then stones were carbonated by continuous heating over 400°C. At this stage, A very-high-carbon-rich charcoal is obtained. At last, the Carbonated DS were cooled at room temperature and ground for homogeneous granules of 1 mm in size.

Characteristics & Preparation of MB Adsorbate

MB is a phenazathion(odimethylamin)-bis -3,7um ($C_{16}H_{18}N_3SCl$); molecular weight 319.85 g; λ_{max} 665 nm) [21]. It is used in this study as a model molecule for organic pollutants in general and basic dyes in particular, and thus, no further purifications were needed. The molecular structure of MB dye is illustrated in (Figure 1). MB dye stock solution (1000 mg/l) was prepared by accurately weighing the required quantity of dye in double-distilled water. The working solutions of different concentrations were prepared by diluting the stock solution to give the appropriate concentrations. All chemicals used throughout this study were of analytical-grade reagents.

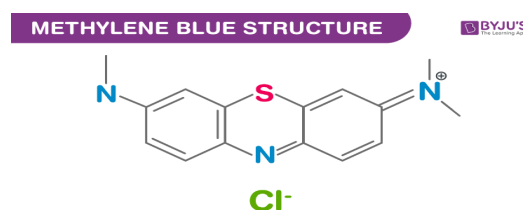


Fig. 1. Molecular Structure of Methylene blue [16]

Instrumentations

Several equipment was used in this study: (i) UV / visible spectrophotometer (Specord 205, UV-Analytikjena, Germany) at $\lambda = 665$ nm for the determination of the MB concentrations; (ii) 740 Inolab WTW model pH meter using a SenTix 20 pH model double electrode calibrated with standard buffer solutions was used for measurements of pH of the solutions; (iii) digital shaker (GFL 3005 model, Germany) was used for Batch mode adsorption experiments. All equipment involved in this study was supplied by Tajoura Nuclear Research Center (TNRC) in Tripoli-Libya.

Batch Adsorption

Batch mode sorption experiments were performed in a shaker at a constant agitation rate of 200 rpm and room temperature of $(25 \pm 2)^\circ\text{C}$ for different periods of contact time (5–30 min) and a pH of (3.0–9.0) using 100 ml Erlenmeyer flasks. All sorption experiments were conducted by mixing different quantities (30, 50, 70, 100 mg) of BCDS with MB solutions containing different initial concentrations of (5, 10, 20, 30 mg/l). After termination of the adsorption experiments, the remaining concentration of MB in each sample was determined by UV spectroscopy after filtering the adsorbent with Whatman filter paper to make it carbon-free. The amount of adsorption at equilibrium, q_e (mg/g), was calculated as follows (1):

$$q_e = (C_0 - C_e) \cdot V / W \quad \dots \dots \dots (1)$$

Where C_0 and C_e (mg/l) are the liquid-phase concentration of dye at initial and final, respectively. V (l) is the volume of the solution, and W (g) is the mass of dry sorbent used.

The percentage adsorption (%) was calculated using the following equation (2):

$$\% \text{ Adsorption} = (C_0 - C_e) \cdot 100 / C_0 \quad \dots \dots \dots (2)$$

In this study, variations in contact time, adsorbent dose, initial MB concentrations, pH, and the investigations of their effect were all aimed by studied.

Results & Discussions

The Effect of BCDS Adsorbent Dose

The effect of adsorbent BCDS doses (30, 50, 70, 100 mg) on MB dye adsorption capacity (the amount of MB dye sorbed per unit mass of BCDS sorbent, i.e. x/m) is shown in (Figure 2); these data have been obtained from starting constant pH of 7.0, agitation rate of 200 rpm, contact time of 30 min, and working solution temperature of normal room temperature. The results showed that as the adsorbent BCDS dose is increased from 30 mg to 100 mg, the MB dye concentration, which remained in the solution (residual), decreased from 30.0 (mg/l) to 2.8 (mg/l). The reason for this is attributed to the increase in the number of active sites available for adsorption of MB molecules with an increase in the quantity (weight) of BCDS, causing higher MB percentage removal [22-25]. Equation (1) was used to calculate the adsorption capacity, which could be seen that it has been gone down from 53.1 (mg/g) using 30 mg of BCDS to 14.1 (mg/g) using 100 mg of the same BC. The active sites may not be available during the MB adsorption process due to the overlapping between these active sites themselves at high doses, which reduces the total surface area and thus the amount of the Adsorbates (i.e. MB molecules) adsorbed by the adsorbents (i.e. BCDS) is decreased; it has been reported in a number of articles [22, 26].

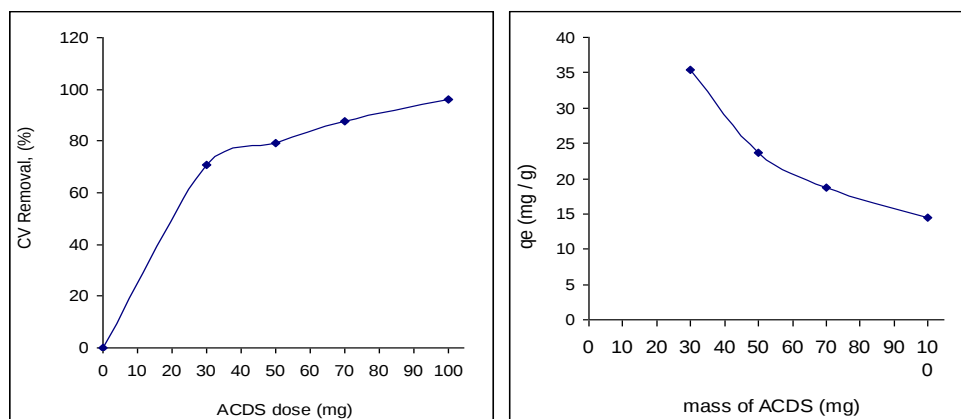


Fig. 2: (left) Variation of MB adsorption as a function of BCDS amounts (50 ml of 30 mg/l of MB, temp. 25°C and pH 7.0). (right) The effect of BCDS dose on the MB adsorption (percentage removal)

The Effect of pH

The initial pH of MB dye solutions (30 mg/ l) was adjusted to 3.0, 5.0, 7.0, and 9.0 while the MB batch mode adsorption was carried out at a room temperature of 25°C , agitation rate at 200 rpm, contact time of 30 min (Figure 3). The pH is a very effective factor in removing the MB dye molecules under the conditions employed, through the protonation of the amino groups located at the aromatic rings (Figure 1). The three amino groups of the MB molecule become protonated at low pH, and the number of them decreases from three to one with the increase of pH.

It was observed that the MB solution had different colours as pH was changed from 3.0 to 9.0, which agreed with reported findings (31). Figure 5 demonstrates that the adsorption capacities of MB increased with the increase of pH; for $\text{pH} < 7.0$, the residual MB dye decreased with an increase in pH from 3.0 to ≤ 7.0 , and above this pH value, the MB residual became nearly steady. This was attributed to the fact that, at low pH (3.0 & 5.0), the protonation of the negatively binding active sites was enhanced and thus the number of these active sites became lower for the adsorption of MB molecules in contrast, when the pH was higher ($\geq$

7.0) the BCDS possibly and gradually become deprotonated (i.e negatively charged) and the electrostatic process of attraction of the cationic MB dye molecules became enhanced [24-27].

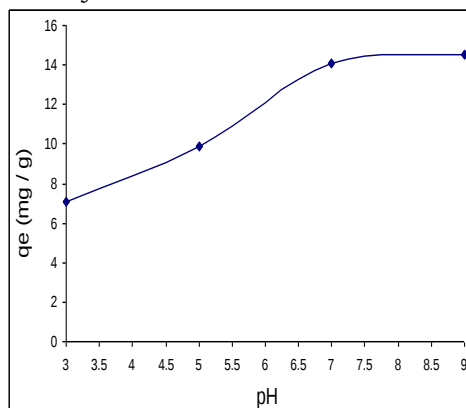


Fig. 3: The effect of the pH on the removal of MB basic dye by the BCDS (50 ml of 30 mg/l of MB, temp. 25 °C, agitation rate of 200 rpm, and contact time 30 min)

The Effect of Contact Time

A batch process was conducted at different contact times ranging from (5 – 30) minutes. The effect of contact time on MB dye adsorption capacity at an MB initial concentration of 30 mg/l is presented in (Figure 4). From the figure, it can be observed that the adsorption capacity increased rapidly with the increase of contact time for the first ten minutes. It seemed thereafter the adsorption process continued slowly until it gradually reached saturation, and the adsorption capacity was said to reach equilibrium, which was attained after 30 minutes at the employed conditions. The rate of adsorption capacity was higher in the beginning due to the larger surface area and the availability of the binding active sites of the adsorbent BCDS at the start [22] and the driving force provided by the initial concentration at the beginning, which overcomes all mass transfer resistance of the MB between the aqueous and solid phases [18, 27]. It is worth mentioning that data on the adsorption kinetics of dyes by a number of adsorbents have demonstrated a range of adsorption rates. For example, Sharma *et al.* (2009) reported that Methylene Blue (MB) basic dye was adsorbed onto an activated carbon (AC) and equilibrium was reached within 60 minutes when the initial concentration of MB was 150 mg/l [19]. Rammel *et al.* (2011) have reported a contact time of 15 minutes as sufficient for the attainment of equilibrium for the adsorption of CV onto *Chaetophora elegans* algae [24]. Saeedeh *et al.* (2013) reported that equilibrium of MB with 72% removal onto Spent Tea Leaves STL was attained at 60 minutes [28]. Alaa reported that equilibrium in the solution of CV dye was attained within 30 minutes when ACDS was applied as an adsorbent [29]. However, in 2006, Mall *et al.* reported that a contact time of 4 hr was accepted for reaching a quasi-equilibrium situation for the adsorption of Orange-G and CV by bagasse fly ash [30].

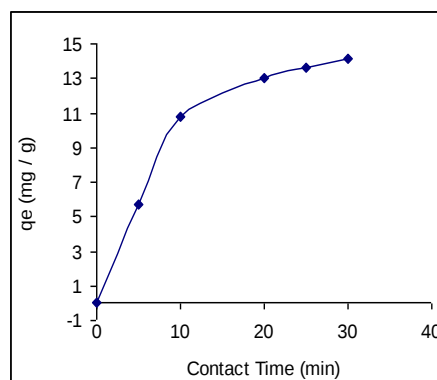


Fig. 4: The effect of contact time on the removal of MB basic dye by BCDS at the following conditions: 50 ml of 30 mg/l of MB, pH of the solution at 7.0, temp. of 25 °C, and an agitation rate of 200 rpm

The Effect of Initial MB Concentrations

The initial dye concentration of 5, 10, 20, and 30 mg/l were used at room temperature, an adsorption pH of 7.0, constant contact time of 30 min and agitation rate of 200 rpm and in conjunction with BCDS adsorbent dose of 50 (mg/l), and their effects on the MB dye removal were thereafter shown in figure 5 (right), while the adsorption capacities of MB was in (Figure 5) (left). From the figure, it can be observed that the MB dye adsorption percentage decreased from 96.7 % to 86.0% with the increase of initial MB concentration from 5.0 mg/l to 30.0 mg/l. However, further examination of the data by using equation (3) revealed that the amount of MB absorbed per unit mass of adsorbent (q_e) increased from 2.42 mg/g to 12.9 mg/g (Figure 5;

right), with the increase in initial concentration from 5.0 mg/l to 30.0 mg/l. This may be attributed to the fact that the initial concentrations provide an important driving force to overcome all mass transfer resistance of the MB between the aqueous and the solid phases, as referred to in a number of literature [18, 25, 31].

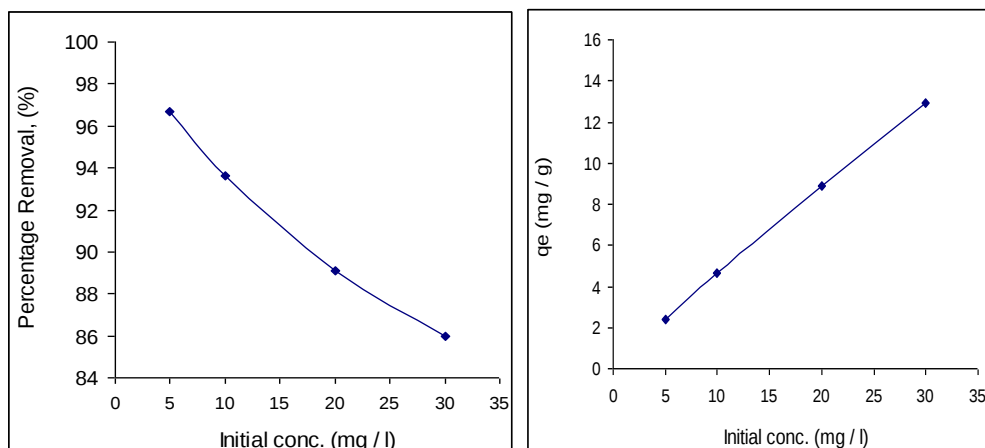


Fig. 5: (left) Variation of MB adsorption as a function of MB concentrations (50 mg of BCDS, temp. 25 °C and pH 7.0). (right) The effect of MB concentrations on the MB adsorption (percentage removal)

Conclusion

The results of the study show that BC obtained from the low-cost and locally abundant date stone materials can be successfully used as an adsorbent for the removal of MB from aqueous solution. The adsorption process was influenced by a number of factors, such as BCDS Adsorbent dose concentration, pH, contact time, and the initial MB concentration. The highest MB removal was obtained at pH 7.0. The removal efficiency increased with an increase in BCDS dose, contact time, and MB initial concentration. The BCDS used in this work is abundantly available, requires almost no cost, and is, more importantly, very effective in removing MB from aqueous solution. Therefore, the eco-friendly adsorbent is expected to be economically feasible for the removal of MB from wastewater treatment, i.e., textile industries, tanning industries, and even at some scientific laboratories, such as medical, biological, and pharmaceutical ones, where dyes are involved in research.

Conflict of interest. Nil

References

1. Senthilkumar P, Ramalingam S, Senthamarai C, Niranjanaa M, Vijayalakshmi M, Sivanesan M. Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*. 2010;261:52-60.
2. Hunger K. Industrial dyes: chemistry, properties, and application. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2003.
3. Sayan E. Optimization and modeling of decolorization and COD reduction of reactive dye solutions by ultrasound-assisted adsorption. *Chem Eng J*. 2006;119:175-81.
4. Kadirvelu K, Namsivayam C. Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd (II) from aqueous solution. *Adv Environ Res*. 2003;7:471-8.
5. Crini G. Kinetics and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes Pigm*. 2008;77:415-26.
6. Gupta VK, Carrott PJM, Carrott MMLR. Low-cost adsorbents: growing approach to wastewater treatment, a review. *Crit Rev Environ Sci Technol*. 2009;39(10):783-842.
7. Lanubi C. La degradation du bleu methylene par la photocatalyse heterogene (TiO₂/Ultraviolet): Memoire de Master. Oum El Bouaghi: University Larbi Ben Mhidi; 2017.
8. Allen SJ, Koumanova B. Decolourization of water/wastewater using adsorption (review). *Univ Chem Technol Metall*. 2005;40(3):175-92.
9. Hazrat A, Muhammad SK. Biosorption of crystal violet from water on leaf biomass of *Calotropis procera*. *Environ Sci Technol*. 2008;1(3):143-50.
10. El Qada EN, Allen SJ, Walker GM. Adsorption of basic dyes from aqueous solution onto activated carbons. *Chem Eng J*. 2008;135(1-2):174-84.
11. Casaletto A, Ferreira J, Tambourgi B, Morase R, Silverira E. Biodegradation of textile azo dyes by *Shewanella putrefaciens* (CCT 1967). *Chem Eng Trans*. 2011;24:871-6.
12. Fan L, Zhou Y, Yang W, Chen G, Yang F. Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model. *Dyes Pigm*. 2008;76(2):440-6.
13. Zourro A, Fidaleo M, Lavecchia R. Response surface methodology (RSM) analysis of photodegradation of sulfonated diazo dye Reactive Green 19 by UV/H₂O₂ process. *J Environ Manage*. 2013;127:28-34.

14. Wu JS, Liu CH, Chu KH, Suen SY. Removal of cationic dye Methyl Violet 2B from water by cation exchange membranes. *J Membr Sci.* 2008;309(1-2):239-45.
15. Senthilkumaar S, Kalaamani P, Porkodi K, Varadarajan PR, Subburaam CV. Adsorption of dissolved Reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste. *Bioresour Technol.* 2006;97(14):1618-25.
16. Lussier MG, Shull JC, Miller DJ. Activated carbon from cherry stones. *Carbon.* 1994;32(8):1493-8.
17. Ahmed AA, Hameed BH, Aziz N. Adsorption of direct dye on palm ash: kinetics and equilibrium modeling. *J Hazard Mater.* 2007;141(1):70-6.
18. Hameed BH, Mahmoud DK, Ahmad AL. Sorption of basic dye from aqueous solution by pomelo peel in a batch system. *Colloids Surf A Physicochem Eng Asp.* 2008;316(1-3):78-84.
19. Sharma C, Uma, Upadhyay SN, Gode F. Adsorptive removal of a basic dye from water and wastewater by activated carbon. *J Appl Sci Environ Sanit.* 2009;4(1):21-8.
20. Shrood O, Farag Z, Adel E, Mansour Z, Hamed AS. Medicinal and nutritional values of Libyan dates. *Biotechnologies Bulletin.* 2004;2(3).
21. Gouamid M, Ouahrani MR, Bensaci MB. Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm leaves. *Energy Procedia.* 2013;36:898-907.
22. Satish P, Vaijanta D, Sameer R, Naseems P. Kinetics of adsorption of Crystal Violet from aqueous solutions using different natural materials. *Int J Environ Sci.* 2011;1(6):1116-34.
23. Chao HP, Rong ZR, Li L, Zhang XY. Adsorption of phenol from aqueous solution using activated carbon prepared from Crofton weed. *Desalination Water Treat.* 2012;37(1-3):230-7.
24. Rammel RS, Zatiti SA, El-Jamal MM. Biosorption of crystal violet by *Chaetophora elegans* algae. *Univ Chem Technol Metall.* 2011;46(3):283-92.
25. Kumar S, Jain A. Sorptive removal of Crystal Violet from aqueous solution using spent tea leaves: part I optimization of sorption conditions and kinetics studies. *Acta Chim Slov.* 2010;57(4):751-7.
26. Bharathi KS, Ramesh ST. Equilibrium, thermodynamic and kinetics studies on adsorption of basic dye by *Citrullus lanatus* rind. *Iranica J Energy Environ.* 2012;3(1):23-34.
27. Uddin MT, Rukanuzzaman M, Khan MMR, Islam MA. Removal of methylene blue by tea waste. *J Hazard Mater.* 2009;164(1):53-60.
28. Hashemian S, Karimi Ardakani MK, Salehifar H. Kinetics and thermodynamics of adsorption methylene blue onto tea waste/CuFe₂O₄ composite. *Am J Anal Chem.* 2013;4(01):1-7.
29. Al-Gidsawi AJK. A study of ability of adsorption of some dyes on activated carbon from date stones. *Aust J Basic Appl Sci.* 2011;5(11):1397-403.
30. Mall ID, Srivastava VC, Agarwal NK. Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses. *Dyes Pigm.* 2006;69(3):210-23.
31. Ashley LP, Thirumalisamy S. Adsorption of hazardous cationic dyes from aqueous solution onto *Acacia nilotica* leaves as an eco friendly adsorbent. *Sustain Environ Res.* 2012;22(2):113-22