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Process Optimization and Kinetics Study of Locally Produced Activated Carbon from Carica Papaya Seeds on Methylene Blue Adsorption

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Abstract

The process optimization of methylene blue removal from aqueous solution using a locally produced activated carbon from the seeds of carica papaya and its kinetics study were carried out. The effects of operating variables such as time, adsorbent dose, pH and temperature were investigated towards achieving the optimum process. Results showed that optimum time (50mins), optimum adsorbent dose (200mg), optimum pH (6.5) and optimum temperature (60^{o}C) were needed to achieve an optimum equilibrium adsorption (320.14 mg/Lmg) of methylene blue from an initial methylene blue concentration of 350 mg/L, which amounted to percentage removal of 91.46 %. The kinetic study however, showed that the adsorption process obeyed the pseudo first order.

Key words: Methylene blue, activated carbon, caricapapya, kinetics, thermodynamics

1. Introduction

Methylene Blue as shown in Figure 1 is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odourless, dark green powder that yields a blue solution when dissolved in water. Methylene Blue (MB) is one of the most widely used dyes in Nigeria, which happens to be a model cation dye used by industries such as textile, as a chemical agent for dyeing cotton wool, silk etc. (Rafatullah et al., 2010). The presence of dye such as MB in effluents is a major concern due to its adverse effects to many forms of life. Industries such as textile, leather, paper, plastics, etc., use dyes in order to colour their products. When improperly discharged into the environment, these dyes may affect aquatic life due to their toxicity and the reduction of light penetration. Methylene blue, being an environmental pollutant from industries has raised great concern, and as such, efforts are being explored on the use of activated carbon to control its menace in the environment.

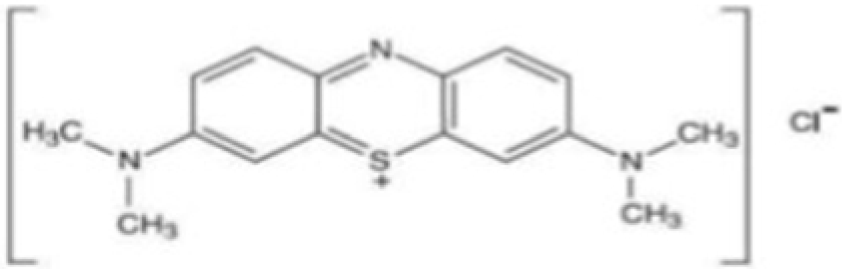

Figure 1: Structure of methylene blue (MB)

Activated carbon is a porous carbonaceous material with ever growing areas of application, especially in water treatment and desalination, waste water treatment and air purification due to its unique characteristics (Kosheleva et al., 2019). It is a very diverse adsorbent material possessing a high degree of porosity and high surface area. While up to 90% of it may be constituted from carbon (Gopinath et al.,2018), oxygen, hydrogen, sulphur and nitrogen are present in the form of functional groups or chemical atoms in the activated carbon structure. It has wide acceptance for use because of its relative cheapness and universal adsorptive capacity for majority of impurities over other adsorbents, such as silica gel and molecular sieves (Adewumi, 2009). The unique adsorption properties depend on the existing functional groups of activated carbon, which are derived mainly from activation processes, precursors and thermal purification (Bhatnagar et al., 2013). The use of papaya seeds as adsorbent to remove dyes from aqueous solutions is particularly attractive in Brazil. Recently, papaya seeds have been used for the removal of tannery dye in aqueous solution, which showed adsorption capacity 60mg$g^{-1}$of 440mgg^{-1} (Weber et al., 2013). Despite its high adsorption capacity, the use of papaya seeds in the adsorption of textile dye with large size molecule has not been reported. Consequently, the use of papaya seeds for MB dye adsorbent is considered interesting from both environmental and economic points of view, since it is an agricultural residue that is available at low cost. Commercially, available activated carbons are usually derived from natural materials such as biomass, lignite or coal, though almost any carbonaceous materials may be used as a precursor for the preparation of carbon adsorbent (El-Khaiary et al.,2009). The excellent ability and economic promise of the activated carbons prepared from biomass is known to exhibit high sorption properties. Kannan and Sundaram, (2001)reported the adsorption capacities of 472.10 mg/g of activated carbons made from straw. However, with the promising nature of carica papaya seeds for dye adsorbent, this study is poised in investigating its process optimization andthe kinetics study of its adsorption ability on methylene blue.

2. Materials and Methods

2.1 Chemicals and equipment: All the chemicals used in this study are of analytical grade (> 98 %). They include hydrochloric acid solution, sodium thiosulfate, iodine, potassium iodide, sodium carbonate, potassium iodate, zinc chloride and methylene blue. They were obtained from Pyrex laboratory limited, Warri, Delta State.

Sample preparation

Carica papaya seeds used as the raw material for the adsorbent were obtained from a fruit shop at Polokor market, Warri, Delta State. Dirt and slime covering the seeds were removed by washing the seeds with distilled water several times, and thereafter, sun dried for 3 months and then air dried for another 3 months for use in preparing the activated carbon.

Preparation of the activated carbon

Both the semi-carbonization and chemical activation processes were deployed in the making of the activated carbon from the previously processed carica papaya seeds.Following the semi-carbonization process, the papaya seeds were heated to a temperature of 300 ^{O}C using a muffle furnace for about 1hr and then cooled to a room temperature, where the resulting material was labeled as semi-carbonized carbon (SCC). The SCC was then subjected to chemical activation by first interacting it with aqueous solution of 200 mL zinc chloride ($ZnCl2$) in ratio 1:1 (wt:wt) of $ZnCl2$:SCC, and then subjected to heat using the muffle furnace at 500 ^{O}C for 2 hrs and then all allowed to cool. Thereafter, the sample was washed using 5% HCl and then with deionized water five times.

Batch equilibrium adsorption

The adsorption experiments were carried out in a batch process at 30, 40, 50 60 and 70 ˚C at varying parameters such as time, adsorbent dosage, adsorbate concentration and pH. At the initial trial, 50 mg weight of CPSAC was added to 50 ml of the dye solution with an initial concentration of 50 mg/L - 400 mg/L, prepared from 1000 mg/L of methylene blue stock solution. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at different time intervals and the final concentration of methylene blue was determined via UV/Vis spectrophotometer at 645nm. The amount of methylene blue adsorbed was thus calculated using Equation (1):

$$q_e = (C_o - C_e)\frac{V}{M} \quad (1)$$

where: q_e is the amount of dye in mg per gram of adsorbent; Co (mg L^{-1}) is the concentration of the methylene blue solution at starting time (t = 0); Ce (mg L^{-1}) is the concentration of the methylene blue solution at equilibrium time; V is the volume of solution and M is the mass of adsorbent, respectively.

2.2 Effect of contact time and initial dye concentration

The effect of contact time on the amount of dye adsorbed was investigated by varying time from 0-70 mins, while keeping pH, concentration, temperature and adsorbent dosage constant. At the end of each batch experiment, the final equilibrium concentration of methylene blue was determined.

Effect of adsorbate concentration

The optimum adsorbate (MB) concentration adsorbed by the locally prepared activated carbon was determined by varying its initial concentrations from 50 mg/L - 250 mg/L at an already predetermined time and keeping temperature and pH constant.

Effect of adsorbent dosage

The adsorption of the methylene blue dye on CPSAC was studied by varying the adsorbent dose (50 – 300 mg/50ml) for 50 mg/L of dye concentration, at already predetermined time above, while keeping temperature and pH constant. At the end of each batch experiment, the final concentration of methylene blue was determined.

Effect of solution pH

The solution pH is one of the most important factors that control the adsorption of dye on the sorbent material. The pH determination was achieved at already predetermined equilibrium of time, adsorbate concentration, adsorbent dosage and varying the pH from 2.0-10.0, by adding concentrated hydrochloric acid to the stock solution. At the end of each batch experiment, the final concentration of methylene blue was determined.

Effect of temperature

To study the effect of temperature on the adsorption of dye adsorption by CPSAC, the experiments were performed at temperatures of 25, 40, 50, 60 and 70°C, respectively while keeping time, concentration of adsorbate, adsorbent dosage and pH constant. At the end of each batch experiment, the optimum concentration of methylene blue adsorbed was determined.

2.3 Surface Morphological Study

While using Jeol 840 electron scanning microscope to analyze the surface structure of the produced activated carbon, 35 mg of CPSAC was placed on aluminium stubs, using colloidal graphite as a mounting medium. Thereafter, a thin layer of gold palladium was deposited unto the samples to make it conductive, where the surface study was carried out at 100 µm magnification.

2. Results and Discussion

2.1 Effect of contact time and initial dye concentration

The effect of time on methylene blue removal (%) from aqueous solution was investigated from 0 - 70 mins. It was observed as shown in Figure 1 that the percentage removal of MB dye increased rapidly with an increase in contact time initially, and thereafter, beyond a contact time of 50 min, no noticeable change in the percentage removal was observed, and the percentage removal at 50 min was 85%.

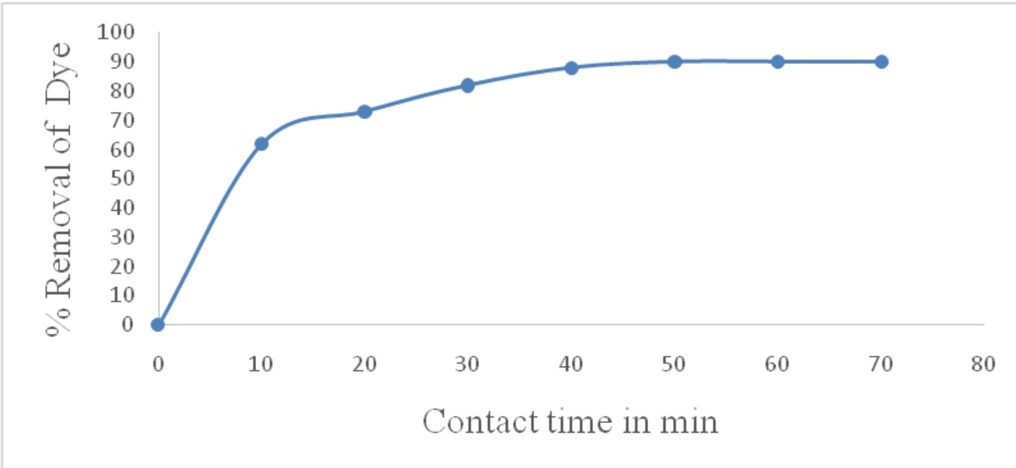

Figure 1: Effect of contact time on methylene blue removal.

Therefore, the optimum contact time for methylene adsorption onto the locally produced CPSAC was considered to be 50 min.

Effect of adsorbent dosage

The effect of adsorbent dosage was studied using 50–300mg of the locally produced activated carbon. Results as presented in Figure 2 showed that 200mg gave the optimum equilibrium adsorbent dosage for the adsorption of MB on the adsorbent, as dosage above 200mg (0.2 g) did not show further adsorption; hence the graph flattened out above 250 to 300mg.

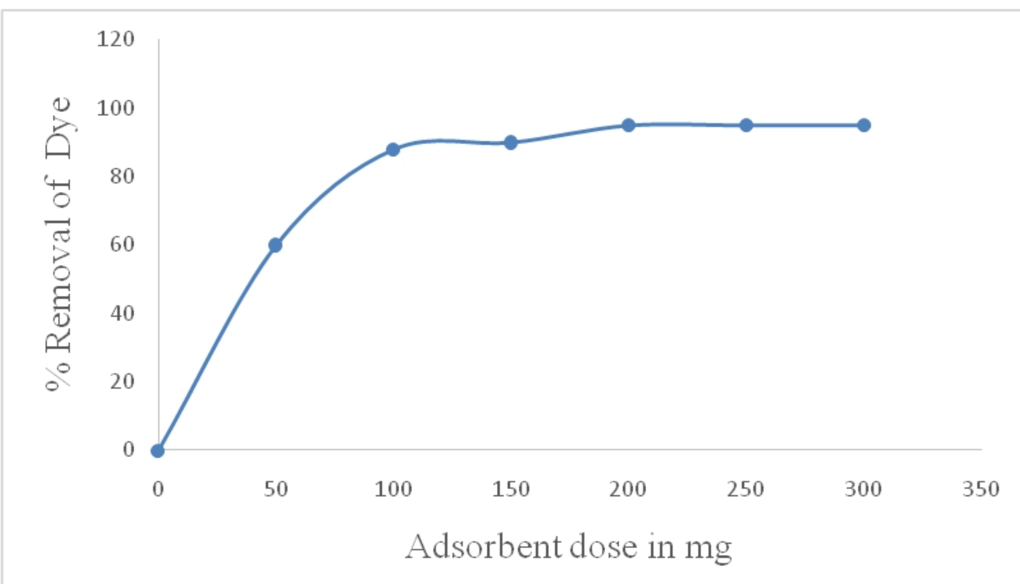

Figure 2: Effect of adsorbent (CPSAC) on methylene blue removal.

Effect of solution pH

To determine the effect of pH on the % removal of MB dye, the solution pH were varied from 2.0 to 10.0 by adding concentrated hydrochloric acid or concentrated sodium hydroxide respectively, to the stock solution. Results as shown in Figure 3 revealed that adsorption increased linearly with increasing pH, where a pH of 6.5 gave an optimum adsorption of 89%. There was decrease in adsorption at pH > 6.5. This signifies that the adsorption of MB on the locally produced activated carbon from carica papaya is found in the pH near neutral.

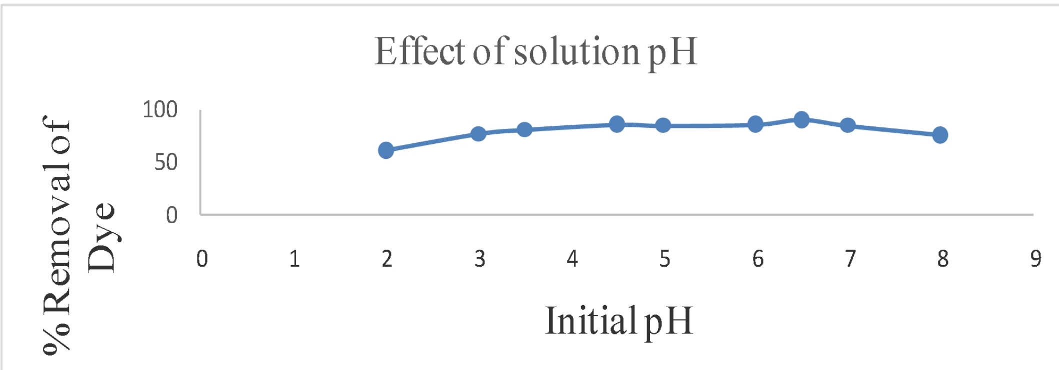

Figure 4: Effect of solution pH on adsorption of methylene blue on adsorbent (CPSAC)

Effect of temperature on adsorption

The effect of temperature ranging from 25°C – 70 °C on the removal of methylene blue from aqueous solution onto CPSAC was investigated. Results as shown in Table 1 revealed that optimum adsorption equilibrium was achieved at 60°C(320.14 mg/L), as increasing the

Table 1: Different initial adsorbate concentrations and the amount adsorbed in batches.

MB_o Conc. (mg/L)	C_e (mg/L) Equilibrium conc. of Adsorbate				q_e (mg/L) Amount of Adsorbate Adsorbed				Amount Removed (%)			
	25 °C	40°C	60°C	70°C	25°C	40°C	60°C	70°C	25°C	40°C	60°C	70°C
50	4.20	4.28	3.26	3.84	45.8	45.72	46.74	46.16	91.6	91.44	93.48	92.32
100	11.05	10.30	9.05	10.00	88.95	89.70	90.95	90.00	88.95	89.70	90.95	90.00
200	38.60	29.00	22.54	23.57	161.40	171.00	177.46	176.43	80.70	85.50	88.73	88.23
350	41.75	40.75	29.86	37.74	308.25	318.14	320.14	312.26	88.07	88.35	91..46	89.21
400	150.40	148.23	140.89	145.55	249.6	251.77	259.11	254.45	62.40	62.94	64.77	63.61

temperature above 70°C showed decrease in adsorption process (312.26 mg/L) when an initial concentration (350 mg/L) of MB was used. However, the initial increase in temperatures facilitates increase in adsorption due to enhanced mobility of molecules, as kinetic energy increased mobility of the MB molecules onto the pores of the adsorbent. As at when saturation of the pores was achieved at 60°C, increasing the temperature above 60°C was of negative effect, which could be due to desorption. Thus the optimum temperature for MB removal onto CPSAC was determined to be 60 °C using 350 mg/L of MB and 200mg of adsorbent, where the highest percentage removal was 91.46 %.

Kinetics of Adsorption

The pseudo-first-order kinetic model is widely used in adsorption process until equilibrium is attained (Idibie and Iyuke, 2008). The applicability of the pseudo-first order was tested fit for the adsorption of MB onto the locally produced CPSACas depicted in Figure 5, as the linear regression correlation coefficient, R^2value obtained was 0.992.

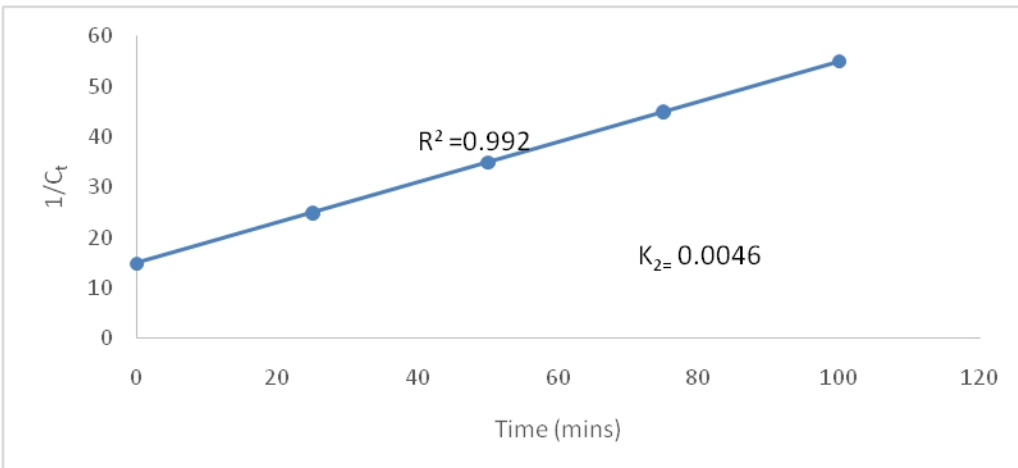

Figure 5: Pseudo first order model for the methylene blue adsorption on CPSAC.

Surface Morphological Studies

The Scanning Electron Microscope (SEM) study of the locally produced activated carbon from the seed of carica papaya before and after adsorption is shown in both Figure 6 & 7. The scanned (Figure 6) showed a porous carbonaceous solid with irregular pore sizes, which accommodated the molecules of the MB on contact. Figure 7, showed less of the activated carbon, as less of the white appearing solid surfaces were reduced significantly after adsorption, indicating that the adsorption of MB on the locally produced carbon is a physisorption.

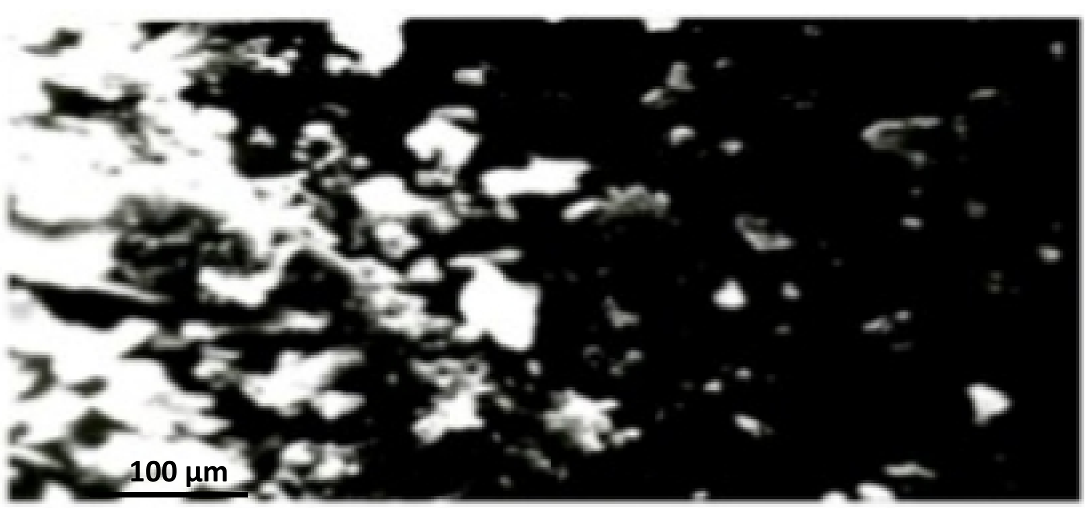

Figure 6: SEM image showing the morphology of the locally produced CPSAC before adsorption.

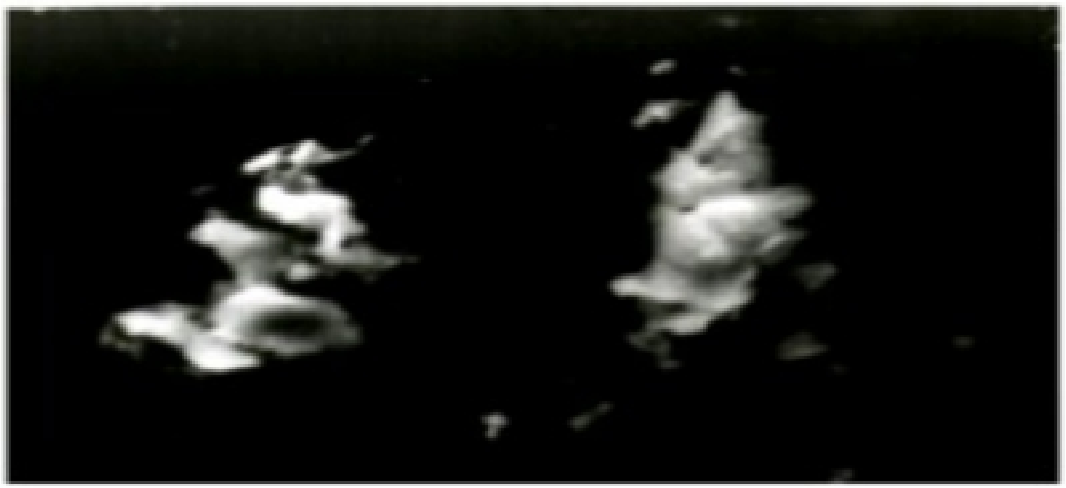

Figure 7: SEM image showing the morphology of the locally produced CPSAC after adsorption

Conclusion

Study of the process optimization of methylene blue removal from aqueous solution using a locally produced activated carbon from the seeds of carica papaya showed that process parameters that favoured the optimum adsorption of methylene blue were the optimum time of 50mins, optimum adsorbent dose of 200mg, optimum pH of 6.5 and an optimum temperature of 60^{o}C,which achieved an optimum equilibrium adsorption of 320.14 mg/L of methylene blue from an initial methylene blue concentration of 350 mg/L.In overall, the optimum process was able to achieve a percentage removal of 91.46 %. The kinetics study showed that the adsorption process obeyed the pseudo first order model.

References

Adewumi I.K. (2009). Activated Carbon for Water Treatment in Nigeria: Problems and Prospects. In: Yanful E.K. (eds) Appropriate Technologies for Environmental Protection in the Developing World, 2:112-121. Springer, Dordrecht.

Bhatnagar, A., Hogland W., Marques, M. and Sillanpää, M., (2013). An overview of the modification methods of activated carbon for its water treatment applications. Chem. Eng. J., 219:499–511.

El-khaiary, M.I., Gad, F.A. and Mahmoud, M.S., (2009). Adsorption of methylene blue from aqueous solution by chemically treated water hyacinth, Toxicol. Env. Chem., 91: 1079–1094.

Gopinath, A., and Kadirvelu, K., (2018). Strategies to design modified activated carbon fibres for the decontamination of water and air. Env. Chem. Lett., 16:1137–1168.

Idibie, C. A and Iyuke,S. E., (2008). Thermodynmic study of linamarin sorption during its isolation from cassava. Colloid and Surfaces A: Physicochm and Eng. Aspects., 326:18 – 22.

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 Pigs., 51:25 – 40.

Kosheleva, R.I., Mitropoulos A.C., and Kyzas, G. Z., (2019). Synthesis of activated carbon from food waste. Env. Chem. Lett., 17:429–438.

Rafatullah M., Sulaiman. O., Hashim, R. and Ahmad A., (2010). Adsorption of ethylene blue on low-cost adsorbents: A rev. J. Hazard. Mater., 177:70–80.

Webar, C.T., Foletto, E.L and Meili, L., (2013). Removal of tannery dye from aqueous solution using papaya seed as an effluent natural biosorbent. Wat. Air Soil Poll. 224:1-8.

Yang, B., Xue, N., Zhou, L., Li, F., Cong, X., Han, B., Li, H., Yan, Y., and Liu, B. (2012). Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. *Ecotoxicity and Environmental Safety,* 84:304-310.