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Research Article
Adsorption of Aniline Blue from Aqueous Solution Using *Litchi chinensis* Peel: Kinetic and Equilibrium Studies

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Abstract
Background and Objective: Residual dyes from textiles are a growing threat to aquatic ecosystem. This study aims to describe the removal of aniline blue from aqueous matrices using *Litchi chinensis* peel as an eco-friendly adsorbent. **Materials and Methods:** The *Litchi chinensis* peels were finally grounded to powder and sieved for uniform particle size 60 µm. The obtained adsorbent was been characterized by SEM and FTIR studies. The batch adsorption parameters such as pH, adsorbent dose, Initial concentration, contact time, adsorption kinetics and isotherm were observed in this study. **Results:** Obtained data suggest that the pseudo second order model fitted the adsorption data than the Lagergren first order model. The observed data were analyzed by well known isotherms like Freundlich, Langmuir, Dubinin-Radushkevich adsorption isotherm model. **Conclusion:** The results showed that The Langmuir adsorption capacity was found to be 5.2 mg g^{-1} and *Litchi chinensis* peel has the ability to remove the dye from aqueous solution.

Key words: Aniline blue, isotherm, pseudo-second order, freundlich

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Many countries use a variety of dyes in their industries like printing, textile, paper, cosmetics, rubber, plastics and dyestuff for coloration of the products[1]. The residual dyes from textile and printing industries are considered a wide variety of organic pollutants entering into the water resources[2]. The colored effluents from the above sources, on mixing with surface and ground water system, also pollute the drinking water. Color is a visible pollutant, the water contaminated with dyes is not only unfit for drinking purpose, but is also not suitable for agriculture due to its inhibitory action on photosynthetic process in plants. In textile industries, treatment of effluents is one of the most important economic problems. Dyes are highly toxic to some organisms and hence it affects the ecosystem[3]. Dyes are harmful to aquatic life in rivers where they are discharged[4]. Furthermore dyes can also cause severe damage to human beings such as malfunction of kidney, reproductive system, liver, brain and central nervous system[5].

As per ETAD (Ecological and Toxicological Association of Dyes) risk paused by any chemical substance on human health is a function of toxicity and exposure. Humans are exposed to dyes through 4 different channels inhalation, dermal exposure, ingestion and eye contact. The health effects caused are mainly due to inhalation and ingestion. Aniline Blue, an organic dye has been an important dye discharging into the water stream. Ingestion of aniline blue results in some adverse reactions in certain organs of the human[6]; contact with external organs like eyes results in severe irritation[7] while inhalation gives rise to difficulty in breathing[8].

Various wastewater treatment methods including, coagulation-flocculation, biodegradation, ion exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods, have been adopted for the removal of dye contents from various wastewater effluent[9,10]. But these methods are unsuccessful sometime for the removal of dyes due to high operational cost and sludge disposal problem[3]. When compared to this, adsorption technique is most efficient and economical process to remove dyes from the adsorbent and also it can control the biochemical oxygen demand. Different biosorbents are teak tree bark[11], sunflower seed husk[12], peanut hull[13], banana peel[14], wheat straw[15], guava leaf powder[16], *Dolichos lablab* peel[3], respectively.

The objectives of the study are:

- To use *Litchi chinensis* peels and to assess the efficiency of the adsorbent produced for the removal of the aniline blue from aqueous solution
- To analyze the equilibrium uptake capacity of the adsorption process from various isotherm models like Langmuir[17], Freundlich[18] and Dubinin and Radushkevich[19]

MATERIALS AND METHODS

Preparation of adsorbent: The *Litchi chinensis* peels were obtained from the market of Kadapa. This peel was cut into smaller size and then it was dried in a hot air oven and was crushed by using crusher or grinder to obtain uniform powder form. The powder was sieved for uniform particle size of 60 µm. The work was carried out during the period December, 2018 to March, 2019.

Preparation of dye solutions: Stock solutions were prepared by dissolving 1 g of the aniline blue dye in 1 L of double distilled water and made up to 1000 mL. The solutions were stored in brown glass bottles to avoid degradation of light. Absorbance measurements were carried out using LabIndia UV-Vis spectrophotometer. The maximum absorbance of dye was used as monitoring wavelength (580 nm).

Adsorbate: In this study, the dye aniline blue was selected as an adsorbate, supplied by Hi-Media (Fig. 1). Aniline blue is basically a cationic dye. The molecular formula of this cationic dye is $C_{37}H_{27}N_3Na_2O_9S_3$ with a molecular weight of 799.8 g mol^{-1}. It is a derivative of an anionic sulfonate triphenylmethane dye.

The adsorption kinetics is desirable as it describes information about the rate of adsorption, which is important for efficiency of the process. Adsorption kinetics can be modeled using Lagergren[20] first order and second order[21].

The lagergren[20] first order model can be represented as:

$$\text{Log}\ (q_e\text{-}q) = \log q_{e\text{-}}k_1 t/2.303 \qquad (1)$$

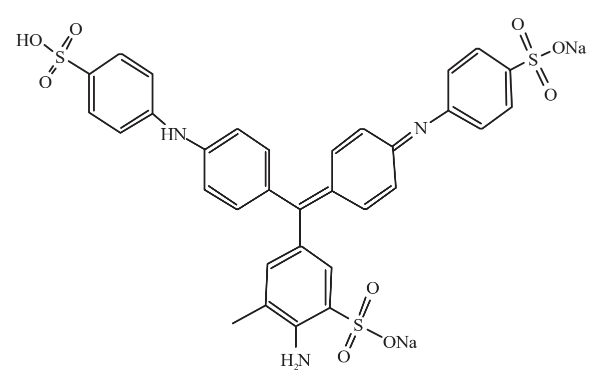

Fig. 1: Structure of aniline blue

where, q_e and q are the amounts of aniline blue adsorbed (mg g^{-1}) at equilibrium and at time t, respectively and k_1 is the rate constant of first order adsorption (1 min). Values of q_e and k_1 were calculated from the slope and intercept of the plot of log (q_e-q) vs. t for different concentrations of aniline blue.

The second order kinetic model is represented as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

The Langmuir[17] isotherm can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

where, C_e is the equilibrium concentration (mg adsorbate/L of solution) and q_e is the amount adsorbed (mg adsorbate/g of adsorbent) at equilibrium. Langmuir[17] isotherms were obtained by agitating the fixed adsorbent dose and different concentrations of aniline blue for a contact time greater than the equilibrium time. The constant Q_o signifies the monolayer adsorption capacity (mg g^{-1}) and b is related to the energy of adsorption (mg L^{-1}).

Freundlich isotherm: The Freundlich[18] isotherm is an empirical equation employed to describe heterogeneous surface systems. It is common model used in wastewater studies, which relates the residual impurity in solution at equilibrium to the amount adsorbed as follows:

$$\text{Log } q_e = \log k_f + 1/n \log C_e \quad (4)$$

where, k_f denotes approximate adsorption capacity and n is related to intensity of adsorption.

Dubinin-radushkevich isotherm: Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich[19]:

$$q_e = q_m \exp(-B\varepsilon^2) \quad (5)$$

where, q_m is D-R constant and ε can be correlated as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), C_e is the equilibrium concentration of adsorbate in solution (mol L^{-1}) and T (K) is the absolute temperature:

$$E = \frac{1}{\sqrt{2B}}$$

RESULTS AND DISCUSSION

Batch mode adsorption studies of aniline blue: Laboratory batch mode studies were conducted with powered peel of *Litchi chinensis* for the aniline blue. Parameters, that influence the adsorption process are contact time, adsorbent dose and pH on uptake, were investigated. Langmuir[17], Freundlich[18] and Dubinin and Radushkevich[19] isotherm equations were used to calculate the adsorption parameters. Results of the kinetic studies were analyzed using first and second order models with respect to aniline blue concentration.

Effect of agitation time and concentration on adsorption of aniline blue: The effect of agitation time on the adsorption of aniline blue onto the adsorbent was studied and the equilibrium time increased with the increase in the initial dye concentration (Table 1). The uptake of aniline blue at equilibrium (q_e) was 0.680 mg g^{-1} at 32°C for an initial dye concentration of 10 mg L^{-1}. At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of aniline blue uptake (q)/unit weight of adsorbent (mg g^{-1}). It is seen that for low initial concentrations, the percent uptake of aniline blue was relatively high. Similar study has been reported for the adsorption of activated carbon prepared from *Delonix regia* pod[22].

Table 1: Comparison of first order and second order model for adsorption of aniline blue

Initial concentration (mg L^{-1})	q_e (exp) (mg g^{-1})	First order kinetics			Second order kinetics		
		k_1 (1/min)	q_e (cal) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (cal) (mg g^{-1})	R^2
10	0.68	0.193	0.265	0.9	0.594	0.787	0.999
20	1.537	0.101	0.147	0.815	1.515	1.55	0.999
30	2.034	0.172	1.116	0.751	0.18	2.00	0.995
40	2.668	0.062	1.088	0.883	0.124	2.739	0.998

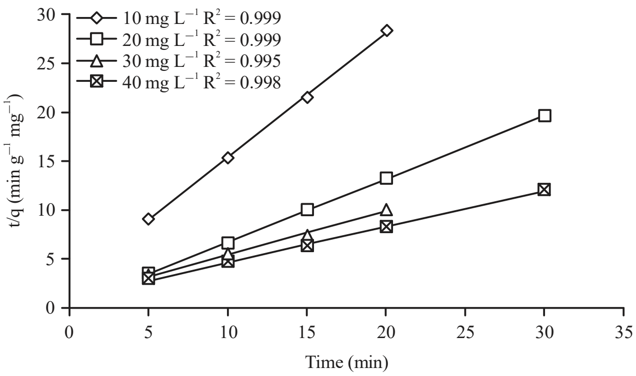

Fig. 2: Second order kinetics for adsorption of aniline blue

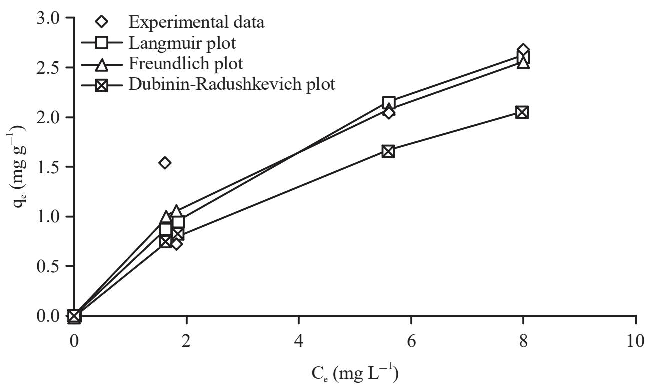

Fig. 3: Adsorption isotherms of aniline blue

Table 2: Adsorption isotherm constants for adsorption of aniline blue

Langmuir[17]		Freundlich[18]		
Q_0 (mg g^{-1})	b (mg L^{-1})	k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	n	R^2
5.2	0.124	0.759	1.718	0.621

Adsorption kinetics: The values of q_e and K_2 were calculated from the intercept and slope of the plots t/q vs. t (Fig. 2). The results of the kinetic fitting data to the first and second order model are presented in Table 1. There was a good fitting between the experimental q_e values and the calculated q_e values from second order equation for the aniline blue by adsorbent. This indicates that the adsorption process of the aniline blue follows second order kinetic model. The regression coefficients for the linear plots from the second order equations are also good. Similar phenomenon has been observed in the adsorption of aniline blue onto activated carbon prepared from *Delonix regia* pod[22], by *Zizyphus oenoplia* seeds[1], onto magnetically modified activated sludge[23].

Effect of adsorbent dosage on removal of aniline blue: Adsorption experiments were set up with various amounts of powdered *Litchi chinensis* (100, 200, 300, 400, 500 and 600 mg/50 mL) and aniline blue concentration (10 and 20 mg L^{-1}). The percent removal of aniline blue increased with the increase in adsorbent dose and reached a constant value after a particular adsorbent dose. A larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more surface area of the adsorbent, maximum removal of aniline blue were found to be around 83.63% for the adsorbent for the initial concentration of 10 mg L^{-1}. Similar results have been reported for the adsorption of aniline blue onto *Zizyphus oenoplia* seeds[1], by activated carbon prepared from *Delonix regia* pod[22].

Adsorption isotherms: The relationship between the solution concentration and the species uptake can be described and the equilibrium data are evaluated using Langmuir[17], Freundlich[18] and Dubinin and Radushkevich[19] isotherms.

Langmuir isotherm: Langmuir[17] isotherm is based on a homogenous surface of the adsorption, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms on its surface. Langmuir[17] equation was found to give the best data correlation despite its normal applicability to homogenous equal energy site adsorption.

Plot of aniline blue dye adsorbed at equilibrium q_e vs. equilibrium dye concentration C_e showed an agreement of experimental data with Langmuir[17] plots (Fig. 3). Values of Q_o and b are presented in Table 2. At room temperature 32°C, the observed Q_o value, an index of adsorption efficiency of the adsorbate (dye) on the adsorbent was found to be 5.2 mg g^{-1}. The adsorption capacity of aniline blue onto miswak was found[24] to be 0.37 mmol g^{-1}. The monolayer adsorption capacity depends on the particle size, surface groups and pore distribution of the adsorbent.

Effect of pH on removal of aniline blue: The pH was studied in the range 2-10 for the initial dye concentration of 30 and 40 mg L^{-1} and the percent removal decreased from 85.9-77.8% for 40 mg L^{-1} of aniline blue concentration for *Litchi chinensis*. From the various pH values, the pH value 2 shows the higher percentage removal of aniline blue dye as compared to other pH values (Fig. 4). In acidic medium, the number of H^+ ions would be large and they are likely to neutralize some of the anionic functional groups present on the surface of the adsorbent. This is in accord to the report of several authors for the adsorption of aniline blue onto *Dolichos lablab* peel[3], using A-site doped perovskite[2].

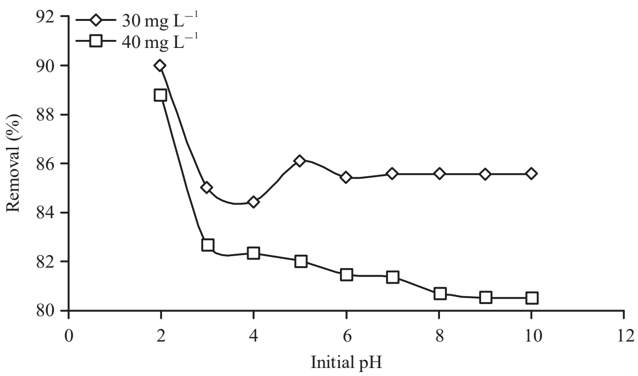

Fig. 4: Effect of pH on adsorption of aniline blue

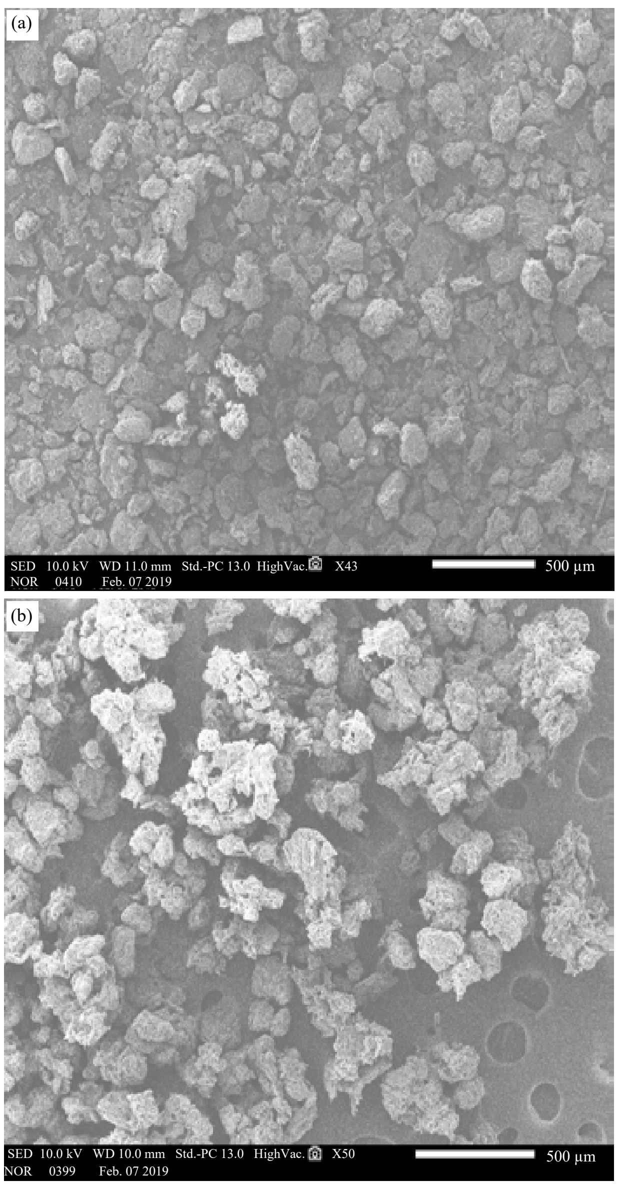

Fig. 5(a-b): SEM image for *Litchi chinensis* peel powder, (a) Before and (b) After aniline blue adsorption

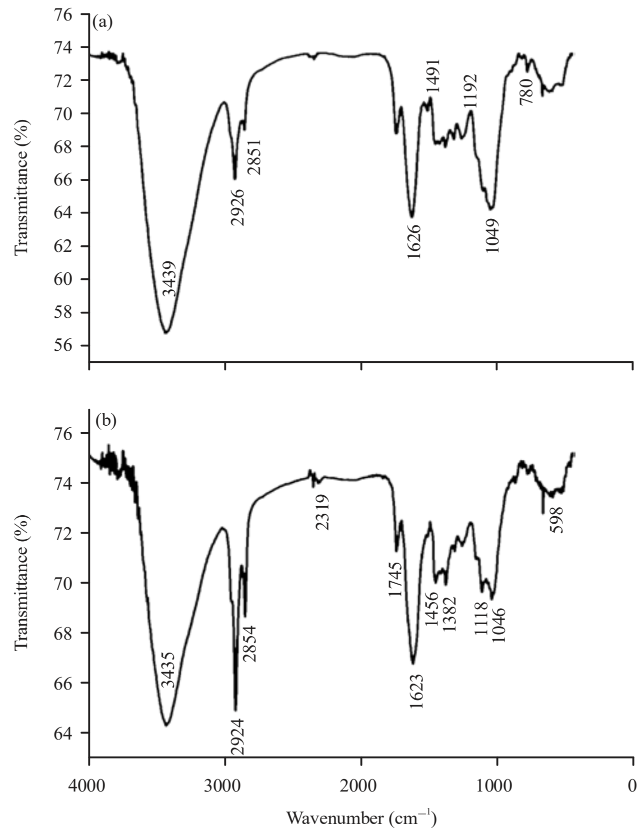

Fig. 6(a-b): FTIR spectra of *Litchi chinensis* peel powder, (a) Before and (b) After aniline blue adsorption

Adsorption mechanism: At pH lower than the pHzpc (7.0), the surfaces of the *Litchi chinensis* peel are positively charged. Therefore the aniline blue molecules are adsorbed due to electrostatic interaction with the positively charged surface of the *Litchi chinensis* peel in acidic medium (2.0). The adsorption mechanism is probably a 2 step mechanism involving the adsorption of the hydrogen ion from solution onto the adsorbent surface followed by electrostatic attraction between the positive surface and the anionic adsorbate[24].

Characteristics of the adsorbent: The pHzpc of the adsorbent was recorded as 7.0. SEM images show that *Litchi chinensis* peel powder possesses a rough surface morphology with some pores. The surface morphology of aniline blue loaded adsorbent shows that the surface of the adsorbent is covered with dye molecules (Fig. 5).

FTIR analysis: The FTIR spectra of *Litchi chinensis* peel powder showed that there were various functional groups detected onto the surface of the adsorbent (Fig. 6). The strong and broad peak at 3439 and 3435 cm^{-1} indicates the presence of OH group. There is the appearance of new peaks in the position of 2319, 1745, 1382 and 1118 cm^{-1}, respectively in dye loaded adsorbent. Shift in the peaks are also detected in the dye loaded and unloaded adsorbent (Fig. 3).

CONCLUSION

The percent of dye removal increases exponentially with an increase in the adsorbent dose. The SEM images showed fully covered pores in the after adsorption of aniline blue dye molecule which supports the adsorption process. It was observed that Freundlich isotherm model described well for the adsorption of aniline blue and the kinetic study revealed that the adsorption process followed the pseudo-second order kinetics. The maximum removal of aniline blue was recorded at pH 2.0. From this work we can conclude that *Litchi chinensis* peel has the ability to remove the dye from aqueous solution.

SIGNIFICANCE STATEMENT

Aniline blue is widely used in many industries like textile, leather, paper etc. which is very harmful upon contact may cause irritation. Toxic by ingestion causing hemoglobinemia. *Litchi chinensis* peel is an eco-friendly adsorbent and it has been characterized by SEM and FTIR studies. This study has optimized the effective pH of 2.0 that can be used for the removal from aqueous solutions. Further this study will help the researchers to explore and enhance the adsorption capacity of the adsorbent by investigating on other parameters like temperature and surface modification studies.

REFERENCES

1. Kumar, M., G. Elangovan, R. Tamolarasan, G. Vijayakumar, P.C. Mukeshkumar and S. Sendhilnathan, 2015. Biosorption of aniline blue from aqueous solution using a novel biosorbent *Zizyphus oenoplia* seeds: Modeling studies. Pol. J. Chem. Technol., 17: 70-77.
2. Labib, A.A., A.E.R. Mahmoud, M.E. Abdunnaser, N.A. Mohamed and W.A. Makholf, 2018. Removal of aniline blue from aqueous solutions using Ce_{1-x} Bi_x CrO_3 (x = 0, 0.5,1). Open J. Inorganic Non-Metallic Mater., 8: 1-10.
3. Pandiaraj, N. and K. Ananthakumar, 2017. Dolichos lablab peel powder: A novel and economical adsorbent for removal of aniline blue from aqueous solution. Asian J. Chem., 29: 563-567.
4. Gurses, A., C. Dogar, M. Yalcin, M. Acikyildiz, R. Bayrak and S. Karaca, 2006. The adsorption kinetics of the cationic dye, methylene blue, onto clay. J. Hazard. Mater., B131: 217-228.
5. Cazetta, A.L., A.M.M. Vargas, E.M. Nogami, M.H. Kunita and M.R. Guilherme *et al*., 2011. NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption. Chem. Eng. J., 174: 117-125.
6. Kurniawan, T.A., G.Y. Chan, W.H. Lo and S. Babel, 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci. Total Environ., 366: 409-426.
7. Otero, M., F. Rozada, L.F. Calvo, A.I. Garcia and A. Moran, 2003. Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges. Biochem. Eng. J., 15: 59-68.
8. Yasin, Y., M.Z. Hussein and F.H. Ahmad, 2007. Adsorption of methylene blue onto treated activated carbon. Malays. J. Anal. Sci., 11: 400-406.
9. Blackburn, R.S., 2004. Natural polysaccharides and their interactions with dye molecules: Applications in effluent treatment. Environ. Sci. Technol., 38: 4905-4909.
10. Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioresour. Technol., 97: 1061-1085.
11. Patil, S., S. Renukdas and N. Patil, 2011. Removal of aniline blue, a basic dye from aqueous solution by ad-sorption using teak tree (*Tectona grandis*) bark powder. Int. J. Environ. Sci., 1: 711-725.
12. Ong, S.T., P.S. Keng, S.L. Lee, M.H. Leong and Y.T. Hung, 2010. Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*). Int. J. Phys. Sci., 5: 1270-1276.
13. Gong, R., S. Zhu, D. Zhang, J. Chen, S. Ni and R. Guan, 2008. Adsorption behavior of cationic dyes on citric acid esterifying wheat straw: Kinetic and thermodynamic profile. Desalination, 230: 220-228.
14. Annadurai, G., R.S. Juang and D.J. Lee, 2002. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J. Hazard. Mater., 92: 263-274.
15. Gong, R., M. Li, C. Yang, Y. Sun and J. Chen, 2005. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. J. Hazard. Mater., 121: 247-250.
16. Ponnusami, V., R. Madhuram, V. Krithika and S.N. Srivastava, 2008. Effects of process variables on kinetics of methylene blue sorption onto untreated guava (*Psidium guajava*) leaf powder: Statistical analysis. Chem. Eng. J., 140: 609-613.
17. Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403.
18. Freundlich, H.M.F., 1906. Over the adsorption in solution. J. Phys. Chem., 57: 385-470.
19. Dubinin, M.M. and L.V. Radushkevich, 1947. Equation of the characteristic curve of activated charcoal. Proc. Acad. Sci. Phys. Chem. Sect., 55: 331-333.

20. Lagergren, S., 1898. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar, 24: 1-39.
21. Ho, Y.S. and G. McKay, 1998. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Process Saf. Environ. Protect., 76: 332-340.
22. Adebisi, S.A., O.S. Amuda, A.L. Adejumo, A.O. Olayiwola and A.G. Farombi, 2015. Equilibrium, kinetic and thermodynamics studies of adsorption of aniline blue from aqueous media using steam-activated carbon prepared from *Delonix regia* pod. J. Water Resour. Prot., 7: 1221-1233.
23. Maderova, Z., E. Baldikova, K. Pospiskova, I. Safarik and M. Safarikova, 2016. Removal of dyes by adsorption on magnetically modified activated sludge. Int. J. Environ. Sci. Technol., 13: 1653-1664.
24. Moawed, E.A., 2013. Effect of heating processes on *Salvadora persica* (Miswak) and its application for removal and determination of aniline blue from wastewater. J. Taibah Univ. Sci., 7: 26-34.