Poll Res. 36 (3) : 445-450 (2017)

ISSN 0257–8050

REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTIONS USING PINE SHELL ASH

MEHDI SAEIDI[1], HAMED BIGLARI[2,*], MARZIEH SOLEIMANI[3], MOHAMMAD MEHDI BANESHI[4], MOHAMMAD MOBINI[5], GHOLAMREZA EBRAHIMZADEH[6], EHSAN ABOUEE MEHRIZI[7] AND MOHAMMAD REZA NAROOIE[8]

[1]Department of Environmental Health Engineering, School of Health, Torbat Heydariyeh University of Medical Sciences, Torbat Heydariyeh, Iran.
[2]Department of Environmental Health Engineering, School of Public Health, Gonabad University of Medical Sciences, Gonabad, Iran.
[3]Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran.
[4]Social Determinants of Health Research Center, Yasuj University of Medical Sciences, Yasuj, Iran.
[5]Department of Environmental Health Engineering, School of Health, Rafsanjan University of Medical Sciences, Rafsanjan, Iran.
[6] Department of Environmental Health Engineering, School of Public Health, Zabol University of Medical Sciences,Zabol, Iran.
[7]Department of Environmental Health Engineering, Faculty of Public Health, North Khorasan University of Medical sciences, Bojnurd, Iran.
[8]Department of Environmental Health Engineering, School of Public Health, Iranshahr University of MedicalSciences, Iranshahr, Iran.

(Received 1 February, 2017; accepted 30 July, 2017)

ABSTRACT

Wastewater treatment and removal of dyes has always been considered as an important measure for the control of pollution originated from industrial wastes especially that of textile and dying industries. The objective of the present study was to evaluate the potential of ash prepared from pine shell as a natural adsorbent to remove methylene blue dye from aqueous solutions in lab conditions. The effect of variables such as pH (3-13), contact time (30-180), adsorbent dose (0.55 g/L) and methylene blue initial concentration on the efficiency of removal of dye from a synthetic wastewater was investigated. The greatest removal efficiency was 92.75% that was achieved at pH of 9, 120 min contact time, adsorbent dose of 3 g/L and dye initial concentration of 100 mg/L. Removal efficiency of over 90% indicates that pine shell ash can be considered as a natural, effective and low-cost adsorbent for the removal of methylene blue dye and wastewater treatment. Therefore, this technique is recommended to eliminate colored pollutants from aqueous environments.

KEY WORDS: Pine shell, Methylene blue, Aqueous environments, Adsorption

INTRODUCTION

Textile is one of the largest water consuming and water body polluter industries that produce colored wastewater with different quantitative and qualitative chemical properties containing substantial amount of colored substances (Saeidi *et al.,* 2017; Biglari *et al.,* 2016c). Textile dyes are the largest class of artificial water soluble colors possessing the biggest variation regarding color type and structure. Increased global production and application of colors has led to the production of highly polluted wastewaters and increased environmental concerns (Garg *et al.,* 2003,

Corresponding author's email: Hamed.biglari@gmail.com

Masombaigi *et al.,* 2009; Biglari *et al.,* 2016b, Biglari, 2016; Ahamadabadi *et al.,* 2016). Most substances present in wastewaters are toxic and have carcinogenic property (Mirzabeygi *et al.,* 2016; Liu *et al.,* 2010; Bazrafshan *et al.,* 2012b; Bazrafshan *et al.,* 2012a; Mohammadi *et al.,* 2015; Biglari *et al.,* 2016a). Various industries like textile, paper, color printing, pharmacy, food, cosmetic, and electric industries use these dyes (Song *et al.,* 2011; Biglari *et al.,* 2017). Some wastewater treatment methods in these industries include biologic treatment, coagulation, adsorption, oxidation, and filtration (Liu *et al.,* 2012; Ponnusami *et al.,* 2010; Samiey and Ashoori, 2012; Unuabonah *et al.,* 2009; Vargas *et al.,* 2011; Alipour *et al.,* 2014; Sajjadi *et al.,* 2016). Among these methods, the adsorption appears to be the most effective one to remove dyes from wastewater of these industries due to its high potential in removal of dyes and organic substances (Rafatullah *et al.,* 2010; Weng *et al.,* 2009; Rahdar *et al.,* 2016). Lower sensitivity to fluctuations in wastewater flow, lack of influence of toxic chemical substances on the process, high flexibility in designation and implementation, and high efficiency of organic material removal are some of the advantages of adsorption method over other common treatment processes (Djahed *et al.,* 2016; Khaksefidi *et al.,* 2016). Several studies have been carried out to develop effective and low-cost adsorbents which have ended at the introduction of materials like sugar cane waste, corn husk, rice bran, banana waste, coconut shell, sewage sludge, and carbon raw material like coal, petroleum coke etc. (Abechi *et al.,* 2011; Doðan *et al.,* 2009; Han *et al.,* 2011; Kavitha and Namasivayam, 2007; Nasuha and Hameed, 2011). In the present study we evaluated pine shell ash as a natural low-cost adsorbent for the removal of methylene blue dye from aqueous environments.

MATERIALS AND METHODS

Methylene blue dye was used without purification and after mixed with distilled water. Other chemicals were purchased from the Merck (Germany). Following extraction, Pine shell was dried, ground and placed in oven at 600 ^{o}C for two hours to produce ash (Khaksefidi *et al.,* 2017). In order to prepare dye stock solution, 1 g methylene blue was dissolved in 1 L of distilled water and the solution was stored at 4 ^{o}C until the start of the experiment. All experiments were performed in 100 mL Erlenmeyer flask shaker set at 150 rpm (Shams *et al.,* 2016). Samples taken for determination of final dye concentration following each experiment were filtered through 0.45µm pores and the absorption of samples was read by spectrophotometer (UV/VIS model) at 665 nm wavelength (Aksu *et al.,* 2010). Sodium hydroxide and sulfuric acid 1N were used for the adjustment of pH throughout the experiment (Sohrabi *et al.,* 2016). Factors studied in the present study included initial pH (3, 5, 9, 11 and 13), adsorbent dose (0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 gr/L), contact time (30, 60, 90, 120, 150 and 180) and dye initial concentration (25, 50, 75, 100, 125 and 150 mg/L). As the first step, pH was changed in previously mentioned range to determine the optimum pH by keeping other variables constant (100 mg/L dye concentration, 1.5 g/L adsorbent dose and 60 min contact time). Subsequently, the experiment was repeated to determine the optimum condition for each of other variables (dye initial concentration, adsorbent dose or contact time) by keeping 3 other factors constant in each step.

RESULTS AND DISCUSSION

Effects of pH

Results of optimum pH determination experiment are presented in diagram 1. At constant 100 mg/L of dye concentration and 1.5 g/L of adsorbent dose, the efficiency of dye removal increased from 72.25 to 88.32% by changing pH from 3 to 13 with insignificant difference between values obtained at pH of 9 and 13 (86.22 and 88.32%, respectively). Since adjusting pH at higher values (Abechi et al., 2011), involves consumption of additional sodium hydroxide and increased cost of the process, pH of 9 was considered as optimum and maintained at the next experimental steps. Findings of the experiment showed that the efficiency of removal increased with increasing pH from 3 to 13 and the highest efficiency (86.22%) was achieved at pH of 9. This can be explained by the electrostatic force between negative charges of adsorbent surface and methylene blue dye. In other word, with increasing pH, the concentration of H^{+} in the solution decreases and that of OH^{-} increases that result in elevated positive charged ions on the adsorbent surface (Del Río *et al.,* 2011, Fanchiang and Tseng, 2009). Kushwaha *et al* (2011) studied the effect of activated carbon obtained from agricultural waste on the removal of two dyes (methylene blue and green) from aqueous solutions and reported that the efficiency of removal increases at higher pH values (Kushwaha *et al.*, 2014).

The high efficiency of 96% with increasing pH up to 12 has also been reported by Pava (2008) *et al.* (Pavan *et al.*, 2008).

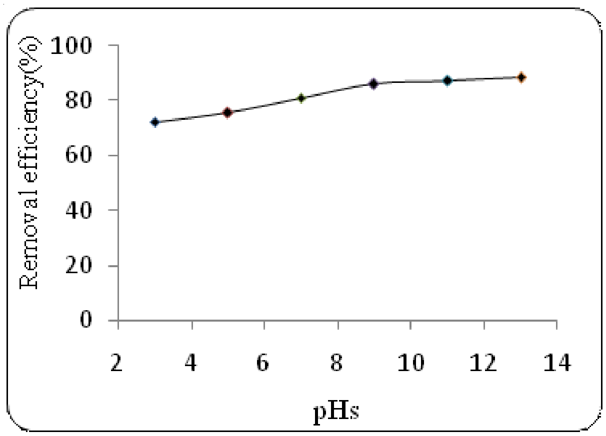

Fig. 1. The Effect of pH on the removal efficiency of MB dye (Initial concentration dye 100 mg/L, contact time 60 min, adsorbent dosage 1/5 g/L)

Effect of adsorbent dose

According to diagram 2, the efficiency of removal rises from 48.52 to 91.42% with increasing adsorbent dose from 0.5 to 5 g/L. Therefore, 3 g/L was taken as the optimum adsorbent dose which corresponded to 89.63% removal efficiency.

With increasing adsorbent dose, the efficiency of process considerably increased from 48 to 92% during the time of reaction in this study. This might be attributed to increased availability of active sites on the adsorbent surface for the adsorbent-dye interaction that leads to decreased adsorption capacity of pine shell ash (Mahmoud *et al.*, 2013).

This effect has also been reported by Gong *et al.* (2005) who used peanut hull powder to remove cationic dye form a synthetic wastewater (Gong *et al.*, 2005).

Effect of contact time

Results indicated that with the progress of contact time the amount of dye remaining in the solution decreased with the highest removal efficiency of 95.11% at 120 minutes above which the efficiency remained constant. Contact time is an effective parameter in assessing the efficiency of the process and we observed that dye residual concentration in solution decreases and the removal efficiency increased with increased time of contact.

The amount of methylene blue removed from aqueous solution was the highest at less than two hours above which the efficiency of the process remained relatively constant that may be indicative of an equilibrium state due to the reduction in adsorbent active sites over time. Generally, removal efficiency increases during the time of contact and reaches a steady state at specific time after which the dye is not further removed from the solution. In this state, the amounts of adsorbed and re-adsorbed dye are in equilibrium. The finding of the current study agrees with those of others (Ponnusami *et al.*, 2007; Sohrabnezhad and Pourahmad, 2010; Gök *et al.*, 2010).

Effect of dye concentration

The effect of Methylene blue initial concentration is presented in diagram 4. It can be seen that with increasing initial concentration at constant condition of 3 g/L adsorbent dose, 120 min contact time, and

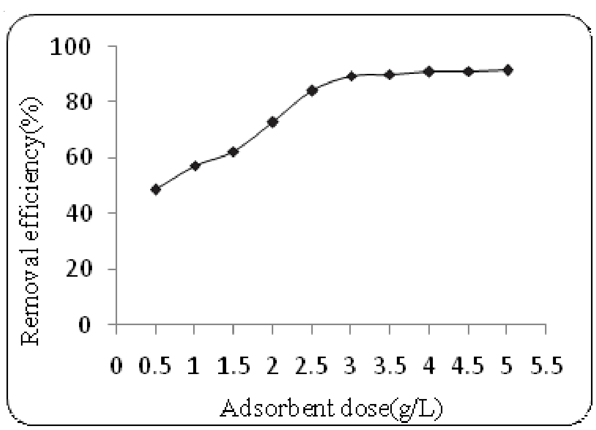

Fig. 2. The Effect of Adsorbent dose (g/L) on the removal efficiency of MB dye (Initial concentration dye 100 mg/L, contact time 60 min, pH 9)

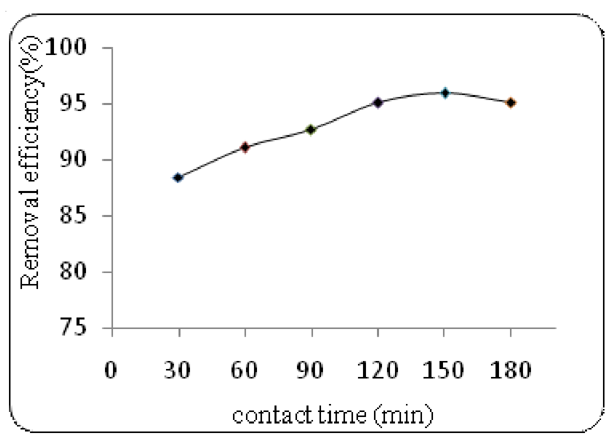

Fig 3. The Effect of contact Time (min (on the removal of efficiency of MB dye(Initial concentration dye 100 mg/L, adsorbent dosage 3 g/L, pH 9)

pH of 9, the efficiency of dye removal shows an initial increase that decreases later on. It is also observed that adsorption capacity increases with increasing dye initial concentration. There was an increasing trend in removal efficiency to 91.63% from 25 to 100 mg/L of initial concentration. However, the efficiency declines to 83.74% with further increase in initial concentration of dye in the solution. These results indicate that the amount of dye removed from the solution showed an initial increase and gradual decline later with further increases in initial concentration. At constant condition (regarding adsorbent dose and contact time), with increasing initial concentration from 25 to 100 mg/L, there is an initial increase in removal rate while with further increases in initial dye concentration, the efficiency of process declines. This might be due to the fact that at lower dye concentrations, dye molecules occupy rapidly the adsorbent surface and, with increased dye initial concentration, lead to early saturation of adsorbent surface or to increased repulsion force between dye molecules and thus decreased adsorption rate (Kushwaha *et al.*, 2014; Gulnaz *et al.*, 2011). In a study by Entezari *et al* (2008) on the rapid and effective elimination of reactive black 5 by combination of ultrasound and adsorption methods, decreased efficiency of elimination with increased dye concentration was attributed to the limited adsorption sites on unit of adsorbent surface area (Entezari *et al.,* 2008). In another study, Khattri *et al* (2009) showed that the adsorption efficiency of malachite green onto sawdust decreases with increasing dye concentration (Khattri and Singh, 2009).

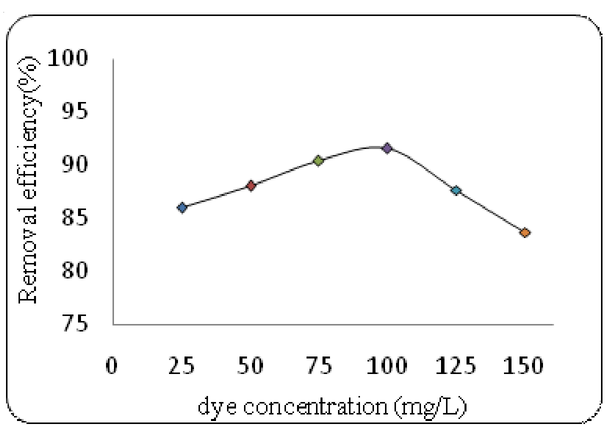

Fig 4. The Effect of initial concentration dye (mg/L) on the removal of efficiency of MB dye(contact time 120 min, adsorbent dosage 3 g/L, pH 9)

CONCLUSION

The present study showed that ash prepared from pine shell can be an effective adsorbent for the removal of methylene blue dye from textile industry wastewater. The optimum adsorbent dose of 3 g/L ash was determined at pH of 9, 100 mg/L dye concentration and 120 minutes of contact time that yielded the removal efficiency of 93.25%. In this study, the efficiency of removal was associated positively with adsorbent dose, contact time and pH and negatively with dye concentration. Overall, it can be concluded that ash obtained from pine shell can be used as natural low cost adsorbent for the removal of methylene blue dye from textile industry wastewater.

ACKNOWLEDGEMENTS

This research was partially funded by the Gonabad University of Medical Science with grant number of 96/18. (Gonabad, Iran). The authors gratefully acknowledge the Student Research Committee (Deputy of Research and Technology, Gonabad University of Medical Sciences) for financial support and also the respectable personnel of the department of Environmental Health Engineering for logistical and technical support Gonabad. Also the Authors thank the environmental health lab staffs for sampling assistance.

REFERENCES

Abechi, E., Gimba, C., Uzairu, A. and Kagbu, J. 2011. Kinetics of adsorption of methylene blue onto activated carbon prepared from palm kernel shell. *Archives of Applied Science Research.* 3 : 154-164.

Ahamadabadi, M., Saeidi, M., Rahdar, S., Narooie, M. R., Salimi, A., Alipour, V., Khaksefidi, R., Baneshi, M. M. and Biglari, H. 2016. Assessment of the chemical quality of groundwater resources in Chabahaar City using GIS software in 2016. *Research Journal of Applied Sciences.* 11 : 1399-1403.

Aksu, Z., Ertuðrul, S. and Dönmez, G. 2010. Methylene Blue biosorption by Rhizopusarrhizus: Effect of SDS (sodium dodecylsulfate) surfactant on biosorption properties. *Chemical Engineering Journal.* 158 : 474-481.

Alipour, V., Nasseri, S., Nodehi, R. N., Mahvi, A. H. and Rashidi, A. 2014. Preparation and application of oyster shell supported zero valent nano scale iron for removal of natural organic matter from aqueous solutions. *Journal of Environmental Health Science* *and Engineering.* 12 : 1.

Bazrafshan, E., Biglari, H. and Mahvi, A. H. 2012a. Humic acid removal from aqueous environments by electrocoagulation process using iron electrodes. *Journal of Chemistry.* 9 : 2453-2461.

Bazrafshan, E., Biglari, H. and Mahvi, A. H. 2012b. Phenol removal by electrocoagulation process from aqueous solutions. *Fresenius Environmental Bulletin.* 21 : 364-371.

Biglari, H., Afsharnia, M., Alipour, V., Khosravi, R., Sharafi, K. and Mahvi, A. H. 2017. A review and investigation of the effect of nanophotocatalytic ozonation process for phenolic compound removal from real effluent of pulp and paper industry. *Environmental Science and Pollution Research.* 24 : 4105-4116.

Biglari, H., Chavoshani, A., Javan, N. and Hossein Mahvi, A. 2016a. Geochemical study of groundwater conditions with special emphasis on fluoride concentration, Iran. *Desalination and Water Treatment.* 1-8.

Biglari, H., Saeidi, M., Alipour, V., Rahdar, S., Sohrabi, Y., Khaksefidi, R. and AL., E. 2016b. Prospect of disinfection byproducts in water resources of Zabol. *International Journal of Pharmacy and Technology.* 8 : 17856-65.

Biglari, H., Saeidi, M., Alipour, V., Rahdar, S., Sohrabi, Y., Khaksefidi, R., Narooie, M. R., Zarei, A. & Ahamadabadi, M. 2016c. Review on hydrochemical and health effects of it in Sistan and Baluchistan groundwater's,Iran. *International Journal of Pharmacy and Technology.* 8 : 17900-17920.

Biglari, H., S. M., Alipour, V., Rahdar, S., Sohrabi, Y. and Khaksefidi, R. 2016. Review on hydrochemical and health effects of it in Sistan and Baluchistan groundwater's, Iran. *International Journal of Pharmacy and Technology.* 8 : 17900-20.

Del Río, A., Fernández, J., Molina, J., Bonastre, J. and Cases, F. 2011. Electrochemical treatment of a synthetic wastewater containing a sulphonated azo dye. Determination of naphthalenesulphonic compounds produced as main by-products. *Desalination.* 273, 428-435.

Djahed, B., Shahsavani, E., Khalili Naji, F. and Mahvi, A. H. 2016. A novel and inexpensive method for producing activated carbon from waste polyethylene terephthalate bottles and using it to remove methylene blue dye from aqueous solution. *Desalination and Water Treatment.* 57 : 9871-9880.

Dođan, M., Abak, H. and Alkan, M. 2009. Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. *Journal of Hazardous Materials.* 164 : 172-181.

Entezari, M., Al-hoseini, Z. S. and Ashraf, N. 2008. Fast and efficient removal of Reactive Black 5 from aqueous solution by a combined method of ultrasound and sorption process. *Ultrasonicssonochemistry.* 15 : 433-437.

Fanchiang, J.M. and Tseng, D. H. 2009. Degradation of anthraquinone dye CI Reactive Blue 19 in aqueous solution by ozonation. *Chemosphere.* 77 : 214-221.

Garg, V., Gupta, R., Yadav, A. B. and Kumar, R. 2003. Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresource Technology.* 89 : 121-124.

Gök, Ö., Özcan, A. S. and Özcan, A. 2010. Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite. *Applied Surface Science.* 256 : 5439-5443.

Gong, R., Li, M., Yang, C., Sun, Y. and Chen, J. 2005. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. *Journal of Hazardous Materials*. 121 :: 247-250.

Gulnaz, O., Sahmurova, A. and Kama, S. 2011. Removal of Reactive Red 198 from aqueous solution by Potamogetoncrispus. *Chemical Engineering Journal.* 174 : 579-585.

Han, X., Wang, W. and Ma, X. 2011. Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf. *Chemical Engineering Journal.* 171 : 1-8.

Kavitha, D. and Namasivayam, C. 2007. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresource Technology.* 98 : 14-21.

Khaksefidi, R., Biglari, H., Rahdar, S., Baneshi, M. M., Ahamadabadi, M., Narooie, M. R., Salimi, A., Saeidi, M. and Alipour, V. 2016. The removal of phenol from aqueous solutions using modified saxaul ASH. *Research Journal of Applied Sciences.* 11 : 1404-1410.

Khaksefidi, R., Rahdar, S., Saeidi, M., Narooie, M. R., Salimi, A., Afsharnia, M., Baneshi, M. M. and Ahamadabadi, M. 2017. Bio-adsorption of aniline from aqueous solutions using activated raw sludge. *Journal of Global Pharma Technology.* 9 : 5-12.

Khattri, S. and Singh, M. 2009. Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of Hazardous Materials*. 167 : 1089-1094.

Kushwaha, A. K., Gupta, N. and Chattopadhyaya, M. 2014. Removal of cationic methylene blue and malachite green dyes from aqueous solution by waste materials of Daucuscarota. *Journal of Saudi Chemical Society.* 18 : 200-207.

Liu, F., Teng, S., Song, R. and Wang, S. 2010. Adsorption of methylene blue on anaerobic granular sludge: Effect of functional groups. *Desalination.* 263 : 11-17.

Liu, T., Li, Y., Du, Q., Sun, J., Jiao, Y., Yang, G., Wang, Z., Xia, Y., Zhang, W. and Wang, K. 2012. Adsorption of methylene blue from aqueous solution by graphene. *Colloids and Surfaces B: Biointerfaces.* 90 : 197-203.

Mahmoud, M. S., Farah, J. Y. and Farrag, T. E. 2013. Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes. *Egyptian Journal of Petroleum.* 22 : 211-216.

Masombaigi, H., Rezaee, A. and Nasiri, A. 2009. Photocatalytic degradation of Methylene Blue using ZnO nano-particles. *Iranian Journal of Health and Environment*. 2 : 188-195.

Mirzabeygi, M., Naji, M., Yousefi, N., Shams, M., Biglari, H. and Mahvi, A. H. 2016. Evaluation of corrosion and scaling tendency indices in water distribution system: a case study of Torbat Heydariye, Iran. *Desalination and Water Treatment.* 1-9.

Mohammadi, S., Zamani, E., Mohadeth, Z., Mogtahedi, F., Chopan, H., Moghimi, F., Mohammadi, M., Karimi, M., Abtahi, H. and Tavakkoli, K. 2015. Effects of Different Doses of Simvastatin on Lead-Induced Kidney Damage in Balb/C Male Mice. *Pharmaceutical Sciences.* 20 : 157.

Nasuha, N. and Hameed, B. 2011. Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. *Chemical Engineering Journal.* 166 : 783-786.

Pavan, F. A., Mazzocato, A. C. and Gushikem, Y. 2008. Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. *Bioresource Technology.* 99 : 3162-3165.

Ponnusami, V., Krithika, V., Madhuram, R. and Srivastava, S. 2007. Biosorption of reactive dye using acid-treated rice husk: factorial design analysis. *Journal of Hazardous Materials.* 142 : 397-403.

Ponnusami, V., Rajan, K. and Srivastava, S. 2010. Application of film-pore diffusion model for methylene blue adsorption onto plant leaf powders. *Chemical Engineering Journal.* 163 : 236-242.

Rafatullah, M., Sulaiman, O., Hashim, R. and Ahmad, A. 2010. Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials.* 177 : 70-80.

Rahdar, S., Khaksefidi, R., Alipour, V., Saeidi, M., Narooie, M. R., Salimi, A., Biglari, H., Baneshi, M. M. and Ahamadabadi, M. 2016. Phenol adsorptive by cumin straw ash from aqueous environments. *Journal of Dispersion Science and Technology*. 7 : 536-541.

Saeidi, M., Biglari, H., Rahdar, S., Baneshi, M. M., Ahamadabadi, M., Narooie, M. R., Salimi, A. and Khaksefidi, R. 2017. The adsorptive acid orange 7 using Kenya tea pulps ash from aqueous environments. *Journal of Global Pharma Technology.* 9 : 13-19.

Sajjadi, S., Asgari, G., Biglari, H. and Chavoshani, A. 2016. Pentachlorophenol removal by persulfate and microwave processes coupled from aqueous environments. *Journal of Engineering and Applied Sciences*. 11 : 1058-64.

Samiey, B. and Ashoori, F. 2012. Adsorptive removal of methylene blue by agar: effects of NaCl and ethanol. *Chemistry Central Journal.* 6 : 1.

Shams, M., Qasemi, M., Afsharnia, M. and Hossein Mahvi, A. 2016. Sulphate removal from aqueous solutions by granular ferric hydroxide. *Desalination and Water Treatment.* 57 : 23800-23807.

Sohrabi, Y., Saeidi, M., Biglari, H., Rahdar, S., Baneshi, M. M., Ahamadabadi, M., Narooie, M. R., Khaksefidi, R. and Alipour, V. 2016. Heavy metal concentrations in water resources of rural areas of Kermanshah, Iran. *IIOAB Journal.* 7 : 542-546.

Sohrabnezhad, S. and Pourahmad, A. 2010. Comparison absorption of new methylene blue dye in zeolite and nanocrystal zeolite. *Desalination*. 256 : 84-89.

Song, J., Zou, W., Bian, Y., Su, F. and Han, R. 2011. Adsorption characteristics of methylene blue by peanut husk in batch and column modes. *Desalination.* 265 : 119-125.

Unuabonah, E. I., Adie, G. U., Onah, L. O. and Adeyemi, O.G. 2009. Multistage optimization of the adsorption of methylene blue dye onto defatted Carica papaya seeds. *Chemical Engineering Journal.* 155 : 567-579.

Vargas, A. M., Cazetta, A. L., Kunita, M. H., Silva, T. L. and Almeida, V. C. 2011. Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonixregia): Study of adsorption isotherms and kinetic models. *Chemical Engineering Journal.* 168 : 722-730.

Weng, C.H., Lin, Y.T. and Tzeng, T. W. 2009. Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder. *Journal of Hazardous Materials.* 170 : 417-424.