Pak. j. sci. ind. res. Ser. B: biol. sci. 2023 **66B**(1) 45-51

Adsorption Study of Orange G Dye on Thermally Modified Rice Husk from Aqueous Medium

Abdul Malik[a]*, Abbas Khan[b], Sana Ullah[c], Faisal Safi[c], Shakeel Ahmad[c], Naseem Ullah[c] and Shakeel Ahmad Khan[c]

[a]Department of Chemistry, Govt. Degree College Toru Mardan 23200, Pakistan
[b]Department of Chemistry, Abdul Wali Khan University, Mardan 23200, Pakistan
[c]Department of Chemistry, Govt. Post Graduate College Mardan 23200, pakistan

(received November 23, 2020; revised May 2, 2021; accepted May 24, 2021)

Abstract. Thermal modification of rice husk in open air environment was carried out by burning of rice husk, followed by a heat action in tube furnace at 973 K̊ for one hour. The material obtained was whitish in colour and termed as rice husk ash (RHA), which was applied to adsorbed the Orange G-dye from aqueous medium. The adsorption process was studied in various experimental conditions that could greatly affect the adsorption process. The optimum conditions for the maximum adsorption of dye, were investigated as; pH 4, temperature 303 K̊ and 80mg/L of initial dye concentration containing 2g/L of the adsorbent concentration. At optimum conditions the dye removal was investigated as 57.6% with adsorption capacity 23.05 mg/g. Thermodynamic study indicated that the adsorption process is exothermic and spontaneous. Kinetic data for the adsorption of Orange-G on the RHA-adsorbent, best followed the pseudo-S second order kinetic model, whereas equilibrium experimental data is fit to Langmuir-model, suggested that adsorption of OG on RHA is a chemical adsorption.

Keywords: Orange G, dye, RHA, modified rice, adsorption

Introduction

Dye stuffs are dangerous to human beings, especially to the workers of dyeing industries. Dyes could cause several disorders in the human bodies including respiratory issues like sharpening respiratory tract, watery eyes, sniffling and asthma etc. (Hassaan *et al*., 2016). The aggravation is one of the most dominant issues, caused by the colouring and dyeing processes. Dyeing and completing procedures may cause skin irritation, blocked noses, sniffling and sore eyes. Formaldehyde based gums, smelling salt, soft drinks sinders, optical whiteners and acid corrosive etc. are the colouring objects that cause irritation and sensitivity in human body. Several hazardous effects of textile dyeing processes on human health and environment have been reported. One of the imperative harmful effects observed, is the skin irritation (Hassaan *et al*., 2017). Textile industries and other material enterprises are the key sources of coloured waste fluids which contain numerous organic dyes and inorganic pigments. Most of the colours are firmly connected to the texture however, some colours have not firm connection to the texture that may washed out (Hassaan and Al- Nemr, 2017). The effluents contain numerous colours and synthetic materials that may be carcinogenic and harmful to the well being on the earth (Hassaan *et al*., 2016).

Dyes are released into aquatic environment through the dyeing process especially in textile industries (Mohan *et al*., 2007), dye manufacturing, industrial operations (Hema and Arivoli, 2007; Jumasiah *et al*., 2005) and textile processing etc. (Kingye and Yang, 2003) and could badly affect the aquatic environment. Even though if only one mg/L of dye is added to water, it could make the water coloured and harmful to be used for drinking purposes (Malik *et al*., 2007).

Dyes are harmful to human as well as aquatic life. For humans they could cause failure of kidneys, malfunction of liver and central nervous system (Sheng *et al*., 2009). Due to the toxic nature of dyes, their removal from water is very crucial to save humans as well as the aquatic life. Several methods have been used to treat the coloured waste water. These methods include coagulation. Flocculation, irradiation and adsorption (Tim *et al*., 2001). Decomposition and degradation of dye have also been applied to treat the coloured waste water. Rhodamin-B 'RH-B' was decolourized by catalytic oxidation (Hang *et al*., 2017), whereas the same dye was decomposed on the surface of zinc oxide

*Author for correspondence;
E-mail: abdulmalikpk811@gmail.com

catalyst to eliminate the colour from coloured waste water (Saeed *et al*., 2017).

Adsorption is an efficient method which have been employed to remove colour from the coloured water (Malik *et al*., 2019). Adsorption is a sludge-free process and could remove colour from waste water completely.

Rice husks are the waste agricultural products and could be easily collected during the rice grain processing. Primarily, rice husk is composed of cellulose, hemi-cellulose, lignin and amorphous silica (Chen *et al*., 2018). The rice husk has hard and rough surface which is not easily decomposable by bacteria and hence it could pollute the environment (Chen *et al*., 2014). Rice husks have been used as raw material for the manufacturing of ceramics (Shibata *et al*., 2012). Silica is the main constituent in ceramics industries. Rice husks and rice husk ash have been used for the extraction of silica (Rehman *et al*., 2013). The rice husk silica has been prepared by acid leaching technique and employed for adsorption purposes (Wina *et al*., 2013). Alkali treatment of rice husk ash has been employed to prepare mesoporous silica for the adsorption of carbon dioxide (Margandan *et al*., 2010). In this study, the rice husk (RH) was thermally modified into rice husk ash (RHA) and was employed for removal of OG from waste water.

Materials and Methods

The rice husk was taken from rice-processing mills located in district Mardan (Pakistan). The Orange G (Orange Gelb) was got from 'Sigma-Aldrich', NaOH, HCl and were employed without further purifications. Distilled water was employed to prepare dye solutions. 'Pyrex-glass-wares' were used to carry out the adsorption experiments. 'Tube Furnace' (PT-1200T) was employed for the preparation of adsorbent, whereas the residual dye concentrations were measured using UV-visible-spectrophotometer (Perkin Elmer Lambda-25).

Preparation of 'rice husk ash' (RHA). The rice husk was subjected to a wash treatment with distilled water, acidic and basic solutions chased by dehydration in electric-oven at 333 $\mathring{K}$ for four hours. The prepared rice husk was first burnt in open air and then activated in tube furnace at 973 $\mathring{K}$ for 1 h to prepare the rice husk ash (RHA) which was grinded and sieved through a mesh of 250 micrometer. The prepared RHA was applied for adsorption of Orange G (OG) from coloured waste water.

Adsorption experiment. The effect of different experimental variable on removal of OG had been studied. For this purpose one condition was varied whereas the remaining conditions were kept constant. To study the effect of dye-concentration, a known quantity of varied dye concentration ranging 20-120 mg/L were employed, while the temperature, adsorbent dose, time and initial pH were kept constant. In similar way, the effects of other conditions were determined. The residual dye concentration was measured with Uv-Visible 'Spectrophotometer'. Adsorption capacity (mg/g) and % dye adsorption have been calculated with the help of equations 1 and 2.

$$qe = \frac{V(Co-Ce)}{m} \quad \text{.....(1)}$$

$$\% \text{ Dye adsorption} = \frac{(Co-Ce)}{Co} \quad \text{.....(2)}$$

where, qe is the adsorption capacity (mg/g); V is the volume of dye solution (L); Co and Ce are initial and equilibrium dye concentrations (mg/L) respectively and m = mass of adsorbent (g).

Results and Discussion

Effect of contact time. Varied time ranging 10 to 70 min i.e (10, 20, 30…..70 min) were employed to investigate the consequences of contact time on adsorption of OG on RHA-surface. The other experimental conditions (temperature, adsorbent dose, dye concentration and pH) were kept constant. The adsorption rate was found high in the initial 10 min however, gradual decrease in the adsorption rate was investigated after 10 min and remained almost constant after 60 min, hence this time was considered as the optimum/equilibrium time for highest removal of OG on RHA-surface from aqueous medium as indicated in Fig 1. At optimum time the adsorption capacity was investigated as 23.05 mg/g and the % dye removal was noted as 57.6%.

Effect of adsorbent dose. The quantity of RHA had great effect on adsorption of OG on RHA-surface. Varied adsorbent dose ranging from 1 to 5 g/L at pH 4, initial-dye concentration 80g/L and temperature 303$\mathring{K}$ were employed to study the role of adsorbent concentration on dye adsorption process. A decrease in the adsorption capacity was noted for the high concentrations of adsorbent however, the availability

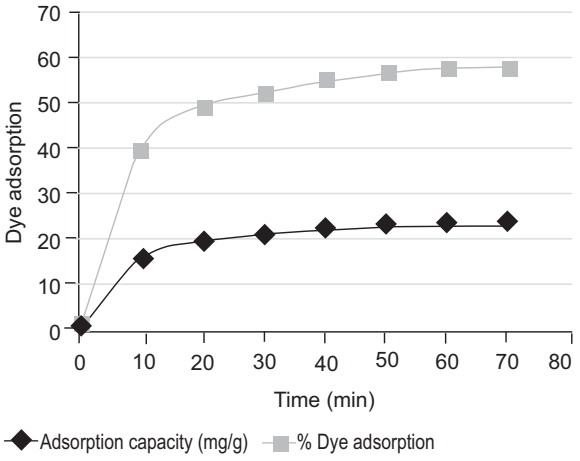

Fig. 1. The effect of contact time on removal of OG on RHA-surface from aqueous-medium (experimental conditions were pH=4; T = 303K̊; adsorbent-conc. = 2g/L; and initial dye-conc. Co= 80 mg/L).

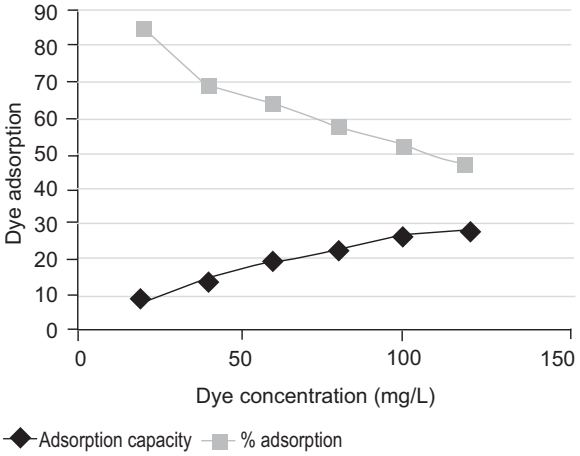

Fig. 3. The effect of initial dye-conc. on adsorption of OG on RHA-surface (experimental conditions where: pH = 4; T = 303K̊; Co = 80 mg/L).

of active sites are high at high concentration of RHA-adsorbent which enhances the % removal of OG-dye from coloured water as indicated in Fig 2. Highest adsorption capacity was found as 26.9g/L for 1g/L of adsorbent dose.

Effect of dye concentration. The dye concentrations in the range of 20 to 120 mg/L, were used in different experiments at temperature 303K̊, adsorbent dose of 2g/L, pH 4 and contact time 60 min. Fig 3 indicated that the adsorption capacity is high at high initial dye concentration, whereas % adsorption of dye was noted lower at this concentration. The highest adsorption capacity was noted as 27.9 mg/g for 120mg/L of initial dye-concentration whereas % dye adsorption was examined as 85.5 % for 20 mg/L of dye concentration. The highest adsorption capacity of OG on RHA at high initial dye concentration is ascribed to multi layer formation. This fact could be verified by the high value of regression constant in the Freundlich Isotherm, as indicated in Table 3. The %removal of OG on the surface of RHA was observed to be lowered for the high initial dye concentration; this is due to the fact that the active sites of RHA become shorter to remove the OG completely. However, for low dye-concentration available active sites of RHA are enough to adsorb the dye molecules almost completely.

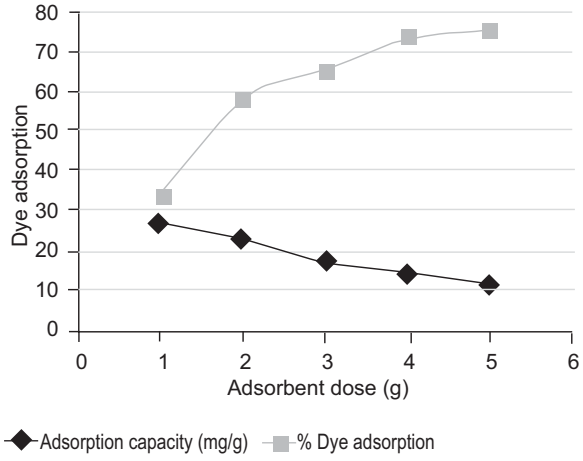

Fig. 2. The effect of adsorbent concentration on adsorption of OG-dye on RHA. (experimental conditions where: pH = 4; T = 303K̊; C_o = 80 mg/L).

Effect of pH. Initial pH range 2-6 was employed to study its effects on the adsorption of OG on the RHA-surface. Experiments were performed at initial dye concentration 80mg/L, temperature 303K̊, and adsorbent dose 2g/L. The maximum adsorption of OG on RHA was observed at pH 4 as indicated in Fig 4. The adsorption capacity was noted as 23.05 mm/g and % dye adsorption was 57.6%. At pH 4 the interaction of anionic dye with adsorbent surface was high. At pH less than 4, the concentration of H+ ions is very high that may interact with anionic dye and hence decreasing the interaction of dye with the adsorbent, hence low

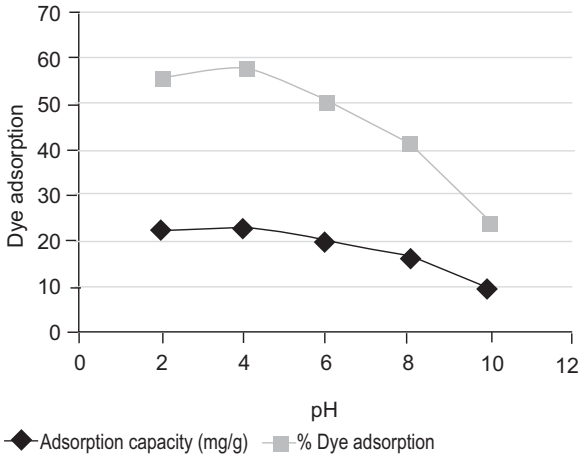

Fig. 4. Role of pH on removal of Orange G on the RHA-surface at adsorbent dose = 2g/L; T = 303K̊; Co = 80 mg/L.

adsorption was observed. At pH greater than 4 the degree of protonation of adsorbent was very low hence low adsorption was noted at high pH.

Temperature effect. The temperature could also affect the dye adsorption process. The adsorption experiments were performed at varied temperatures, 303, 313, 323, 333 and 343 K̊±3, to measure the role of temperature upon the dye removal practice. It was examined that at high temperature the adsorption of dye on RHA was decreased as indicated in the Fig 5, this shows that the removal of OG on RHA is exothermic process and at elevated temperature the interaction of dye with solvent is high as compare to that with RHA surface. The highest adsorption capacity and % removal of dye was noted at 303K̊.

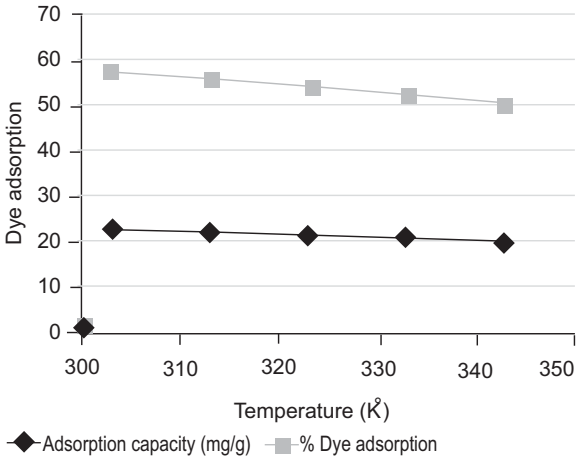

Fig. 5. Effect of temperature on removal of Orange G on RHA-surface. (experimental conditions were: initial pH= 4; adsorbent dose = 2g/L; initial-dye concentration; Co= 80 mg/L).

Thermodynamic studies. Thermodynamic-parameters like 'Gibbs free energy ($\Delta\mathring{G}$) enthalpy ($\Delta\mathring{H}$) entropy ($\Delta\mathring{S}$) and equilibrium constant *(K)* for the adsorption process were computed with the help of equation 3, 4 and 5 which were listed in the Table 3.1. The 'negative values' of $\Delta\mathring{G}$ indicated that removal of 'OG-dye' on RHA-adsorbent is spontaneous. The $\Delta\mathring{S}$ and T are interrelated with each other as given in equation 3.3 (Malik *et al*., 2019). 'Plot of $\Delta\mathring{G}$ Vs T is indicated in Fig. 6. Values of entropy change $\Delta\mathring{S}$ and enthalpy change ($\Delta\mathring{H}$) were calculated from slope and intercept of the plot. Negative values of $\Delta\mathring{H}$ and $\Delta\mathring{S}$ indicated that removal of OG on RHA was exothermic process and randomness was decreased at the adsorbent adsorbate interface.

$$\Delta\mathring{G} = -RT \ln k. \quad \text{..... (3)}$$

$$\mathring{K} = C_{ads}/C_e. \quad \text{..... (4)}$$

Table 1. Thermodynamic parameters, for the adsorption of OG on RHA-adsorbent

Temperature (K̊)	$\Delta\mathring{G}$ (kJ/mol)	Values of (K)	$\Delta\mathring{H}$ (kJ/mol)	$\Delta\mathring{S}$ (kJ/mol/K)
303	-0.774	1.359	-6.289	-0.018
313	-0.614	1.266		
323	-0.444	1.179		
333	-0.263	1.102		
343	-0.042	1.015		

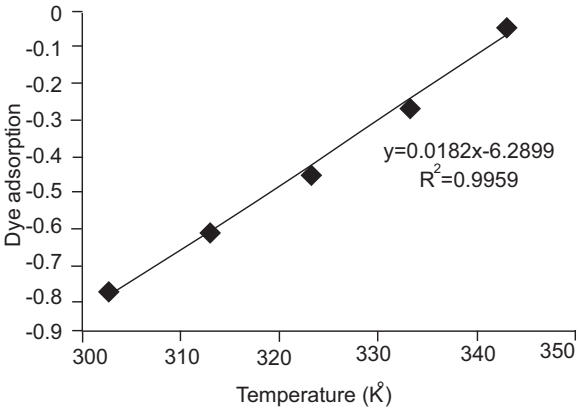

Fig. 6. Plot of ΔG Vs T for removal of Orange G on RHA-surface from aqueous-medium.

$\Delta\mathring{G} = \Delta\mathring{H} - T\Delta\mathring{S}$ ..... (5)

Adsorption kinetics. Kinetics study suggests for the rate and mechanism of the reaction. Both 'pseudo-first' and 'pseudo-second' order equations were employed to investigate physical and chemical interaction of dye molecules with the adsorbent surface. The linear equations of 'pseudo-first' and 'pseudo-second' order reactions are given in equation 6 and 7 respectively (Bassyouni *et al*., 2017).

$$\text{Log}\ (q_e - q_t) = \log q_e - K_1 t/2.303 \quad \text{..... (6)}$$

$$t/q_t = t/q_e + 1/k_2\, q_e^2 \quad \text{..... (7)}$$

Plots of the two order ('pseudo-first' and 'pseudo-second') reactions are given in Fig. 7 and 8. Values of rate-constants, '$\mathring{K}_1$', '$\mathring{K}_2$', qe and R^2 were computed from 'slopes' and 'intercepts' of the plots which are listed in the Table 2. The kinetic studies indicated that the experimental data best fits to the 'pseudo-second order' kinetic model, which suggested removal of OG-dye on RHA, is mostly chemical in nature.

Adsorption isotherm models. ***Langmuir.-isotherm model.*** Experimental-data was evaluated with

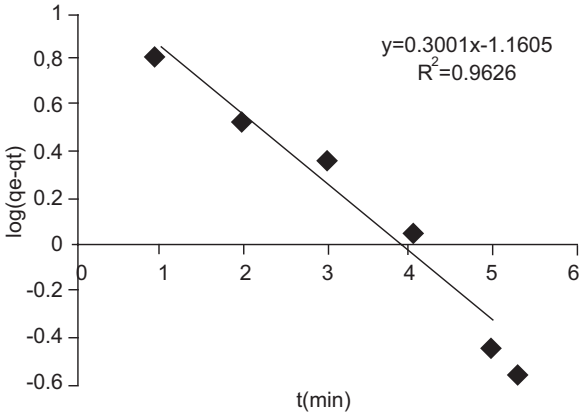

Fig. 7. The pseudo first-order kinetic model for removal of Orange G-dye on RHA-adsorbent.

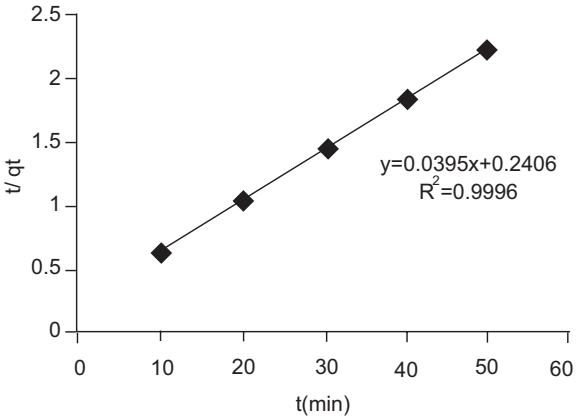

Fig. 8. The pseudo-second-order kinetic model for the removal of orange G-dye on RHA-surface.

'Langmuir-model'. Linear equation of this model is specified as;

$$Ce/qe = Ce/qm + 1/Kqm \quad \text{..... (8)}$$

where:

Ce = eq. dye- conc. "mg/L"; qe = Uptake capacity "mg/g"; qm = Maximum uptake-capacity for mono layer coverage and K 'Lmg^{-1}' is the Langmuir equilibrium-constant (Suantak *et al*., 2011). Plot 'Ce/qe' Vs Ce' is given in Fig. 9.

Table 3. Parameters in Langmuir and Freundlich adsorption-isotherms for removal of OG on RHA-adsorbent.

Adsorption isotherm model	Parameters	Values
Langmuir	qm mg /g	33.33
	K_L L/mg	0.073
	R^2.	0.981
Freundlich	n	1.838
	K_F L/mg	4.017
	R^2.	0.824

Table 2. Values of rate constants $\mathring{K}_1$, $\mathring{K}_2$, adsorption capacities 'qe' and correlation factors 'R^2' for adsorption of OG on RHA

Adsorbent	Pseudo-1st order model			Pseudo-2nd order model		
	K_1/ (min)	R^2	qe (mg/g)	K_2(g/mg/min)	R^2	qe.(mg/g)
RHA	1.30×10^{-2}	0.962	14.45	6.33×10^{-3}	0.999	25.64

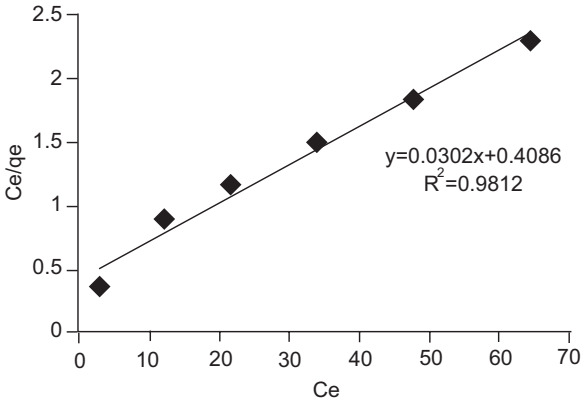

Fig. 9. Langmuir-model for removal of OG on RHA-surface.

Freundlich-isotherm model. This model could usually be applied to heterogeneous system and could be referred for multilayer adsorption (Indiran *et al*., 2018). The linear expression of this model is given as:

$$\log qe = \log K_F + \frac{1}{n} \log Ce \quad \text{..... (9)}$$

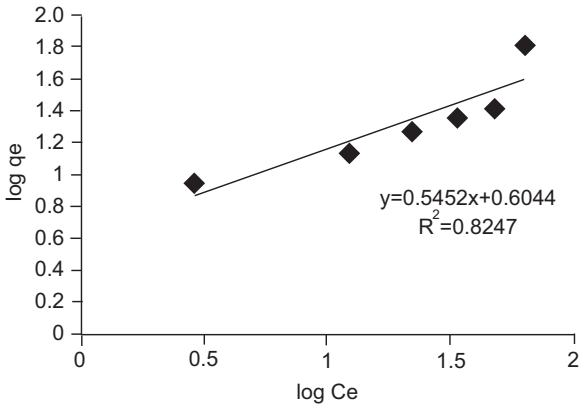

Fig. 10. Freundlich-model for removal of OG-dye on RHA-surface.

where;

'K_F' and 'n' are Freundlich adsorption constant, which are referred for adsorption capacity and intensity (Gurusamy *et al*., 2002). The plot of log qe Vs log Ce is shown in Fig. 10. Experimental data is best fit to Langmuir model for which the regression constant value is very close to unity (0.999), which suggested that the adsorption is mostly chemical with mono-layer formation.

Conclusion

Rice-husk. (.an agricultural by product), was thermally modified into rice-husk ash. (RHA), which was employed for adsorption of Orange G-dye from coloured waste water. The adsorbent was prepared by the aerobic burning followed by the heating in tube furnace at 973K̊. Different experimental variables were tested on the adsorption process to compute the optimum condition for maximum removal of OG-dye from aqueous medium. It was investigated that the removal of Orange G-dye on RHA was significantly affected by changing the experimental conditions. The highest adsorption efficiency was noted at 303K̊ and pH 4 from 80 mg/L dye solution containing 2g/L of adsorbent dose. Thermodynamics of the process suggested for its spontaneous and exothermic nature. The adsorption of OG on RHA followed the pseudo second order mechanism and the experimental data is fit to the Langmuir isotherm, which suggested for the chemical nature of the process.

References

Ahmit, S., Tuzen, M., 2009. Kinetic and equilibrium studies of biosorption of Pb (II) and Cd (II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. *Journal of Hazardous Materials*, **164:** 1004-1011.

Bassyouni, D.G., Hamad, H.A., El-Ashtoukhy, E.Z., Amin, N.K., Abd El-Latif, M.M. 2017. Comparative performance of anodic oxidation and electro-coagulation as clean processes for electro-catalytic degradation of diazo dye Acid Brown 14 in aqueous medium. *Journal of Hazardous Materials*, **335:** 178-187.

Chen, D., Gao, A., Ma, Z., Fei, D., Chang, Y., Shen, C. 2018. In-depth study of rice husk torrefaction: characterization of solid, liquid and gaseous products, oxygen migration and energy yield. *Bioresource Technology*, **253:** pp.148-153.

Chen, D., Zhou, J., Zhang, Q., Zhu, X., Lu, Q. 2014. Up-grading of rice husk by torrefaction and its influence on the fuel properties. *Bio Resources*, **9:** 5893-5905.

Gurusamy, A., Juang, R.S., Lee, D.J., 2002. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *Journal of Hazardous Materials*,

92: 263-274.

Hang, S., He, Q., She, P., Zeng, S., Xu, K., Li, J., Liang, S., Liu, Z. 2017. One-pot synthesis of Au@ TiO_2 yolk-shell nanoparticles with enhanced photocatalytic activity under visible light. *Journal of Colloid and Interface Science*, **505:** 884-891.

Hassaan, M.A., El Nemr, A. 2017. Advanced oxidation processes for textile wastewater treatment. *International Journal of Photochemistry and Photobiology*, **2:** 85-93.

Hassaan, M.A., El Nemr, A., Hassaan, A., 2017. Health and environmental impacts of dyes: mini review. *American Journal of Environmental Science and Engineering*, **1:** 64-67.

Hassaan, M.A., El Nemr, A., Madkour, F.F. 2016. Application of ozonation and UV assisted ozonation for decolourization of direct yellow 50 in Sea water. *The Pharmaceutical and Chemical Journal*, **3:** 131-138.

Hema, M., Arivoli, S., 2007. Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon. *International Journal of Physical Sciences*, **2:** 10-17.

Indiran, M., Agilan, S., Selvakumar, R., Vairam, S., 2018. Synthesis of Co_3O_4/graphene nano-composite using paraffin wax for adsorption of methyl violet in water. *IET Nanobiotechnology*, **12:** 787-794.

Jumasiah, A., Chuah, T.G., Gimbon, J., Choong, T.S.Y., Azni, I. 2005. Adsorption of basic dye onto palm kernel shell activated carbon: sorption equilibrium and kinetics studies. *Desalination*, **186:** 57-64.

Malik, A., Khan, A., Humayun, M. 2019. Preparation and chemical modification of rice husk char for the removal of a toxic dye (Orange G) from aqueous medium. *Zeitschrift für Physikalische Chemie*, **233:** 375-392.

Malik, R., Ramteke, D.S., Wate, S.R. 2007. Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Management*, **27:** 1129-1138.

Margandan, B., Yun, L.J., Anuradha, R., Jang, H.T. 2010. Utilization of rice husk ash as silica source for the synthesis of mesoporous silicas and their application to CO_2 adsorption through TREN/TEPA grafting. *Journal of Hazardous Materials*, **175:** 928-938.

Mohan, N., Balasubramanian, N., Basha, C.A. 2007. Electrochemical oxidation of textile wastewater and its reuse. *Journal of Hazardous Materials*, **147:** 644-651.

Kingye, S., Yang, L. 2003. The adsorption of basic dyes from aqueous solution on modified peat–resin particle. *Water Research*, **37:** 1535-1544.

Rehman, M.S.U., Umer, M.A., Rashid, N., Kim, I., Han, J.I. 2013. Sono-assisted sulphuric acid process for economical recovery of fermentable sugars and mesoporous pure silica from rice straw. *Industrial Crops and Products*, **49:** 705-711.

Saeed, M., Siddique, M., Usman, M., Ul Haq, A., Khan, S.G., Raoof, H.A. 2017. Synthesis and characterization of zinc oxide and evaluation of its catalytic activities for oxidative degradation of rhodamine B dye in aqueous medium. *Zeitschrift für Physikalische Chemie*, **231:** 1559-1572.

Shen, D., Fan, J., Zhou, W., Gao, B., Yue, Q., Kang, Q. 2009. Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. *Journal of Hazardous Materials*, **172:** 99-107.

Shibata, K., Yamaguchi, T., Urabe, T., Hokkirigawa, K. 2012. Experimental study on microscopic wear mechanism of copper/carbon/rice bran ceramics composites. *Wear*, **294:** 270-276.

Suantak, K., Balomajumder, C., Chand, S. 2011. Removal of As (III) from aqueous solution by biosorption onto maize (*Zea mays*) leaves surface: parameters optimization, sorption isotherm, kinetic and thermodynamics studies. *Research Journal of Chemical Sciences*, **1:** 73-79.

Tim, R., McMullan, G., Marchant, R., Nigam, P. 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, **77:** 247-255.

Wina, R., Sophiphun, O., Rintramee, K., Prayoonpokarach, S., Wittayakun, J. 2013. Paraquat adsorption on porous materials synthesized from rice husk silica. *Water Science and Technology*, **68:** 863-869.