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Diamond green dye adsorptive removal from water by carrot pulpy waste and potato peels

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Diamond green dye is an example of textile dye. In this study, *Daucus carota* (carrot) waste and *Solanum tuberosum* (potato) peels were used for dye removal from water. These are low-cost and commonly available materials. Their adsorption capacity for Diamond green dye was tested for the first time in this study for possible application on industrial scale water treatment. Optimum conditions for the removal of 25 ppm of Diamond green dye from 100 mL of synthetic wastewater by carrot pulpy waste were: 0.6 g adsorbent dose, pH 2.0, 40 min contact time, 30ºC temperature and 150 rpm agitation speed. Using potato peels, the optimum conditions were: 0.4 g adsorbent dose, pH 1.0, 15 min contact time, 30ºC temperature and 50 rpm agitation speed. Various conditions affecting the sorption of Diamond green dye from water were optimized by carrying out isothermal and kinetic studies. Isothermal studies indicated that chemisorptive mode is predominant over physio-sorption with maximum removal capacities for carrot waste and potato peels of 4.14 and 3.13 mg/g, respectively. Kinetic studies pointed to a pseudo-second order model. Both materials are suitable for bulk-scale removal of Diamond green dye from waste water streams.

Keywords: Diamond green dye; Carrot pulpy waste; Potato peels, Isotherm; Kinetic models.

INTRODUCTION

Rapid growth in population in recent years resulted in higher development of industrialization to support people economically and to offer them better living standards. But this leads to environmental pollution which may be lethal for living creatures. It acts as a slow poison, e.g., toxic metals or excessive organic pollutants discharged into water bodies. Mainly dyes, colorants, synthetic drugs, pesticides, herbicides, germicides, and detergents are the common examples of organic pollutants found in industrial waste water streams. Organic pollutants are sometimes biodegradable, but synthetic dye stuff is resistible to biodegradation. So, its removal from waste streams is necessary.

Dyes removal by adsorption process is getting more important nowadays. Different researchers are working with various types of waste materials from indigenous sources to remove toxic matter from water by adsorption.

Agricultural waste, like leaves, peels, seeds, pulp, etc., is more popular among them due to its easy handling, availability and non-toxic nature [1-8].

In this work, the removal of Diamond green dye from water by carrot waste and potato peels was studied. Its λ_{max} is 625 nm and the formula is given in Fig. 1. It is a textile dye with synonyms used in various texts: Brilliant green, Astradiamant green GX, Basic green 1, Emerald green, Ethyl green, Malachite green G and Solid green JO.

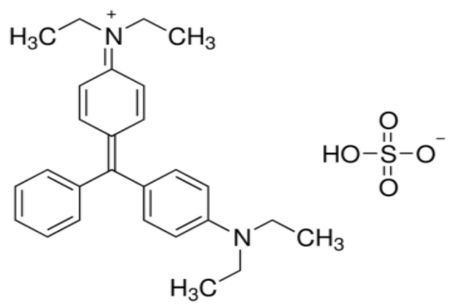

Fig. 1. Structure of Diamond green.

It is injurious to health if comes in skin or eye contact or orally ingested. Burning of items coated with this dye results in NO_x and SO_x fumes, causing air pollution, leading to eye infection and skin ulcer [9-11].

Various adsorbents were used for its removal from aqueous medium, e.g., saklikent mud, cactus fruit peels, saw dust, rice husks, fly ash, eucalyptus wood, bottom ash, de-oiled soya, palm kernels, sunflower, rubber wood, babassu coconut epicarp, etc. [12-32].

Potato (*Solanum tuberosum*) peels and carrot (*Daucus carota*) pulpy waste were used for adsorption of Diamond green dye. Carrots and potatoes are extensively used as food. They are not only used in homemade food items, but also extensively employed in industrial level-processed food like chips, French fries, carrot juice, muraba,

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pickles, desserts, cakes and soups [33-41]. Both of them are nutritionally rich and economical food. They are easily available all over the world. Their adsorption capacity for removing Diamond green dye was tested for the first time in this study for possible application on industrial scale water treatment. Their use on a large scale can significantly increase the organic matter in water due to leaching, but that organic matter is decomposable; moreover, it usually contains different chelating agents that can reduce toxic metallic ions concentration in waste water streams. So their usage as adsorbents is preferable as compared to synthetic adsorbents.

EXPERIMENTAL

Materials and instrumentation

Diamond green dye (λ_{max} = 625 nm), HCl (Merck), NaOH (Merck), Vis spectrophotometer 721, grinder (Philips), digital balance, FT-IR spectrometer (Perkin Elmer), oven (Haier).

Sorbent matter preparation

Potato peels and carrot pulpy waste were collected from cafeteria of home institutes making potato chips and carrot juice. They were washed, strained, dried in sunlight and ground to fine powder. The ground material was sieved through 60 mesh and stored in plastic jars. Potato peels were labeled as S.T.P and carrot waste - as D.C.W. Their FT-IR spectra were recorded on a Perkin Elmer spectrometer (ATR supported) and are given in Figs. 2 and 3, respectively. Their physical characterization was carried out using standard methods and is reported in Table 1.

Adsorption studies

Adsorption studies were carried out with synthetic Diamond green dye solutions. The effect of various parameters on the rate of the biosorption process was investigated by varying biosorbent amount (0.2-2.0 g), contact time, (5-60 min), initial pH of the solution (1-10), agitation speed (0-200 rpm) and temperature (20-70 °C) using potato peels and carrot waste. The solution volume (V) was kept constant (50 mL). 25 ppm dye solution was used and photometric measurement was done at λ_{max} = 625 nm. Diamond green (B.G) dye adsorption was calculated by the following equation:

$$\% \text{ adsorption of B.G dye} = (C_o - C_e)/C_o \times 100 \qquad (1)$$

After completion of the adsorption process, the adsorbents were separated from water by vacuum filtration using a Büchner funnel.

Isothermal modeling

Optimized operational conditions were applied on dye solutions of various concentrations (from 15 to 80 ppm) for isothermal modeling of equilibrium data. Langmuir model equation is [35]:

$$\frac{1}{q} = \frac{1}{bq_mC_e} + \frac{1}{q_m} \qquad (2)$$

where q is the adsorption capacity (mg/g) [33-35].

The value of *b* was used to calculate the separation factor R_L and ΔG^o.

Separation factor is determined by:

$$R_L = 1/(1+bC_0) \qquad (3)$$

When its value is greater than 1, the adsorption process is unfavorable using that specific adsorbent.

$$\Delta G^o = -RT \ln K \qquad (4)$$

Here K = 1/b and Gibbs free energy is given in KJ/mol [7-12].

Freundlich isotherm is [12]:

$$\log q = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

Kinetic modeling

Optimized operational conditions were applied on a 50 ppm dye solution for different time periods ranging from 5 to 120 min for kinetic modeling of the equilibrium data. Kinetic modeling was done using equation 6 and equation 7 [12]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \qquad (7)$$

Here *t* corresponds to the time interval of contact between sorbent and dye solution in min, k_1 is a first-order constant and k_2 is a second-order constant.

RESULTS AND DISCUSSION

Characterization of adsorbent samples

Different functional groups were identified by FT-IR studies on the biosorbent samples that can interact with dye molecules and ionized species in aqueous medium (see Fig. 2 for *Solanum tuberosum).* –OH, C-H, C=O, N-H bonds at peaks 3300.20, 2924.09, 1244.09, 1149.57 and 1639.49, 1537.27 cm^{-1} were found in the spectrum of potato peels. The FT-IR spectrum of carrot waste (Fig. 3) shows the same trend.

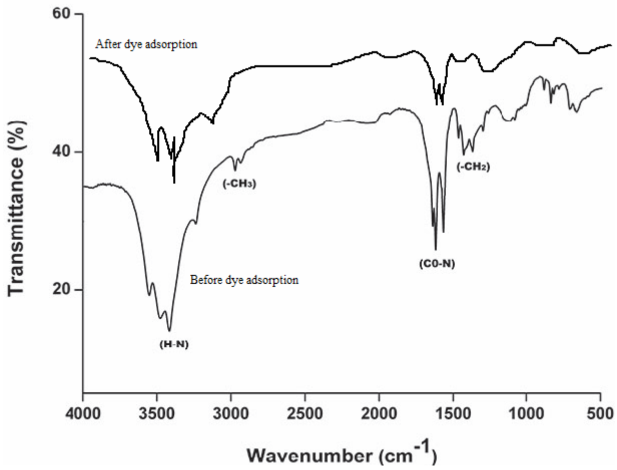

Fig. 2. FT-IR spectrum of potato peels.

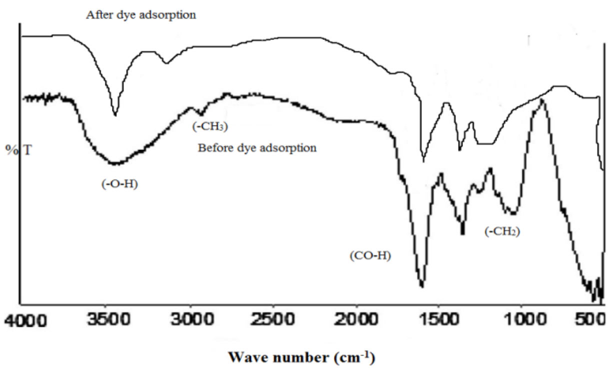

Fig. 3. FT-IR spectrum of carrot pulpy waste.

After dye adsorption, the samples were again analysed for observing if changes took place. After comparing with the original adsorbent before adsorption, it was observed that the wavenumber values shifted towards lower numbers, indicating that chemisorption mode is predominant.

Table 1 indicates that potato peels have a more acidic nature which will help to adsorb cationic dye more efficiently.

Table 1. Physical characteristics of adsorbents

Physical properties	*Carrot pulpy waste*	*Potato peels*
pH	7	6
Moisture content (%)	7.4	8.6
Ash (%)	3.51	3.93
Volatile matter (%)	18.8	21.4

The moisture, ash and volatile matter contents were higher in potato peels than in carrot waste. This is an evidence for the easy decomposition of potato peels after usage, which will help in dumping of waste after adsorption of dye. Higher ash content indicates that the physisorption capacity of potato peels for dye removal is higher as compared to carrot waste. This was further confirmed by isothermal modeling of equilibrium data.

Results of optimized operational conditions

Adsorbent dose

The effect of adsorbent dose is shown in Fig. 4 which indicates that the maximum removal of Diamond green dye by D.C.W occurred at 0.4 g and by S.T.P at 0.6 g. The use of a lower quantity with maximum removal of dye within 20 min revealed that carrot waste contains a larger number of binding sites for chemisorption of Diamond green dye. So, it is better than potato peels for adsorption of Diamond green on bulk scale removal of dye.

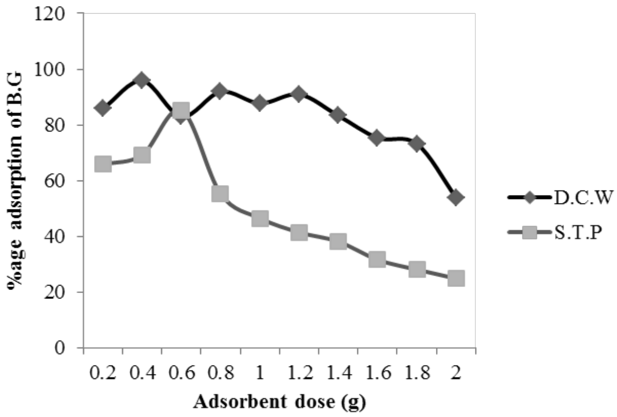

Fig. 4. Adsorbent dose effect on the removal of Diamond green dye.

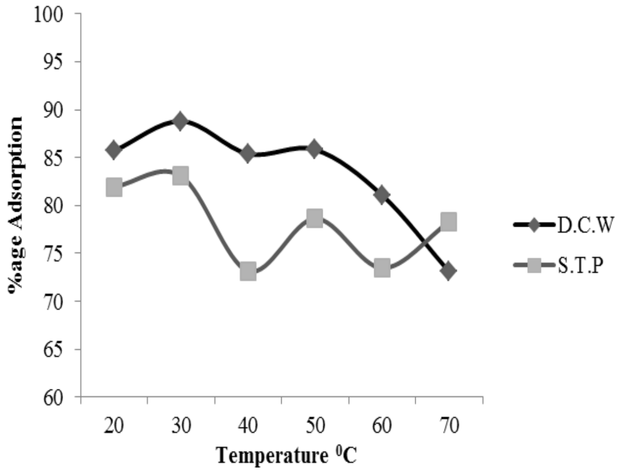

Fig. 5. Temperature effect on the removal of Diamond green dye.

Temperature

The effect of temperature on the adsorption of Diamond green dye by potato peels and carrot pulpy waste is presented in Fig. 5 which indicates that the maximum removal occurs at 30^{o}C using both adsorbing materials, carrot pulpy waste providing a higher percent removal.

This means that higher temperature does not favour the removal of Diamond green dye, because it is an exothermic process. Additional movement of molecules surges with rise in temperature; therefore depression in adsorption occurred at higher temperatures [28].

Dye solution pH

Dye solution pH alters the various ionized species present in solution that can interact with biosorbent surface. So its effect was monitored and is shown in Fig. 6.

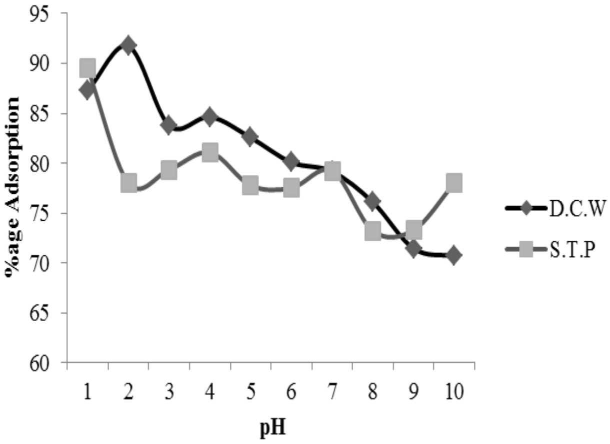

Fig. 6. Dye solution pH effect on the removal of Diamond green dye.

It indicates that the maximum removal of Diamond green dye takes place at pH of the dye solution of 2 and 1 for carrot pulpy waste and potato peels, respectively. Depression in adsorption occurs at higher pH of Diamond green dye solution. Alteration in the molecular structure of Diamond green dye due to ionization and protonation in acidic medium along with changes in functional groups of the carrot pulpy waste and potato peels are responsible for this effect. In basic conditions, the higher concentration of hydroxide ions leads to polarization of the adsorbent surface that in turn can easily remove a cationic dye like Diamond green by stronger electrostatic attraction. This can be pictured by the following equations [16, 25]:

$$[\text{Adsorbent surface}]\text{---OH} + \underset{\text{(in aqueous dye solution)}}{OH^-} \rightarrow [\text{Adsorbent surface}]^- + H_2O$$

$$[\text{Adsorbent surface}]^- + Dye^+ \rightarrow [\text{Adsorbent surface}]\text{----Dye}$$

Contact time

The effect of contact time is shown in Fig. 7 which indicates that the maximum removal of Diamond Green dye occurs in 40 min using carrot waste and in 15 min using potato peels. This trend is due to the fact that carrot waste is more porous and contains a larger number of binding sites as compared to potato peels, so it needs more time for attaining adsorption equilibrium with Diamond green dye molecules. Also, the adsorbed amount is larger than with potato peels. At the initial stage of the process, the removal of Diamond green dye is rapid, but with passage of time, the process slows down because now the surface binding sites are covered by dye molecules. Further removal of dye can only occur, if the dye molecules penetrate into deeper layers of the sorbent. So after the saturation point of the sorbent, further adsorption was suppressed [30].

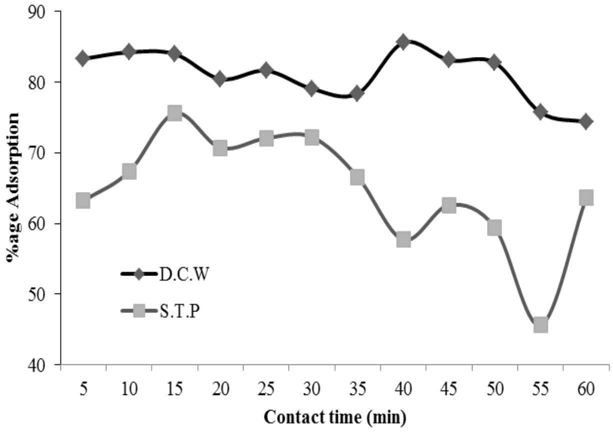

Fig. 7. Contact time effect on the removal of Diamond green dye.

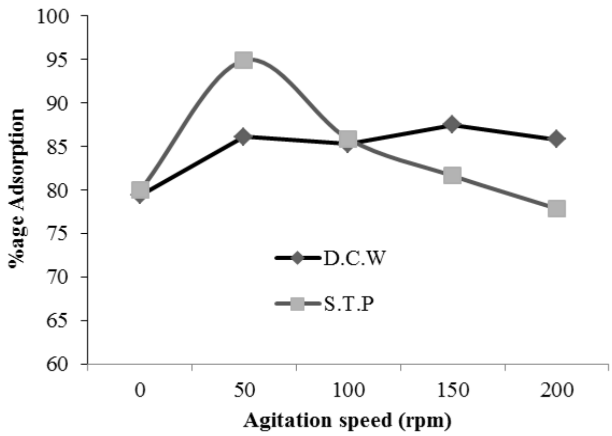

Fig. 8. Agitation speed effect on the removal of Diamond green dye.

Agitation speed

Agitation of the dye solution helps the penetration of dye molecules into deeper layers of the sorbent, which enhances the contact with.

Table 2. Langmuir isothermal parameters for the adsorption of Diamond green dye

Adsorbent	*Slope*	*Intercept*	R^2	q_{max} *(mg/g)*	*b* *(L/mg)*	ΔG^0 *(KJ/mol)*
Carrot pulpy waste	0.8856	0.2044	0.921	4.44	0.674	-9.772
Potato peels	6.754	-0.479	0.937	3.13	0.949	-0.13

Table 3. Freundlich isothermal parameters for the adsorption of Diamond green dye

Adsorbent	*Slope*	*Intercept*	R^2	K_F ($mg^{1-(1/n)}L^{1/n}\ g^{-1}$)	*n*
Carrot pulpy waste	0.707	0.078	0.900	0.77	6.86
Potato peels	1.464	0.906	0.896	0.124	0.68

Table 4. Kinetic modeling parameters for the adsorption of Diamond green dye.

Adsorbent	*Pseudo-first order*			*Pseudo-second order*			$q_{e(exp)}$ *mg/g*
	k_1	$q_{e(cal)}$ *mg/g*	R^2	k_2	$q_{e(cal)}$ *mg/g*	R^2	
Carrot pulpy waste	0.0311	0.758	0.938	0.0351	1.354	0.991	1.2
Potato peels	0.0223	0.203	0.929	0.0397	2.287	0.996	2.2

binding sites. However, very high agitation speeds have a negative effect on adsorption, because in that case less time is available to contact dye molecules with the active sites of the sorbent. It is clear from Fig. 8 that the maximum removal of Diamond green dye is achieved at 150 rpm for carrot pulpy waste and at 50 rpm for potato peels

Isothermal studies of adsorption data

Isothermal studies were carried out on the mechanism of removal of Diamond green dye by carrot pulpy waste and potato peels and the results are presented in Tables 2 and 3.

R^2 (regression coefficient) value is greater for Langmuir isotherm than for Freundlich model using both carrot pulpy waste and potato peels. This means that chemisorption occurred on homogenously distributed active binding sites rather than physio-sorption in multilayer fashion.

The greater value of q_{max} (4.44 mg/g) for carrot waste proves it a better adsorbent as compared to potato peels. In this study, the separation factor R_L value less than unity using both carrot pulpy waste and potato peels points to the favorable sorption of Diamond green dye on these sorbents [40, 41]. ΔG^0 values are negative, indicating the spontaneous and exothermic nature of Diamond green dye removal process using carrot pulpy waste and potato peels.

The values of K_F and *n* for carrot pulpy waste and potato peels indicating that first one provides more removal of Diamond green dye.

Sorption kinetics

Generally, the pseudo-first order kinetic equation is not applicable for biosorption of dye systems. Same is the case here. Kinetic parameters are given in Table 4. The correlation coefficient of the pseudo-second order model was greater than that of the other model using carrot waste and potato peels for Diamond green dye removal from water. This indicated that the adsorption system is not a first-order reaction. Secondly, the $q_{e(cal)}$ values of the pseudo-second order kinetic model are closer to $q_{e(exp)}$. So both these parameters suggest that the pseudo-second order kinetic model is followed in Diamond green dye adsorption by carrot pulpy waste and potato peels.

CONCLUSIONS

It is found that Diamond green dye can be easily removed from water by employing carrot waste (D.C.W) and potato peels (S.T.P) as sorbents with maximum adsorption capacity of 4.44 mg/g for carrot pulpy waste and 3.13 mg/g for potato peels. Optimum conditions for the removal of 25 ppm of Diamond green dye from 100 mL of synthetic wastewater by carrot pulpy waste were: 0.6 g adsorbent dose, pH 2.0, 40 min contact time, 30ºC temperature and 150 rpm agitation speed. Using potato peels, the optimum conditions were: 0.4 g adsorbent dose, pH 1.0, 15 min contact time, 30ºC temperature and 50 rpm agitation speed. Kinetic modeling of equilibrium data indicated that pseudo-second order model was followed and thermodynamic studies revealed the spontaneous nature of this process. Both of these adsorbents, i.e., carrot pulpy waste and potato peels, can be easily employed for bulk-scale Diamond green dye removal from waste water streams.

REFERENCES

1. K.A. Adegoke and O.S. Bello, *Water Resources and Industry*, **12**, 8 (2015).
2. I. Anastopoulos and G.Z. Kyzas, *Journal of Molecular Liquids*, **200**, Part B, 381 (2014).
3. M. Asgher and H.N. Bhatti, *Ecological Engineering*, **38**, 79 (2012).
4. A. Bhatnagar, M. Sillanpää and A. Witek-Krowiak, *Chemical Engineering Journal*, **270**, 244 (2015).
5. A. Bhatnagar, V.J.P. Vilar, C.M.S. Botelho and R.A.R. Boaventura, *Advances in colloid and interface science*, **160**, 1 (2010).
6. K.G. Bhattacharyya and A. Sharma, *Journal of Environmental Management*, **71**, 217 (2004).
7. M. Feizi and M. Jalali, *Journal of the Taiwan Institute of Chemical Engineers*, **54**, 125 (2015).

8. E. Forgacs, T. Cserháti and G. Oros, *Environment International*, **30**, 953 (2004).
9. M. Ghaedi, H. Hossainian, M. Montazerozohori, A. Shokrollahi, F. Shojaipour, M. Soylak and M.K. Purkait, *Desalination*, **281**, 226 (2011).
10. Y. Kismir and A.Z. Aroguz, *Chemical Engineering Journal*, **172**, 199 (2011).
11. M. R. Kosseva, Processing of Food Wastes. In *Advances in Food and Nutrition Research*, Chapter 3, Academic Press:, **58**, 57 (2009).
12. R. Kumar and M.A. Barakat, *Chemical Engineering Journal*, **226**, 377 (2013).
13. A.K. Kushwaha, N. Gupta and M.C. Chattopadhyaya, *Journal of Saudi Chemical Society*, **18**, 200 (2014).
14. V.S. Mane and P.V.V. Babu, *Desalination*, **273**, 321 (2011).
15. V.S. Mane, I. Deo Mall and V.C. Srivastava, *Journal of Environmental Management*, **84**, 390 (2007).
16. V.S. Mane, I.D. Mall and V.C. Srivastava, *Dyes and Pigments*, **73**, 269 (2007).
17. V.S. Mane and P.V. Vijay Babu, *Journal of the Taiwan Institute of Chemical Engineers*, **44**, 81 (2013).
18. A. Mittal, D. Kaur and J. Mittal, *Journal of Colloid and Interface Science*, **326**, 8 (2008).
19. B.K. Nandi, A. Goswami and M.K. Purkait, *Journal of Hazardous Materials*, **161**, 387 (2009).
20. T. Nharingo and M. Moyo, *Journal of Environmental Management*, **166**, 55 (2016).
21. A.E. Ofomaja and Y.S. Ho, *Dyes and Pigments*, **74**, 60 (2007).
22. G.B. Oguntimein, *Journal of Environmental Chemical Engineering*, **3**, 2647 (2015).
23. V. Ponnusami, S. Vikram and S.N. Srivastava, *Journal of Hazardous Materials*, **152**, 276 (2008).
24. S. Rangabhashiyam, N. Anu and N. Selvaraju, *Journal of Environmental Chemical Engineering*, **1**, 629 (2013).
25. M.S.U. Rehman, M. Munir, M. Ashfaq, N. Rashid, M.F. Nazar, M. Danish and J.I. Han, *Chemical Engineering Journal*, **228**, 54 (2013).
26. M.A. Salem, R.G. Elsharkawy and M.F. Hablas, *European Polymer Journal*, **75**, 577 (2016).
27. A.T. Shah, M.I. Din, F.N. Kanwal and M.L. Mirza, *Arabian Journal of Chemistry*, **8**, 579 (2015).
28. M.P. Tavlieva, S.D. Genieva, V.G. Georgieva and L.T. Vlaev, *Journal of Colloid and Interface Science*, **409**, 112 (2013).
29. K. Vasanth Kumar and S. Sivanesan, *Dyes and Pigments*, **72**, 124 (2007).
30. A.P. Vieira, S.A.A. Santana, C.W.B. Bezerra, H.A.S. Silva, J.A. Chaves, J.C.P. Melo, E.C.S. Filho and C. Airoldi, *Chemical Engineering Journal*, **173**, 334 (2011).
31. W.S. Wan Ngah and M.A.K.M. Hanafiah, *Bioresource Technology*, **99**, 3935 (2008).
32. M.T. Yagub, T.K. Sen, S. Afroze and H.M. Ang, *Advances in Colloid and Interface Science*, **209**, 172 (2014).
33. H.N. Bhatti, A.W. Nasir and M.A. Hanif, *Desalination*, **253**, 78 (2010).
34. F. Güzel, H. Yakut and G. Topal, *Journal of Hazardous Materials*, **153**, 1275 (2008).
35. T. Aman, A.A. Kazi, M.U. Sabri and Q. Bano, *Colloids and Surfaces B: Biointerfaces*, **63**, 116 (2008).
36. A.C. Arampatzidou and E.A. Deliyanni, *Journal of Colloid and Interface Science*, **466**, 101 (2016).
37. G.Z. Kyzas and E.A. Deliyanni, *Chemical Engineering Research and Design*, **97**, 135 (2015).
38. G.Z. Kyzas, E.A. Deliyanni and K.A. Matis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **490**, 74 (2016).
39. Y. Li, Y. Deng and B. Chen, *Journal of Environmental Sciences*, **24**, 675 (2012).
40. J.C. Moreno-Piraján and L. Giraldo, *Journal of Analytical and Applied Pyrolysis*, **90**, 42 (2011).

Z. Zhang, X. Luo, Y. Liu, P. Zhou, G. Ma, Z. Lei and L. Lei, *Journal of the Taiwan Institute of Chemical Engineers*, **49**, 206 (2015).

ОТСТРАНЯВАНЕ НА БАГРИЛОТО ДИАМАНТЕНО ЗЕЛЕНО ОТ ВОДИ ЧРЕЗ АДСОРБЦИЯ ВЪРХУ ОТПАДЪЧНА МОРКОВЕНА ПУЛПА И КАРТОФЕНИ ОБЕЛКИ

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(Резюме)

Багрилото диамантено зелено е пример за текстилна боя. В това проучване е използвана отпадъчна пулпа от моркови (*Daucus carota)* и обелки от картофи (*Solanum tuberosum)* за отстраняване на багрилото от водата. Това са евтини и лесно достъпни материали. Техният адсорбционен капацитет за отстраняване на багрилото диамантено зелено е тестван за пръв път в това проучване с оглед възможно приложение за индустриално пречистване на водата. Оптималните условия за отстраняване на 25 ppm диамантено зелено багрило от 100 mL синтетична отпадна вода чрез отпадъци от моркови са: 0.6 g адсорбент, pH 2.0, 40 минути контактно време, 30 °C температура и 150 rpm скорост на разбъркване. Когато се използват обелки от картофи, оптималните условия са: 0.4 g адсорбент, pH 1.0, 15 минути контактно време, 30 °C температура и 50 rpm скорост на разбъркване. Различните условия, влияещи върху сорбцията на багрилото диамантено зелено от вода, са оптимизирани чрез изотермични и кинетични изследвания. Изотермичните проучвания показват, че хемисорбцията преобладава над физисорбцията, като максималният капацитет за отстраняване чрез отпадъци от моркови и обелки от картофи е съответно 4.14 и 3.13 mg/g. Кинетичните изследвания сочат модел от псевдо-втори порядък. И двата сорбента са подходящи за отстраняване на багрилото диамантено зелено от отпадни води.